

## Electrochemical behaviour of few vinyl quinolones at glassy carbon electrode

P. LALITHA\* and S. SIVAKAMASUNDARI

Department of Chemistry, Avinashilingam University For Women, Coimbatore - 641 043 (India).

(Received: April 19, 2010; Accepted: May 23, 2010)

### ABSTRACT

Many quinolones, substituted quinolines and thiones are well known for their biological activity. The redox characteristics of such biological substances may provide valuable information about the redox behaviour in living systems. The present paper is aimed at carrying out a methodical cyclic voltammetric investigation of the peak potential values of 4-methyl/phenyl -3- vinyl quinoline-2(1H) one(MVQ/PVQ), 2-chloro-4- methyl/phenyl -3-vinyl quinoline (CMVQ/CPVQ), 4- methyl/phenyl -3-vinyl quinoline-2(1H)-thione (TMVQ/TPVQ), in tetrahydrofuran (THF) with tetra butyl ammonium bromide (TBAB) as supporting electrolyte at glassy carbon electrode (GCE) with varying scan rate . All the voltammograms showed only irreversible diffusion controlled reduction.

**Key words:** Electrochemical behaviour, Vinyl quinolones, Glassy carbon electrode.

### INTRODUCTION

Many quinolones, substituted quinolines and thiones are well known for their biological activity. The redox characteristics of such biological substances may provide valuable information about the redox behaviour in living systems. The present paper is aimed at carrying out a methodical cyclic voltammetric investigation of the peak potential values of 4-methyl/phenyl -3- vinyl quinoline-2(1H) one(MVQ/PVQ), 2-chloro-4- methyl/phenyl -3-vinyl quinoline (CMVQ/CPVQ), 4- methyl/phenyl -3-vinyl quinoline-2(1H)-thione (TMVQ/TPVQ), in tetrahydrofuran (THF) with tetra butyl ammonium bromide (TBAB) as supporting electrolyte at glassy carbon electrode (GCE) with varying scan rate . The reduction of vinyl quinolones has been studied at dropping mercury electrode (DME) polarographically with buffers-acetic acid/sodium acetate; ammonium

chloride /ammonium hydroxide; and in sodium hydroxide in the presence of tetra ethyl ammonium iodide and benzyltrimethyl ammonium iodide as supporting electrolytes. Three reduction waves and the difference in their  $E_{1/2}$  values were attributed to the structural effects on the reduction mechanism. This provoked our interest in studying the reduction behaviour of the foresaid compounds at glassy carbon electrode since the reduction behaviour is anticipated to vary with DME and GCE

### MATERIAL AND METHODS

#### Stock solutions of compounds

Stock solutions of all compounds were prepared by dissolving appropriate amounts of the compound in THF. From the stock solutions appropriate amounts were taken to get the working solution of approximately 0.05mM.

Compound	Abbreviation used	Compound	Abbreviation used
4-Methyl -3-vinyl quinoline-2(1H)-one	MVQ	2-Chloro-4-phenyl-3-vinyl quinolines	CPVQ
2-Chloro-4-methyl-3-vinyl quinoline	CMVQ	4-Phenyl-3-vinyl quinoline-2(1H)-thione	TPVQ
4-Methyl -3-vinyl quinoline-2(1H)-thione	TMVQ	4-Phenyl -3-vinyl quinoline-2(1H)-one	PVQ

These compounds were purified and recrystallized and used in the study. Tetra butyl ammonium bromide was obtained from Lancaster (U.K) and used as such. Britton Robinson Buffer <sup>1</sup> was used to maintain pH ~6 .

### Instrumentation

The experimental set-up for CV measurement consisted of a Solartron model number 1280 ZT electrochemical system (1280 B+ USB 128087S) – CIF analyzer controlled by a personal computer with the Corrware program.

### Analytical measurements

#### Electrochemical cell

Cyclic voltammetric experiments were performed using a three electrode system consisting of a 3 mm diameter glassy carbon ( MF 2012) as working electrode , saturated calomel as reference electrode and a platinum counter electrode immersed in a small glass cell with provision for inserting electrodes and nitrogen purging. All potentials are referred to the reference electrode.

#### Electrochemical measurement

Before each measurement, the working electrode was washed with ethanol, rinsed with water, then cleared by cycling between  $-0.20$  V and  $+1.20$  V at a scan rate of  $0.10$  V/s for 10 min in  $0.10$  M  $H_2SO_4$  and finally carefully washed with water <sup>2</sup>. The GCE was polished before each set of experiments. In each study a blank run of the solvent and quaternary salts were recorded to ascertain the wave due to the organic compounds and also to ascertain background current before every experiment.

About 20ml of  $0.01$  M supporting electrolyte solution was dispensed into an electrochemical cell. To it was added appropriate volumes of Britton Robinson buffer and compound ( $\sim 10^{-5}$  M) in THF. Oxygen was typically removed by bubbling nitrogen through the solution for about 15 minutes. A blanketing layer of inert gas over the solution was maintained during the experiment. The working electrode (GCE), reference electrode (Calomel electrode) and auxiliary electrode (Pt wire electrode) were placed in the deoxygenated solution. The electrodes were connected to the potentiostat and cyclic voltammograms were obtained at sweep rates:

$0.01, 0.02, 0.05, 0.1, 0.15$  and  $0.2$  V  $s^{-1}$ .

## RESULTS AND DISCUSSION

In the present work cathodic cyclic voltammograms were obtained for all the individual compounds in presence of supporting electrolytes. All the voltammograms showed only irreversible nature as exemplified from the shape of the voltammograms (Fig. 1 to 6).

### Scan rate dependence

It was observed in all cases, that the peak potential ( $E_{pc}$ ) value shifts towards more negative side as the sweep rate  $u$  increases. The electrochemical data obtained are summarized in tables 1 to 6. It is well evident from the results that the cathodic peak current ( $i_{pc}$ ) increases with increasing sweep rate. The cathodic shift of peak potential with sweep rate <sup>3</sup>, absence of anodic wave on reverse scan and fairly constant value of  $i_p/u^{1/2}$  at higher scan rates confirm the reduction process to be a diffusion controlled irreversible one. Plots of current peak intensity ( $i_{pc}$ ) against  $t^{1/2}$  were linear ( $R > 0.9$ ) and passed through the origin, which also proved that the reduction process was diffusion-controlled. The current function ( $ip/Cv^{1/2}$ ) has been found to be fairly constant with respect to high sweep rates indicating that the electrode process is diffusion controlled <sup>4,5</sup>.

The product of  $i_{pc}$  and  $v^{-1/2}$  increases with potential scan rate, but for a simple irreversible electron transfer reaction, it should remain constant. The variation at low scan rate suggests a complex set of mechanisms for the reaction. At high scan rates the product remains almost constant indicating a simple irreversible electron transfer reaction.

The compounds MVQ, CMVQ, CPVQ and TPVQ gave one peak at  $E_p$  0.8 to 1.1 while the compounds TMVQ and PVQ gave an additional cathodic peak only at low scan rates (10,20) at  $E_p$  1.9-2.02 at glassy carbon electrode with Britton Robinson buffer at pH 6. These results show that two groups are reduced in the latter set of compounds.

### Mechanism of Reduction

Based on the results of the CV studies the

**Table 1: Cyclic peak parameters obtained for the reduction of 0.05081mm MVQ at different scan rates in THF- TBAB system with britton robinson buffer at pH 6(7.84)**

Scan rate $\nu$ (V/s)	Peak potential $-E_p$ (V)	Peak current $I_p$ ( $\mu$ A)	$i_p/\nu^{1/2}$ $\mu$ AV <sup>-1/2</sup> S <sup>-1/2</sup>	$i_p/C\nu^{1/2}$
0.01	0.840	1.40	14.00	275.54
0.02	0.910	3.00	21.20	417.5
0.05	1.020	7.50	33.54	660.1
0.10	1.067	8.40	26.50	523.0
0.15	1.087	10.2	26.33	518.0
0.20	1.107	13.3	29.70	585.3

Plot of  $i_p$  vs  $\nu^{1/2}$ 

$$y = 31.627x - 1.2168; r = 0.98$$

Plot of  $E_p$  vs  $\log \nu$ 

$$y = -0.2072x - 1.2649; r = 0.99$$

Plot of  $\log i_p$  vs  $\log \nu$ 

$$y = 0.77x - 1.65; r = 0.97$$

**Table 2: cyclic peak parameters obtained for the reduction of CMVQ at different scan rates in THF- TBAB system with britton robinson buffer at pH 6.06(7.8)**

Scan rate $\nu$ (V/s)	Peak potential $-E_p$ (V)	Peak current $I_p$ ( $\mu$ A)	$i_p/\nu^{1/2}$ $\mu$ AV <sup>-1/2</sup> S <sup>-1/2</sup>	$i_p/C\nu^{1/2}$
0.01	0.910	0.60	6.00	119.7
0.02	0.930	2.04	14.4	287.8
0.05	1.007	6.18	27.64	551.4
0.10	1.020	8.80	27.83	555.2
0.15	1.030	11.2	28.90	576.9
0.20	1.040	13.01	29.10	580.4

Plot of  $i_p$  vs  $\nu^{1/2}$   $y = 35.882x - 2.6909; r = 0.996$ Plot of  $E_p$  vs  $\log \nu$   $y = -0.1051x - 1.1212 r = -0.97$ Plot of  $\log i_p$  vs  $\log \nu$   $y = 0.99x + 1.90 r = 0.97$ **Table 3: Cyclic peak parameters obtained for the reduction of TMVQ at different scan rates in THF- TBAB system with britton robinson buffer at pH 6.19(7.9)**

Scan rate $\nu$ (V/s)	Peak potential $-E_{p1}$ (V)	Peak current $I_{p1}$ ( $\mu$ A)	$i_{p1}/\nu^{1/2}$ $\mu$ AV <sup>-1/2</sup> S <sup>-1/2</sup>	$i_{p1}/C\nu^{1/2}$	Peak potential $-E_{p2}$ (V)	Peak current $I_{p2}$ (mA)	$i_{p2}/\nu^{1/2}$ $\mu$ AV <sup>-1/2</sup> S <sup>-1/2</sup>
0.01	0.940	5.60	56.00	1103	1.96	31.6	316
0.02	0.960	4.80	33.90	669	2.05	33.7	238
0.05	1.030	6.40	28.62	564	-	-	-
0.10	1.050	9.50	30.04	592	-	-	-
0.15	1.070	11.50	30.00	585	-	-	-
0.20	1.064	18.97	42.41	835	-	-	-

Plot of  $i_p$  vs  $\nu^{1/2}$   $y = 35x + 0.02; r = 0.91$ Plot of  $E_p$  vs  $\log \nu$   $y = -0.106x - 1.15; r = -0.98$ Plot of  $\log i_p$  vs  $\log \nu$   $y = 0.39x + 1.42; r = 0.89$

**Table 4: Cyclic peak parameters obtained for the reduction of pvq at different scan rates in thf- ttab system with britton robinson buffer at pH 6.06(8.06)**

Scan rate $\nu$ (V/s)	Peak potential $-E_{p1}$ (V)	Peak current $I_{p1}$ ( $\mu$ A)	$i_{p1}/\nu^{1/2}$ $\text{mAV}^{-1/2}\text{s}^{-1/2}$	$i_{p1}/C\nu^{1/2}$	Peak potential $-E_{p2}$ (V)	Peak current $I_{p2}$ ( $\mu$ A)	$i_{p2}/\nu^{1/2}$ $\mu\text{AV}^{-1/2}\text{s}^{-1/2}$
0.01	0.84	5.90	59.00	729	1.91	71.4	714
0.02	0.87	6.90	48.80	603	1.94	56.8	402
0.05	0.92	9.30	41.60	514	-	-	-
0.10	0.95	11.80	37.30	461	-	-	-
0.15	0.98	16.50	42.60	526	-	-	-
0.20	0.99	28.50	63.70	787	-	-	-

Plot of  $i_p$  vs  $\nu^{1/2}y = 55.5x - 1.8$ ;  $r = 0.91$

Plot of  $E_p$  vs  $\log \nu y = -0.117x - 1.07$ ;  $r = -0.99$

Plot of  $\log i_p$  vs  $\log \nu y = 0.46x + 1.63$ ;  $r = 0.94$

**Table 5: Cyclic peak parameters obtained for the reduction of CPVQ at different scan rates in THF- TBAB system with britton robinson buffer at pH 6.06(8.08)**

Scan rate $\nu$ (V/s)	Peak potential $-E_p$ (V)	Peak current $I_p$ ( $\mu$ A)	$i_p/\nu^{1/2}$ $\text{mAV}^{-1/2}\text{s}^{-1/2}$	$i_p/C\nu^{1/2}$
0.01	0.89	09.60	96.0	1920
0.02	0.92	11.30	80.0	1598
0.05	1.00	16.20	72.4	1449
0.10	1.02	11.80	37.3	746
0.15	1.06	14.20	36.7	733
0.20	1.07	15.01	33.6	671

Plot of  $i_p$  vs  $\nu^{1/2}y = 11.5x + 9.9$ ;  $r = 0.63$

Plot of  $E_p$  vs  $\log \nu y = -0.14x - 1.17$ ;  $r = -0.99$

Plot of  $\log i_p$  vs  $\log \nu y = 0.12x + 1.26$ ;  $r = 0.73$

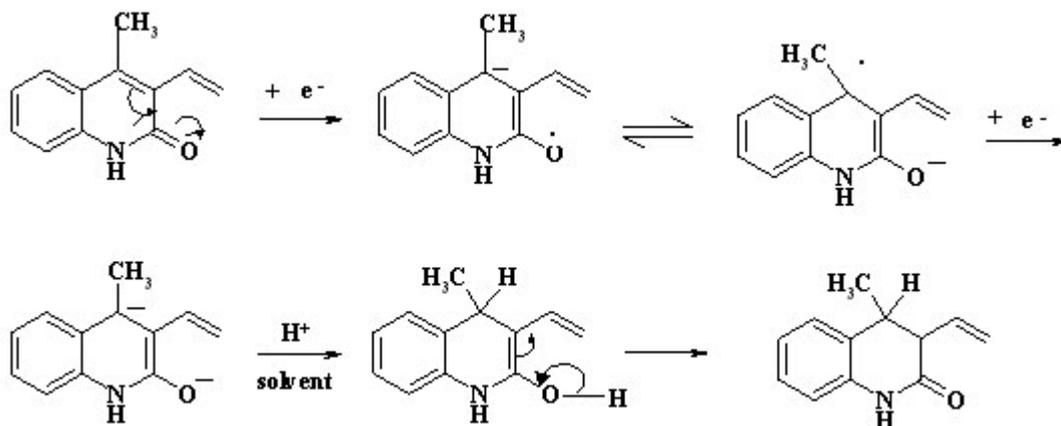
**Table 6: Cyclic peak parameters obtained for the reduction of TPVQ at different scan rates in THF- TBAB system with britton robinson buffer AT pH 6.06(8.07)**

Scan rate $\nu$ (V/s)	Peak potential $-E_p$ (V)	Peak current $I_p$ (mA)	$i_p/\nu^{1/2}$ $\mu\text{AV}^{-1/2}\text{s}^{-1/2}$	$i_p/C\nu^{1/2}$
0.01	0.940	06.32	63.2	1264
0.02	0.960	08.40	59.4	1188
0.05	1.010	10.20	45.6	912
0.10	1.028	12.10	38.3	765
0.15	1.034	19.50	50.3	1007
0.20	1.044	25.30	56.6	1131

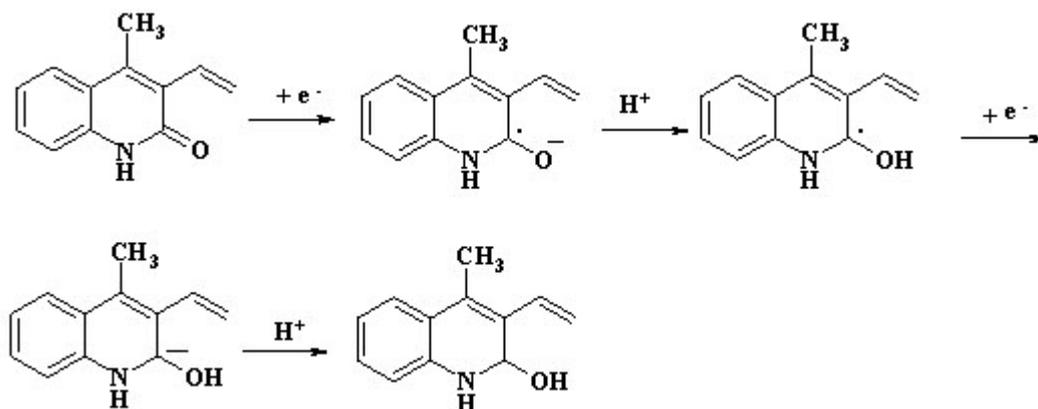
Plot of  $i_p$  vs  $\nu^{1/2}y = 50.1x + 0.13$ ;  $r = 0.95$

Plot of  $E_p$  vs  $\log \nu y = -0.08x - 1.1$ ;  $r = -0.99$

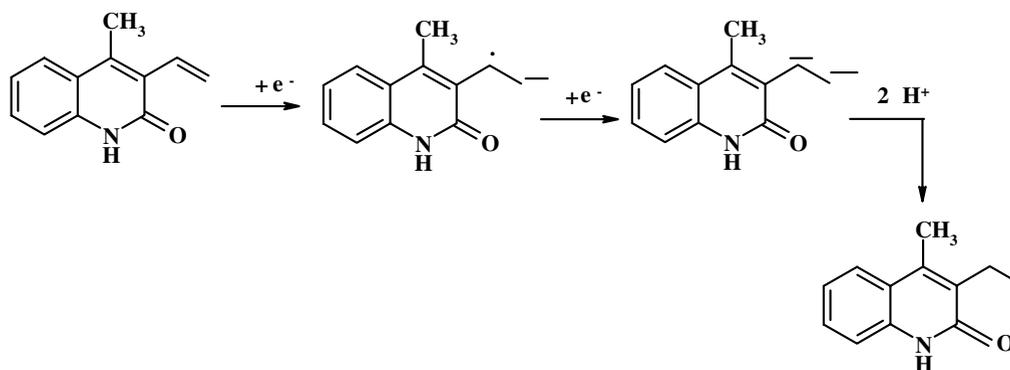
Plot of  $\log i_p$  vs  $\log \nu y = 0.42x + 1.6$ ;  $r = 0.95$



The reduction of the carbonyl group may be visualized as in the following:



A possible mechanism for the reduction of the vinyl group in vinylquinolones may be visualized as shown in the reaction sequence below:



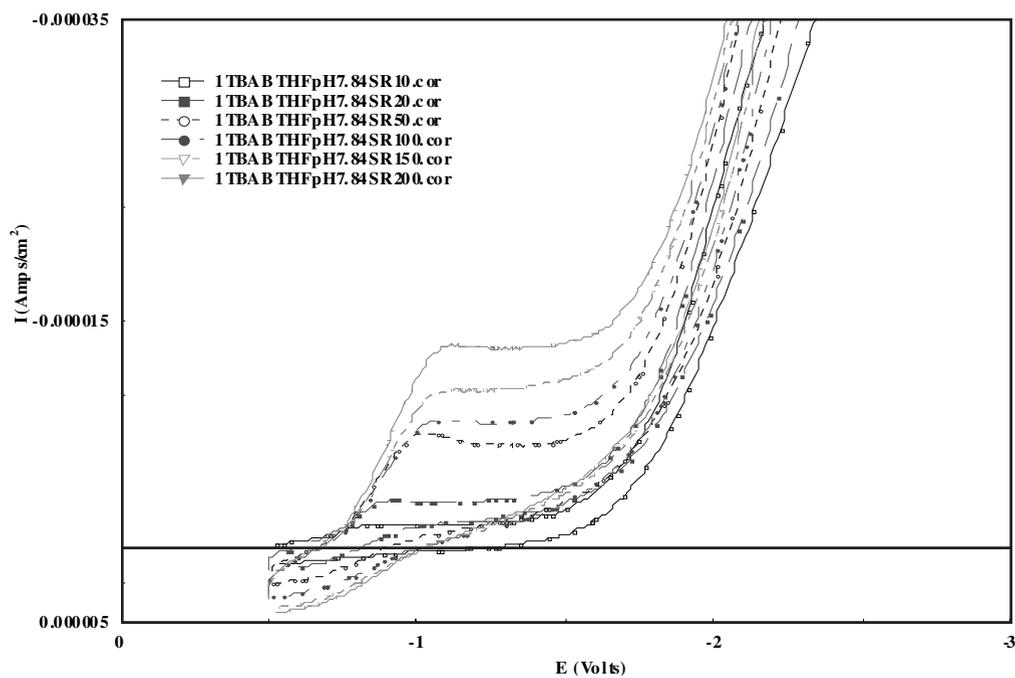


FIG. 1: Cyclic voltammogram of 0.05069mM MVQ in TBAB-THF system at different scan rates with br buffer [pH 6 (7.84)]

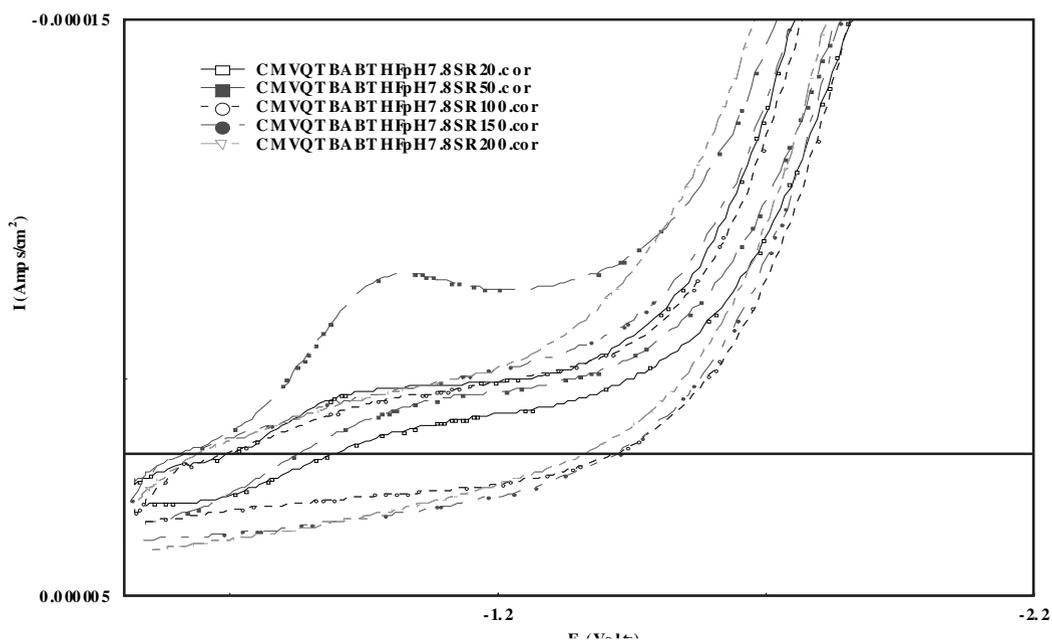


FIG. 2: Cyclic voltammogram of 0.05012mM CMVQ in TBAB-THF system at different scan rates with br buffer [pH 6.06 (7.8)]

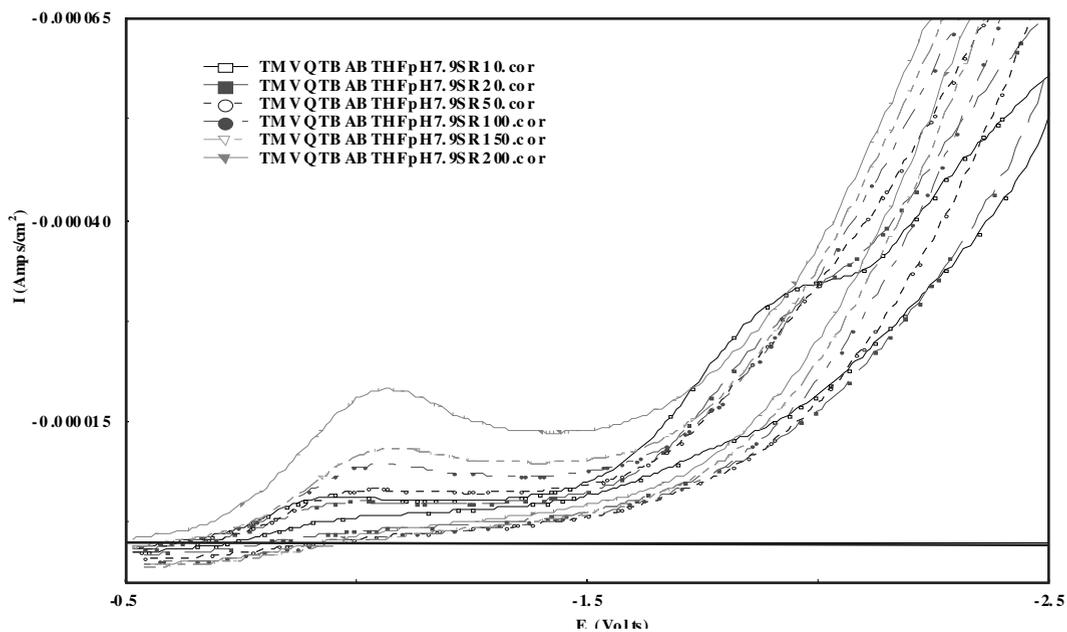


Fig. 3: Cyclic voltammogram of 0.05075mm TMVQ in TBAB-THF system at different scan rates with BR buffer [ph 6.19 (7.9)]

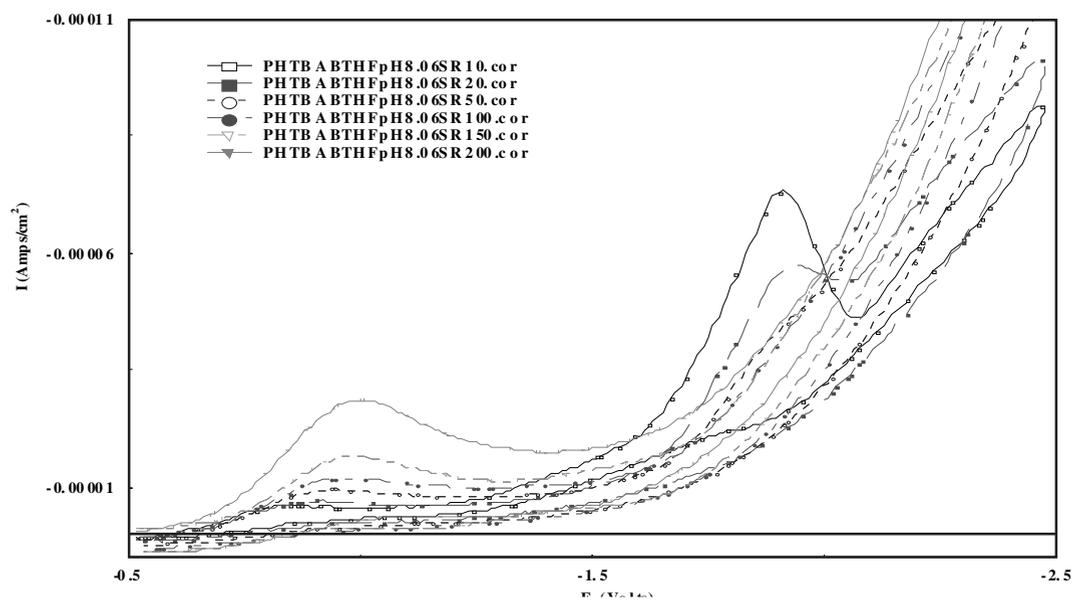
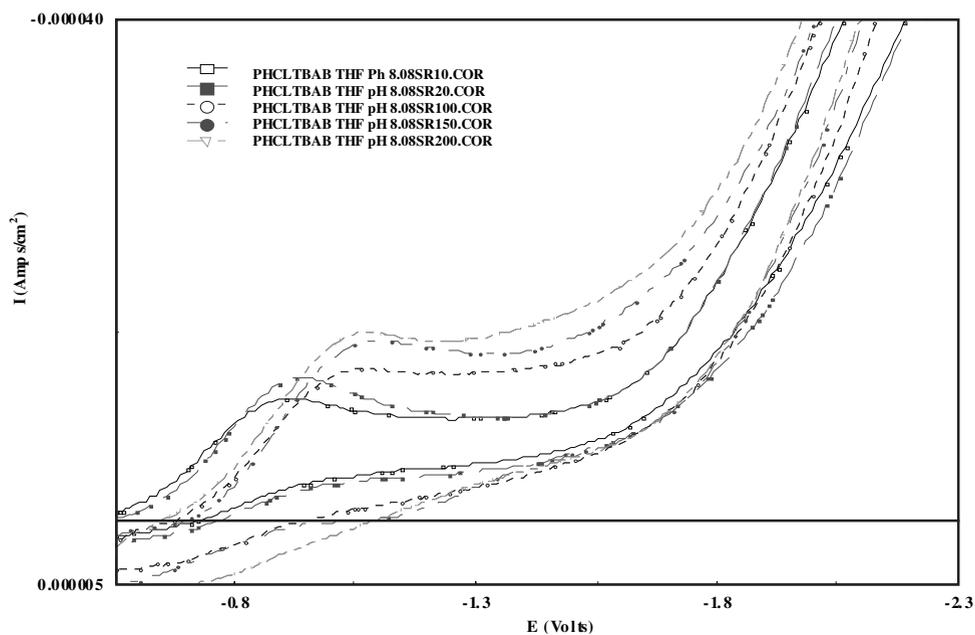


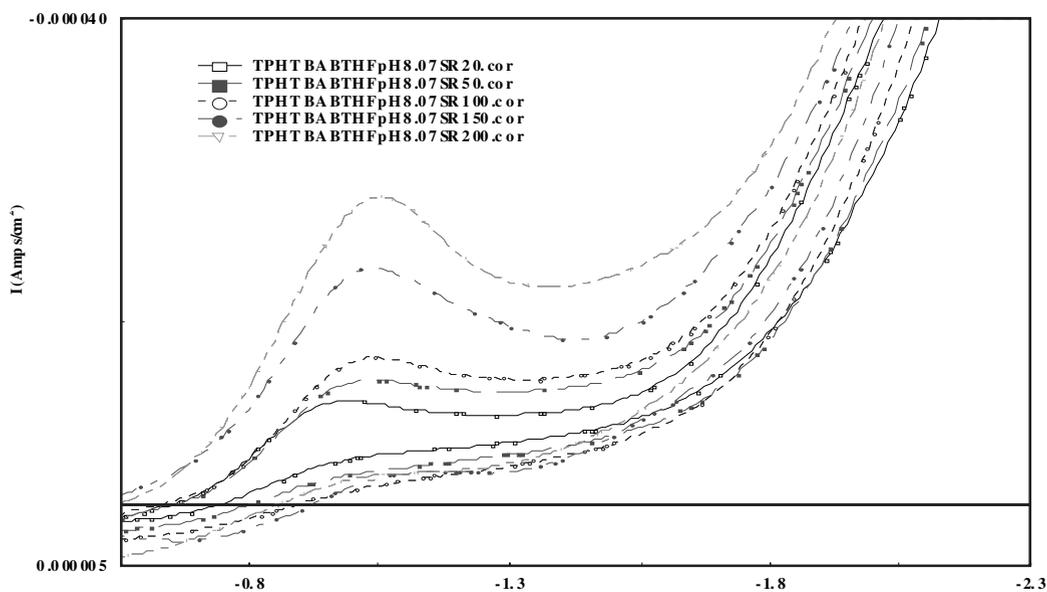
Fig. 4: Cyclic voltammogram of 0.08097mm PVQ in TBAB-THF system at different scan rates with BR buffer [ph 6.06 (8.06)]

electrochemical reduction mechanism of the compounds under study is proposed in the following paragraphs.

In order to arrive at the mechanism of reduction of the compounds under study, an analysis of the  $E_p$  values of all the compounds at pH 6 in



**Fig. 5: Cyclic voltammogram of 0.05000mm CPVQ in TBAB-THF system at different scan rates with BR buffer [ph 6.06 (8.08)]**



**Fig. 6: Cyclic voltammogram of 0.05000mm TPVQ in TBAB-THF system at different scan rates with BR buffer [ph 6.06 (8.07)]**

**Table 7: Comparison of peak potentials of compounds at pH 6 in THF-TBAB system**

Compound	BR pH(Test pH)	-E <sub>p</sub> (V) for $\nu$ 0.01 to 0.20 (V.s <sup>-1</sup> )		
		Peak 1	Peak 2	Peak 3
MVQ	6.0	0.84-1.0	1.8 ( $\nu$ 0.01)	-
	(7.84)		1.86( $\nu$ 0.02)	
PVQ	0.06	0.84-0.99	1.91 ( $\nu$ 0.01)	-
	(7.8)		1.94( $\nu$ 0.02)	
CMVQ	6.06	0.91-1.04	-	-
	(7.8)		-	
CPVQ	6.06	0.89-1.07	-	-
	(7.08)		-	
TMVQ	6.19	0.94-1.06	1.96( $\nu$ 0.01)	-
	(7.9)		2.05 ( $\nu$ 0.02)	
TPVQ	6.06	0.94-1.044	-	-
	(8.07)		-	

THF-TBAB system at different scan rates (0.01, 0.02, 0.05, 0.1, 0.15 and 0.2 V s<sup>-1</sup>) was carried out (Table 7). It is quite obvious from the results that all the compounds gave the first wave at E<sub>p</sub> 0.8 to ~1.0V. The 4-substituted vinyl-2-quinolones gave an additional peak at 1.8 to 1.9V. The corresponding wave as expected was found missing for the 2-chloro substituted 4-methyl and 4-phenyl quinolines. This shows that the second peak must be due to the reduction of the -C=O group. The second wave obtained for the quinolones disappeared slowly at higher scan rates. This may be attributed to the adsorptive effect of the compound onto the glassy carbon electrode. The thione compounds gave additional waves at 1.9 to 2.05V at low scan rates. This might be due to the reduction of the -C=S bond and formation of the thiol moiety (-C-SH).

Reactions of thiones with several cyclizing agents showed that the 4-methyl substituted thiones easily forms the thiols, which subsequently ring closes to form a stable 5-membered ring – dihydrothienoquinolines<sup>6</sup>. Observations also indicate that 4-phenyl substituted thiones easily form the dimer–disulphide and the corresponding dihydrothienoquinolines. This is quite evident from the cyclic voltammetric results since the 4-methyl thione gives a second wave at low scan rates while no prominent peaks or waves were obtained with 4-phenyl substituted thiones.

Thus it can be concluded from the results obtained that at neutral pH, (BR pH ~6 and test pH ~7) the quinoline- and oxo- moieties are reduced which can be mechanistically viewed as follows:

### CONCLUSION

The cathodic shift of peak potential with sweep rate, absence of anodic wave on reverse scan and fairly constant value of  $i_p/u_{1/2}$  at higher scan rates confirm the reduction process to be diffusion controlled irreversible one. The compounds MVQ, CMVQ, CPVQ and TPVQ gave one peak at E<sub>p</sub> 0.8 to 1.1, while the compounds TMVQ and PVQ gave an additional cathodic peak at low scan rates (10, 20) at E<sub>p</sub> 1.9-2.02 at glassy carbon electrode with Britton Robinson buffer at pH 6 indicating the presence of two reducible groups in the compounds. Compatibility of glassy carbon electrode with organic solvents was quite obvious. This electrode can be used for the quantitative determination of compounds like vinyl quinolines, quinolones and thiones based on their cathodic reduction using CV with a limit of determination around 10<sup>-6</sup>M.

### ACKNOWLEDGEMENTS

The authors thank the concerned authorities of the Avinashilingam University for Women, Coimbatore for providing facilities to carry out this work.

**REFERENCES**

1. Prabavathi, N., Electrochemical Studies of Some Flavonoid Compounds, Ph.D Thesis, Bharadhidasan University, Tiruchirapalli, South India, (1993).
2. Kissinger, P.T., Heineman., W.R. Marcel Dekker., *Laboratory Techniques in Electro Analytical Chemistry*, 2<sup>nd</sup> ed., revised and expanded, **2**: 314 (1996).
3. Honglan Qi., Chengxiao Zhang., Electro generated chemiluminescence behaviour of lucigenin with isatin at a platinum electrode, (2004).
4. Brown, O.R and Harrison, J.A., *J.Electroanal.Chem.*, **21**: 387 (1969).
5. Nicholson R. S., Shain I., *Anal. Chem.*, **36**: 706 (1964).
6. Lalitha, P., S.Sivakamasundari and Shanmugam P , poster on Reaction of 4-methyl-3-vinyl quinoline-2(1H)-thione with various reagents presented and abs. in the proceedings of the One Day Symposium on Future directions of NMR and users meeting organized by NMR Research Centre, Indian Institute of Science, Bangalore in August (2007).