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Research Article

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Cyclicvoltammetric studies on anodic alkoxylation of selective aromatic systems in aqueous medium on glassy carbon electrode

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INTRODUCTION

Aromatic compounds are used in many industrial processes and particularly, benzene is the simplest of these aromatic compounds and has been studied for several purposes. Direct functionalization of the aromatic ring using several electrochemical techniques [1,2] especially in the preparation of conductive polymers, in organic / aqueous media finds its applications [3-5]. Fundamental studies performed on platinum surfaces in the gas phase and in an electrochemical environment have also been reported [6-9]. Some studies have shown that the orientation and mode of attachment of the aromatic compounds, irreversibly adsorbed from aqueous solutions onto smooth platinum electrodes, are dependent on the chemical structure and concentration of the adsorbate, the surface activity, the supporting electrolyte and the pH of the solution [9]. The study of the electrochemical oxidation from aqueous solution is a preliminary step in order to analyze the possible treatment of these compounds by an electrochemical method. The adsorption and electrooxidation of benzene and its homologues on polycrystalline platinum electrodes have been examined in some papers [7,9]. The influence of the orientation of the platinum electrode on the adsorption of benzene has also been studied [7,8].The approach of electroanalytical methodologies in general and cyclic voltammetric technique, in particular,serves to be an effective tool to researchers to understand the subtle aspects of electrochemical reaction routes [10-14].

This paper deals with electroanalytical interpretations on the electrochemical oxidation of mono substituted benzenes in acid media on glassy carbon electrode. The cyclicvoltammetry technique is exploited to bring out the molecular behavior in the electrochemical field under the stipulated conditions.

EXPERIMENTAL METHODS

The cyclic voltammetric studies were carried out with a computerized cyclic voltammogram [*Chi620a – Electrochemical Analyzer, CH Instruments Inc. USA*]. The glassy carbon electrode was washed with distilled water and rinsed with conductivity water. The surface was polished with velvet cloth and was used afresh. Before obtaining the voltammograms, the electrode was first pre-polarized, keeping it immersed in the solvent-electrolyte and running a few sweeps, in the scan range chosen for the study. The special cell was cleaned with concentrated nitric acid, washed thoroughly with water, rinsed with doubly distilled water followed with conductivity water. 1M sulfuric acid in 0.5M alcohol-water mixture was taken. The working electrode - glassy carbon was introduced. A 1x2 cm^2 area Platinum foil served as the cathode. The reference electrode *Ag / AgCl* was inserted in such a way the distance between the two electrodes was kept the minimum.

The nitrogen gas employed to deaerate the cell, was purified by passing it through wash bottles, the first containing alkaline Pyrogallol and the second containing the triply distilled water. Purified nitrogen gas was initially purged through the electrolytic solution with stirring for 20 minutes and then kept above the solution during the measurement to blanket the surface so as to prevent re-absorption of oxygen.

The cell was introduced into the computer controlled circuit. The initial and final potentials between which the sweep was to take place along with the scan rate in the range of 100 – 500 mV / sec and the nature of the scan as single or multiple was loaded in the software. The sweep was performed and the cyclic voltammograms were obtained.

The cyclic voltammetric studies were exhaustively exploited to generate supportive evidence for analyzing the core electroalkoxylation studies under the following variables.

Substrate variation studies
To confirm the site of electroalkoxylation and to observe the influence of various functional groups on the peak potentials, cyclic voltammograms were run for substrates with

a. Electron releasing groups : Anisole and Bromobenzene
b. Electron withdrawing groups : Acetophenone, Methyl benzoate and Nitrobenzene

Alcohol variation studies
Cyclic voltammograms were run under the identical stipulated condition with 0.5M aqueous solutions of different alcohols viz., Ethanol, 2-Propanol and 2-Methyl-2-propanol on glassy carbon electrode with 0.1M Anisole, in order to study the effects of primary, secondary and tertiary alcohols on electroalkoxylation.

pH variation studies
With the intention of understanding the impact of pH variation on the peak potentials and the ease of the anodic process, cyclic voltammetric scans on Bromobenzene with Ethanol were run in solutions of pH = 1, 4, 7, 10 and 13.

Scan rate variation studies
Cyclic voltammograms with variable sweep rates along the range of 100 – 500 mV / second, for the systems as shown in the scheme by providing identical environment as far as the other parameters are concerned .

Cyclic Voltammetric Studies

[Substrate] : 0.1M *[Electrolyte] :1M H_2SO_4 / KOH*
Solvent : 0.5M alcohol -water Temperature : 30 $\pm$ 1° C
Working electrode : C glassy *Counter electrode : Pt*

SUBSTRATE	ALCOHOL	pH	SCAN RATE mV / sec
Anisole	Ethanol	1	100, 200, 300, 400 and 500
Anisole	2-Propanol	1	100, 200, 300, 400 and 500
Anisole	2-Methyl-2-propanol	1	100, 200, 300, 400 and 500
Acetophenone	1-Propanol	1	100, 200, 300, 400 and 500
Methyl benzoate	1-Propanol	1	100, 200, 300, 400 and 500
Nitrobenzene	Ethanol	1	100, 200, 300, 400 and 500
Bromobenzene	Ethanol	1,4,7,10 & 13	100, 200, 300, 400 and 500

Multiple scan studies
For all those systems shown in the table, in addition to the single sweep, multiple scannings at a scan rate of 100 mV/sec, were performed, in order to clarify any formation of anode filming, due to polymer formation or otherwise.

RESULTS AND DISCUSSION

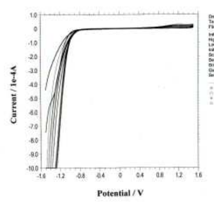
Cyclic voltammetric studies on the systems under consideration in general and on Anisole in particular provide substantive and supportive evidences for the electrochemical pathways suggested for these systems. The electroanalytical data generated in this study are interpreted with the perspective of its supportive nature. However, these data may very well be utilized as a useful and important resource to approach the physicochemical aspects of the electrochemical reaction and for the evaluation of electron transfer kinetics, based on similar such studies reported by earlier workers [15-17].

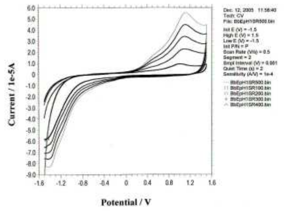
SUBSTRATE VARIATION STUDIES

The cyclic voltammograms for the following combinations of the substrate-alcohol mixtures in a medium of pH=1 are considered for the purpose of rationalizing the salient features of electrochemical processes proposed.

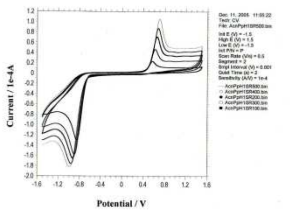
Anisole + Ethanol; Bromobenzene + Ethanol ;Acetophenone + 1-Propanol ; Methyl benzoate + 1-Propanol ; Nitrobenzene + Ethanol

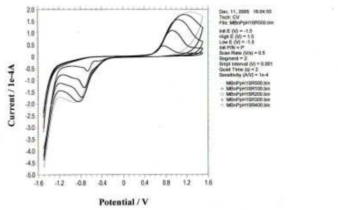
All the runs are observed in the range of scan rates from 100 to 500 mV/sec



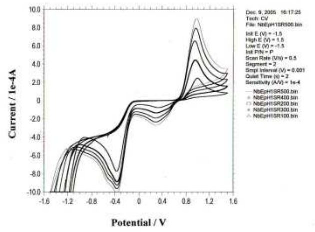


Anisole + Ethanol Bromobenzene + Ethanol





Acetophenone + 1-PropanolMethylbenzoate + 1-Propanol



Nitrobenzene + Ethanol

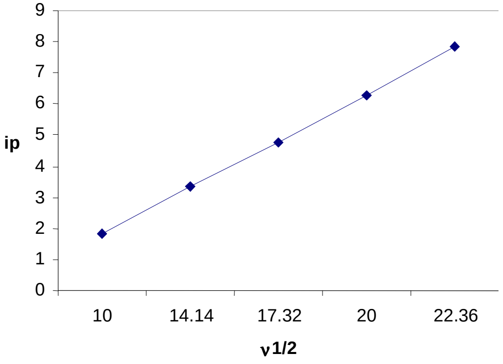
The cyclic voltammograms of Anisole and Bromobenzene clearly depicts two distinct peak potentials, almost at the same positions, namely 0.4 and 0.9V. These two peak potentials are indicative of two 1-electron oxidations with a chemical process in between. That is an *ECE* process. When the peak heights are considered, the height of the second peak is observed to be higher than that of the first peak. This indicates the fact that the second electron oxidation is more difficult than the first electron oxidation.

On the other hand, the curve pattern for compounds containing electron withdrawing groups namely $–NO_2$, $-COOCH_3$ and $–COCH_3$, looks to be different. The anodic portion of the curve has a well pronounced single peak around 1.2V with an extended peak height. The groups under consideration having unsaturated positions are bound to destabilize the aromatic system. As a result the potential for the first electron oxidation must have shifted to the level at which the second electron oxidation occurs. Therefore the merger of two peaks occurs even at low scan rate. Commonly the phenomenon of merger of two peaks is observed when the scan rate is increased. For these systems with unsaturated positions in the functional groups, the cathodic peaks do appear on the reverse sweep, as the voltammetric sweep is in undivided cells. The peak height is indicative of the extent of current flow. Higher the peak, more the current flow. The peak current signifies the Faradaic current due to charge transfer and to charge the electrical double layer. Indirectly it is proportional to the duration of current.

On the basis of electro kinetic principle, the peak height has direct correlation with the rate of the reaction[18-19]. Accordingly as the peak height increases, the rate of the reaction is slow and the formation of the reactive intermediate corresponding to the summit of the peak is difficult[20]. Hence the cyclic voltammograms obtained for the two sets of substrates with electron donating and electron withdrawing groups explain the proposed mechanistic pathway.

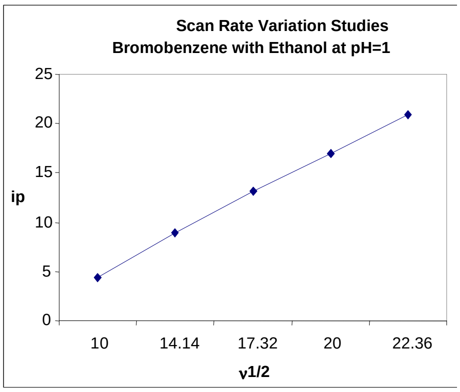
The various electroanalytical parameters derived from the cyclic voltammograms are provided. The peak current (i_p) values are plotted against the square root of the scan rate ($\nu^{1/2}$). The slope values for the linear curves derived, for these systems are observed to be higher than 0.5. This emphatically conveys that these electrochemical processes conducted on carbon electrode are only adsorption controlled phenomena[21,22]. This analytical interpretation accomplishes a vital support for the electrochemical behavior of substrates assumed in this study at Graphite.

Parameters	Scan rate ν (mV/s)				
	100	**200**	**300**	**400**	**500**
ν1/2	10	14.14	17.32	20	22.36
ip (μA)	1.854	3.364	4.74	6.262	7.829
Ep (V)	0.999	1.117	1.119	1.120	1.122



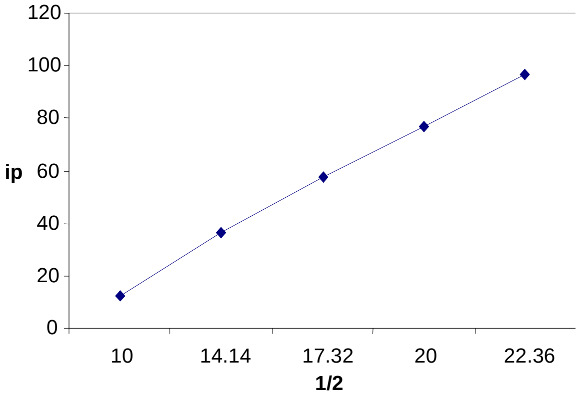
Scan Rate Variation Studies
Anisole with Ethanol at pH=1

Parameters	Scan rate ν (mV/s)				
	100	**200**	**300**	**400**	**500**
ν1/2	10	14.14	17.32	20	22.36
ip (μA)	4.362	8.951	13.14	16.93	20.96
Ep (V)	0.995	1.062	1.071	1.082	1.096



Scan Rate Variation Studies
Bromobenzene with Ethanol at pH=1

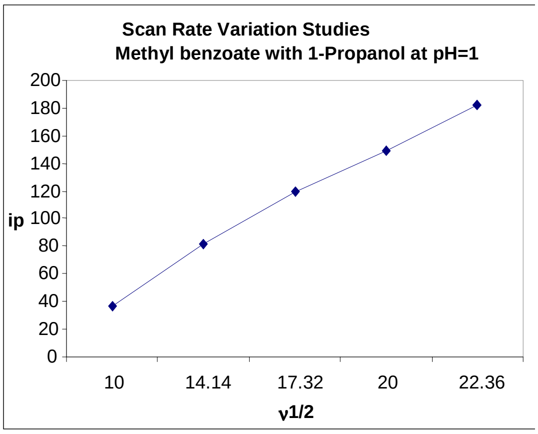
Parameters	Scan rate ν (mV/s)				
	100	**200**	**300**	**400**	**500**
ν1/2	10	14.14	17.32	20	22.36
ip (μA)	12.37	36.3	57.34	76.86	96.51
Ep (V)	0.566	0.617	0.649	0.675	0.696



Scan Rate Variation Studies
Acetophenone with 1-Propanol at pH=1

Further the diagnostics of cyclic voltammogram of systems under study correlate to the ECE mechanism [23]. As the scan rate gets increased, the $(i_p)/(\nu^{1/2})$ value also increases still it reaches a steady value at higher scan rate. This characteristic observation is phenomenal for ECE reactions.

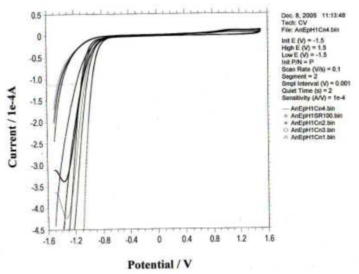
Parameters	Scan rate ν (mV/s)				
	100	**200**	**300**	**400**	**500**
v1/2	10	14.14	17.32	20	22.36
ip (μA)	37.09	82.18	119.2	149.2	182.4
Ep (V)	0.751	0.916	0.997	1.072	1.080

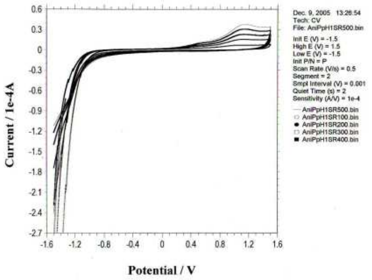


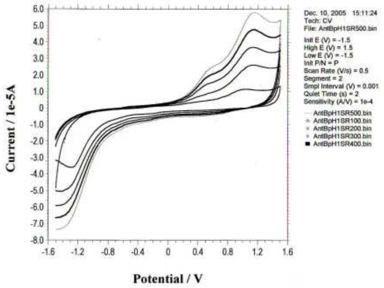
In addition, the absence of reverse peaks in Anisole and Bromobenzene indicates irreversible electron transfer reactions in these cases.

ALCOHOL VARIATION STUDIES

The cyclic voltammograms for Anisole with Ethanol, 2-Propanol and 2-Methyl-2-Propanol can be analyzed





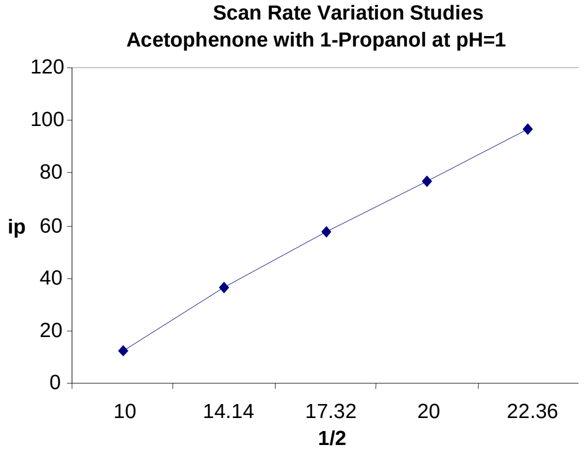


Irrespective of the alcohol used, not much deviation in the peak potential values for the first and the second electron oxidation on carbon in acidic solutions is observed. This prompts to infer that oxidation does not occur on alcohols. It must be the aromatic π cloud that is involved in both the oxidation steps.

Further when the peak current values are observed, there is a slight increase in these values for the first electron oxidation from 1^0alcohol to 3^0 alcohol and a well pronounced increase for the corresponding second electron oxidation.

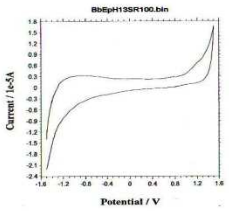
As far as the first electron oxidation is concerned, there is not much observable impact on the rate of electron transfer, due to the variation in alcohols. The obvious increase in the peak currents for the second electron oxidation varies with the nature of alcohols. In other words, the rate of reaction of the C process prior to oxidation seems to be slow. This must be due to the steric hindrance the 3^0 alcohols experience in accessing the radical cation in the chemisorbed state.

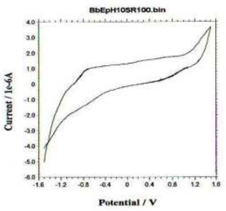
Parameters	Scan rate ν (mV/s)				
	100	**200**	**300**	**400**	**500**
ν1/2	10	14.14	17.32	20	22.36
ip (μA)	12.37	36.3	57.34	76.86	96.51
Ep (V)	0.566	0.617	0.649	0.675	0.696

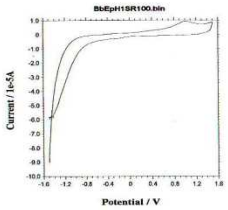


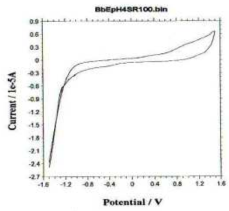
pH VARIATION STUDIES

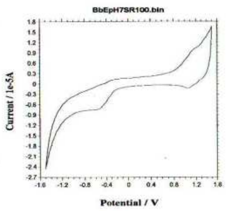
When the cyclic voltammograms generated for Bromobenzene with Ethanol on Glassy carbon at the scan rate of 100mV/sec in solutions of pH ranging from 1 to 13, are analyzed, not much of observable variations in the pattern of the cyclic voltammogram are detected. This suggests that the initial oxidation occurs at the aromatic π cloud only irrespective of the medium present. In other words, the change in the pH of the medium does not influence the mechanistic pathway through the aromatic radical cation formation, though it may produce different varieties of products.











SCAN RATE VARIATION STUDIES

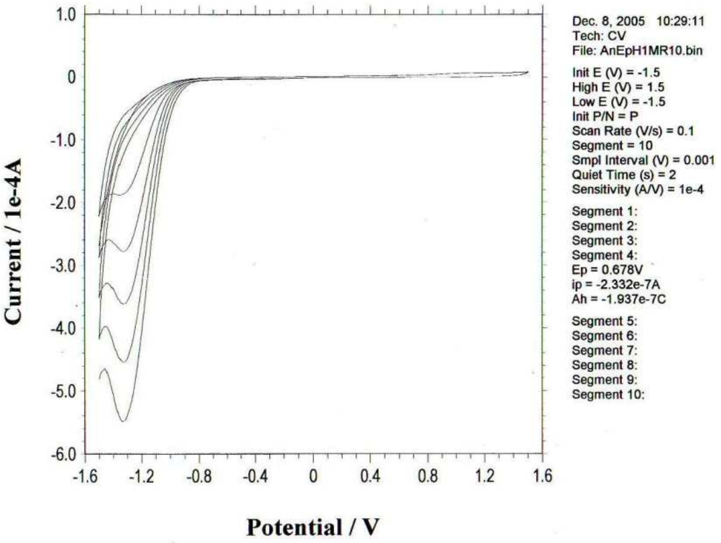
The cyclic voltammograms obtained at different scan rates mainly describes the reversible or irreversible character of the electrochemical process. The cyclic voltammograms for Anisole and Bromobenzene accomplishes the same peak potential irrespective of the increase in the scan rates. This behavior is characteristic of an irreversible electron transfer pathway. On the contrary, the well known reversible electrochemical conversions in the form of Acetophenone, Methyl benzoate and Nitrobenzene show a shift in the higher peak potential value as the scan rate is increased.

Further the plot between the peak current (i_p) and the square root of the scan rate ($\nu^{1/2}$), produces a straight line which does not pass through the origin suggesting the irreversible character for electron transfer processes involving Anisole and Bromobenzene. The other conversions must be reversible as the plot generates straight lines passing through the origin[24].

MULTIPLE RUN STUDIES

In the multiple scan technique, the potential sweep at a specific scan rate namely 100 mV/sec is repeatedly performed for 10 segments through the same solution, without disturbing the assembly of the experiment. This technique finds its use in ascertaining the probable formation of any polymer films on the surface of the working electrode.

For a system capable of forming polymer coats, the potential sweep is responsible for the first segment by way of initiating polymerization. As the electrode gets coated with the polymer of conducting nature, the subsequent sweeps cannot show any peak current.



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Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4
Segment 1:
Segment 2:
Segment 3:
Segment 4:
Ep = 0.678V
ip = -2.332e-7A
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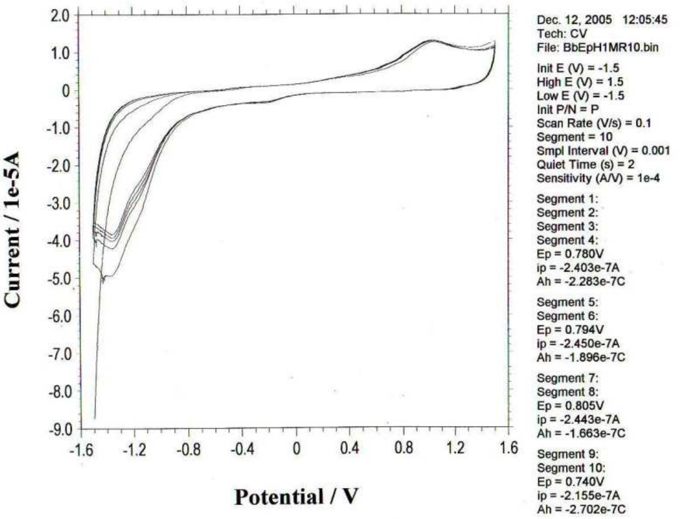
Segment 5:
Segment 6:
Segment 7:
Segment 8:
Segment 9:
Segment 10:



Dec. 12, 2005 12:05:45
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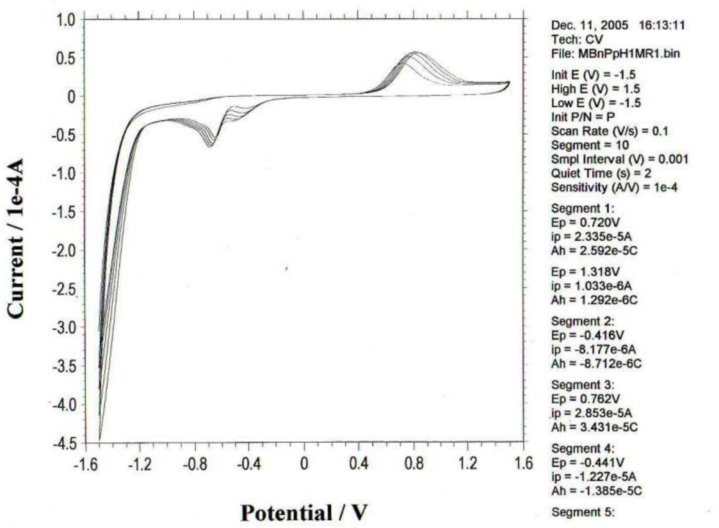
Low E (V) = -1.5
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 10
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4
Segment 1:
Segment 2:
Segment 3:
Segment 4:
Ep = 0.780V
ip = -2.403e-7A
Ah = -2.283e-7C
Segment 5:
Segment 6:
Ep = 0.794V
ip = -2.450e-7A
Ah = -1.896e-7C
Segment 7:
Segment 8:
Ep = 0.805V
ip = -2.443e-7A
Ah = -1.663e-7C
Segment 9:
Segment 10:
Ep = 0.740V
ip = -2.155e-7A
Ah = -2.702e-7C

In the present study the cyclic voltammograms with such multiple scans for Anisole, Phenol, Bromobenzene, Acetophenone and Nitrobenzene in aqueous solution are studied. It is clearly understood that no polymeric coatings seem to have occurred in the systems except in phenol. This decision has been derived from the observation that the peak current fluctuations at the respective peak potential do appear at multiple scan rates.



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Low E (V) = -1.5
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Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4

Segment 1:
Ep = 0.720V
ip = 2.335e-5A
Ah = 2.592e-5C

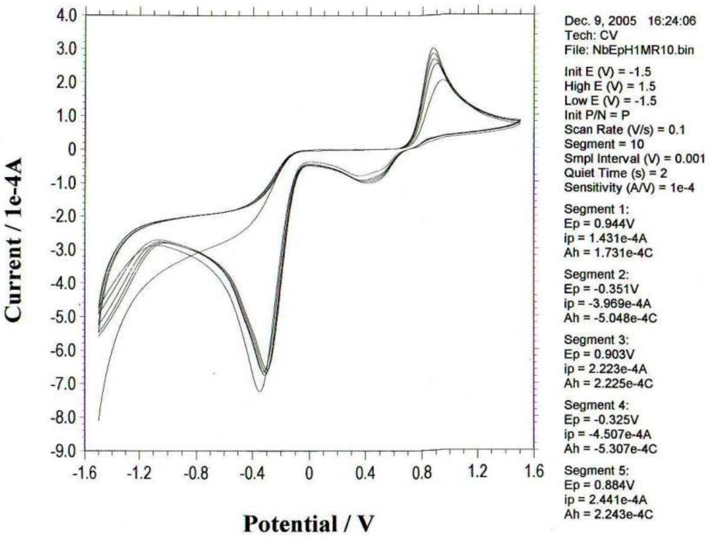
Ep = 1.318V
ip = 1.033e-6A
Ah = 1.292e-6C

Segment 2:
Ep = -0.416V
ip = -8.177e-6A
Ah = -8.712e-6C

Segment 3:
Ep = 0.762V
ip = 2.853e-5A
Ah = 3.431e-5C

Segment 4:
Ep = -0.441V
ip = -1.227e-5A
Ah = -1.385e-5C

Segment 5:



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Low E (V) = -1.5
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Scan Rate (V/s) = 0.1
Segment = 10
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4

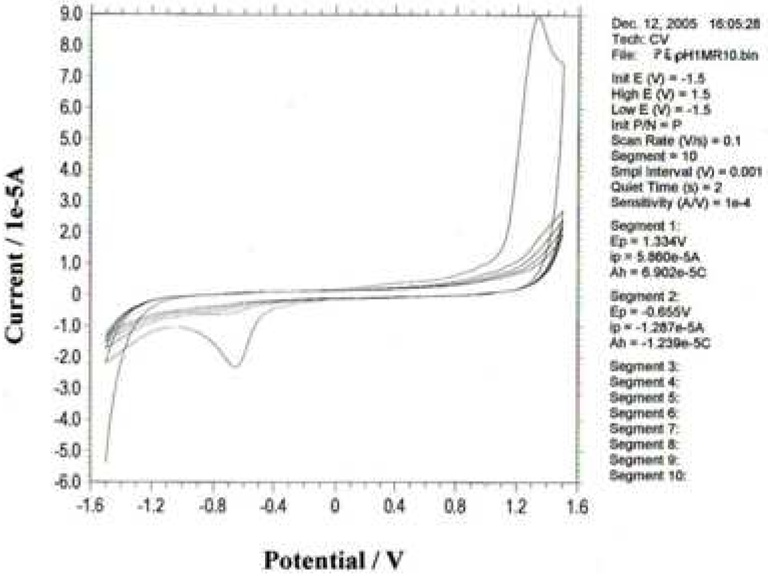
Segment 1:
Ep = 0.944V
ip = 1.431e-4A
Ah = 1.731e-4C

Segment 2:
Ep = -0.351V
ip = -3.969e-4A
Ah = -5.048e-4C

Segment 3:
Ep = 0.903V
ip = 2.223e-4A
Ah = 2.225e-4C

Segment 4:
Ep = -0.325V
ip = -4.507e-4A
Ah = -5.307e-4C

Segment 5:
Ep = 0.884V
ip = 2.441e-4A
Ah = 2.243e-4C



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Low E (V) = -1.5
Init P/N = P
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Segment = 10
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4

Segment 1:
Ep = 1.334V
ip = 5.860e-5A
Ah = 6.902e-5C

Segment 2:
Ep = -0.655V
ip = -1.287e-5A
Ah = -1.239e-5C

Segment 3:
Segment 4:
Segment 5:
Segment 6:
Segment 7:
Segment 8:
Segment 9:
Segment 10:

When the multiple scan cyclic voltammogram of phenol is analyzed the sensing of peak potential with an appropriate peak current value appears during its first segment. This peak current hub disappears in the subsequent segments. This characteristic observation is indicative of the fact that only the initiation of the reaction has occurred which have propagated to a conducting polymer film of phenol, because of the coating of this film no peak current is realized, at the peak potential in the subsequent segments.

CONCLUSION

Cyclicvoltammetric studies on selective aromatic systems with 1^0, 2^0 and 3^0 alcohols reveal an adsorption controlled electrode process with ECE mechanism. The cyclic voltammograms reveal the participation of aromatic ring in the first electron transfer. Diversified behavior with changes in Substrates was identified from multiscans and scan rate variation studies.

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