Anodic Coupling of Aniline

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Summary: Electrochemical behavior of aniline at platinum electrode was studied in acetonitrile. The results are compared with those of carbon paste electrode. Our results show little variation from the carbon paste electrode when the picric acid / picrate are present in the setup while without picric acid / picrate our results are comparable to that of the carbon paste electrode. Mechanism can be diagnosed from number of possibilities by taking the consideration of the slopes -dEp / dlogC and dEp / dlogv and dEp / dlogX by comparing the theoretical and experimental values.
Results are also compared with the slopes obtained in distilled water and in 9:1 acetonitrile /water, shows great variation.

Introduction

Factors Affecting Electro-Polymerization of Aniline

A number of conjugated polymer systems could be generated via electropolymerization, including polyanilines. The process occurs anodically via radical coupling with aniline nitrogen playing vital role. The proposed elctropolymerization mechanism involved removal of a nitrogen lone pair electron, followed by a chemical step resulting in radical contribution at the 2-position of the thiophene ring 1-2. The electropolymerization of aniline-functionalized carbon nanotubes and thioaniline-modified glucose oxidase on a thioaniline monolayer-modified Au electrode has also been reported yielding a composite cross-linked by the redox-active bis-aniline units [3].

A bis-aniline cross-linked Au nanoparticle composit was electropolymerized onto the Au surface by Riskin et al and on a rough Pt film supported Au by Frasconi et al. The electrochemical oxidation of the bis-aniline units to the quinoid state released protons to the electrolyte solution, while the reduction of the quinoid bridges resulted in the uptake of protons from the electrolyte. In addition, trinitrotoluene imprinted Ah composites revealed high selectivity [4-5].

A number of researches have been made on the factors affecting the rate of electropolymerization of aniline and its derivatives. Ferrocenesulfonic acid is shown to play an important role in increasing the rate with a rather high electrochemical activity of the produced polyaniline [6]. Electropolymerization of aniline has also been investigated in the presence of various organic substances [7-9], surfactant [10], ions and inorganic acids [11,12], light [13] and in aqueous solutions at a wide pH range [14].

The synthesis and electrochemical properties of aniline and aniline like molecules substituted with ferrocene was described by Horwitz. All compounds polymerized upon electrochemical oxidation of the aromatic amine portion of the complex in a CH_3CN solution containing Bu_4NClO_4 as supporting electrolyte. The polymers, were characterized by cyclic voltammetry and showed well defined couples for ferrocence with no electrochemical indication about the electroactive nature of polymer backbones [15]. Mechanistic study of the initial stage of electropolymerization of aniline and substituted aniline was performed in aqueous solution and in acetonitrile respectively [16-18]. Electroless polymerization of aniline on platinum was investigated for polyaniline micro- and nano-structuring into practical electronic devices and adapted to estimate its usefulness in a lithographic process [19].

Activity of Ferrocene

There continues to be considerable effort directed at electron transfer reaction for ferrocene at solid electrodes. Recent work addresses the kinetics of the heterogeneous electron transfer in oxidative electrochemistry of ferrocene [20]. On the other hand, ferrocene has been used as a probe to investigate dynamics of micro-heterogeneous and micellar systems and redox reactions of organic substrates [21-23].

Ferrocene-ferrocenium electrode process at platinum in acetonitrile has been used to compare

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two and three-electrode configurations [24]. Most work involving ferrocene as redox couple in electrochemical investigations gave same results in the presence and absence of oxygen [25-26].

The previous studies of aniline have been made on carbon paste electrode but on platinum they are very rare. We studied aniline on platinum in comparison with carbon paste.

This work reports the catalytic activity of ferrocene for organic compounds.

Result and Discussion

Electrolytic Studies

Current Potential Curves

In case of electrolytic studies a wide separation of currents between background (acetonitrile containing sodium perchlorate) and the solution of ferrocene(in background) was observed, the linear rise at about 0.4 V indicates formation of ferrocenium while the decomposition of acetonitrile is not significant until after about 2.5 V. A plateau appears in the same curve extending from 1 to 2 V, with a slight downward slope, represents limiting current for one electron oxidation of ferrocene.

Whereas oxidation of aniline, in case of electrolytic experiments exhibits a plateau beyond 1 V and when the ferrocene added the current falls, the falling part is consistent with the coating of the platinum surface with products of ferrocene anodic oxidation in acetonitrile [26] containing dissolved oxygen. The rising part of the same curve beginning at about 2 V is indicative of the oxidation of acetonitrile. A similar value for the oxidation of acetonitrile is revealed under potentiostatic conditions Fig. 1, as noted from the rising part of a normal pulse voltammogram, not shown here, recorded for the background electrolyte. In case of a mixture of aniline and ferrocene two well-separarted oxidation processes were observed under potentiostatic conditions, as evident from the cyclic voltammogram, Fig. 1.

In case of ethanol, two well-separated oxidation processes were revealed for ferrocene [27]. The value of apparent electrochemical reaction order involving the second (higher potential) oxidation of ferrocene was found to be 2, as evaluated from anodic current vs. concentration of ferrocene plot, Fig not shown [28].

Voltammetric Studies

Studies of Aniline in Presence of Ferrocene

Fig. 1 shows the difference in the cyclic voltammetric anodic peak current with and without an internal standard: ferrocene. The enhancement of oxidation current of aniline in the presence of internal standard can be observed rather than in the case of absence. The peak current of the cyclic voltammogram without internal standard ferrocene is -2.033 μA while the peak current for the cyclic voltammogram with internal standard: ferrocene is -2.844 μA and difference of peak currents of the both peaks shows that the increase in current in the presence of an internal standard : ferrocene is 10-20% Fig. 1.

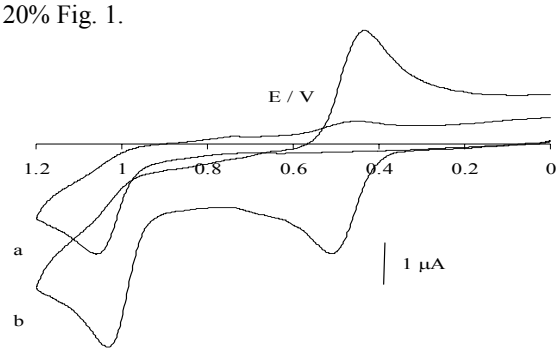

Fig. 1: Cyclic voltammogram of (a) 0.66 mM aniline (b) 0.66 mM aniline in presence of aninternal standard: 0.44 mM ferrocene. Containing 0.1 M sodium perchlorate in acetonitrile at platinum electrode (0.00785 cm^2) versus silver /silverchloride, chloride reference electrode. Scan rate 0.1 Vs^{-1}.

Scan Rate Dependence of Aniline in the presence of Internal Standard: Ferrocene

Overlay of cyclic voltammograms of scan rate dependence of 0.66 mM aniline in the presence of internal standard: 0.44 mM ferrocene reveals that current increases with the scan rate.

Influence of scan rate on anodic peak current of 0.66 mM aniline in the presence of an internal standard: 0.44 mM ferrocene was studied. Peak potential for aniline is shifted to more positive values when the scan rate in cyclic voltammetry was increased. Such behavior is consistent with the occurrence of chemical reactions following a reversible electron transfer step [29].

The influence of square root of scan rate on cyclic voltammetric anodic peak current for the oxidation of 0.6 mM aniline in the presence of an

internal standard: 0.44 mM ferrocene shows linear trend with the slope, intercept and regression y = 9.0164x + 0.0313, R^2 = 0.994, which means that the process is diffusion controlled (Fig. not shown).

Influence of log of scan rate on cyclic voltammetric half peak potential for the oxidation of 0.6 mM aniline in the presence of an internal standard: 0.44 mM ferrocene exhibit linear trend with the slope, intercept and regression y = 0.0221x + 1.0062, R^2 = 0.9916.

The influence of log of scan rate on cyclic voltammetric peak potential for the oxidation of 0.6 mM aniline in the presence of an internal standard: 0.44 mM ferrocene is evident from Fig. 2. The slope, intercept and regression of the almost all the readings are y = 0.0338x + 1.0608, R^2 = 0.9768. While the Fig. shows two linear portions and the slope, intercept and regression of the first linear portion are y = 0.011x + 1.0429, R^2 = 0.9132 and that of second linear portion are y = 0.038x + 1.0607, R^2 = 0.9851.

It was observed that the current function of aniline increased with increasing scan rate in the presence of an internal standard: ferrocene, in contrast to the aniline itself [29] because ferrocene forms filming at the surface of platinum.

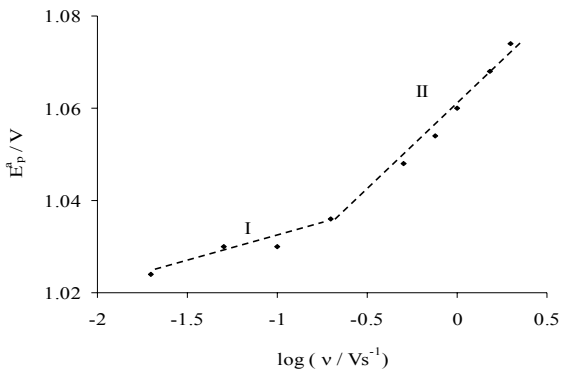

Fig. 2: Influence of log of scan rate (0.02-2 Vs^{-1}) on cyclic voltammetric anodic peak potential for the oxidation of 0.6 mM aniline in the presence of an internal standard: 0.44 mM ferrocene containing 0.1 M sodium perchlorate in acetonitrile at platinum electrode (0.00785 cm^2) versus silver/silverchloride, chloride reference electrode. (I) y = 0.011x + 1.0429, R^2 = 0.9132 (II) y = -0.0622x + 1.0408, R^2 = 0.9894.

The slopes obtained from platinum electrode are compared (Table-1) with that of carbon paste electrode [29], they show a little variation due to the presence of an internal standard: ferrocene

Concentration Dependence of Aniline

The overlay of concentration dependence cyclic voltammograms of aniline at 0.1 Vs^{-1} shows the current increases as the concentration increase.

The influence of concentration on cyclic voltammetric anodic peak current for the oxidation of aniline at a scan rate of 0.1 Vs^{-1} exhibit the linear trend with the values of slope, intercept and regression y = 3.6384x + 0.1182, R^2 = 0.996, indicating the direct proportionality of anodic current with concentration.

The influence of log of concentration on cyclic voltammetric $i^a_pC^{-1}$ for the oxidation of aniline at a scan rate of 0.1 Vs^{-1} shows inclined behaviour.

Fig. 3 shows the influence of log of concentration on cyclic voltammetric peak potential for the oxidation of aniline. The slope, intercept and regression of the almost all the readings are y = -0.034x + 1.0457, R^2 = 0.9746 (Table-1). While the Fig. shows two linear portions and the slope, intercept and regression of the first linear portion are y = -0.0294x + 1.0498, R^2 = 0.999 and that of second linear portion are y = -0.0622x + 1.0408, R^2 = 0.9894 (Table-1).

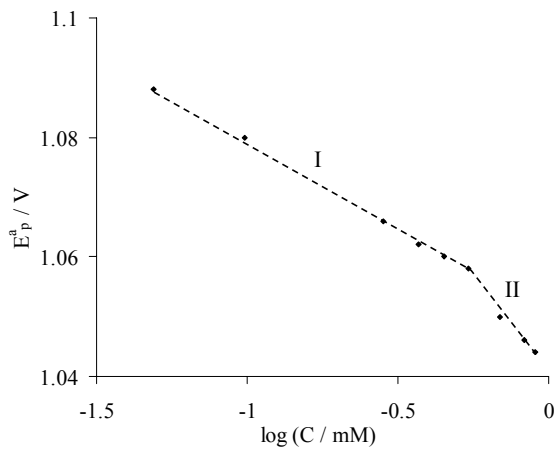

Fig. 3: Influence of log concentration (0.049-0.901 mM) on cyclic voltammetric anodic peak potential for the oxidation of aniline at a scan rate of 0.1 Vs^{-1} in acetonitrile containing 0.1 M sodium perchlorate at platinum electrode (0.00785 cm^2) versus silver/silverchloride, chloride. (I) y = -0.0294x + 1.0498, R^2 = 0.999 (II) y = -0.0622x + 1.0408, R^2 = 0.9894.

The influence of log concentration on cyclic voltammetric anodic half peak potential for the oxidation of aniline at a scan rate of 0.1 Vs^{-1} shows two types of linear behavior one with the value y = -0.0237x + 0.9927, R^2 = 0.9945 up to the range of (0.049-0.19mM) and other with the value y = -0.0465x + 0.9901, R^2 = 0.9675, up to the range of (0.28-0.901mM) are mentioned in Table-2.

Scan Rate Dependence of Aniline

Influence of scan rate on anodic peak current of 0.66 mM aniline reveals, as the scan rate increases the anodic peak current also increases while values of peak potential, half peak potential and E^a_p - $E^a_{p/2}$ almost remains constant.

The overlay of scan rate dependence cyclic voltammograms of 0.6 mM aniline shows as the scan rate increases the current increase (Fig. not shown).

The influence of square root of scan rate on cyclic voltammetric anodic peak current for the oxidation of 0.6 mM aniline shows linear trend with the values of slope, intercept and regression y = 6.5509x - 0.0548, R^2 = 0.9975, which means that the process is diffusion controlled.

The influence of log of scan rate on cyclic voltammetric peak potential for the oxidation of 0.6 mM aniline is shown in Fig. 4. The Fig. clearly shows two linear portions and the slope, intercept and regression of the first linear portion are y = 0.0122x + 1.0674, R^2 = 0.9761 and that of second linear portion are y = 0.0368x + 1.0833, R^2 = 0.9648 (Table-1).

Influence of log of scan rate on cyclic voltammetric half peak potential for the oxidation of 0.6 mM aniline with the slope, intercept and regression y = 0.0294x + 1.0235, R^2 = 0.9839.

It was observed that the current function of aniline decreased with increasing scan rate [29].

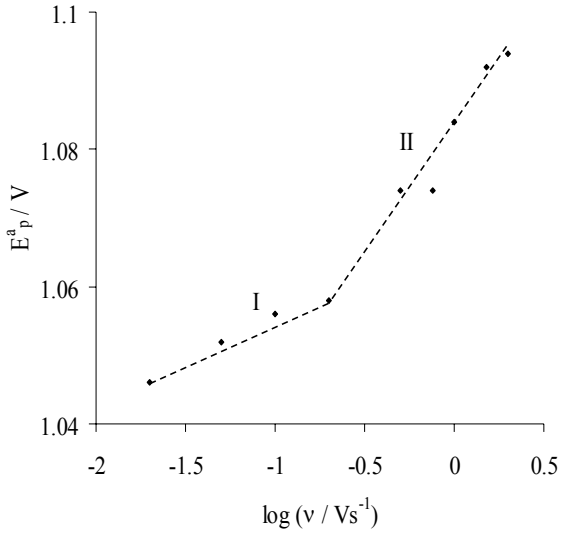

Fig. 4: Influence of log of scan rate (0.02-2 Vs^{-1})on cyclic voltammetric anodic peak potential for the oxidation of 0.6 mM aniline containing 0.1 M sodium perchlorate in acetonitrile at platinum electrode (0.00785 cm^2) versus silver/ silverchloride, chloride reference electrode. . (I) y = 0.0122x + 1.0674, R^2 = 0.9761(II) y = 0.0368x + 1.0833, R^2 = 0.9648.

Table-1: Following are the voltammetric characteristics of aniline[a] in pure acetonitrile.

Compound	Method/Medium/Electrode	dE_p/dlog CmV	dE_p/dlog νmV	$dE_{p/2}$/dlog CmV	$dE_{p/2}$/dlog ν	Ref.
Aniline	C.V/ Acetonitrile /Platinum	-34.0[b] -29.4[c] -62.2[d]	24.6[e] 12.2[f] 36.8[g]	-30.7[h] -23.7[i] -46.5[j]	24.6[k] 21.1[l] 29.4[m]	Our Work
Aniline	C.V/ Acetonitrile /Platinum Picric Acid:Picrate 1:1	-13.3[p] -13.3[q] -28.9r	36.7[s] 24.8[t] 63.7[u]	35.6[v] 31.5[w] 20.6[x]	28.6[s] 20.5[t] 43.5[u]	Our Work
Aniline	C.V/ Acetonitrile /Platinum Picric Acid:Picrate 9:1	115.6[y]	39.0[z] 28.9[ab] 55.4[ac]	132.3[y]	27.6[z] 26.0[ab] 30.5[ac]	Our Work
Aniline	C.V/ Acetonitrile /Platinum C.V/ Phosphate buffer/Carbon paste	-34.0	26.0			(Rusling et al., 1984)

[a]All slopes in mV per 10-fold change of the independent variable. Values given are determined from linear regression analysis. Scan rates for concentration dependences were 100 mV s^{-1};
[b]Concentration range (0.049-0.90 mM); [c]Concentration range (0.049-0.19mM); [d]Concentration range (0.28-0.901mM)
[e]Scan rate range (0.01 – 2 V/s); [f]Scan rate range(0.02 – 0.2 V/s); [g]Scan rate range (0.2 – 2 V/s)
[h]Concentration range (0.049-0.90 mM); [i]Concentration range (0.049-0.19mM); [j]Concentration range (0.28-0.901mM)
[k]Scan rate range (0.01 – 2 V/s); [l]Scan rate range(0.02 – 0.2 V/s); [m]Scan rate range (0.2 – 2 V/s)
[n]Scan rate range (0.01 – 2 V/s); [o]Scan rate range(0.01 – 0.5 V/s)
[p]Concentration range (0.005-1.364 mM); [q]Concentration range (0.918-1.364 mM); [r]Concentration range (0.005-1.364 mM)
[s]Scan rate range (0.05 – 10 V/s); [t]Scan rate range(0.05 – 1.5 V/s); [u]Scan rate range (1.5 – 10 V/s)
[v]Concentration range (0.005-1.364 mM); [w]Concentration range (0.005-1.078 mM); [x]Concentration range (1.078-1.364 mM) [y]Concentration range (0.247-1.496 mM);
[z]Scan rate range (0.025 – 10 V/s); [ab]Scan rate range(0.025 – 0.750 V/s); [ac]Scan rate range (0.750 – 10 V/s)

At C< 0.2 mM for aniline gives 23.7 mV/log c (Table-1). As the concentration of the aniline was increased, $dE_{p/2}$ shifted to more negative values by an average of 46.5 mV/log c (Table-1) for aniline. These shifts are consistent with the occurrence of the EC^2 mechanism [30].

Studies of Aniline in Picric Acid and Potassium Picrate

Table-2 shows dependence of potentials of oxidation peak of aniline on different buffer compositions at platinum (0.00785 cm^2) electrode.

Table-2: Dependence of potentials of oxidation peak of aniline on buffer composition.

Buffer Comp./ [HA]:[A^-]	Aniline	$\Delta E_{p/2}$
$E_{p/2}$ / V vs. Ag/AgCl,Cl^- (saturated)		
9:1	0.954	-0.02
8:2	0.983	0.003
6:4	0.98	-0.011
5:5	0.991	0.052
4:6	0.939	-0.016
2:8	0.955	-0.006
1:9	0.961	0.961

Experimental

Chemicals

Ferrocene (assay > 98% Fluka), sodium perchlorate monohydrate (E-Merk Germany), acetonitrile HPLC grade (assay 99.9 %+water 0.02 % Riedel-de Haen), aniline (Fluka 98%HPLC grade) and picric acid (B&H of analytical grade were used. Potassium picrate was synthesized in laboratory. Solutions were not purged free of oxygen.

Working Electrode

Platinum disk of was used as working electrode. Polishing of the platinum working electrode was done on a nylon-texture synthetic cloth pad soaked with γ-alumina (0.05micron) slurry in water. Polishing was followed by thorough rinsing with triple distilled water.

Electrolytic Studies

A home-built power supply unit was used to record manually polarization curves at a platinum semi-micro disk ($8x10^{-4}$ cm^2) anode, with a platinum short-wire cathode serving also as a quasi reference electrode in a two-electrode configuration.

Cell Configuration for Potentiostatic Studies

All experiments were performed in a three-electrode cell containing platinum disk working electrode of area 0.00785 cm^2, platinum short-wire or platinum spiral counter electrode and silver/silver chloride, chloride reference electrode.

Potentiostatic Studies

Voltammetry was carried out using EG & G, Princeton Applied Research Corp, Versastat II. All experiments were performed in a three-electrode cell containing platinum semi-micro disk (0.00785 cm^2) working electrode, platinum wire counter electrode and a silver/silver chloride, chloride reference electrode. Data was acquired using M270 Electrochemistry Research Software on a dedicated P II micro–processor coupled to the potentiostat. Background electrolyte was sodium perchlorate dissolved in acetonitrile.

Three set of experiments were performed:

a) Studies of aniline in presence of an internal standard: Ferrocene.
b) Studies of aniline.
c) Studies of aniline in picric acid and potassium picrate.

Conclusions

Electrolytic Studies

(1) Under electrolytic conditions, decomposition potentials of a solvent in two-electrode and three-electrode configurations in case of simple charge transfer, such as oxidation of ferrocene, show marginal correlation. It was noted that acetonitrile oxidizes at 2.4 V in electrolytic process whereas in potentiostatic process the potential for its decomposition was about half volt lower. In case of aniline the two configurations do not manifest similar behavior.

(2) Under electrolytic conditions homogeneous catalysis of aniline driven by the ferrocinium formed in the electrode reaction cannot be ruled out [31]. On the other hand, voltammetric results seem to indicate otherwise.

Voltammetric Studies

The results of aniline at platinum electrode are comparable to that of at carbon paste electrode.

It is obvious from the Figures, and statistical data also shows that the current of cyclic voltammogram of aniline in the presence of an internal standard: ferrocene is greater than the current of aniline in the absence of ferrocene. This clearly shows that ferrocene act as a catalyst for the oxidation of aniline. So the presence of ferrocene can increase the rate of reaction by facilitating the electron transfer process in irreversible systems.

Our system is non-aqueous so instead of considering buffered or unbuffered mechanisms we will consider either mechanism [32].

Mechanism can be diagnosed from number of possibilities (Scheme 1-2) by taking the consideration of the slopes $-dE_p$ / dlogC and dE_p / dlogν and dE_p / dlogX̃T he comparison of theoretical and experimental values for the scheme 1-2 is given in Table-3.

Radical-Substrate Coupling

$$\textbf{Step 1:}\quad HA \rightleftharpoons HA^{\cdot+} + e^-$$
$$\textbf{Step 2:}\quad HA^{\cdot+} + HA \rightleftharpoons D^{\cdot+}$$
$$\textbf{Step 3:}\quad D^{\cdot+} + BH \rightleftharpoons DH^{\cdot} + B^+$$
$$\textbf{Step 4:}\quad DH^{\cdot} \rightleftharpoons DH^+ + e^-$$
$$\textbf{Step 5:}\quad BH^+ + BH \rightleftharpoons DH_2 + B^+$$

Scheme 1: Radical-Substrate Coupling, rds Step 3.

$$\textbf{Step 1:}\quad HA \rightleftharpoons HA^{\cdot+} + e^-$$
$$\textbf{Step 2:}\quad HA^{\cdot+} + HA \rightleftharpoons D^{\cdot+}$$
$$\textbf{Step 3:}\quad D^{\cdot+} + BH \rightleftharpoons DH^{\cdot} + B^+$$
$$\textbf{Step 4:}\quad DH^{\cdot} + HA^{\cdot+} \rightleftharpoons DH^+ + HA$$
$$\textbf{Step 5:}\quad BH^+ + BH \rightleftharpoons DH_2 + B^+$$

Scheme 2: *Radical-Substrate Coupling, rds Step.*

Table-3: Comparison of theoretical and experimental values of slopes of aniline[a] for scheme-2 and 3.

	r.d.s	$-dE_p$ / dlog CmV	dE_p / dlog νmV	dE_p / dlogXmV
Theoretical Value [33-34]	3	29.6	29.6	29.6
Experimental Value Without Picric acid:Picrate		29.4[c]	24.6[e]	----
Experimental Value With Picric acid:Picrate1:1		-28.9[r]	24.8[t]	25.3[ae]
Experimental Value With Picric acid:Picrate 9:1		115.6[y]	28.9[ab]	25.3 [ae]

[a,,c,e,r,t,y,ab,ae] Values are given in Table-1, [ae] Picric acid:Picrate(4:6,2:8,1:9)

By comparing the slopes of aniline in pure acetonitrile with results obtained in distilled water and in 9:1 acetonitrile/water, shows great variation as shown in Table-4 and 5.

Table-4: Following are the voltammetric characteristics of aniline[a] in distilled water.

Compound	Method /Medium/Electrode	dE_p/dlog CmV	$dE_{p/2}$/dlog CmV
Aniline	C.V/ water /Platinum Picric Acid:Picrate 9:1	-184.46[b] -44.732[c] -371.63[d]	-202.39[b] -36.06[c] -411.04[d]
Aniline	C.V/ water /Platinum Picric Acid:Picrate 1:1	-150.98[b]	-161.29[b]

[a]All slopes in mV per 10-fold change of the independent variable. Values given are determined from linear regression analysis. Scan rates for concentration dependences were 100 mV s^{-1}; [b]Concentration range (0.2-2 mM); [c]Concentration range (0.2-0.8mM); [d]Concentration range (0.8-2mM)

Table-5: Following are the voltammetric characteristics of aniline[a] in 9:1 acetonitrile/water.

Compound	Method /Medium/Electrode	dE_p/dlog CmV	$dE_{p/2}$/dlog CmV
Aniline	C.V/ 9:1 acetonitrile/water /Platinum Picric Acid:Picrate 9:1	-223.79[b]	-173.86[b] -21.969[c] -284.19[d]
Aniline	C.V/ 9:1 acetonitrile/water /Platinum Picric Acid:Picrate 1:1	-7.731[b] -11.145[e] -62.362[f]	-13.346[b] -9.1747[g] -35,281[h]

[a]All slopes in mV per 10-fold change of the independent variable. Values given are determined from linear regression analysis. Scan rates for concentration dependences were 100 mVs^{-1};[b]Concentration range (0.2-2 mM); [c]Concentration range (0.2-0.8mM); [d]Concentration range (0.8-2mM);[e]Concentration range (0.2-1.4 mM); [f]Concentration range (1.6-2mM); [g]Concentration range (0.2-1.2mM) ; [h]Concentration range (1.2-1.8mM);

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