Asian Journal of Chemistry; *Vol. 24, No. 6 (2012), 2472-2478*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Electrochemical Behaviour of *para*-Amino benzoic acid and its Cadmium Complex

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(*Received*: 21 April 2011; *Accepted*: 9 January 2012) AJC-10925

The electrochemical behaviour of *p*-amino benzoic acid (PABA) has been investigated at glassy carbon electrode by cyclic voltammetry in aqueous methanolic medium (1:1, v/v). The effects of pH, sweep rate and concentration have been studied. The reduction process of *p*-amino benzoic acid has been found to be irreversible which involves four electron transfers. The kinetic parameters have been evaluated. Also, the electrode reaction mechanism is proposed and discussed. Controlled current electrolysis of *p*-amino benzoic acid was also carried out using stainless steel (SS-316) electrodes in acidic medium. The product was isolated, purified and characterized by combined application of chromatographic and spectroscopic techniques. The electrochemical reduction behaviour of synthesized cadmium complex with *p*-amino benzoic acid in DMF has also been studied cyclic voltammetrically using tetrabutylammonium perchlorate as supporting electrolyte. The reduction is quasi-reversible and involves two electrons transfer. The complex was characterized on the basis of elemental analysis, IR and ^{1}H NMR spectra.

Key Words: Electrochemical, *p*-Amino benzoic acid, Cadmium(II), Complex.

INTRODUCTION

Amino benzoic acids (ABA) are widely used as additives in many products such as drugs, corrosion inhibitors, sunscreen products and other skin care products. *p*-Amino benzoic acid (PABA), also called vitamin B_x or bacterial vitamin H, has been used in dermatomyositis[1], infertility (female)[2], pemphigus[3], peyronie's disease[4], scleroderma[5] and vitiligo[6]. It helps to protect skin from sunburn and cancer from excess ultraviolet light exposure[7]. *p*-Amino benzoic acid is also used in repigmentation of hair caused by either stress or a nutritional deficiency[8]. It supports folic acid production by the intestinal bacteria and has wide applications in the manufacture of esters and azo dyes. All the three isomers of amino benzoic acid inhibit the corrosion of mild steel both in HC1 and H_2SO_4 in the order *ortho* > *meta* > *para*[9]. A survey of literature reveals the applications of amino benzoic acid as poly(amino benzoic acid) modified electrode and electro-synthesis of conducting polymers derived from amino benzoic acids[10-12].

Due to great applicability of *p*-amino benzoic acid and in order to bring better understanding about its electrochemical reactions, the aim of this work is to study the voltammetric behaviour of *p*-amino benzoic acid using cyclic voltammetry in acidic, neutral and basic medium and the electrochemical reduction at stainless steel electrodes in acidic medium using controlled current electrolysis. Stainless steel electrodes have been used in our laboratory for the electrochemical reduction of some carbonyl compounds[13-16].

Cadmium is a toxic element and may compete with Zn(II), Cu(II), Ca(II) and Fe(II) for the active site in important biological molecules[17]. The research of the new drugs capable of treating heavy metals poisoning including cadmium also involves investigation of metal complexes. Thus, it seems important to study Cd(II) complexes and compare them with analogous complexes of other metals.

EXPERIMENTAL

All chemicals used in the present investigation were of analytical grade and all the solvents were dried and then distilled out. Doubly distilled water was used to prepare the required solutions. Potassium chloride was used as supporting electrolyte for electrochemical studies. A series of Britton-Robinson buffer solutions was prepared to maintain the pH of the solutions.

Synthesis of the metal complexes: Cadmium complex of *p*-amino benzoic acid was synthesized by dropwise addition of aqueous solutions of cadmium chloride (1 mM) to hot aqueous-methanolic solution of sodium salt of *p*-amino benzoic acid (2 mM) in the molar ratio 1:2. The mixing of the solution yielded the solid metal complex, which was filtered, washed with water several times and dried in a vacuum desiccator over anhydrous calcium chloride. Purity of the complexes was checked by TLC. Yield 52 %; anal. calcd. (%) for $C_{14}H_{12}N_2O_4Cd$: C, 43.7; H, 3.12; N, 7.28; Cd, 29.24; found (%): C, 48.09; H, 2.92; N, 8.13; Cd, 28.16; m.p. 157 ºC.

Physical measurements: Elemental analyses (C, H, N) of cadmium complex of *p*-amino benzoic acid was performed at Central Drug Research Institute, Lucknow. The melting point was determined in open capillary tubes using Prefit model. The magnetic susceptibility measurement has been done on the EG & G Princeton Applied Research Co. (PARC) make vibrating sample magnetometer (VSM) model 155 at 25 ºC in field up to 8.5 k De. The molecular weight was determined by cryoscopic method using glacial acetic acid as solvent. The spectra of *p*-amino benzoic acid and its cadmium complex were recorded in KBr wafer phase with a system 8400S model FTIR spectrophotometer (Shimadzu) and 300.4 MHz FT NMR spectrometer (model Jeol AL 300), using $CDCl_3$ as solvent and TMS as an internal standard. The model ECDA-001 basic electrochemistry system was used to record cyclic voltammograms having three electrode cell assembly with glassy carbon as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. BR series of buffer solutions were used to maintain the pH of the solutions (3.0, 5.0, 7.0, 9.0 and 11.0). A digital pH meter (ELICO Digital pH Meter 100) was used to measure the pH of solutions. The electrolyte solutions were purged with purified nitrogen for 15 min prior to each measurement. All the experiments were carried out at the ambient temperature (25 ºC). The area of the electrode was calibrated using 10 mM $K_4Fe(CN)_6$ in 0.1M KCl by recording the current voltage curve. From the cyclic voltammetric peak current (17.3 μA), it was calculated[18] by using the following equation:

$$i_{pa} = (2.69 \times 10^5)\, n^{3/2} A D^{1/2}\, \nu^{1/2} C^* \quad (1)$$

where n = number of electrons transferred, A = area of the electrode, D = diffusion coefficient (6.538×10^{-6} cm^2 s^{-1}), ν = sweep rate (0.05 V s^{-1}) and C* = concentration of electro active species (10 mM). The area of the electrode was found to be 0.058 cm^2.

Controlled current electrolysis was carried out by employing galvanostat, assembled by CDPE (Center for Development of Physics Education, University of Rajasthan, Jaipur, India). Stainless steel (SS-316) electrode was used as cathode as well as anode. A two-limbed H-cell was used as reaction vessel. The solution was stirred by a Remi 2LH hot plate cum stirrer throughout the electrolysis. The electrolysis of *p*-amino benzoic acid (0.1 M) was carried out at constant current (1 amp.) in acidic medium (pH = 1.7) using glacial acetic acid and CH_3COONa (1 M) for 7 h. After electrolysis, extraction with diethyl ether followed by crystallization gave the reduced product. The product was characterized by spectral analysis and TLC.

RESULTS AND DISCUSSION

The white coloured Cd complex of the *p*-amino benzoic acid is air- and light-stable, nonhygroscopic and insoluble in water, benzene, petroleum ether, methanol and ethanol. They are slightly soluble in chloroform and readily soluble in dichloromethane, acetic acid, DMF and DMSO. The analytical data of the complex correspond well with the formula CdL_2. Magnetic susceptibility measurement shows that the complex is diamagnetic.

Spectral characterization: In order to ascertain the mode of bonding of *p*-amino benzoic acid to the metal ion, the IR spectra of the free ligand was compared with their metal complex. The IR spectrum of the *p*-amino benzoic acid shows absorption band at 3440 cm^{-1} ν(N-H) asymm. and 3350 cm^{-1} ν(N-H) symm. In the spectrum of the Cd(II) complex, there is an appreciable shift towards lower frequency in the ν(N-H) region was observed, indicating the participation of the nitrogen in chelation.

In the free ligand, strong absorption bands are observed around 1685 and 1340 cm^{-1}, due to ν(C=O) stretching and δ(O-H) deformations of carboxylic acid, respectively. These bands are replaced with new bands in the ranges of 1553-1540 and 1388-1372 cm^{-1} corresponding to ν(COO$^-$) asymmetric and ν(COO$^-$) symmetric vibrations in the spectrum of the complex, supporting the fact that the oxygen atom of the carboxylic acid is participating in chelation[19,20]. The coordination of the oxygen atom of the ligand to cadmium is also indicated by the disappearance of a broad band in the range of 3300-2500 cm^{-1} ν(O-H). The metal complex show new bands in the regions 480-450 and 400-350 cm^{-1} which are due to the formation of Cd-N bond and Cd-O bonds respectively[21]. The involvement of *p*-amino benzoic acid in polymer structure and as a bridging ligand between Cd(II) metal ion is also evident from IR spectral data as reported in literature[22].

In ^{1}HNMR spectra, the chemical shift observed for the OH proton in *p*-amino benzoic acid (10.2 and 10.7 ppm) was not observed in its Cd complex. This confirms the participation of the hydroxyl oxygen in the C-O-Cd bond. The multiplets of aromatic protons appeared within the range 7.1-8.0 ppm and they were not affected by chelation.

Electrochemical behaviour: The cyclic voltammograms of *p*-amino benzoic acid were recorded at glassy carbon electrode using Britton-Robinson buffer solution with an initial potential (E_i) of 1.4 V and switching potential (E_s) of -1.3 V at different pH (3.0, 5.0, 7.0, 9.0 and 11.0) using KCl as supporting electrolyte in methanol/water mixture (1:1). *p*-amino benzoic acid gave a well-defined reduction wave with two cathodic peaks in all the pH range studied. The first cathodic peak, p_{1c} in the potential range 0.32 V to -0.06 V and corresponding anodic peak, p_{1a} between 0.42-0.03 V can be attributed to the reduction of -C=N- group (system I). Second reduction peak, p_{2c} in the potential range -0.57 V to -0.65 V (corresponds to no anodic peak, system II) may be also attributed to the reduction of >C=O moiety to -CH-OH moiety for all the pH range studied (Fig. 1). Double cyclic voltammograms were also recorded to monitor the fate of products generated in first cycle. The voltammetric data of *p*-amino benzoic acid is summarized in Table-1.

The two-electron nature of all above peaks has been established by comparing its cyclic voltammograms with similar peaks displayed by N-aryl benzohydroxamic acids having functional group similar to that of *p*-amino benzoic acid after coupling (Fig. 2).

TABLE-1
EFFECT OF SWEEP RATE VARIATION ON THE CYCLIC VOLTAMMETRIC PARAMETERS FOR THE REDUCTION OF *p*-AMINO BENZOIC ACID IN AQUEOUS-METHANOLIC SOLUTION CONTAINING BR BUFFER AT 5.0 pH

ν (mVs^{-1})	System I				System II			
	E_{pc1} (mV)	E_{pa1} (mV)	ΔE_p (mV)	i_{pa1}/i_{pc1}	E_{pc2} (mV)	$E_{pc/2}$ (mV)	i_{pc2} (µA)	$i_{pc2}/\nu^{1/2}$ (µA s$^{1/2}$/mV$^{1/2}$)
75	252	311	59	0.9	-602	-481	244	28.17
100	247	316	69	0.87	-608	-484	273	27.30
200	232	332	100	0.88	-632	-496	371	26.24
300	223	335	112	0.87	-656	-502	459	26.50
400	217	340	123	0.88	-664	-504	539	26.95
500	212	343	131	0.87	-671	-507	606	27.10
700	210	349	139	0.86	-692	-511	729	27.56

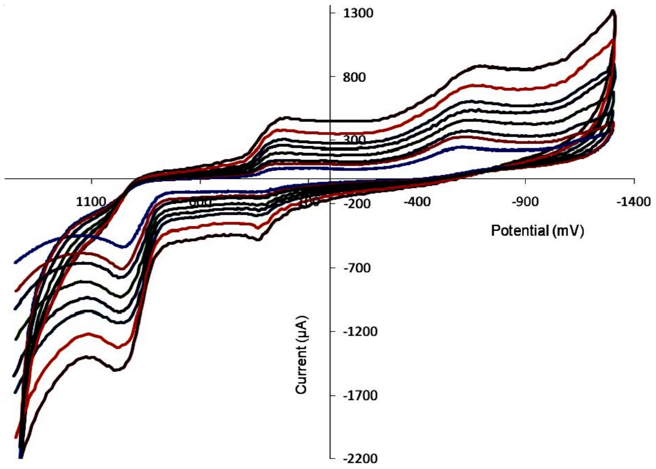


Fig. 1. Cyclic voltammograms of 0.002 M *p*-amino benzoic acid in aqueous methanolic medium at sweep rate: (1) 75, (2) 150, (3) 200, (4) 300, (5) 400, (6) 500, (7) 700, (8) 1000 mV/s at pH 5

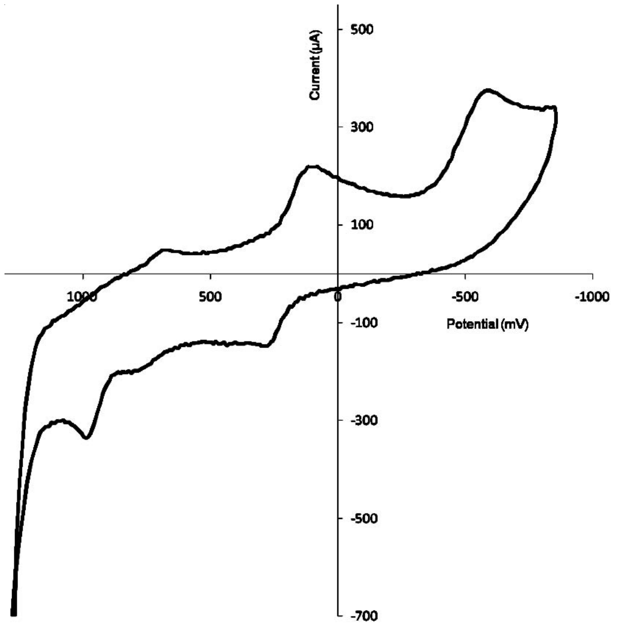


Fig. 2. Cyclic voltammogram of 0.002 M N-phenyl benzohydroxamic acid in aqueous methanolic medium at (sweep rate 200 mV/s, pH 6)

Effect of scan rate: The effect of scan rate on the peak potential and peak current of 2 mM of *p*-amino benzoic acid was studied at different scan rates in aqueous methanolic solution within the range of 75-1000 mV S^{-1} at pH 5 (Fig. 1). For the system I, the difference between the cathodic and anodic peak potentials ΔE_p is of the order 0.07-0.164 V, a somewhat large peak to peak separations in comparison to Nernstian value (0.059 V) observed for reversible electron transfer couple and the ratio of anodic to cathodic peak currents i_{pa}/i_{pc} is less than the unity, indicates the quasi-reversible nature of the couple. The criteria for quasi-reversibility of the process is further satisfied as on increasing the scan rate, a slight displacement of the cathodic and anodic peak potential values is observed toward cathodic and anodic direction respectively, leading therefore, to an increase in the potential difference, ΔE_p[23]. The cathodic peak potential of second reduction wave, p_{2c} was shifted towards more negative values as scan rate increases, indicating the irreversible nature of the electrode processes. The irreversibility was also confirmed from the linear dependence of the cathodic peak potential, $E_{p_{2c}}$ with decimal logarithm of the sweep rate[24] (Fig. 3). The small influence on current function of scan rate *i.e.*, $i_{pc2}/\nu^{1/2}$ reveals no significant adsorption at the electrode and thus the electrochemical reaction is followed by a chemical reaction (Table-1). The plots of peak currents *versus* $\nu^{1/2}$, for anodic (p_{1a}) and cathodic (p_{1c}, p_{2c}) peaks are found to be linear which is indicative of the diffusion control behaviour of the redox system[25] (Fig. 4).

Effect of pH: The influence of pH on the reduction process was examined using 2 mM *p*-amino benzoic acid in Britton-Robinson buffer at different pH values 3, 5, 7, 9 and 11. The cathodic peak potentials for the system I show considerable shift towards more negative potential with increase in pH and the peak current is varied in a nonlinear mode (Fig. 5). This indicates the participation of hydrogen ions in the electrode

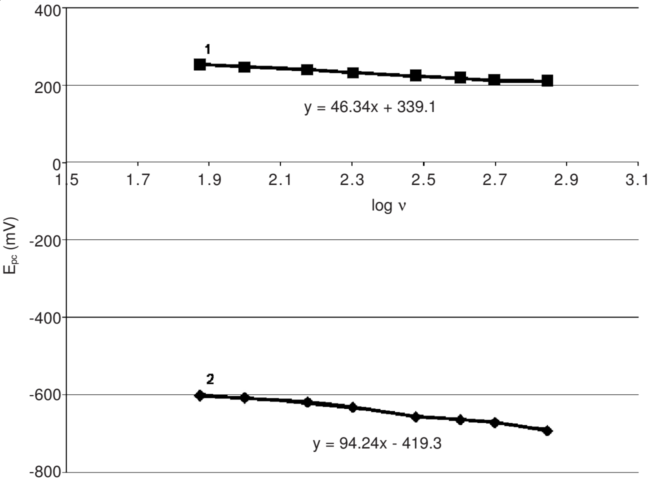


Fig. 3. Variation of the cathodic peak potential with the sweep rate (on a semi-log scale) for (1) system I, (2) system II (pH 5, concentration 0.002 M)

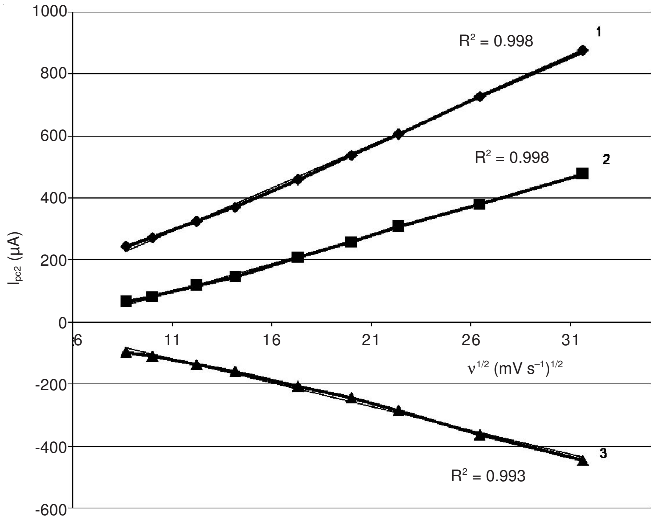


Fig. 4. Variation of the height of peak currents: (1) I_{pc2}, (2) I_{pc1}, (3) I_{pa1} for reduction of *p*-amino benzoic acid with square root of sweep rate (pH 5, concentration 0.002 M)

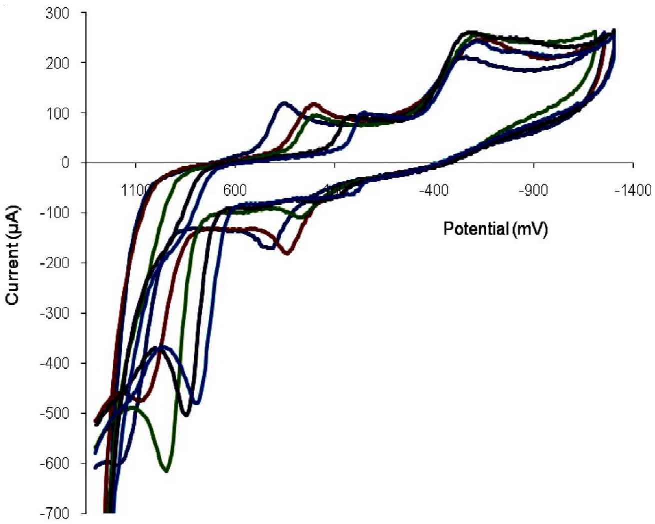


Fig. 5. Cyclic voltammograms of 0.002 M *p*-amino benzoic acid in aqueous methanolic medium at different pH: (1) 3, (2) 5, (3) 7, (4) 9, (5) 11 (sweep rate 100 mV/s)

process[26] and the decreased ease of reduction at high pH values. It can be seen from Fig. 6 that the formal potential E° (defined as average of cathodic and anodic peak potentials) of redox couple have a linear relationship with pH. The slope of the above plot was found to be approximately close to the theoretical value of -59.0 mV pH-1 at 25 ºC indicates that the number of protons participating in the electrode reaction is same as that of electrons[27]. The corresponding equation is,

$$E^o = -0.0505\ \text{pH} + 0.545 \qquad (2)$$

The reduction wave for system II presents a relationship where the peak potential is independent of pH suggesting the occurrence of an electrodic process without preprotonation reaction.

Effect of concentration: The effect of concentration was studied by recording the cyclic voltammograms at different concentration of *p*-amino benzoic acid (0.1, 0.3, 0.5, 0.75, 1.0, 1.5 mM) in aqueous methanolic solution (Fig. 7). The linear plot of cathodic peak currents, i_{p1c} and i_{p2c} *versus* concentration reveals that both currents increase with increase in concentration. This further suggests that the process is diffusion controlled[28].

Effect of substituent: In the presence of electron withdrawing and electron donating groups, reduction occurs at lower and higher potentials respectively[29]. Accordingly *p*-amino benzoic acid and benzoic acid got reduced at -715 and -652 mV (at pH 4.0 and scan rate 200 mV/s). Amino group has positive mesomeric effect (+M) which increases electron density in the aromatic ring. Thus it is more difficult to reduce *p*-amino benzoic acid than benzoic acid which is also evident from their reduction potentials (Fig. 8).

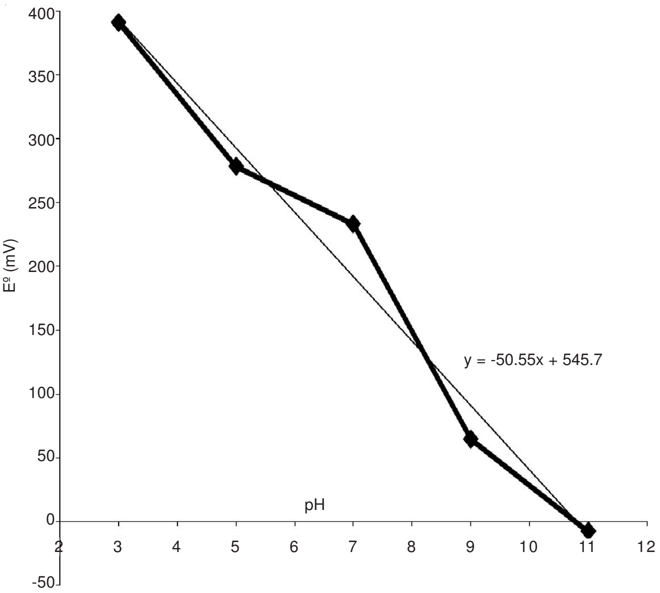


Fig. 6. Variation of the formal potential, E° with pH for system I for reduction of *p*-amino benzoic acid (sweep rate 100 mV/s, concentration 0.002 M)

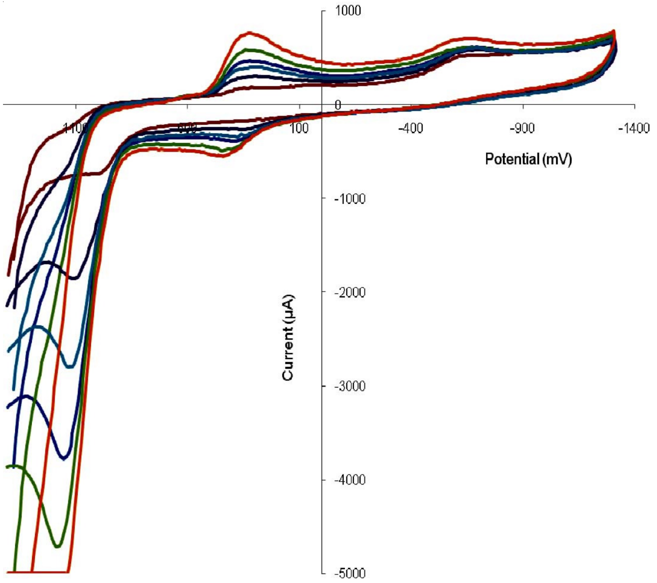


Fig. 7. Cyclic voltammograms of *p*-amino benzoic acid in aqueous methanolic medium (1:1, v/v) at different concentration: (1) 0.1, (2) 0.3, (3) 0.5, (4) 0.75, (5) 1.0, (6) 1.5 mM (sweep rate 500 mV/s)

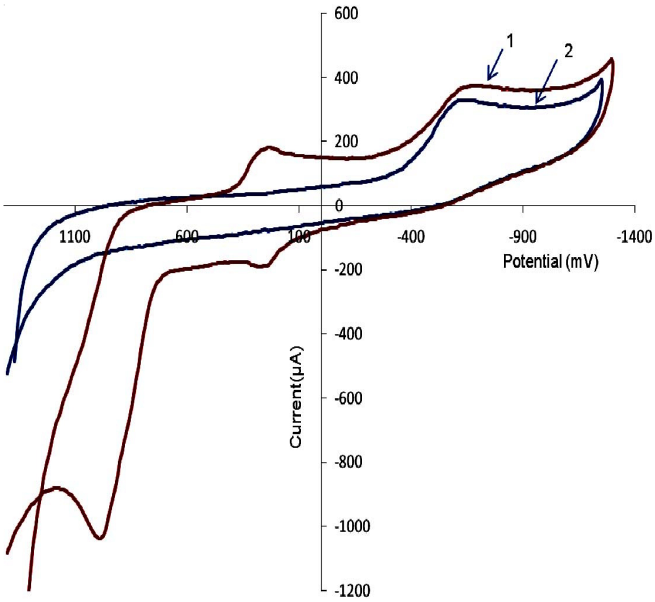


Fig. 8. Cyclic voltammograms of (1) *p*-amino benzoic acid, (2) benzoic acid in aqueous methanolic medium (1:1, v/v) (at pH 4 and scan rate 200 mV/s)

Electro-kinetic studies: The heterogeneous electron-transfer rate constant, ks for system I can be estimated from the variations of a peak separation (ΔE_p) by using an equation[30].

$$\psi = \frac{\gamma ks}{(\alpha aD)^{1/2}} \quad (3)$$

where, $\gamma = (D_O/D_R)^{1/2}$ and $a = nF\nu/RT$. Assuming that γ is *ca.* 1, the heterogeneous electron-transfer rate constant can be calculated from the slop of ψ *versus* $\nu^{1/2}$ plot according to eqn. 1. As can be seen the heterogeneous electron-transfer rate constant is determined to be 0.2455 s^{-1}. On the basis of the graph of E_{pc1} *versus* logarithm of the scan rate, the values of $\alpha = 0.63$ were calculated. For irreversible electrode reaction process II, we may use equations[30],

$$E_{pc2} = E^0 - RT/\alpha n_a F\{0.780 - \ln ks + 0.5 \ln [\gamma n_a DF\nu/RT]\} \quad (4)$$

$$E_{pc2} - E_{pc/2} = 1.857RT/\alpha n_a F = 47.7 \text{ mV}/\gamma n_a \quad (5)$$

where E^0 is the formal potential and $E_{p/2}$ is the half wave potential. According to eqn. 4, the curve of E_{pc2} *versus* log ν should be linear (Fig. 3). The charge transfer coefficients (α) for the reduction process can be determined from the slope of this line and ks can be calculated from the intercept, if the values of E^0 and D are known. The value of E^0 in eqn. 4 can be obtained from the intercept of E_{pc2} *versus* ν plot on the ordinate by extrapolating the line to $\nu = 0$. And also, 'a' can be calculated from the eqn. 5. The average value of 'a' is 0.32 and an apparent electron transfer rate constant, ks = 7.152×10^{-4} cm s^{-1} was estimated.

The diffusion coefficient, D is determined to be 3.52×10^{-5} and 2.237×10^{-4} cm^2 s^{-1} for system I and system II respectively by the formula given below[31].

$$ipa = (2.99 \times 105)n(\alpha n_a)^{1/2}AD^{1/2}\nu^{1/2}C_o^* \quad (6)$$

where, n = number of electrons, A = area of the electrode, D = diffusion coefficient, ν = scan rate, C_o^* = concentration of electroactive species.

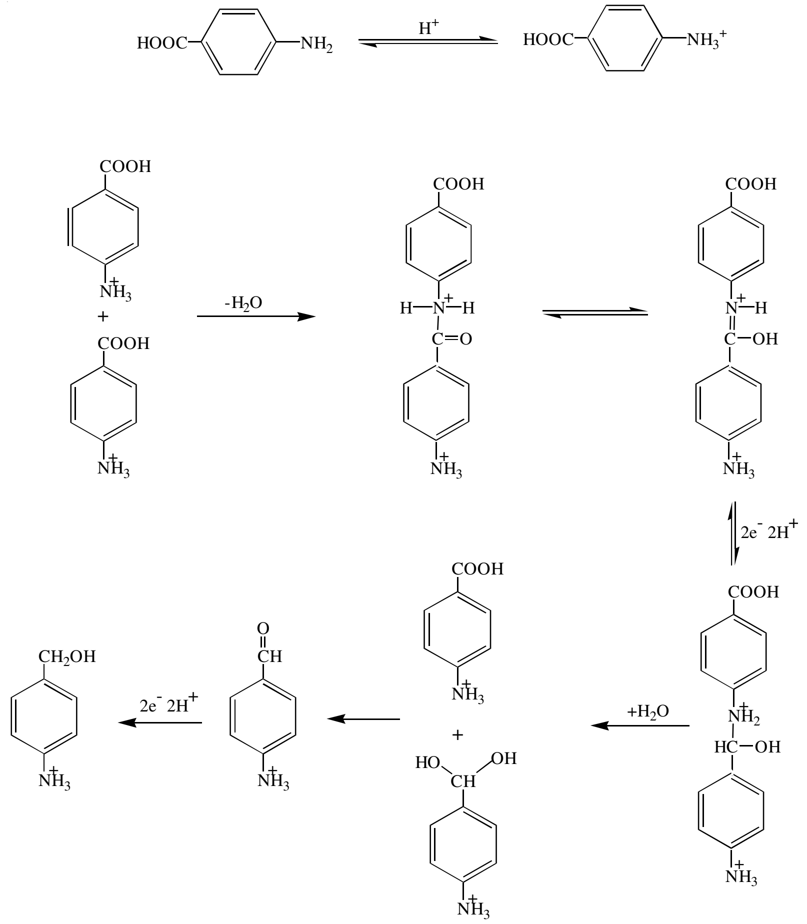
Controlled current electrolysis: Electrolysis was carried out to identify *p*-aminobenzyl alcohol as the product of reduction of *p*-amino benzoic acid using H-type cell separating the anode and cathodic compartments by a fine glass sinter. The reduced product by bulk electrolysis was obtained in reasonably good yield (yield = 77.29 %). The purity of the compound was checked by single spot TLC. The product has been identified to be *p*-aminobenzyl alcohol [H_2N-(C_6H_4)-CH_2OH] on the basis of m.p. (81.5 ºC), elemental and spectral analysis. The IR spectrum of *p*-aminobenzyl alcohol shows the absorption bands at 3300 cm^{-1}(ν_{O-H} broad band), 3450 cm^{-1} ν(N-H) asymm., 1600, 1580 and 1500 cm^{-1} ν(C-C) Ar, 1620 cm^{-1} δ(N-H), 1050 cm^{-1} ν(C-O), 790 cm^{-1} δ(C-H) *para*-substituted benzene, out-of-plane. The stretching absorption band obtained at 1685 cm^{-1} due to -(C=O) group in the IR spectrum of *p*-amino benzoic acid, disappeared in the product. The ^1H NMR data for *p*-aminobenzyl alcohol shows signals at δ 2.6 ppm (s, -OH proton), δ 4.0 ppm (s, -NH_2 protons), δ 4.7 ppm (s, -CH_2 protons), δ 6-7.5 ppm (m, aromatic protons). Anal. calcd. (%) for C_7H_9ON: C, 68.29; H, 7.32; N, 11.39; found (%): C, 69.09; H, 7.92; N, 10.63.

The mechanism as shown in **Scheme-I**, is proposed for electrochemical reduction of *p*-amino benzoic acid in acidic, aqueous and alkaline medium. The IR and NMR spectral data of products obtained after controlled current electrolysis further confirms the proposed reaction mechanism.

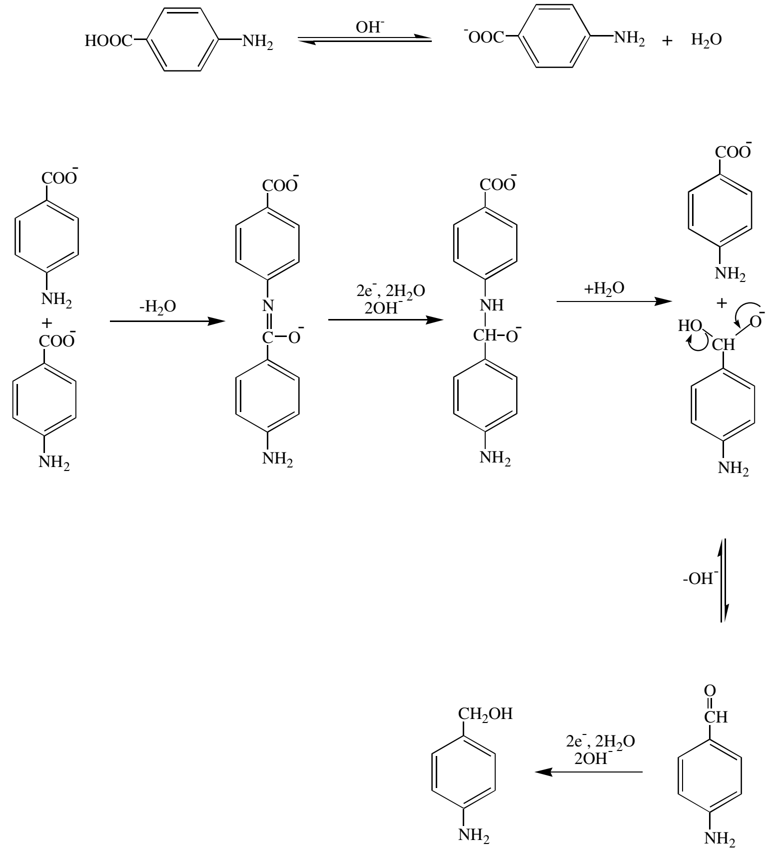
Complexation with Cd(II): The cyclic voltammograms of 0.2 mM cadmium complex with an initial potential (E_i) of 0.02 V and switching potential (E_s) of -1.3 V at different scan rates *viz.*, 75, 100, 150, 200, 300, 400, 500 and 700 mV/s in DMF using TBAP as supporting electrolyte are shown in Fig. 9. At all scan rates a redox couple was observed due to transfer of two electron[18] (E_{pc} = -0.839 V and E_{pa} = -0.645 V at 200 mV/s scan rate). A slight displacement of the anodic and cathodic peaks is observed as the sweep rate increases thus ΔE_p increases with sweep rate and was found to be more than 0.12 V (Table-2). The ratio of anodic (i_a) and cathodic (i_c) peak currents is not equal to unity. All these characteristics are assigned to quasi-reversible electrode reaction due to a slow electrochemical reaction or a slow chemical reaction such as complex dissociation followed by a reversible electron transfer. A linear relationship was observed between the peak currents for both anodic and cathodic peak and the square root of the scan rate with a significant correlation coefficient of 0.9935 and 0.9955 respectively, indicating thereby that the electrode process is diffusion-controlled[25] (Fig. 10).

TABLE-2
EFFECT OF SWEEP RATE VARIATION ON THE CYCLIC VOLTAMMETRIC PARAMETERS FOR THE REDUCTION OF Cd(II) COMPLEX OF *p*-AMINO BENZOIC ACID
(MEDIUM = DMF; CONCENTRATION = 2 mM)

ν (mV s^{-1})	E_{pc1} (mV)	E_{pa1} (mV)	ΔE_p (mV)	i_{pa1}/i_{pc1}	$i_{pc1}/\nu^{1/2}$ (μA $s^{1/2}/mV^{1/2}$)
100	-822	-656	166	0.81	42.3
150	-827	-652	175	0.84	40.11
200	-832	-648	184	0.87	38.54
300	-845	-639	206	0.89	36.95
400	-853	-632	221	0.87	37.25
500	-865	-622	243	0.85	37.05
700	-881	-612	269	0.88	34.41



(a) In acidic medium



(b) In aqueous and alkaline medium

Scheme-I: Proposed reaction mechanism for electrochemical reduction of *p*-amino benzoic acid in (a) acidic, (b) aqueous and alkaline medium

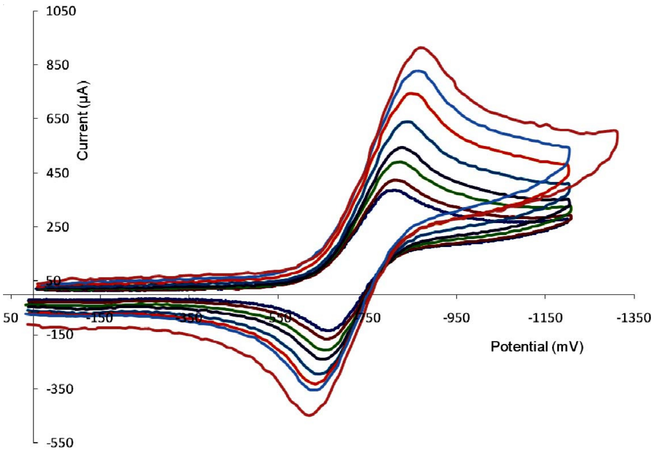


Fig. 9. Cyclic voltammograms of 0.2 mM cadmium(II) complex of *p*-amino benzoic acid in DMF at a sweep rate: (1) 75, (2) 100, (3) 150, (4) 200, (5) 300, (6) 400, (7) 500, (8) 700 mV/s

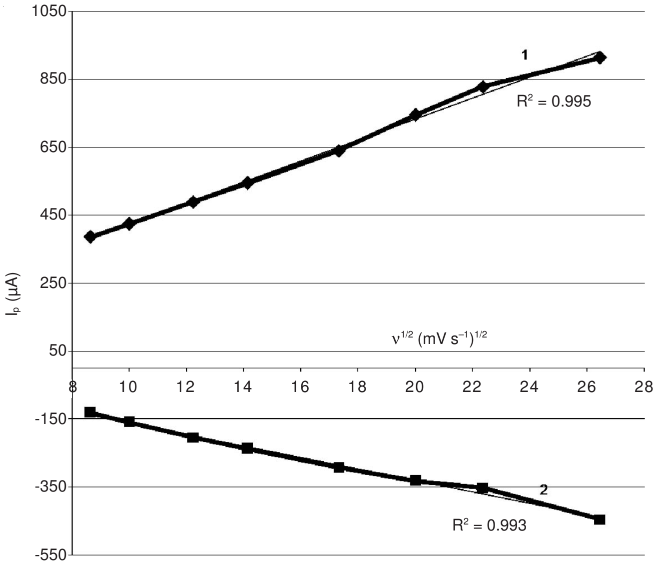


Fig. 10. Variation of the height of peak currents: (1) I_{pc}, (2) I_{pa} for reduction of Cd(II) complex of *p*-amino benzoic acid with sweep rate (concentration 0.2 mM)

Conclusion

Reduction of *p*-amino benzoic acid involves the transfer of four electrons and four protons resulting in the formation of its alcohol derivative. The system I has quasi-reversible and system II has irreversible electrode process. The cathodic peak currents were found to increase linearly with square root of sweep rate and also with concentration of electroactive species, suggesting that the overall process is diffusion controlled process. Cadmium complex of *p*-amino benzoic acid is reduced quasi-reversibly involving one step with the transfer of 2 electrons. The electrochemical behaviour shows diffusion controlled and metal centered process.

ACKNOWLEDGEMENTS

The authors are grateful to the Head, Department of Chemistry for providing necessary facilities to carry out this investigation & to CSIR, New Delhi, for providing fellowship to one of us (Mrs. Hemlata Agarwal).

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