Electro- reduction of 4-nitrobenzaldehyde in basic medium at Different Electrodes

Sadhana Sharma[1], Mamta Kumari[2] and D.K. Sharma*

[1,2,*]Department of Chemistry, University of Rajasthan, Jaipur – Rajasthan-302004(India)

Email : sadhanasharma_21@yahoo.co.in; sharma-dk@uniraj.ernet.in

Mailing Add: Department of Chemistry, University of Rajasthan,

Jaipur – Rajasthan-302004 (India)

Tel. No. +91-141-2553661(R), +91-9414071373(M), Fax : +91-141-2548050

Abstract: Electro-organic synthesis of 4,4'-bis(hydroxymethyl)hydazobenzene has been carried out by the electroreduction of 4-nitrobenzaldehyde at copper and amalgamated forms of copper and zinc electrodes under alkaline conditions using galvanostatic techniques. The electro reduction of 4-nitrobenzaldehyde has been also studied by cyclic voltammetry at glassy carbon electrode under alkaline conditions, which indicate the reducible behaviour from its cyclic voltammogram. Isolated product was characterized by T.L.C., usual laboratory qualitative tests and IR, NMR spectral analysis to be 4,4'-bis(hydroxymethyl)hydazobenzene. Effect of different parameters like current density, temperature, depolarizer concentration and nature of cathode material on yield percentage and current efficiency have been investigated. Number of electrons have also been calculated to confirm the isolated product to be 4,4'-bis(hydroxymethyl)hydazobenzene. [Nature and Science. 2009;7(3):84-98]. (ISSN: 1545-0740).

Keywords: 4-nitrobenzaldehyde, cyclic voltammetry   galvanostatic technique.

Introduction

Electroreduction of aromatic compounds having nitro and aldehyde groups may be controlled to give aniline, azo, azoxy, hydrazo and alcohol respectively [1-6]. Cathodic reduction of nitro and aldehyde groups containing aromatic compounds and other pharmacologically important compound [7-11] have also been studied at the different electrodes but the formation of 4,4'-bis(hydroxymethyl)hydazobenzene from the reduction of 4-nitrobenzaldehyde has not been reported in literature. The Voltammetric techniques showed themselves to be an excellent alternative for the study of the reaction mechanism [12-13] and analytical determination of organic compounds . Compared with other methods , this new procedure (Cyclic Voltammetry) possesses following advantages, such as a low detection limit, a rapid response, excellent reproducibility , simplicity and low cost[14] . typical Cyclic Voltammograms were recorded within the wide range (200mV to -1600 mV)of the potential at pH 11.0and at different scan rates(50,100,200,500 mVsec^{-1})fig.1. The 4-nitrobenzaldehyde reduction is irreversible as evident by cyclic voltammograms at higher scan rates and anodic waves did not appear under any circumstances. The current function ($I_{pc/v}^{1/2}$) can be scan rate independent (fig:2) while E_{pc} (cathodic peak potential) varies negatively as the scan rate increases.

It is evident form the literature that the reduction 4-nitrobenzaldehyde has not been studied in detail. Reduction of 4-nitrobenzaldehyde has, therefore, been studied at different metal such as Copper, amalgamated copper (Cu-Hg) and amalgamated zinc (Zn-Hg) electrodes galvanostatically. Effect of various experimental parameters such as current density, temperature and concentration of depolarizer on yield percentage has been investigated for the reduction of 4-nitrobenzaldehyde in order to obtain optimum conditions.

Material and Methods

4-nitrobenzaldehyde used was of laboratory grade and other chemicals like sodium hydroxide, sulphuric acid, diethylether etc. were of analytical grade. All the solutions were prepared in conductivity water. Electrolytic cell used was a 250 ml beaker (tall form) with the provision of porous pot, magnetic stirrer, magnet bar, thermometer, cathode and agar-agar gel glass tube (bridge) to measure the cathodic potential (vs Saturated Calomel Electrode, SCE). Other components of the cell assembly were as follows [15-19].

Cathode :   different metal strips

Catholyte   :   5% (w/v) aqueous sodium hydroxide + 4-nitrobenzaldehyde

Total volume of catholyte : 100ml

Anode   :   lead strip (PbO_2)

Anolyte :   aqueous sodium hydroxide solution

Distance between cathode & anode : 2.5 cm (approximately)

Catholyte prepared was of different concentration from 0.05M to 0.2M. The temperature was controlled to the desired value by having ice cold water in outer Jacket of Electrolysis cell. A magnetic stirrer was used for agitation.

The desired current according to current density range was applied from the current regulated power supply (galvanostat) developed by CDPE, Department of Physics, University of Rajasthan, Jaipur. The cathodic potential measured by digital multimeter RISH Multi 14S via saturated calomel electrode (SCE) through agar-agar gel bridge in each case i.e. at all electrode under investigation in the presence and absence of depolarizer to get suitable current density range for reduction under the experimental conditions imposed.

In all cases a theoretical quantity of current was passed depending upon the amount of depolarizer taken.

After electrolysis, the catholyte was neutralized with 5% (w/v) sulphuric acid solution and cooled to 278 – 283 K in ice. This solution was then treated with diethylether to extract the product and the same was washed with ice cold water to remove the base or salt (if any) and allowed to evaporate the ether. After evaporation, a yellowish-orange solid was obtained, which was subject to the usual physiochemical methods of analysis. The following observations were made.

1.   Solid was soluble in ether, acetone, chloroform and partially in water, and burns with sooty flames shows aromatic nature of compound.

2.   The product gave highly pungent and displeasing smell indicating the formation of dimerisation product.

3.   A single clear spot on silica gel-G plate was obtained in iodine chamber. (80% C_6H_6+ 20% ethyl acetate medium) confirming that the product was a single compound and not a mixture.

4.   The melting point of the product was found to be 453K.

5.   The percentage of Carbon ,Hydrogen and Nitrogen in the product was determined by PERKIN ELMER elemental analyzer.

6.   IR spectra were recorded in KBr on a SHIMADZU 400-50 infrared spectrophotometer (ν_{max} in cm^1).

7.   ^{1}H NMR spectra were recorded on JEOL AL 300 ^{1}H NMR spectrophotometer using $CDCl_3$ as solvent and TMS as an internal standard (chemical shift in δppm).

8.   All the characteristic data are collectively given in Table 1.

C, H, N, estimation value

The observed values of the carbon, Hydrogen and Nitrogen, in the product, were 68.34%, 5.96%, 11.78% respectively, as compared to the their theoretical values, which are 68.85%, 6.5%, 11.47% respectively, thus, confirming the product.

Results and Discussions

Polarization curves

The polarization data are given in Table 2(a), 2(b) and 2(c). From which polarization curves have been drawn for 4- nitrobenzaldehyde and are given in figs. 3, 4 and 5 for all the electrodes investigated. Comparison of these polarization curves in presence and in the absence of depolarizer shows suitable current density ranges for reduction. The data for potential vs. time curves are also given in Table 2(d) and curves have been drawn in Fig. 6.

Polarization curves for the reduction of 4-nitrobenzaldehyde at copper, zinc and their amalgamated forms (Cu-Hg and Zn-Hg) show that virtually polarization takes place and hence reaction can be expected.

The proper current density ranges to be 0.057 to 0.067, 0.091 to 0.105 and 0.080 to 0.091 Amp. cm.$^{-2}$ for copper, zinc and their amalgamated forms (Cu-Hg and Zn-Hg) respectively . (Table 3).

After conducting experiments at various current densities optimum current densities have been determined for all three electrodes (Cu, Cu-Hg and Zn-Hg) at 0.062, 0.098 and 0.085 Amp. cm.$^{-2}$ respectively. (Table 4).

Conclusions

The formation of 4,4'-bis(hydroxymethyl)hydazobenzene by the electroreduction of 4-nitrobenzaldehyde in alkaline medium involves ten electrons process, mechanism is given in scheme 1. This is confirmed by working electrode potential Vs time curves (Fig. 6). It is seen from the curves that the cathodic potential becomes constant after theoretical time during electrolysis approximately required for ten electron process according to Faraday's law.

An electrolytic method for its preparation will be of industrial importance. The literature reviewed so far does not propose any method for the preparation of this compound on any scale. Thus , 4,4'-bis(hydroxymethyl)hydazobenzene can be prepared by the cathodic reduction of 4- nitrobenzaldehyde at any of the electrodes investigated.
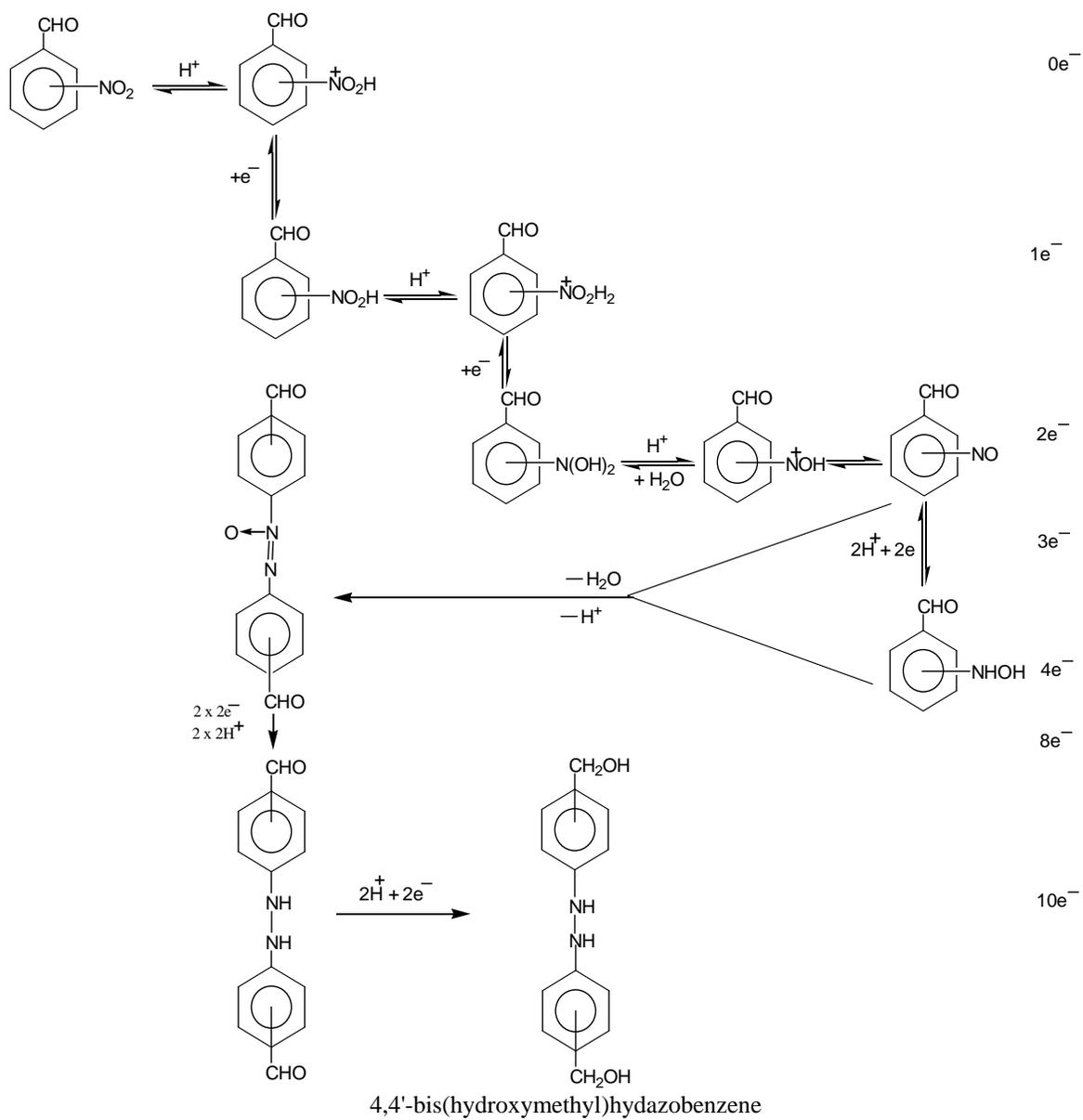
Figure

Table 1: I.R. and N.M.R. data for the product.

Crystal / Amorphous state of compound	M.P.	IR data (c.m^{-1})	NMR data (δ ppm)	Product compound confirmed
Yellow Needle Shaped Crystal	453K	3330 sharp one spike of –NH 3100 – OH 3030 = CH (Aromatic hydrogen) 1450-1550 (Aromatic system) 830– para substituted aromatic compound peak	δ (7.3) aromatic protons (merged) integrated for 8 protons δ (3.9) Two alcoholic protons δ (7.9) for – NH integrated Two protons δ (3.52) Four protons of benzyl group	4,4'-bis(hydroxymethyl) hydrazobenzene
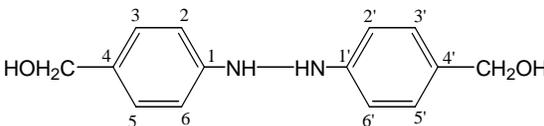
Table 2(a): Cathodic Polarization data of 4- nitrobenzaldehyde at copper (Cu) electrode in aqueous 5 %(w/v) sodium hydroxide and methanol solution.
Cathode area = 19.10 cm^2, Temperature = 25$\pm$1°C

S. No.	Current (Amp.)	Current Density (c.d., Amp.cm^{-2})	-log c.d.	Potential (- V) vs. SCE			
				Without depolarizer	With depolarizer		
					0.05M	0.10M	0.20M
1	0.10	0.005	2.30	0.573	0.511	0.404	0.374
2	0.20	0.010	2.00	0.573	0.511	0.404	0.374
3	0.30	0.015	1.82	0.573	0.511	0.404	0.374
4	0.40	0.021	1.67	0.573	0.511	0.404	0.374
5	0.50	0.026	1.58	0.573	0.511	0.404	0.374
6	0.60	0.031	1.51	0.610	0.523	0.504	0.374
7	0.70	0.036	1.44	1.498	0.637	0.611	0.550
8	0.80	0.041	1.38	1.585	0.741	0.700	0.696
9	0.90	0.047	1.33	1.649	0.844	0.800	0.810
10	1.00	0.052	1.28	1.720	0.938	0.940	0.928
11	1.10	0.057	1.24	1.739	1.040	1.023	1.080
12	1.20	0.062	1.20	1.776	1.175	10116	1.315
13	1.30	0.067	1.17	1.815	1.380	1.190	1.620
14	1.40	0.073	1.13	-	1.660	1.315	2.070

Table 2(b): Cathodic Polarization data of 4- nitrobenzaldehyde at amalgamated copper (Cu-Hg) electrode in aqueous 5 %(w/v) sodium hydroxide and methanol solution. Cathode area= 14.18cm^2, Temperature = 25$\pm$1°C

S. No.	Current (Amp.)	Current Density (c.d., Amp.cm^{-2})	-log c.d.	Potential (- V) vs. SCE			
				Without depolarizer	With depolarizer		
					0.05M	0.10M	0.20M

1	0.10	0.007	2.15	0.609	0.542	0.522	0.500
2	0.20	0.014	1.85	0.609	0.542	0.522	0.500
3	0.30	0.021	1.67	0.609	0.542	0.522	0.500
4	0.40	0.028	1.55	0.609	0.542	0.522	0.500
5	0.50	0.035	1.45	0.609	0.542	0.522	0.500
6	0.60	0.042	1.37	1.215	0.550	0.531	0.500
7	0.70	0.049	1.31	2.191	0.656	0.650	0.550
8	0.80	0.056	1.25	2.223	0.763	0.747	0.630
9	0.90	0.063	1.20	-	0.882	0.830	0.724
10	1.00	0.070	1.15	-	1.007	0.906	0.785
11	1.10	0.077	1.11	-	1.214	0.984	0.850
12	1.20	0.084	1.075	-	1.459	1.085	0.900
13	1.30	0.091	1.040	-	1.736	1.220	0.960
14	1.40	0.098	1.008	-	2.530	1.380	1.100
15	1.50	0.105	0.98	-	-	1.550	1.150

Table 2 (c): Cathodic Polarization data of 4-nitrobenzaldehyde at amalgamated zinc (Zn-Hg) electrode in aqueous 5% (w/v) sodium hydroxide and methanol solution. Cathode area=18.62cm^2, Temperature= 25$\pm$1°C

S. No.	Current (Amp.)	Current Density (c.d., Amp.cm^{-2})	-log c.d.	Potential (- V) vs. SCE			
				Without depolarizer	With depolarizer		
					0.05M	0.10M	0.20M
1	0.10	0.005	2.30	1.543	1.406	1.340	0.713
2	0.20	0.011	1.95	1.543	1.406	1.340	0.713
3	0.30	0.016	1.79	1.543	1.406	1.340	0.713

4	0.40	0.021	1.67	1.543	1.406	1.340	0.713
5	0.50	0.026	1.58	1.543	1.406	1.340	0.713
6	0.60	0.032	1.49	1.548	1.406	1.356	0.713
7	0.70	0.037	1.43	2.143	1.420	1.385	0.730
8	0.80	0.042	1.37	2.216	1.456	1.440	0.753
9	0.90	0.048	1.31	2.234	1.513	1.470	0.789
10	1.00	0.053	1.27	2.283	1.573	1.510	0.820
11	1.10	0.058	1.23	2.321	1.656	1.610	0.863
12	1.20	0.064	1.19	2.358	1.779	1.730	0.916
13	1.30	0.069	1.16	2.393	1.920	1.845	0.979
14	1.40	0.075	1.12	2.426	2.220	1.925	1.038
15	1.50	0.080	1.10	2.457	2.325	2.020	1.097
16	1.60	0.085	1.07	2.490	2.434	2.121	1.065

Table 2(d): Polarization data for long term electrolysis (Potential vs. Time) of 4- nitrobenzaldehyde (0.1M) at copper (Cu) amalgamated copper (Cu-Hg) amalgamated zinc (Zn-Hg) electrodes in aqueous 5 %(w/v) sodium hydroxide and methanol solution. Temperature = 25 ± 1°C

S. No.	Time (min.)	Potential (-V) Vs SCE at copper electrode	Potential (-V) Vs SCE at amalgamated copper (Cu-Hg) electrode	Potential (- V) Vs SCE at amalgamated zinc (Zn-Hg) electrode
1	0	1.085	1.340	1.900
2	20	1.145	1.400	1.960
3	40	1.256	1.700	2.250
4	60	1.386	2.156	2.340
5	80	1.595	2.235	2.396
6	100	1.630	2.250	2.405

7	120	1.650	2.270	2.423
8	140	1.650	2.270	2.428
9	160	1.650	2.270	2.428
10	180	1.650	2.270	2.428

Table 3: Effect of current density on yield at different cathodes [Temperature 298 $\pm$ 1K, catholyte 100 ml (aqueous 5 %(w/v)   sodium hydroxide + methanol solution containing 4-nitrobenzaldehyde (0.1M))]

S.No.	Cathode	Current density (Amp.Cm^{-2})	Yield of the product (%)
1.	Cu	0.057	62
		0.062	70
		0.067	63
2.	Cu-Hg	0.091	71
		0.098	76
		0.105	69
3.	Zn-Hg	0.080	69
		0.085	77
		0.091	72

Table 4: Optimum conditions for electroreduction of 4-nitrobenzaldehyde (medium: aqueous 5% (w/v) sodium hydroxide + methanol solution) with 0.1 M concentration, Temperature 298 $\pm$1

Cathode	Temperature ($\pm$1K)	Depolarizer concentration	Current density (Amp.Cm^{-2})	Current efficiency (%)
Cu	298	0.1 M	0.062	88
Cu-Hg	298	0.1 M	0.098	92
Zn-Hg	298	0.1 M	0.085	92
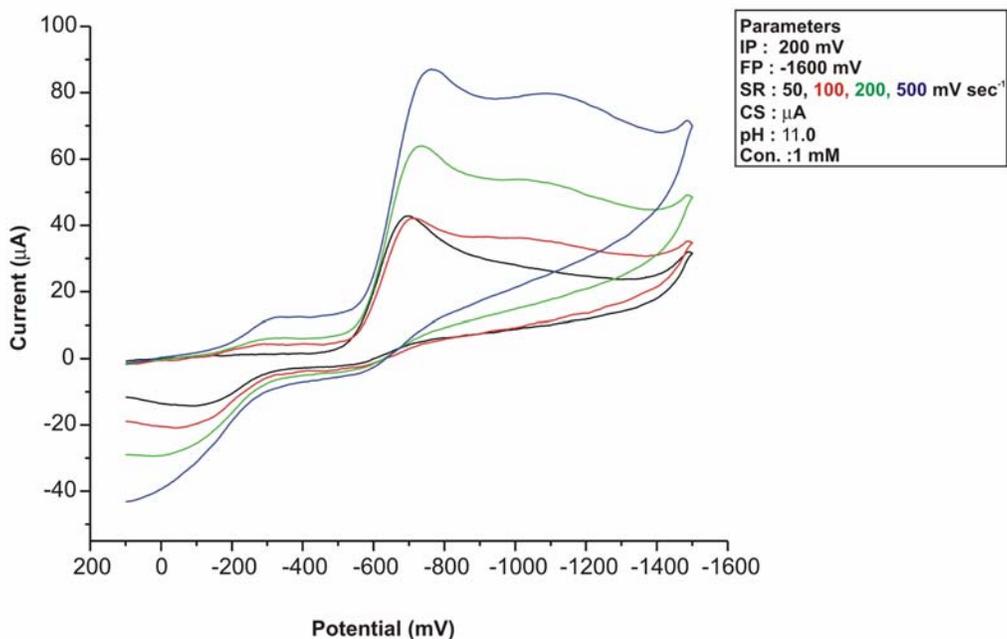
Fig 1: Effect of Scan rate on Cyclic Voltammetric behavior of 4- nitrobenzaldehyde at pH: 11.0
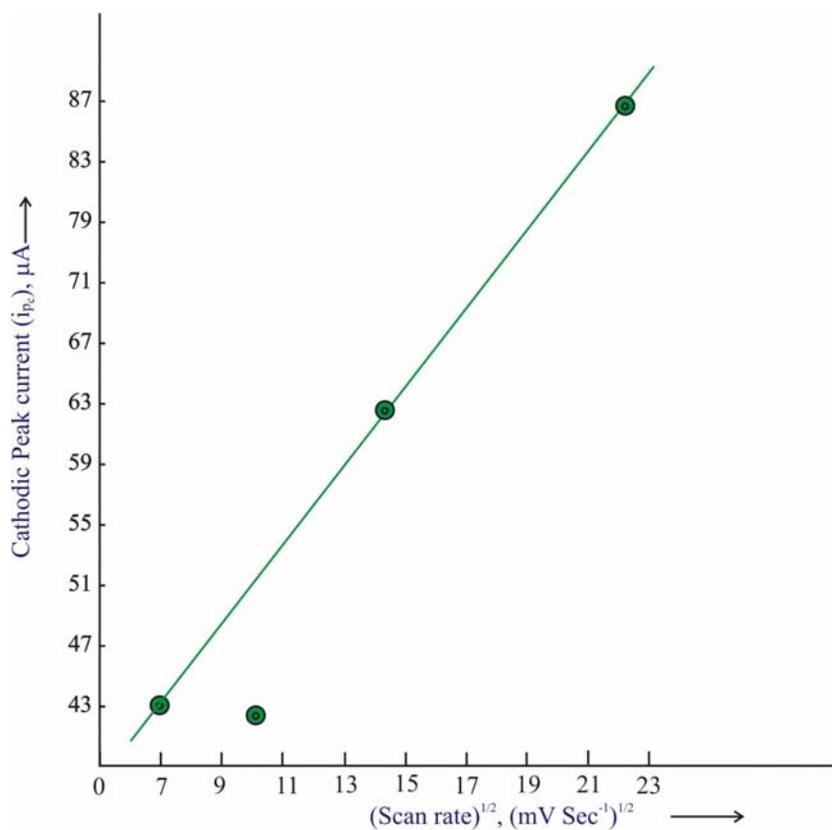
Fig. 2. Plot of I_{pc} versus $_v^{1/2}$ from votammogram in fig. 1 for 4-nitrobenzaldehyde(1Mm) at pH: 11.0.
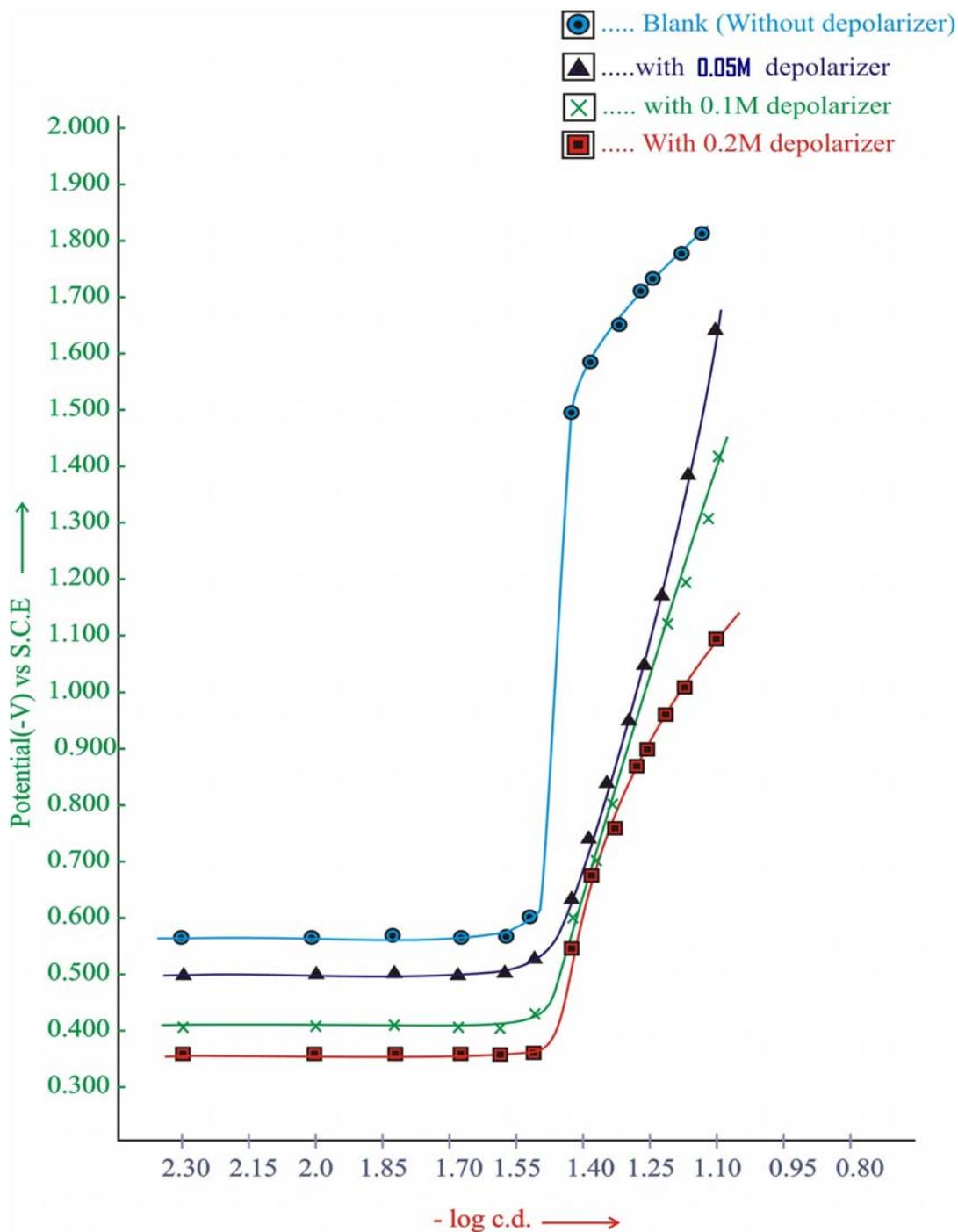
Fig 3: Cathodic Polarization Curves of 4- nitrobenzaldehyde in aqueous 5% (w/v) NaOH + methanol medium, temperature [298+1K] at Copper (Cu) electrode
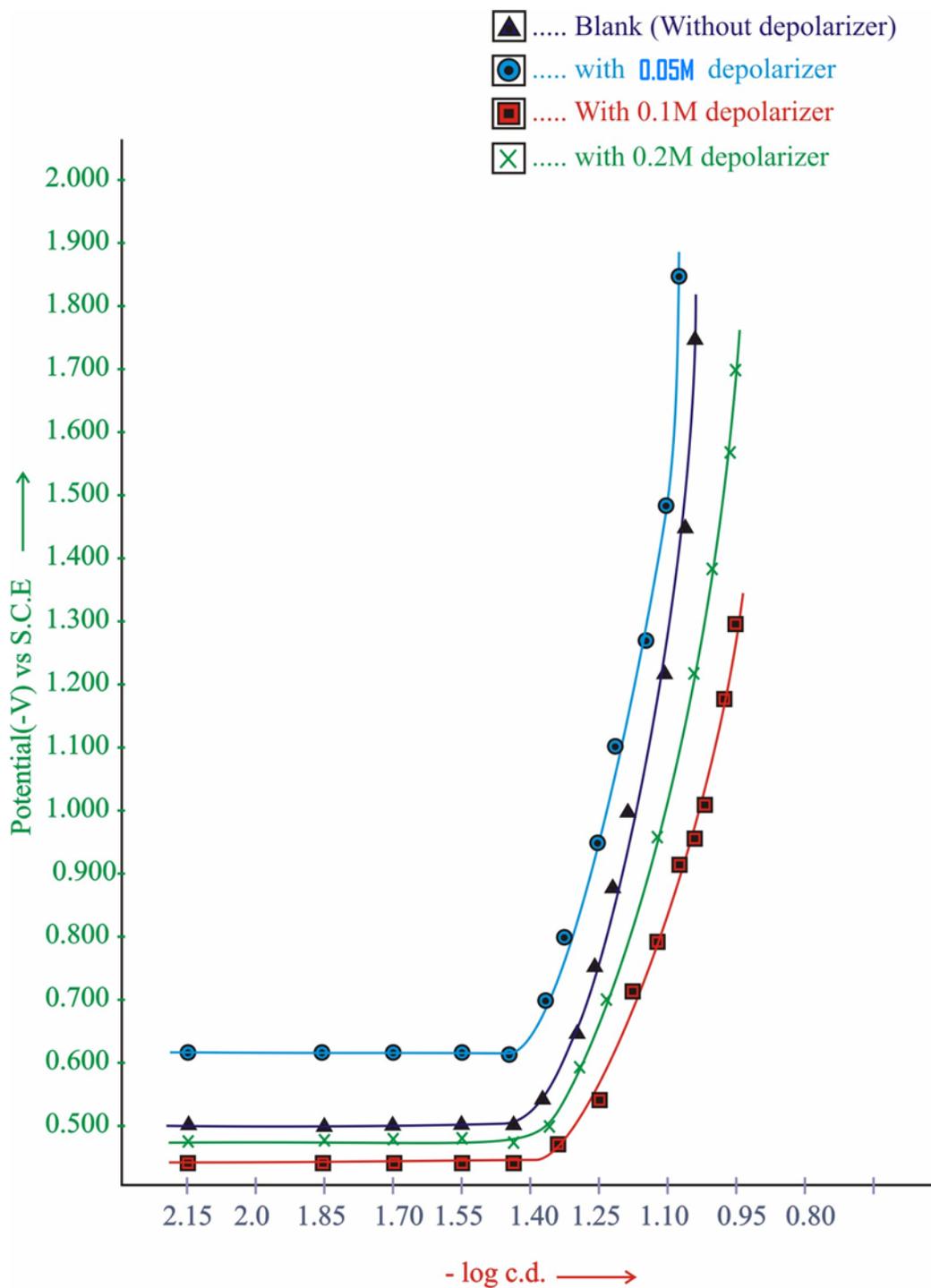
Fig 4: Cathodic Polarization Curves of 4- nitrobenzaldehyde in aqueous 5% (w/v)
NaOH + methanol medium, temperature [298+1K] at amalgamated Copper (Cu-Hg)
electrode
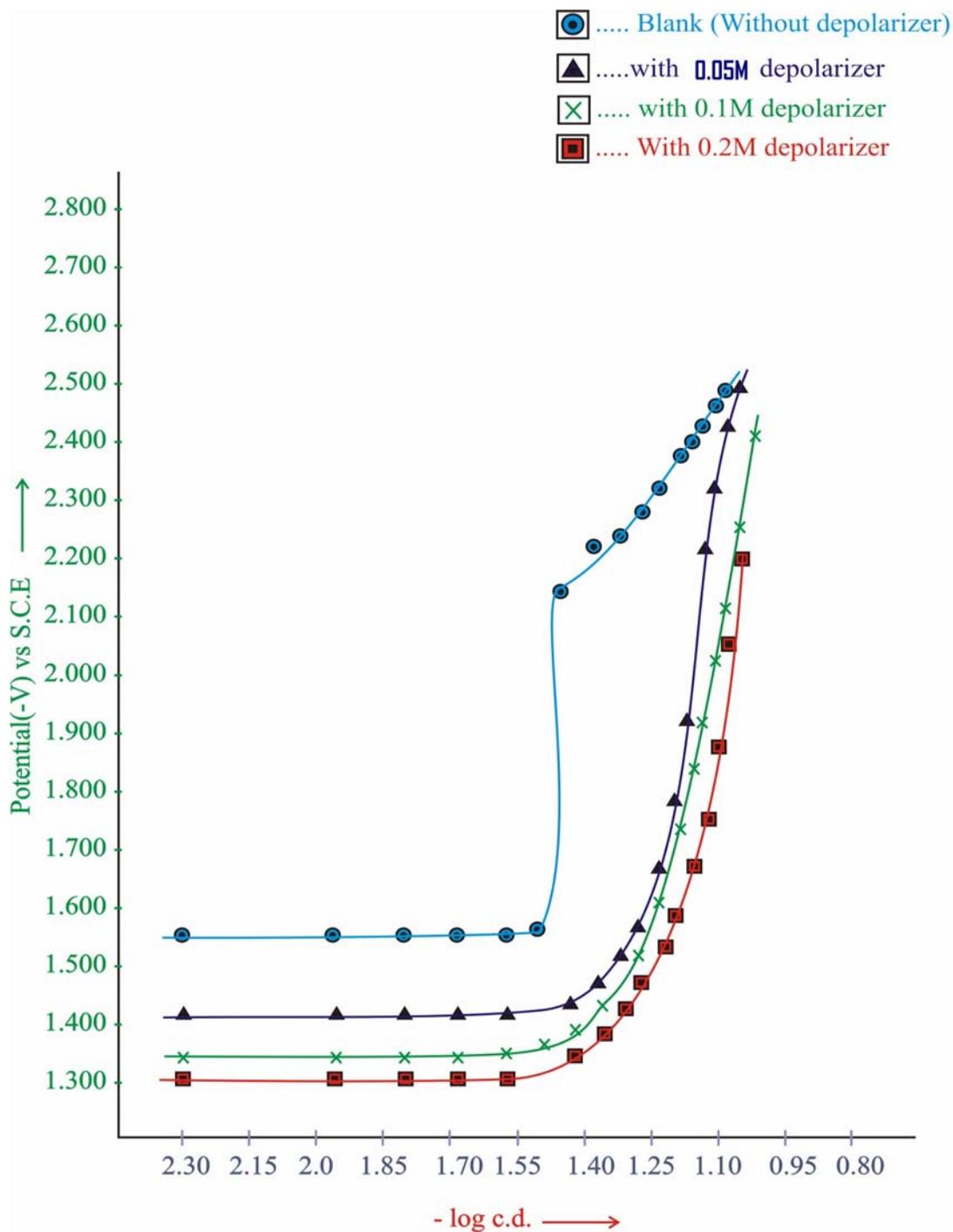
Fig 5: Cathodic Polarization Curves of 4- nitrobenzaldehyde in aqueous 5% (w/v) NaOH + methanol medium, temperature [298+1K] at amalgamated Zinc (Zn-Hg) electrode
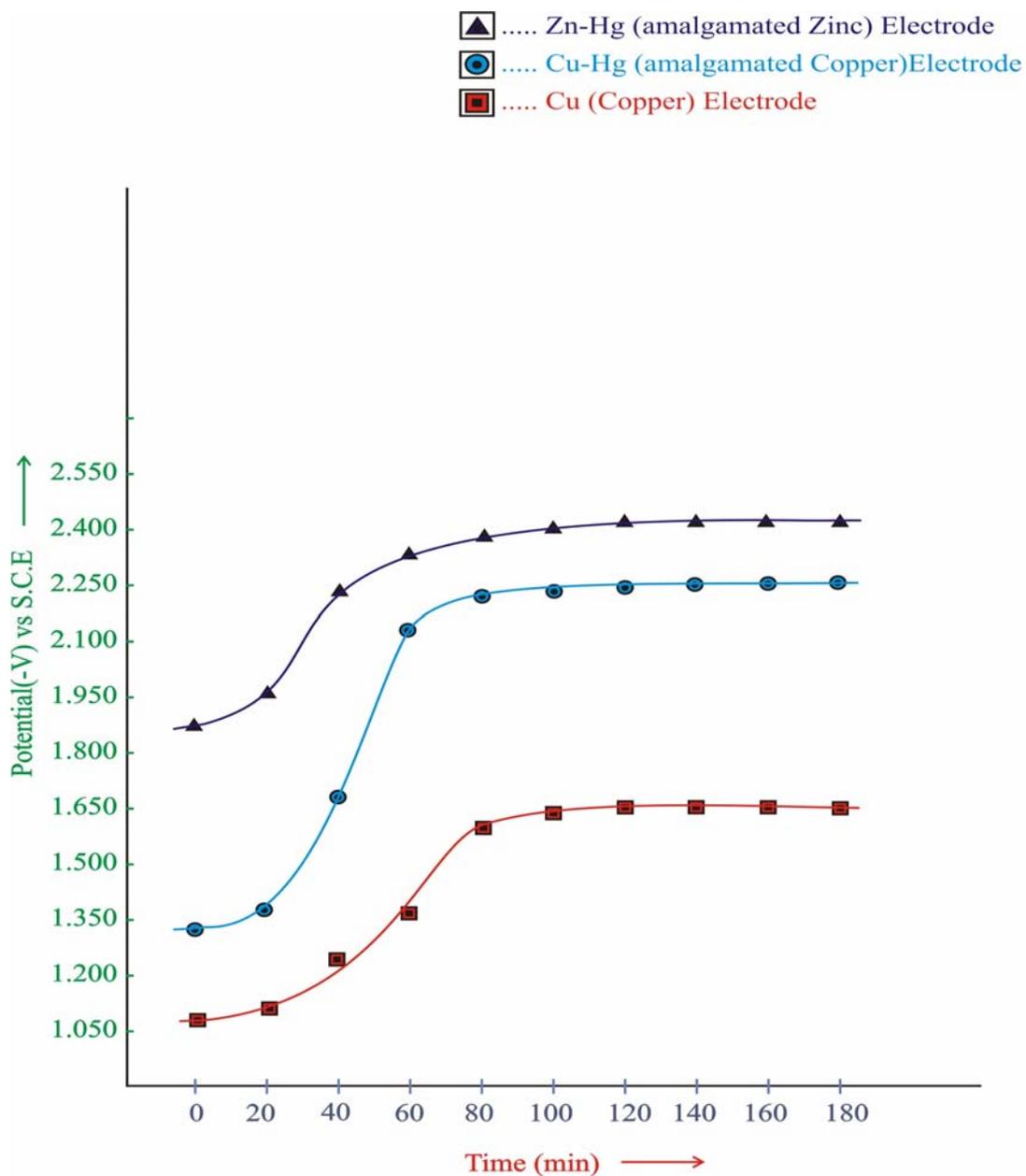
Fig 6: Time vs Potential Curves of 4- nitrobenzaldehyde (0.1M) in aqueous 5% (w/v)NaOH + methanol medium, temperature [298+1K]

REFERENCES

1.   Sharma VK , Sharma DK and Gupta CM, Bull Electrochem., 1989; 5: 359-363.

2.   Kornarev AA (Gosundarstuennyi Nauchnyi Tsentr Rossiiskoi Federatssi "NIOPIK", Russia) Russ. RU2, 2000;159:424.

3.   Rodriguez-Amaro R, Piez R, Lopez V and Ruiz JJ, J. Electroanal Chem. Intrafacial Electrochem., 1990;278: 307-22 (Eng.)

4.   Ahmad ZA, Bull Electrochem., 1994; 10 (08) :322-5(S).

5.   Allen MJ, J. Org. Chem*.,* 1950;15: 435.

6.   Wawzonek S and Laitinen HA, J. Amer. Chem. Soc*.,* 1941;63: 2341.

7.   Jain R, Tomar S and Jain U, J. Electrochem. Soc. India*,* 1998;47:3.

8.   Zhu G, Fang H, Chen H and Zhu D, J. Electrochem. Soc*.* 1996;143: 7.

9.   Ratael MG, Rodriguez M and   Jose M, Collect (Zech Chem. Commun.),   1992;57: 1836-42 (Eng.)

10.   Faliang C, Jinyuan MO and Xiaoyun D, Fenxi Ceshi Xuebao, 1999;18: 21-24 (Ch.)

11.   Rami Reddy YV, Reddy P, Kumar R, Krishna S, Mohan and S. jayarama Reddy M and S, Bull. Electrochem*.,* 1996;12: 446.

12.   Mauro La-Scalea A ,Siliva Serrano HP and Ivano GR , Gutz. J. Braz. Chem Soc.1999;10(2):127.

13.   Chunhai Y. Analytical Sciences 2004;20:821-824.

14.   Knox RI ,Knight RI, Edwards DI ,Biochem Pharmac 1983;32:2149.

15.   Perrin CL, in Progress in Physical Organic Chemistry, (Eds) Cohen SG, Streitwieser A, Jr and Robert Tat. Vol. 3 Wiley, New York 1965: 195.

16.   Vidyottma, Agrawal RS and Sharma DK, Bull. Electrochem*.,* 2002;18(9): 429.

17.   Sharma S and Sharma DK, J. Ultra Chem, 2007;3(1):49

18.   Sharma S and Sharma DK, J. Ultra Chem *&* phy. sc, 2008;20(1):121-130

19.   Sharma DK , Sharma S, Mourya G L & Kumari M J. Ind. Chem Soc., 2009;86:1.

2/14/2009