ROTATING AMALGAMATED MICROELECTRODE IN THE ELECTROLYTIC REDUCTION OF NITROBENZENE AND p-NITROPHENOL

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ABSTRACT

Extensive use of amalgamated, rotating microelectrode for the study of electro-organic reductions does not appear to have been made so far. The design and construction of such an electrode is described. Preliminary results on the depolarisation characteristics of nitrobenzene and p-nitrophenol using the same have been presented. Reproducibility of the results obtained have been studied. Current-voltage curves obtained for the above two compounds are also given.

INTRODUCTION

There are many circumstances where the use of solid microelectrode is not a firm necessity, but just an interesting and simpler alternative to use of mercury electrode. Nernst and Merriam[1] were the first to describe current-voltage curves with a rotating platinum microelectrode. Many attempts have been made later to use electrodes of platinum, gold and other inert metals. Well known examples of solid electrodes which have been developed, especially for polarographic work, are the stationary, rotating and vibrating electrodes[2] and the gas flushed electrode.[3] Levich[4-6] and Frumkin[7] used a rotating disc and a rotating double disc (ring and disc) electrodes for investigating intermediate products in electrochemical reactions and also to study the kinetics of electrode processes. Recently, a carbon paste rotating disc has been described by Galus and Adams[8] and its capability and limitations for the measurement of heterogeneous rate constants for moderately rapid electron transfer processes have been discussed. Carbon paste R.D.E. has also been used to study the mechanism of anodic oxidation of N, N dimethyl aniline[9]. Cooke[10] had used a rotating amalgam electrode in place of dropping mercury electrode in polarographic work. Airey[11] describes the use of solid microelectrodes in conjunction with oscillographic polarography and states that amalgamated electrodes have the advantage of being usable upto the potentials as negative as-2.1. Goldschmidt[12] studied the electro-reduction of nitro-benzene in 0.1N NaOH in 65% alcohol. Russ[13] and Haber and Russ[14] studied the reduction of nitrobenzene and p-nitrophenol using relatively large electrodes of various metals in stirred solutions. No diffusion current regions were observed in these experiments due to the large size of the electrodes and the relatively great concentrations used. In each case the potential of the electrode was found to be a linear function of the logarithm of the current. This relationship indicates the variation of the speed of the electrode reaction as a function of the potential since under the experimental conditions the current is not determined by the rate of diffusion. In recent years, a number of electrochemical reductions have been reported using amalgamated cathodes[15-17]. Particular mention may be made of the use of such cathodes for the reducton of nitro compounds to give corresponding aminophenols[15,16]. References to the studies of electrochemical reduction at an amalgamated rotating microelectrode are scanty and it was considered to be of interest to take up such an investigation.

EXPERIMENTAL

Apparatus: Disc type rotating microelectrode used in our study consists of a cylindrical copper rod (Fig. 1) of 1.25 cm. diameter and 15 cm length. There is a threaded joint in the middle dividing it into 2 pieces A & B of 10cm and 5cm length, respectively. At the lower end of the rod B, there is a groove and at the centre of the groove is attached a fine copper wire which can fit into a 1 mm capillary tube D. The capillary tube is filled with 'Araldite' just

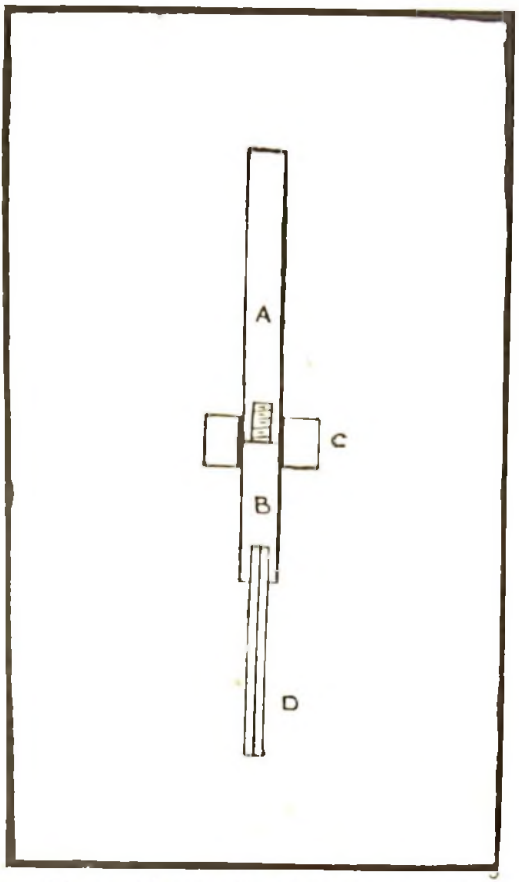


Fig. 1: Line drawing of the amalgamated microelectrode

before introducing the copper wire and fitting it into the groove. The end of the copper wire electrode is carefully ground and made smooth. The diameter of the copper wire is 0.95 mm and the working area of the electrode is 0.0072 cm^2. The microelectrode thus prepared is connected to the shaft of a fractional H.P. motor by a rubber tubing and contact given by pressing on it two carbon brushes C which also act as guide for smooth rotation.

Circuit diagram of the experimental set-up is given in Fig. 2. It includes a power supply unit, P, preferably a constant current generator. e1, e2 and e3 indicate respectively the cathode, the reference electrode and the anode. A platinum foil of large area (4 cm^2) is used as the anode. The cathode is the copper microelectrode described above, which has been amalgamated before use. Potential is measured using a Kintel VTVM.

The classical H-type cell used in polarographic work with a sintered diaphragm dividing the anode and cathode compartments has been used. Finger-type saturated calomel (L.N.) electrode is used as the reference electrode.

Procedure: The microelectrode surface is made smooth and uniform by grinding with fine emery and finally with zero grade emery paper. Then it is washed well with distilled water. The surface of the electrode is amalgamated as follows: A 10% solution of mercuric sulphate is prepared by dissolving 5 g. of $HgSO_4$ in 4 ml of concentrated sulphuric acid and then gradually making it up to 50 ml with distilled water. This solution is used as the electrolyte. Using a lead-foil as the anode and the microelectrode as cathode, 1 mA (c.d. 10 amp/dm^2) current is passed for 5 minutes. The cathode is kept rotating during electrolysis for uniform deposition. The cathode is re-

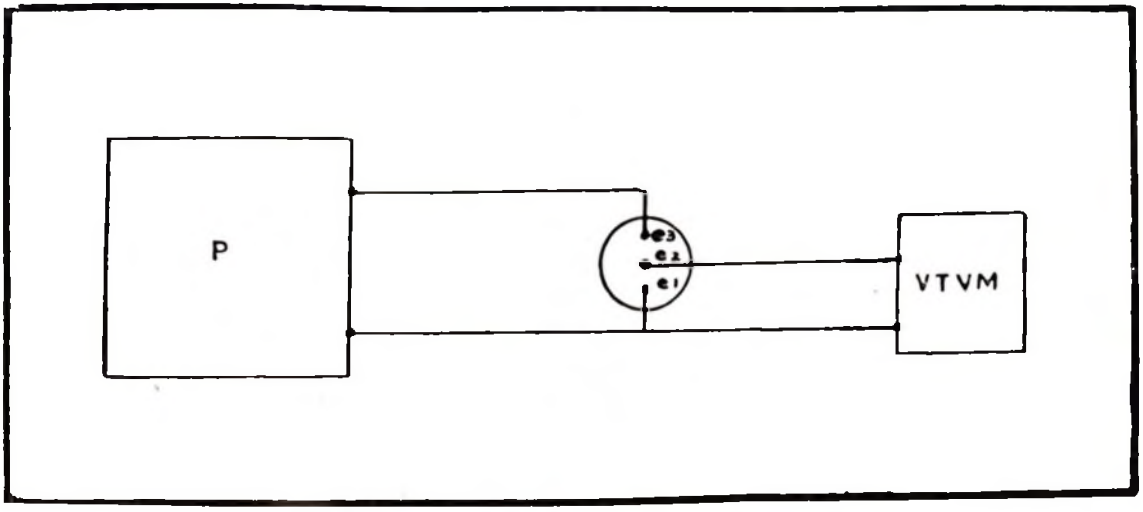


Fig. 2: Diagram of the circuit used in the experiments

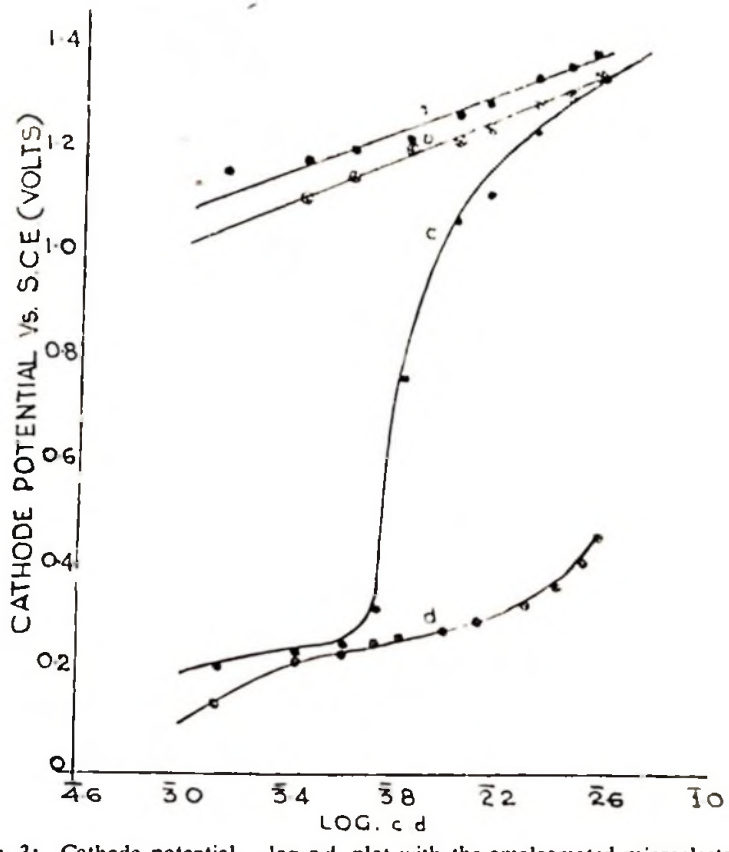


Fig. 3: Cathode potential — log c.d. plot with the amalgamated microelectrode
a) Stationary cathode without nitrobenzene
b) Rotating „ „ „
c) Stationary „ with nitrobenzene
d) Rotating „ „ „

moved and washed well with distilled water before use. After taking each set of reading, the electrode is washed with water, then with organic solvent (say alcohol) and finally with distilled water. Amalgamation of the electrode is done at intervals, say after 3 to 5 trials.

A solution of nitrobenzene is prepared by dissolving 5 ml (5 x 1.18 g) of nitrobenzene in 125 ml of absolute alcohol and making upto 250 ml with distilled water. 10 ml of this solution is diluted with 10 ml of 5M sulphuric acid and 30 ml of distilled water each time and is used as the catholyte. The anolyte is 50 ml of 1M sulphuric acid. The current potential readings are noted both at stationary and rotating cathodes. The r.p.m. was approximately 1200. The readings are compared with the blank.

To study the deploarization of **p**-nitrophenol, a saturated solution of **p**-nitrophenol in 1M sulphuric acid is prepared (estimated by bromination method[14] 13.23 g/litre). 50 ml of this is used as the catholyte. Potential measurements are carried out as above.

To study the effect of alcohol addition on the reduction, log i vs. E curves were plotted, the potential measurements being carried out at a rotating cathode with and without alcohol in the catholyte.

RESULTS AND DISCUSSION

The reproducibility of the results obtained on the same amalgamated copper surface, after washing with water, alcohol and finally with distilled water, have been tried at different current densities and is recorded in Table I. The cathode potential is found to decrease, especially at higher current densities, each time by 2 to 3%. If, on the other hand, the electrode is washed well, and reamalgamated, the results were found to be reproducible (Ref. Table II).

TABLE I: *Cathode potential data using the same cathode repeatedly*

Conditions: Anode, platinum foil; Cathode, rotating amalgamated copper; Anolyte, 10 ml 5M H_2SO_4 + 40 ml distilled water; Catholyte, 10 ml 5M H_2SO_4 + 10 ml nitrobenzene solution + 30 ml distilled water.

Current density (amp/cm² × 10³)	Cathode potential vs S.C.E. (volts)			
Trials	1	2	3	4
0.21	0.26	0.25	0.25	0.25
0.42	0.29	0.29	0.29	0.28
0.69	0.32	0.32	0.32	0.31
1.11	0.34	0.34	0.34	0.33
1.39	0.36	0.36	0.36	0.35
2.08	0.41	0.39	0.38	0.38
2.77	0.47	0.46	0.44	0.43
3.46	0.53	0.52	0.50	0.48

TABLE II: *Cathode potential data measured after every reamalgamation*

Conditions: Same as given in Table I.

Current density (amp/cm² x 10³)	Cathode potential vs. S.C.E. (volts)			
Trials	1	2	3	4
0.21	0.24	0.24	0.24	0.24
0.42	0.28	0.28	0.27	0.28
0.69	0.31	0.29	0.30	0.29
1.11	0.33	0.32	0.33	0.33
1.39	0.34	0.33	0.33	0.34
2.08	0.36	0.35	0.36	0.35
2.77	0.39	0.39	0.39	0.39
3.46	0.42	0.42	0.42	0.42

The cathode potential measured against saturated calomel electrode is plotted against log current density for both nitrobenzene and **p**-nitrophenol in Figs. 3 and 4. They indicate that at a stationary cathode, there is good depolarisation only at very low current density whereas at a rotating cathode good depolarisation is observed at high current density range also. At a rotating cathode, concentration polarisation comes less into picture and accounts for the increased depolarisation.

Alcohol addition lowers the hydrogen overvoltage as well as the depolarisation (Ref. Figs. 5 and 6). The lowering of depolarisation is observed in spite of the increased solubility of the organic depolariser in the aqueous alcoholic medium. Unless it is assumed that the alcohol present in the bath affects adsorption of organic molecule and hence the depolarisaton, this effect cannot be readily explained.

The depolarisation (Δ E) with nitrobenzene

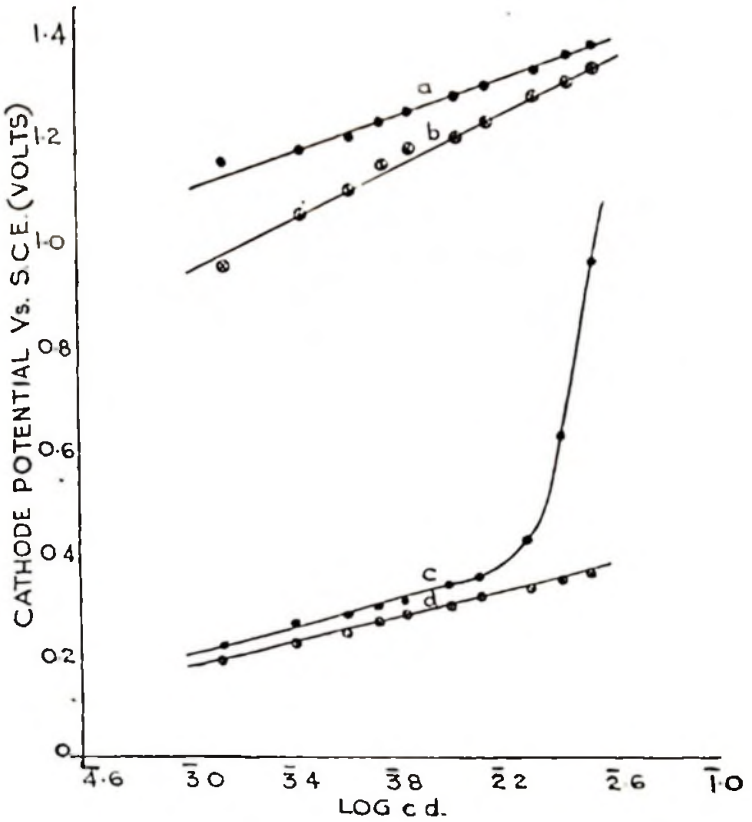


Fig. 4: Cathode potential — log c.d. plot with the amalgamated microelectrode

a) Stationary cathode without p-nitrophenol
b) Rotating ,, ,, ,,
c) Stationary ,, with p-nitrophenol
d) Rotating ,, ,, ,,

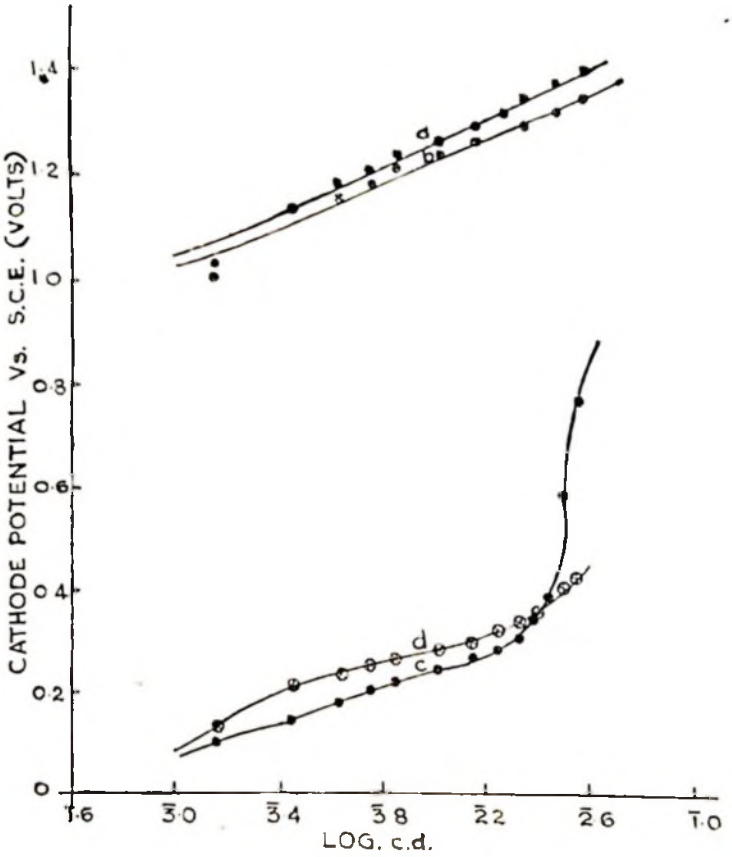


Fig. 5: Cathode potential — log c.d. plot with the amalgamated microelectrode

a) Without nitrobenzene, without alcohol
b) „ „ , with alcohol
c) With nitrobenzene, without alcohol
d) „ „ with alcohol

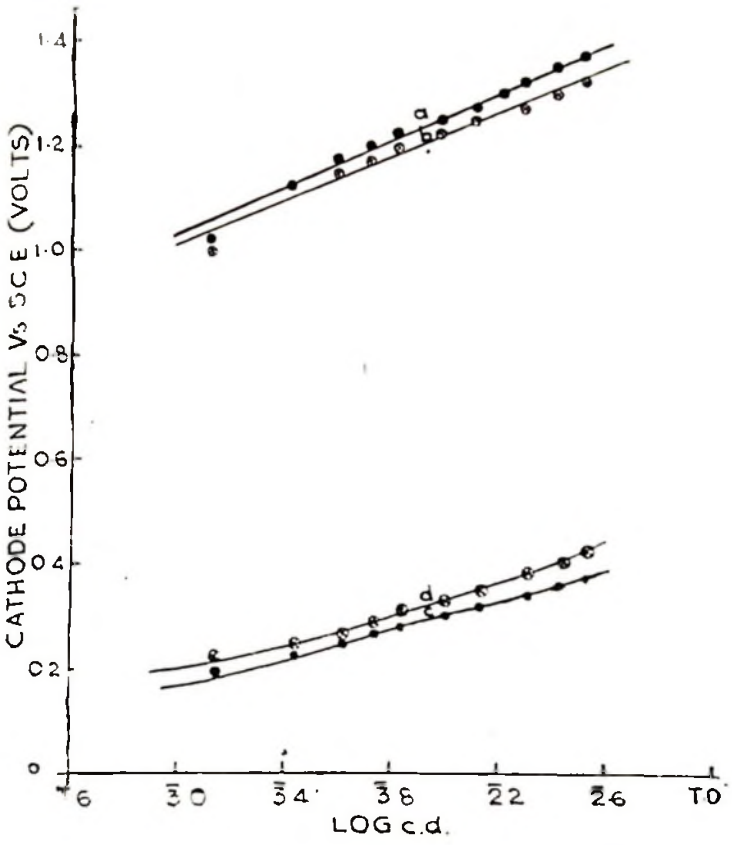


Fig. 6: Cathode potential — lod c.d. plot with amalgamated microelectrode

a) Without p-nitrophenol, without alcohol
b) „ „ with alcohol
c) With p-nitrophenol, without alcohol
d) „ „ with alcohol

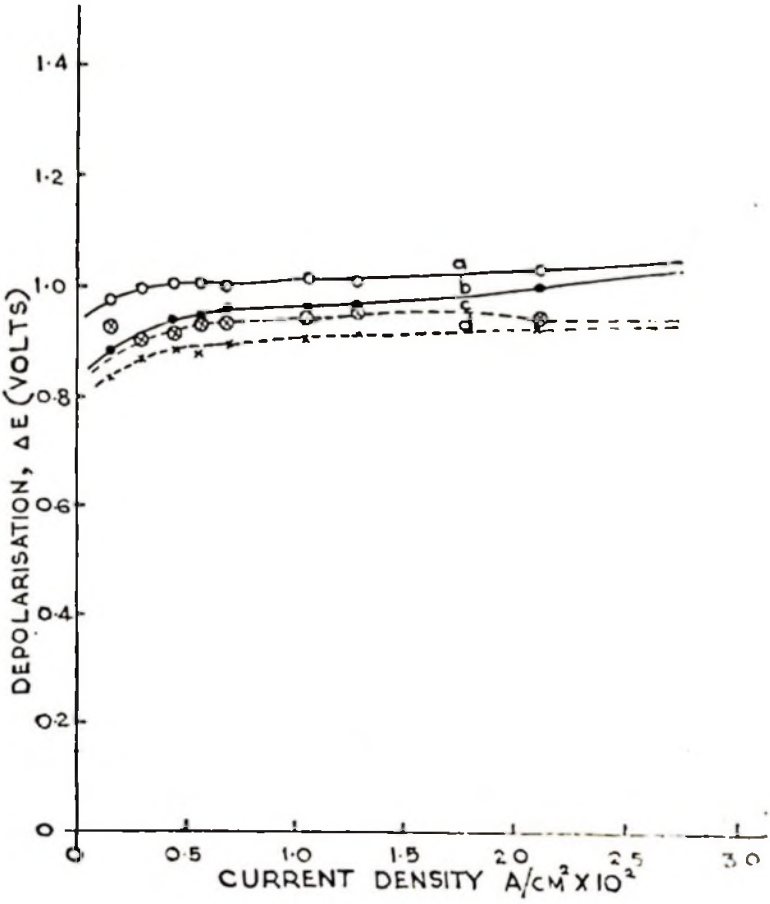


Fig. 7: Depolarisation (E) vs current density

a) Nitrobenzene without alcohol addition
b) p-Nitrophenol ,, ,, ,,
c) Nitrobenzene with alcohol addition
d) p-Nitrophenol ,, ,, ,,

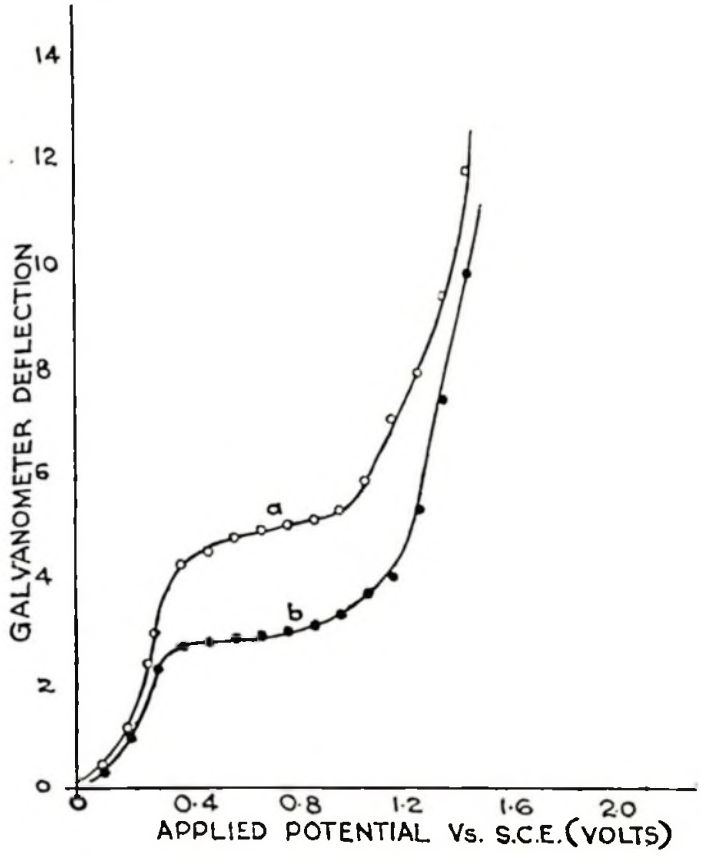


Fig. 8: Current-voltage curves with amalgamated microelectrode
a) For nitrobenzene
b) For p-nitrophenol

and p-nitrophenol at various current densities in the presence as well as in the absence of alcohol are plotted in Fig. 7. It is noted that nitrobenzene is a better depolariser than p-nitrophenol. Thus, it is noted that introduction of the -OH group in the benzene nucleus in the p-position to the nitrogroup decreases the depolarisation in view of the +T effect being greater than the -I effect of the same.

Current-voltage curves drawn using a manual polarograph and the amalgamated microelectrode gave results having the same trend. In obtaining the polarogram, the usual precautions were observed, i.e., by bubbling hydrogen for 15 minutes and adding maxima suppressor also (gelation 0.005%). Sensitivity is kept at 1/500. The supporting electrolyte is 2N sulphuric acid, the nitro compounds being added only in milligram quantities. The readings are plotted in Fig. 8 after correcting for residual current. Only one wave is obtained for both the nitrocompounds. The half-wave potential for nitrobenzene and p-nitrophenol are found to be -0.23V and -0.25V respectively. It is thus noted that $E_{\frac{1}{2}}$ is shifted to more negative value by the introduction of -OH group in the benzene ring in the para position to the nitro group. The shift of $E_{\frac{1}{2}}$ to more negative value indicates that the reduction of the latter compound is more difficult than nitrobenzene. Similar results have been noted by Kolthoff and Lingane[19] using dropping mercury electrode. This order is also in good agreement with the electronegativity rule of Shikata and Tachi[20].

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