Second Reduction Potentials
of
Some Nitroaromatic Compounds.
(CYCLIC VOLTAMMETRIC STUDIES)

By

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ABSTRACT

Second reduction potentials of some nitroaromatic compounds, 3-Nitroaniline, 4-Nitroaniline. 4-Amino-3-Nitrotoluene, I-Nitronaphthalene and 1,3-Dinitrobenzene have been studied by single sweep triangular wave cyclic voltammetry. To check the accuracy and reporducibility of results, investigations were carried out first using gold wire as reference electrode and then using $Ag/AgNO_3$ as reference electrode.

It was found that the first reduction potentials of the compounds studied were reversible. The second reduction potentials were found to be irreversible for all the compounds except 1,3-Dinitrobenzene.

To check the reversibility and irreversibility different types of criteria were used. It was found that for the first reduction potentials $(I_p)_c/(I_p)_a = I$, $(E_{1/2})_c = (E_{1/2})_a$, $E_p - E_{1/2} \approx 28$ to 30 mV, $E_{p/2} - E_{1/2} \approx 28$ to 30 mV, and $(E_p)_c - (E_p)_a \approx 58$ to 60 mV and the value of $\alpha n \simeq I$ all prove that the Ist reduction potentials are reversible. Using the same criteria, second reduction potentials were found to be irreversible and the value of αn found was approximately 0.3, which also confirms that they are irreversible. Thus the overall picture emerged as multistep reversible-irreversible processes.

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1. INTRODUCTION

Since the discovery of polarography in 1922 by Heyrovsky it has undergone many developments and at present it is one of the most reliable analytical tool in chemistry. In the early stages of polarography only the dropping mercury electrodes were used, then for more accurate recording of current-voltage curves oscilloscopic polarography was introduced. The use of stationary electrode added a new dimension to the polarographic studies and opened a new field of cyclic voltammetric studies (4, 15) at solid electrodes as well as stationary mercury drop electrode. The polarographic studies (or in more general terms voltammetry) includes kinetic studies, molecular structure investigation, adsorption phenomenon and thermodynamic properties.

The well known Nernst equation is only applicable to systems having some thermodynamic significane. But only the reversible systems have thermodynamic significance. When measuring the reduction potentials, if Nernst equation is applicable the reduction potential will be reversible. It means the reduction potentials has thermodynamic significance if these are reversible. It can be observed experimentally whether the reduction potential is reversible or irreversible. If the reduction potential is irreversible it means some chemical reaction is coupled with it. Reversibility can be proved both polarographically and cyclic voltammetrically. In polarography if a plot of log $\frac{i_d - i}{i_d}$ vs E gives a straight line, it means the system is reversible. If $E_{3/4} - E_{1/4} \simeq 56$ mv., it is also a proof of reversibility. In cyclic voltammetry there are some criteria for reversibility. For example if

$$(E_p)_c - (E_p)_a \simeq 58 \text{ to } 60 \text{ mv.}$$

$$E_p - E_{1/2} \simeq 28 \text{ to } 30 \text{ mv.}$$

$$E_{P/2} - E_{1/2} \simeq 28 \text{ to } 30 \text{ mv.}$$

It means the system should be reversible. There is one more authentic criteria of reversibility. It is that the ratio of anodic to cathodic peak currents should be unity.

Gokhshtein (13) calculated that if two waves behave as independent reversible waves, a certain minimum potential separation of about $118/_n$ mv is required between the formal reduction potentials. Irreversible wave will be more drawn out and the current corresponding to the irreversible wave will be lower. The irreversible waves depend on the charge transfer co-efficient αn which is calculated by the relation $E_p - E_{p/2} = 47.70/\alpha n$. The smaller the value of αn, the more the wave drawn out and more the changes of it being irreversible. Nicholson and shain along with a team of workers (5-7,10,33-40) did a lot for the development of voltammetric studies. Works of Matsuda, Ayabe, Reinmuth, saveant, Kemula and so many other workers (18,19,46-51,60-61,64,66) are also a valuable asset for those studying electrochemical phenomenon. New

Nitroaromatics have been subject for Polarographic and cyclic voltammetric studies (2,8-9,16,31-32,51). Geski and his callaborators did the polarographic studies of nitroaromatic compounds. They mainly devoted their observations to the changes of σ and ρ alongwith half-wave potential and ~~for~~ E S R spectra for nitro-aromatic compounds having different substituents. Where ρ is a constant characteristic of the reaction series, and σ is a constant peculiar to the substituent. Rieger and Fraenkel (52) also carried out the polarographic studies of Nitroaromatic compounds. They mainly stressed on the M. O. energies and Spin densities and their relation with half-wave potential. Kemula and Kublik (64) carried out the voltammetric study of 4-Nitroaniline in aqueous media.

No cyclicvoltammetric investigation has been reported for nitroanilines particularly the nature of second reduction potential have not been investigated by earlier workers. We carried out cyclic triangular wave voltammetric studies on 3-Nitroaniline (3-NA) , 4-Nitroamiline (4-NA), 4-Amino-3-nitrotoluene (ANT), m-Dinitrobenzene (DNB) and 1-Nitronaphthalene (NN) in acetonitrile solution. Meta-Dinitrobenzene was used as test system, on hanging mercury drop electrode in acetonitrile, to investigate the nature of second reduction potentials.

2. THEORY

1. Voltammetry

A number of new controlled potential techniques have been developed which can be applied to the study of electrode reactions. One of the most useful of these has involved the use of a stationary mercury electrode, the hanging mercury drop electrode (63). The hanging mercury drop electrode has been used in studies of the reduction of nitro-compounds. Voltammetry with continuously varying potential using this electrode is very rapid and reproducible, and is more sensitive, and powerful than conventional polorography.

The use of stationary electrodes in voltammetry offers several distinct advantages over the dropping mercury electrode. In addition to the reduced charging current, the constant area of the electrode makes it possible to scan the current-voltage curve in a relatively short time.

Stationary platinium electrodes have been studied by Laitinen and Kolthoff (25), Rogers, Miller,Goodrich, and Stehney (58) and, Nicholson (35) among others. Mercury pool electrodes were investigated by streuli and Cooke (62) who reported increased sensitivity (due to the large electrode area) and lower charging currents. Unfortunately, it is difficult to reproduce the area of mercury pool electrodes. Furthermore, rather large amounts of mercury are consumed, as the electrode must be removed frequently.

The development of the hanging mercury drop electrode by Gerischer (15) and Berzins and Delahay (4) has made available a very reproducible stationary spherical mercury electrode which shows great promise as an analytical tool. The solution of the equations for spherical diffusion with continously varying potential by Frankenthol and Shain (10) provides a reliable and accurate interpretation of the experimental results. (45).

Although these are significant advantages over the dropping mercury electrode, the major advantage from the stand point of a Kinetic study lies in the fact that the products of the electrode reaction remain in the vicinity of the electrode surface where they can be subjected to further reduction in order to characterize intermediates or to reoxidation in order to characterize the back reaction (63).

A. Polarography At Constant Potential :-

In Polarography at drapping mercury electrode the scan rate of potential is so low that it is about the study of current at constant potential. Since we have carried out cyclic voltammetric studies a very brief summery of this method (Polarographic method) only be given here. For details various books may be consulted (20,29-30,44,69,70).

Using the Nernst equation as fundamental equation the equation of the type given below have been derived (20,29).

$$E = E^{o} - \frac{0.0591}{n} \log \frac{f_{red}\, K_{ox}}{f_{ox}\, K_{red}} - \frac{0.0591}{n} \log \frac{i-(id)_a}{(id)_c-i}$$

$$\underline{E_{1/2}} = E^{o} - \frac{0.0591}{n} \log \frac{f_{red}\, K_{ox}}{f_{ox}\, K_{red}}$$

$$E = E_{1/2} - \frac{0.0591}{n} \log \frac{i-(id)_a}{(id)_c - i}$$

Here $E_{1/2}$ is the half-wave potential. The potential of the point on the current-voltage curve at which the diffusion current is one half of its limiting value is known as the half-wave potential. This potential is independent of the concentration of the reacting ions in the solution, the size of the mercury drops and the instrumentation and is characteristic of the kind of ion being deposited from a given base electrolyte (30).

When one considers the reactions of substance R in a solution containing an excess of background electrolyte. The solution is unsteirred and linear diffusion is maintained. The Nearnst equation is assumed applicable to the electrode process.

B. <u>Polarography at continuously changing potential</u>: Linear Scan Cyclic Voltammetry:-

In this case the potential is swept at perceptable rate. The sweep voltage can be represented by $E = E_i - Vt$ ---------------(1) Where E_i is the initial potential,V the rate of potential change in volts per second, and the time interval of electrolysis. E_i is set at a value where R is not reduced. Substance $R^{=}$ is assumed absent at time $t = 0$.

The diffusion problem was first solved and translated into a current-potential curve independently by Randles (24) and Sevčik (1). An excellent account of the details is given by Delahay (44). A valuable graphical representation of the process in terms of a three-dimensional diagram has been presented by Reinmuth (46). For a reversible reduction taking place at plane electrode.

$$R + n_e \rightleftharpoons R^{*}.$$

The bondary value problem will be

$$\frac{dC_R}{dt} = D_R \frac{d_2C_R}{dx^2} \qquad (1)$$

$$\frac{dC_R^{*}}{dt} = D_R^{*} \frac{d_2C_R}{dx^2} \qquad (2)$$

$$t = o, \quad x \geqslant o$$

$$C_R = CR^{o} \; ; \; C_R^{*} = C_R^{o*} \qquad (3)$$

$$t \geqslant 0, \qquad x \rightarrow \infty$$

$$C_R \rightarrow C_R^{\circ} \qquad ; \qquad \overset{*}{C_R} \longrightarrow 0 \qquad (4)$$

$$t > 0, \quad x = 0$$

$$D_R \frac{dCR}{dx} = -D_R^*\left(\frac{d\overset{*}{CR}}{dx}\right) \qquad (5a)$$

$$\frac{C_R}{C_{R*}} = \exp\left[(nF/RT) \quad (E-E^{\circ})\right]$$

$$\frac{C_R}{C_R^*} = \exp\left((nF/RT) \ (E-E^{\circ})\right) \qquad (5b)$$

Where C_R and C_R^* are the concentrations of substances R and R*, x is the distance from the electrode, t is the time, C_R° and $C_R^{\circ *}$ are the bulk concentrations of substances R and R*, D_R and D_R^* are the diffusion coefficients, n is the number of electrons, E is the potential of the electrode, E° is the formal electrode potential, and R,T, and F have their usual significance. The potential in equation 5b is a function of time, given by the relations.

$$0 < t \leqslant \lambda \qquad E = E_i - vt \qquad (6a)$$

$$\lambda \leqslant t \qquad E = E_i - 2v\lambda + vt \qquad (6b)$$

E_i is the initial potential, v is the rate of potential scan, and λ is the time at which the scan is reversed (the triangular wave voltammetry) The applicability of the Fick's diffusion equations and the initial and boundary conditions has been discussed by Reimmuth (51). Nicholson and Shain (37) solved the boundary value problem by rigorous mathematics and got the equation.

$$E = E^{o} - (RT/nF)\ \ln\gamma + (RT/nF)\left(\ln\gamma\theta + \ln S_{a\lambda}(at)\right) \quad (7)$$

Or

$$(E-E_{1/2})\ n = (RT/F)\left[\ln\gamma\theta + \ln S_{a\lambda}(at)\right] \quad (8)$$

and established the equation showing the values of the

$$i = nFAC_R^{o}\ \sqrt{\pi D_R a}\ \chi(at) \quad (9)$$

The ireversible stationary electrode polarogram for a plane electrode exhibits a maximum value of $i_p/(nFA\sqrt{D_R a}\ C_R^{o}) = 0.4463$ at a potential 28.50/n mv; cathodic of $E_{1/2}$(37) i.e.,

$$(E_p - E^{o})\ n + RT/F\ \ln\gamma = -28.50 \pm 0.05\ \text{mv}. \quad (10)$$

Or

$$E_p = E_{1/2} - (1.109) \pm 0.002)\ \ (RT/nF) \quad (11)$$

Actually, the peak of a reversible stationary electrode polarogram is fairly broad, extending over a range of several millivolts (37). Thus it is sometimes convenient to use the half peak-potential as a reference point (59), although this has no direct thermodynamic significance (37). The half peak potential precedes $E_{1/2}$ by 28.0/n mv; Or

$$E_{p/2} = E_{1/2} + 1.109\ (RT/nF) \quad (12)$$

The $E_{1/2}$ value can be estimated from a reversible stationary electrode polarogram from the fact that it occurs at a point 85.17% of the way up the wave.

Cyclic voltammetry is an extension of the potential sweep technique in which the potential is swept back and forth over the same region several times.

If the working electrode potential is swept negatively, a current peak due to reduction results. During the first part of the sweep, no current flows until the decomposition potential of the substance is reached. Once this point is passed, the current rises rapidly as the substance is consumed at the electrode surface. Since the solution is unstirred, the substance concentration at the electrode surface is soon depleted, and the current begins to drop. This process is repeated when the potential is sufficient to electrolyze the next electoactive species (59).

If, at the end of one potential sweep, the sweep direction is reversed, electrolysis of the products of the forward sweep takes place.

Cyclic voltammetric technique was first practiced by Sevcik (1). An excellent series of papers by Kemula and Co-Workers employing the hanging mercury drop electrode pointed the way to studies of electrode mechanism (64 - 68).

For cyclic voltammetry the sweep rates can be about the same as in single-sweep voltammetry, but values of 10-100 v/min are frequently of interest. Large amplitude signals of 0-3 V are used, depending upon the potential range of interest. The data are best presented on an X-Y recorder (1-Sec pen response), although conventional x-time or strip - chart recording can be used. Oscillographic recording is also used.

A rapid charge-transfer process (reversible system) will show cyclic polerograms. Actually, for a reversible system, the anodic and cathodic peaks are not at exactly the same potential, but a separation is predicted. This is verified by eq.

$$E_p = E_{1/2} \frac{-0.029}{n} \quad V \qquad (13)$$

Which shows that $E_{p,c}$ for a reduction is $\frac{0.029}{n}$ V more cathodic than $E_{1/2}$. Correspondingly, $E_{p,a}$ for the oxidation of the same system will be $\frac{0.029}{n}$ V more anodic than $E_{1/2}$. The potential increment between the peaks for a reversible system will be (44,18).

$$E_{p,a} - E_{p,c} = 2\,(0.029/_{n}) = \frac{0.058}{n}\ \text{V} \qquad (14)$$

Above equation holds for single-sweep polarograms of individual solutions of Ox and Red. Conditions in the actual cyclic polarograms are slightly different. For the reduction of a substance R, the concentration of R at the electrode surface is not zero at the peak potential and only becomes zero at potentials considerably beyond $E_{p,c}$. Since all R^- for reoxidation comes from the cathodic sweep, if the switching potential (cyclic reversal) is too "close" to $E_{p,c}$, the value of R^- will be slightly less than the initial bulk concentration of R. Thus the initial condition for the anodic reversal is not the same as for the starting cathodic sweep. The result is a small anodic shift of the oxidation wave, and the separation of peak potentials will be slightly greater than that predicted by eq. (14) Nicholson and Shain have calculated the shift of E_p for the reverse sweep in terms of the switching potential E_λ. Provided the sweep is carried far enough such that $(E_{1/2} - E_\lambda)\,n$ is of the order of 2-300 mV, the position of the reverse wave is relatively unaffected for sweep rates as slow as 3 V/min. This represents a time interval of only 4-6 sec past the peak.

Now there is a difference between the first two or three cycles and continuing cycles. In the absence of coupled chemical reactions, continuing cycles merely gradually alter the concentration profiles near the electrode surface. The anodic and cathodic peaks slightly change shape and decrease until a steady state is achieved. With slow sweep rates this steady state appears after about 5-10 cycles. For a reversible system Matsuda showed that the difference between initial and steady-state E_p's was only a few millivolts and relatively insignificant. A thorough discussion of cyclic polarograms at steady-state conditions is given in the original paper by Matsanda (19). The slight changes observed in cycling to steady -state conditions are very different from the gross alterations that may occur with coupled chemical reactions. The latter are most marked during the first few cycles. For most cases the most revealing information is contained with in the first five cycles and continuing on to the steady-state level is uninteresting.

C. Coupled Chemical Reactions:-

For coupled chemical reactions, stationary electrode polarography provides an extremely powerful method of investigating the kinetic parameters. A variety of possibilities exist. Chemical reactions may precede a reversible or irreversible electron transfer. Chemical reactions may follow a reversible or irreversible charge transfer.

In addition, an important, more complex, situation is frequently met where a chemical reaction is coupled between two successive electron transfers, i.e., electron transfer-chemical reaction-electron transfer--commonly referred to as an ECE mechanism.

A large group of coupled chemical reactions involves cases in which the electroactive species is produced by a Chemical reaction preceding a reversible charge transfer (37).

$$Z \underset{K_b}{\overset{K_f}{\rightleftharpoons}} R$$

$$R + ne \rightleftharpoons R^{ne}$$

The cases in which a reversible chemical reaction follows a reversible charge transfer

$$R + ne \rightleftharpoons R^{ne}$$

$$R^{ne} \underset{K_b}{\overset{K_f}{\rightleftharpoons}} Z$$

include a fairly large group of organic electrode reactions.

In another case of coupled chemical reaction, an irreversible Chemical reaction follows a reversible charge transfer.

$$R + ne \rightleftharpoons R^{ne}$$

$$R^{ne} \xrightarrow{K_f} Z$$

The boundary value problems for coupled chemical processes are quite involved and has been discussed by Nicholson and Shain (37). Here we give only qualitative discussion. For the case when Ist wave is reversible and IInd irreversible, then the irreversible wave will have the same characteristics as described by Nicholson and Shain (37) earlier Nicholson and Shain (37) derived the relation

$$E_p - E_{p/2} = -1.857 \, (RT/\alpha nF) \qquad (15)$$

and showedt that both the peak potential and the half-peak potential are functions of the rate of potential scan.

$$(E_{p/2})_2 - (E_{p/2})_1 = (E_p)_2 - (E_p)_1 = (RT/\alpha nF) \ln \sqrt{V_1/V_2} \qquad (16)$$

and thus, for a totally irreversible wave, there is a cathodic shift in peak potential or half-peak potential of about 30/αn millivolts for each ten-fold increase in the rate of potential scan. For the cyclic scans no anodic wave is observed for the corresponding cathodic irreversible wave. Xn can be calculated from the relation given above (59).

II. MULTISTEP CHARGE TRANSFERS:-

The case when reduction takes place in steps like

$$R + e \rightleftharpoons R^{-} + ne \longrightarrow R^{*} \qquad (1)$$

the problems is more involved.

Qualitatively if R and R^{-} react at sufficiently separated potentials with R more easily reducible than R^{-}, or we may say that stepwise addition of electrons takes place, then the polarogram for the overall reduction of R to R^{*} consists of two separate waves. The first wave corresponds to the reduction of R to R^{-} and in this potential range, substance R^{-} diffuses into the solution. As the potential is scaned toward cathodic values, a second wave appears which is made up of two parts superimposed. The current related to species R, which is still diffusing towards the electrode, increases since this species now is reduced directly to R^{*} by (1 + ne) electrons. In addition the species R^{-}, which was the product of the first wave is also being reduced in this potential region, and a portion of this material diffuses back toward the electrode and reacts. Gokhshtein and Gokhshtein (12,13) has also discussed such a type of multistep charge transfers involving reversible, quasireversible, or irreversible system in various combinations for any mumber of successive reactions. Later on Polcyn and Shain (7) applying this theory for the interpretation of experimental voltammetry, restricted their treatment to only two species. But they did not limit the addition of electrons one by one. Rather they gernalized that unspecified number of electrons may be added in each step. To correlate these theories with experiment, here addition of one electron in Ist step and ne electrons for IInd step case only are considered.

These voltammetric characteristics depend on many factors, including the nature of the charge steps, the potential separation between the individual charge transfers, the number of electrons in the specific steps, and whether the experiment is performed as a single potential scan or as a cyclic potential scan (7).

For a two-step electron transfer, the boundary value problem is (7).

$$\frac{dC_R}{dt} = D_R \left(d_2C_R / dx^2 \right) \qquad (2)$$

$$dC_{R^-}/dt = D_{R^-} \left(d_2C_{R^-}/dx^2 \right) \qquad (3)$$

$$dC_R^*/dt = D_R^* \left(d_2C_R^*/dx^2 \right) \qquad (4)$$

$$t = 0, \quad X > 0: \quad C_R = C_R^o$$

$$C_R^- = C_R^{o-} \;; \quad C_R^* = C_R^{o*}$$

$$C_{R^-}, \; C_{R^*} \simeq 0 \qquad (5)$$

$$t > 0, \quad x \to \infty: \; C_R \longrightarrow C_R^o$$

$$C_{R^-} \longrightarrow 0 \quad ; \quad C_R^* \longrightarrow 0 \qquad (6)$$

$$t > 0, \quad x = 0$$

$$D_R \left(dC_R/dx \right) + D_R^- \left(dC_R^-/dx \right) + D_R^* \left(dC_R^*/dx \right) = 0 \qquad (7)$$

$$C_R^{+}, C_R^{-}, C_R^{*} = f\ (E,t) \qquad (8)$$

Here x is the distance from the electrode surface, t is the time, C_R^{+}, C_R^{-} and C_R^{*} are the concentrations of the substances R, R^{-}, and R^{*}, C_R^{o} C_R^{o-}, and C_R^{o*} are the bulk concentration and D_R, D_R^{-} and D_R^{*} are the respective diffusion co-efficients. The function f(E,t) for stationary electrode polarography is a periodic triangular variation of the electrode potential. The total current for the two step reaction is given by

$$i_t = FRf_R\ (t) + nFR\ \left[f_R\ (t) + f_{\bar{R}}\ (t) \right] \qquad (9)$$

The solutions to boundary value problesm has also been discussed by (37,38,43).

The flux of substance $\bar{R}$ is the negative of the flux of substance R, in the potential region of first wave; thus the entire second term does not appear and the current merely corresponds to the flux of substance R. Polen and Shain (7) have discussed the integeral equations for R–R R–I, I–R and I-I charge transfer reactions and their solutions in detail (7).

A. Reversible Charge Transfers:-

Effect of Potential Separation:- Gokhshtein (13) have calculated that in order the polarograms of two waves behave as independent reversible waves, a certain minimum potential separation, ΔE^{o}, of about 118/n mv.

is required between the formal reduction potentials.Polycn and Shain (7) have calculated a theoretical polarogram with a potential separation ΔE^{o} of-180 mV and is shown in figure I, it is further said that when ΔE^{o} is less than 100/n mV; the individual waves merge into one broad distorted wave whose peak height and shape are no longer characteristic of a reversible wave. The wave is broadened like irreversible wave, but can be distinguished from the irreversible wave, because the distorted wave does not shift on the potential axis as a function of the scan rate. When $\Delta E^{o} = 0$ and each step involves one electron, then both the waves merge into one another and the peak height observed is that of between a one-electron and two-electron reversible wave and $E_p - E_{1/2}$ is about 21 mV. When it is easier to reduce R^{-} than R, the wave height increases and the peak narrows until it reaches the height and shape of a two-electron wave. The height of the two-electron wave is $(2)^{3/2}$ times that for the single electron reversible wave and $E_p - E_{1/2}$ is 14.25 mV and reaction seems to be direct reduction of R to R^{*}. The effective E^{o} for the eomposite wave of two electrons is given by $(E_1^{o} + E_2^{o})/2$.

<u></u>Effect of Number of Electrons:- As it is known that number of electrons are the multiplying factors in the equations for current and potential, therefore the variation of number of electrons in two-step charge transfer reactions effects both the position and shape of waves. When both the waves are well separated then each wave is proportional to $(n)^{3/2}$ and the potential range covered by each wave is determined by the individual value of $(E - E^{o})$ n. For distorted waves the effect of varying n_1 and n_2 is complicated.

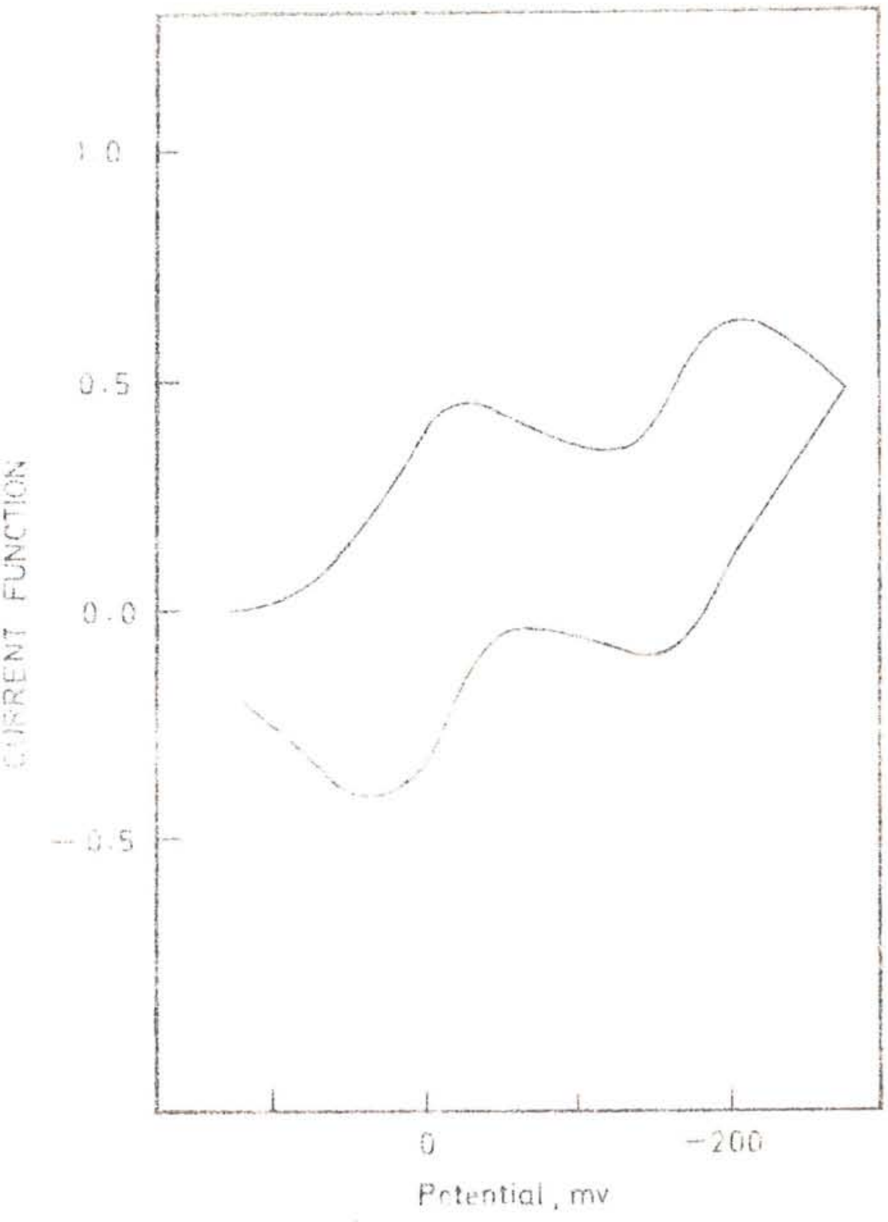

FIG.1 CYCLIC STATIONARY ELECTRODE POLAROGRAM FOR CASE R-R

The effect of single scan and cyclic voltammetry for two-step charge transfer reactions are similar to those as for single step charge transfer reactions (7, 37).

B. Irreversible Charge Transfer:-

(R____ I, I____ R, I____ I):-

(where R stands for reversible and I stands for irreversible).

When one of the waves is reversible and the other is irreversible, the characteristics of the irreversible charge transfer will be like those as discussed by (37). The wave will be more drawn out and the current corsponding to the irreversible wave will be lower. The current function has an value of 0.496 at the peak, $E_p - E_{p/2} = 47.70/\alpha n$ (7). For cyclic scan, no anodic wave is observed for the corresponding cathodic irreversible wave. Irreversible waves depend on the charge transfer co-efficient α. When ΔE^o (potential separation) for two waves is less than about $100/\alpha n$ mV, the waves merge and a distorted wave is obtained. When $\Delta^o E = 0$, then a composite wave having the characteristics of both the waves is observed. When R is easier to reduce than R, then the wave height increases and the peak becomes sharper. Voltammogram for selected systems involving a reversible -irreversible charge transfer step is shown in Fig. 2 by Polcyn and Shain (3).

To investigate the second wave a base line should be established from the descending branch of the preceding wave. Gokhshtein and Gokhshtein (12,14) established equations for this purpose and later on Polcyn and Shain (7) did some imporvements.

Sometimes it becomes difficult to distinguish between multistep charge transfer reactions and systems in which coupled chemical reactions,

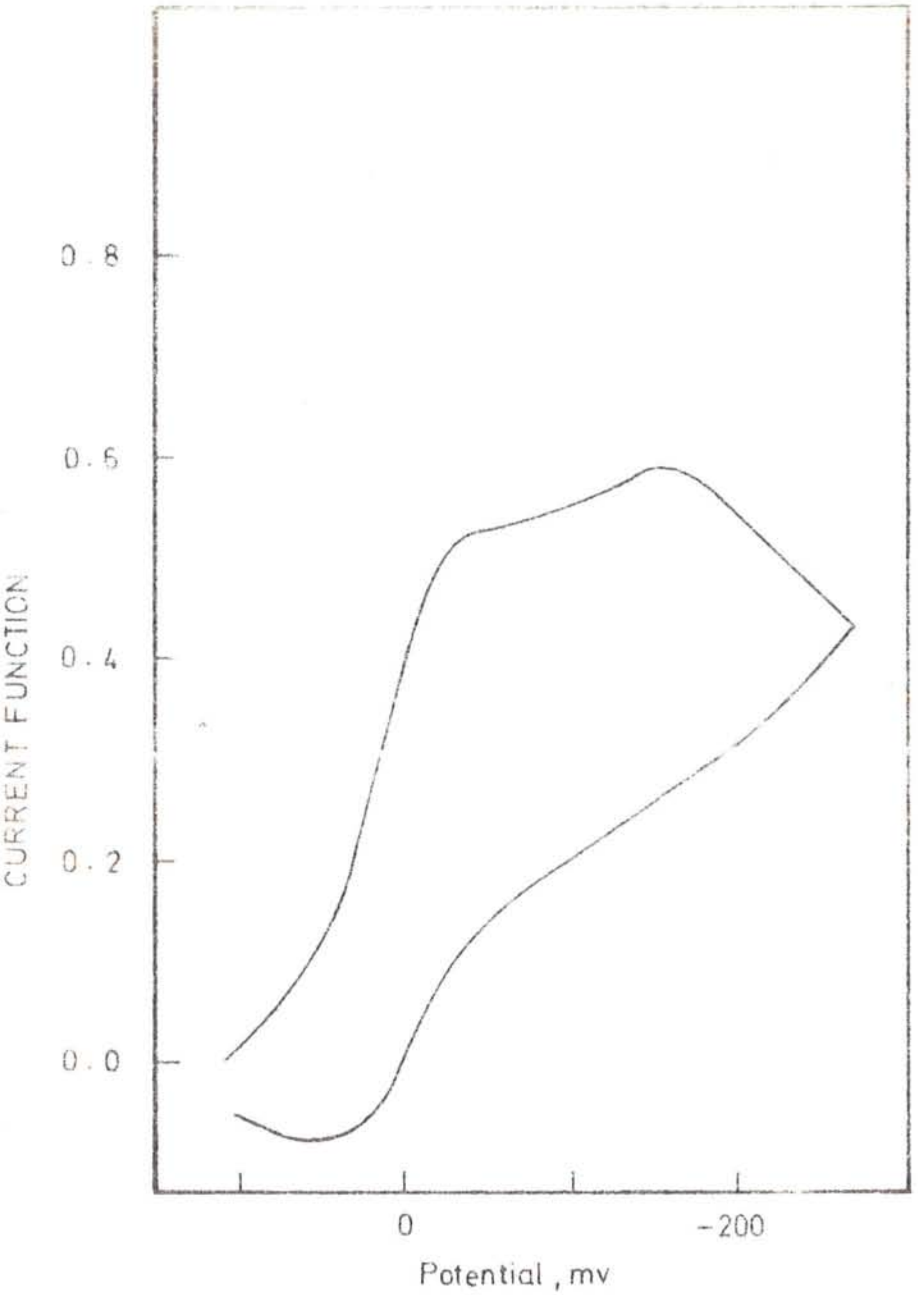

FIG. 2. CYCLIC STATIONARY ELECTRODE POLAROGRAM FOR CASE R-I

are present. But there are two things which can be used as diagnostic criteria. First is that over the entire range of scan rates, the quantity $i_p/\sqrt{V}$ is a constant for systems involving only multistep charge transfers. Secondly if ΔE° is sufficiently negative, the type of multistep charge transfer system can be determined from the number of anodic waves. (7)

III. Criteria of Reversibility:-

As was mentioned before that for the reduction potential to be reversible it should fulfill certain criteria. If it is not fulfilled then it is suspected that some other phenomena are involved. In the following sections these criteria are discussed.

A. Polarographic:-

The fundamental criteria of reversibility is that: if the half-reaction is reversible, the cathodic wave obtained with the oxidized form alone, the anodic wave obtained with the reduced form alone, and the composite wave obtained with the mixture of two must all have the same half-wave potential, and all must obey an equation of the form (26).

$$E = E_{1/2} \frac{-0.05915}{n} \log \frac{i-(i_d)_a}{(i_d)_c - i} \qquad (i)$$

Where $E_{1/2}$ is the half-wave potential, i is the current passing i_d is the diffusion current, c and a represent cathodic and anodic wavesrespectively. Sometimes electroactive impurities may cause invonvenience (2).

From the equations (26) given below it is

$$E = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{(i_d)_c - i} \qquad (i) \quad (\text{cathodic})$$

$$E = E_{1/2} - \frac{0.05915}{n} \log \frac{(i_d)_a - i}{i} \qquad (ii) \quad (\text{anodic}) \qquad (2)$$

$$E = E_{1/2} - \frac{0.05915}{n} \log \frac{i-(i_d)_a}{(i_d)_c - i} \qquad (iii) \quad (\text{compositive wave})$$

apparent that a plot of $-E$ Vs the log term appropriate to the kind of wave being considered should be linear and should have a slope of 59.15/n mv. This linear relation is a proof of reversibility. Meites (26) says that plot in the range of -1.5 to $+1.5$ volts must be linear and any serious divergence in this range is a definite proof of irreversibility, because this corresponds to values of the current ranging from about 3 to 97 % of the diffusion current and error due to residual current is negligible.

From the equations (2) $E_{1/4}$ and $E_{3/4}$ can easily be evaluated.

$$E_{1/4} = E_{1/2} - \frac{0.05915}{n} \log \frac{i_{d/4}}{i_d - i_{d/4}}$$

$$= E_{1/2} - \frac{0.05915}{n} \log \frac{1}{3} \qquad (3)$$

and

$$E_{1/4} = E_{1/2} - \frac{0.05915}{n} \log 3 \qquad (4)$$

so that

$$E_{3/4} - E_{1/4} = -\frac{0.05915}{n} \log 9 \qquad (5)$$

$$= -\frac{0.0564}{n}$$

Here $E_{3/4}$ and $E_{1/4}$ are the potentials at which the current is equal to one-fourth and three-fourths of the diffusion current. Thus eq. (5) is another proof of reversibility.

Sometimes irreversible waves or half-reactions involving two or more electrons may give log plots having about the slope of eqs. (2). Therefore, n should not be calculated from log plot or $E_{3/4} - E_{1/4}$ rather it should be obtained from diffusion-current data (27). Now again there are couples whose reduced forms given anodic waves that seem to be reversible according to these criteria, but whose oxidized forms cannot be reduced at all or can be reduced only at much more negative potentials. This behaviour arises from a mechanism like

$$A + ne \rightleftharpoons B \qquad \text{(reversible)}$$

$$B \longrightarrow C \qquad \text{(slow)}$$

Which shows that a reversible electron-transfer step is followed by an irreversible rearrangment, which may be due to some coupled chemical reaction. This system cannot be calculated as reversible from the simple fact that the slope of the log plot or the value of $E_{3/4} - E_{1/4}$ for the wave of A agrees with the reversible prediction, rather the difference between the cathodic and anodic half-wave potentials will slow that the A ____ C couple is irreversible.

Thus from the preceding discussion it is apparent that these two criteria of log plot and $E_{3/4} - E_{1/4}$ are not definite proof of reversibility. But if the slope of a log plot appreciably exceeds 59.2/n mV. or if the numerical value of $E_{3/4}-E_{1/4}$ appreciably exceeds $\frac{56.4}{n}$ mV. the couple should be taken to be irreversible without further ado. It means that these two criteria should be used to prove irreversibility and not reversibility.

There are some other criteria of reversibility which are rarely used. First is that appreciable variation of $E_{1/2}$ with concentration can be usually taken as conclusive proof of the irreversibility of the half-reaction. The converse does not hold true. The second is that, a large positive temperature co-efficient of the half-wave potential, usually signifies that the half-reaction is irreversible. The temperature co-efficient of the half-wave potential of a reversible wave is usually small, typically between -2 and + 2 mV/deg. Irreversible waves often have half-wave potentials with similarly small temperature co-efficient (28), but there are some whose temperature co-efficients are positive and exceed several millivolts per degree. This is due to substantial heat of activation. Thirdly a comparisón of half-wave potentials theoretically calculated and experimentally determined can also be used as a proof of reversibility or irreversibility.

B: Cyclic Triangular Wave Voltammetric:-

In voltammetry the basic criteria of reversibility is that

$$(i_p)_c = (i_p)_a$$

(i_p is the peak height from the base line and c and a stand for cathodic and anodic respectively). We can directly estimate the electrode reversibility, because the potentials at which oxidation and reduction occur are observed directly. For example, at low frequencies of scanning it may be possible with a given system that electrochemical equilibrium alwa$y is maintained at the electrode surface. Under these conditions the separation of cathodic and anodic peak potentials is about $60/n$ mV, and the reaction is reversible (40)

Thus

$$(E_p)_c - (E_p)_a = 60/_n \text{ mV} = \Delta E_p \qquad (6)$$

For irreversible system, the peak separation ΔE_p is always greater than 60 mV. (40)

The other diagnostic criteria of reversibility is that, when the ratio of anodic to cathodic peak current is unity. This shows that the system is completely reversible and there is no coupled chemical reaction (37). By using for the base line the cathodic wave which would have been obtained if there had been no change in direction of potential scan, all of the anodic curves are the same, independent of switching potential, and indentical in height and shape to the cathodic wave. Experimentally the cathodic base line can be obtained by extending a single scan cathodic sweep beyond the selected switching potential, or if another reaction interferes by stopping the scan at some convenient potential past the peak, and recording the constant potential current-time curve. The latter method of obtaining the base line has been proposed for analytical purposes by Reinmuth (71).

The only reaction which alongwith the reversible case gives a constant value of unity for the ratio of anodic to cathodic peak heights on varying the switching potential is the catalytic reaction.

Matsuda and Ayabe studied the relations in voltammetry for reversible , and totally irreversible systems, i.e; when one must consider the relative rates of charge transfer and mass transfer (18). For the reversible case they found that simple relations exist between the E_p , $E_{p/2}$ (such as at 25°C (55)), and the conventional $E_{1/2}$.

$$E_p = E_{1/2} \quad \frac{-0.029}{n} \text{ V} \quad \text{(i)}$$

$$E_{p/2} = E_{1/2} + \frac{0.028}{n} \text{ V} \quad \text{(ii)} \qquad (7)$$

$$(E_p - E_{p/2}) = \frac{0.057}{n} \text{ V} \quad \text{(iii)}$$

These above equations serve as good criteria of reversibility. It can be seen fro eq (iii)-7 that the peak polarogram of a reversible system in sharp, spanning a voltage range of roughly 0.12 V for a one electron system. The peak potential is 0.029/n mV. more cathodic (for a reduction) than the corresponding $E_{1/2}$ and further, the $E_{p/2}$ is $\frac{0.028}{n}$ V more anodic.

The equations for a totally irreversible peak polarogram are considerably more involved (44). No simple relation exists between E_p and $E_{1/2}$ — the expression involves both the heterogeneous rate constant for the charge transfer and the transfer co-efficient . The product of the transfer co-efficient x and the number of electrons in the rate-determining step n can be found from the effective slope of the peak polarogram.

$$E_{p/2} - E_p = \frac{0.048}{\alpha n} \quad V \qquad (8)$$

It can be observed that as (αn) decreases, the peak polarograms become more spread out and the peaks tend to be rounded rather than sharp.

IV. Electrode System:-

In early stages of polarography two electrode system was used to study the electrochemical processes. The electrodes being the dropping mercury electrode acting as working electrode and a large mercury pool, which in presence of Kcl in aqueous solution, acted as a non-polarizable reference electrode and anode as well. With the development of non-aqueous polarography, where large IR drop was involved three electrode system has been found to be more advantageous.

In two-electrode system by coupling the test-electrode with a non-polarizable reference electrode two quantities can be measured: (i) the changes in the potential of the test electrode and (ii) the potential of the test electrode relative to the reference electrode. Such a two-electrode system is quite adequate for the measurement of equilibrium relative electrode potentials. An electrode through which a finite current is passing has a potential different from its zero current or equilibrium value. This difference is ordinarily called overvoltage or overpotential and is given the symbol η. It has been calculated that (21).

$$\eta = -\frac{RT}{(1-B)^F} \ln i_o + \frac{RT}{(1-B)^F} \ln i \qquad (1)$$

Or

$$\eta = -\frac{2.303\ RT}{(1-B)^F} \log i_o + \frac{2.303\ RT}{(I-B)^F} \log i \qquad (2)$$

All termsin these equations are explained (22). Thus, when the electronation current i becomes too small for consideration, the current producing or the current-produced potential (the overpotential) is a linear function of log i. Now to determine the overpotential, it is necessary to alter the two-electrode system by introducing an extra auxillary electrode, which is also called the counter electrode.

three-electrode arrangement is set up. In such a set up the counter electrode is connected to the test-electrode via a polarizing circuit (e.g; a power source) through which a controllable current is made to pass and produce alterations of the potential of the test electrode. Between the nonpolarizable reference electrode and test electrode is connected an insturment which is capable of measuring the potential difference between these electrodes. The measuring instrument must have a high input impedance (23).

In equilibrium conditions at the test electrode-electrolyte interface the potential difference E_e is given by

$$E_e = \Delta\phi_e + \Delta\phi_{contact} + \Delta\phi_{ref,e} \qquad (3)$$

Here $\Delta\phi_{contact}$ and $\Delta\phi_{ref,e}$ are the potential differences across the metal-metal contact and reference interfaces.

On passing current I through the polarizing circuit, (i) the potential of the test electrode changes from $\Delta\phi_e$ to $\Delta\phi$; (ii) the potential difference across the metal-metal contact can be considered to be unchanged; (iii) the potential of the reference electrode remains at the equilibrium value, $\Delta\phi_{ref,e}$, because no current flows through the measuring circuit (i.e; between the reference and test electrodes) and (iv) a potential drop arises in the electrolyte through which the polarizing current flows. Under these conditions, the measured potential difference between the test and reference electrodes is

$$E = \Delta\phi + \Delta\phi_{contact} + \Delta\phi_{ref,e} - IR \qquad (4)$$

IR is the potential drop developed between when the polarizing current I overcomes the resistance $R = \ell/\sigma A$ of the electrolyte between the test electrode and the so-called Luggin tip or probe by means of which the reference electrode makes ionic or electrolytic contact with the test electrode.

From Eqs (3) and (4)

$$\eta = \Delta\phi - \Delta\phi_e = (E-E_e) + IR \qquad (5)$$

The IR drop can be eliminated by minimizing R, i.e; by choosing high-conductivity electrolytes and using small distances between the test electrode and Luggin tip.

From the preceding discussion it is clear that η can be observed experimentally using a three-electrode system, measuring the potential of the test electrode with respect to a reference half-cell.

Thus, η is the total overpotential η_t, which experimentally may be composed of three quantities (20): Ohmic overpotential n_o or IR, concentration overpotential η_c, and activation overpotential η_a.

Thus,

$$\eta_t = \eta_o + \eta_c + \eta_a \qquad (6)$$

Concentration polarization is the very basis of voltammetry. A current-voltage curve is nothing more than the measurement of concentration overpotential effects at an electrode. The polarizable (test) electrode used in voltammetry is one at which it is possible to obtain extreme evidence of concentration overpotential. When this high degree of η_c develops, limiting currents are obtained.

In the strictest sense there are no nonpolarizable electrodes (41) However, η_c is quite small at a large electrode provided the concentrations of electroactive material are very large. Such an electrode is said to be relatively non-polarizable and serves as reference electrode in voltammetry. The activation overpotential is associated with a slow or rate-determining electron-transfer processes and η_o and η_c are a natural results of the current flow (56).

3- Experimental:-

A:- Purification of Mercury:

In most of the experimental work, hanging mercury drop electrode was used as test electrode. Mercury metal used was of Fisher Scientific Company. According to the certificate of analysis of the company, its specification was as follows: At wt. 200.59. Foreign metals not more than 0.0005 %. Appearance of impurities was nil. This available mercury metal was further purified by passing mercury supplies through a pinhole in the cone of a No. 40 Whatman filter paper. This process was continued and repeated many times until the last drop of mercury left on filter paper was as shining as the other part.

To verify whether mercury was completely purified, one test was applied. Mercury was placed on a clean smooth glass surface. Tailing of the mercury occurs with the contaminated specimens whereas no tailing visible is with very pure mercury. No tailing was observed with the above purified mercury.

B:- Purification of Chemicals:-

Different chemicals used were of laboratory reagent grade , they were further purified to get good results.

i) Purification of 1-Nitronaphthalene:-

1-Nitronaphthalene of Riedel-De Haen Ag Seelze-Hannover, Germany was crystallized twice from ethyl alcohol (42). Very nice yellow coloured and needle shaped crystals were obtained. The melting point of the compound was determined. M.Pt. was found to be 60.0°C and the literature value is 61.0°C (17).

ii) Purfication of 1,3-Dinitrobenzene:-

1,3-Dinitrobenzene of BDH-Chemicals Ltd., was purfied by crystallizing it twice from CCl_4 (42). Its melting point was determined and was found 90.5°C and the literature value (17), is 91°C.

iii). Purfication of 3-Nitroamiline :-

3-Nitroamiline was crystallized twice from benzene (42). Its melting point was found to be at 115°C and literature value (17) in 114°C.

iv) Purfication of 4-Nitroaniline:-

4-Nitroamiline of EGA-Chemicals,Germany was also crystallized twice from benzene. It melting point was found to be 147°C and the literature value (17) is 148°C .

v). Purification of 4-Amino-3-Nitro-Toluene Or 2-Nitro-p-Toluidine:-

4-Amino-3-Nitratoluene of Hopkins and Williams Ltd. was crystallized from benzene twice (42). Its melting point was found to be 116.5°C and the literature value (17) is 117°C.

C: Solvents:

i) Acetonitrile:-

Acetonitrile was used as a solvent to carry out the main experiments. ACS certified acetonitrile of Fisher Scientific Company was used directly. Acetonitrile of BDH chemicals Ltd., was used after distillation with P_2O_5 . Distillate between 81°C to 82°C was collected and used.

ii) Benzene, Carbon Tetrachloride, and Ethyl alcohol:-

Laboratory reagent grades were used directly for crystallizations Alcohol used was Analar Alcohol of BDH Chemicals. Carbon tetrachloride used was P.P.H. Polskie Odezynniki Chemiezne-Gliwice, Poland. Benzene used was of BDH-Chemicals.

D:- Electrolyte:-

Tetrabutylammonium perchlorate of Eastman Kodak Co. was used directly as the electrolyte in all the experiments.

E:- Innert Gas:-

Innert gas N_2 from lecture Bottle (H.P. dry) of Matheson gas products was used to remove dissolved oxygen from the solution by bubbling N_2 through the solution.

F:- Electrodes:-

The electrode system used was as follows:-

i) Test Electrode:-

Hanging mercury drop electrode was used as a test electrode. It was prepared by attaching a small drop of purified mercury to the end of a gold wire sealed in a capillary glass tube of 0.D-6 mm with the help of araldite. No ill effect of araldite was found and the results were reproducible. This electrode is shown in fig. 3.

ii) Counter Electrode:-

A platinium wire electrode (supplied by Heath Co. in their polarographic assembly) was made into a circle surrounding the mercury drop and was used as a counter electrode. This is shown in fig. 4.

iii) Reference Electrodes:-

Different reference electrodes were tried. At first gold gold wire reference electrode was used. fig.5a Reproducible results were obtained with this reference electrode for all the five compounds.

FIG.3. Test electrode

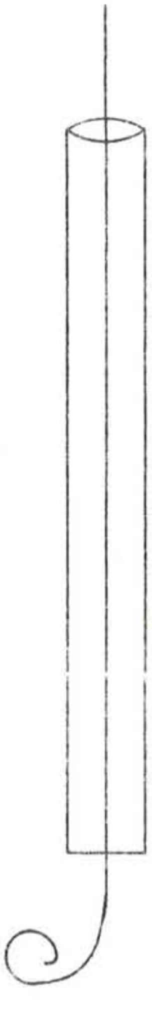

FIG.4. Counter electrode

FIG.5.a.
Reference electrode, Gold wire

An aqueous saturated calomel electrode was also tried as reference electrode. However a Ag/Ag NO_3 electrode is more practical. for the electrochemical studies carried out in acetonitrile (72). All the five compounds were studied using this electrode as reference electrode. To prepare Ag/$AgNO_3$ electrode about 10 ml. of 0.1 molar solution of tetrabutylamonium perchlorate in acetonitrile was taken. It was then made 0.01M in $AgNO_3$. This solution was filled into an outer jacket of a SCE electrode, which had been washed thoroughly to get rid of Kcl. The tip was suitably plugged by the manufacturer (Beckman) of SCE electrode. A silver wire was dipped in the above solution to make Ag/$AgNO_3$ electrode. It is shown in fig.5b

G. Electrolysis Cell:-

For all experiments, a cell of the type shown in fig.6 was used. The teflon cell cap shown in fig. 7 was carefully machined to fit tightly on the cell. Through this cap passed the test electrode, the counter electrode, the reference electrode, the nitrogen inlet tube and nitrogen outlet tube. All of the teflon to glass joints were made as air tight as possible.

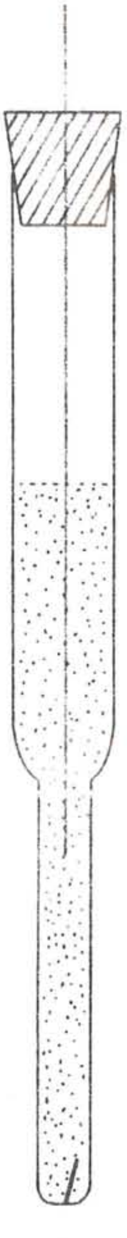

FIG.5.b Reference electrode Ag / $AgNO_3$

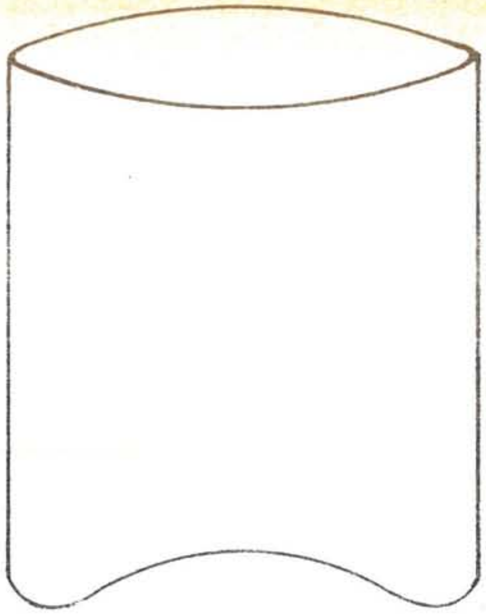

FIG. 6.
Electrolysis Cell

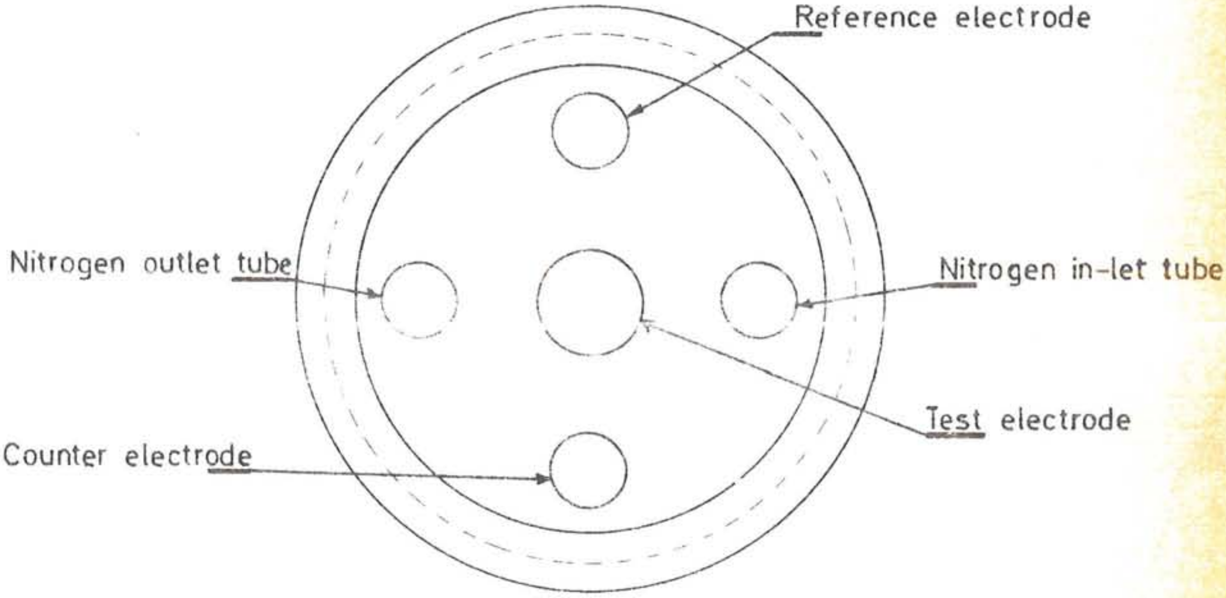

FIG. 7.
Cell cap of teflon

Instrumentation:-

All the first and second reduction potentials of all the compounds were measured on Heath Company's polarography Laboratory model Eu-402 V including EUA-19-2 Polarography Module, EUW-19 B operational Amplifier, EUA-19-4 Amplifier stabilizer, EU-20V Multispeed Recorder, EUA-19-6 Dropping mercury electrode assembly installed in the Institute of Chemistry, University of Islamabad. Dropping mercury electrode was changed to hanging mercury drop electrode. To see the reversibility and irreversibility of waves for first and second reduction potentials, Oscilloscopic recording assembly was also employed besides the chart recorder. For studies at higher scan rates (for triangular cyclic voltammetry) a Tektronix function generator (model TM 501) was used and the signal displayed on an oscilloscope (Tektronix 453 A).

Sweep rate was kept 2V/min for most of the readings. Chart speed and micro-ampere full scale were adjusted accordingly to get best possible graphs of current VS voltage curves. All the measurements were made at the ambient temperature.

Most of the readings were recorded on EU-20V multispeed recorder. To check the accuracy of the instrument waves were also seen on the oscilloscope. Under the experimental conditions and for the purpose of measurement of Ist and IInd reduction potential, EU-20 V multispeed recorder was found to be sufficiently accurate except it seemed to have some artifact for second reduction potential.

4- Results And Discussion

The results of cyclic voltammetric studies are collected in tables (1-3). The cyclic voltammograms of 1-Nitronaphthalene, (I-NN) 3-Nitroamiline (3-NA), 4-Nitroaniline (4-NA), 4-Amino-3-Nitrotoluene and m-Dinitrobenzene (m-DNB) are also shown in figs (8-12). Except for m-Dinitrobenzene, two cathodic and one anodic peaks were observed for the remaining compounds studied. For (m-DNB) two cathodic and two anodic peaks were observed. As for as m-Dinitrobenzene is concerned, it has already been confirmed (73) that its first and second reduction potentials both are reversible. Therefore, it was used overhere as a test and reference system. The second reduction potentials of the remaining compounds in non-aqueous media has not been studied by cyclic voltammetry. To study the reversiblity or irreversibility of these compounds, different criteria were used which has already been discussed in the chapter-2. The $(E_p)_c - (E_p)_a \simeq 60$ mV. on HMD electrode, $(i_p)_c / (i_p)_a$ ratio as unity and $E_{p/2} - E_{1/2}$ (where $E_{1/2}$ is the potential corresponding to 85% of the peak current) $\simeq 28$ mV criteria for reversibility (in addition of the trivial condition $(E_{1/2})_a = (E_{1/2})_c$ calculated as already mentioned) all confirm that the first reduction potential of each compound, is reversible and the reduced species, the anion radicals are stable. It was seen from the recorded voltammogram that the second reduction potentials of these compounds except m-dinitrobenzene are irreversible. This can be seen from the figures (8-12) given for these compounds.

Quantitatively the equations for a totally irreversible peak polarogram are considerably more involved (44,18,37). No simple relation exists between E_p and $E_{1/2}$, the expression involves both the heterogeneous rate constant for the charge transfer and the transfer co-efficient. The product of the transfer co-efficient α and the number of electrons n in the

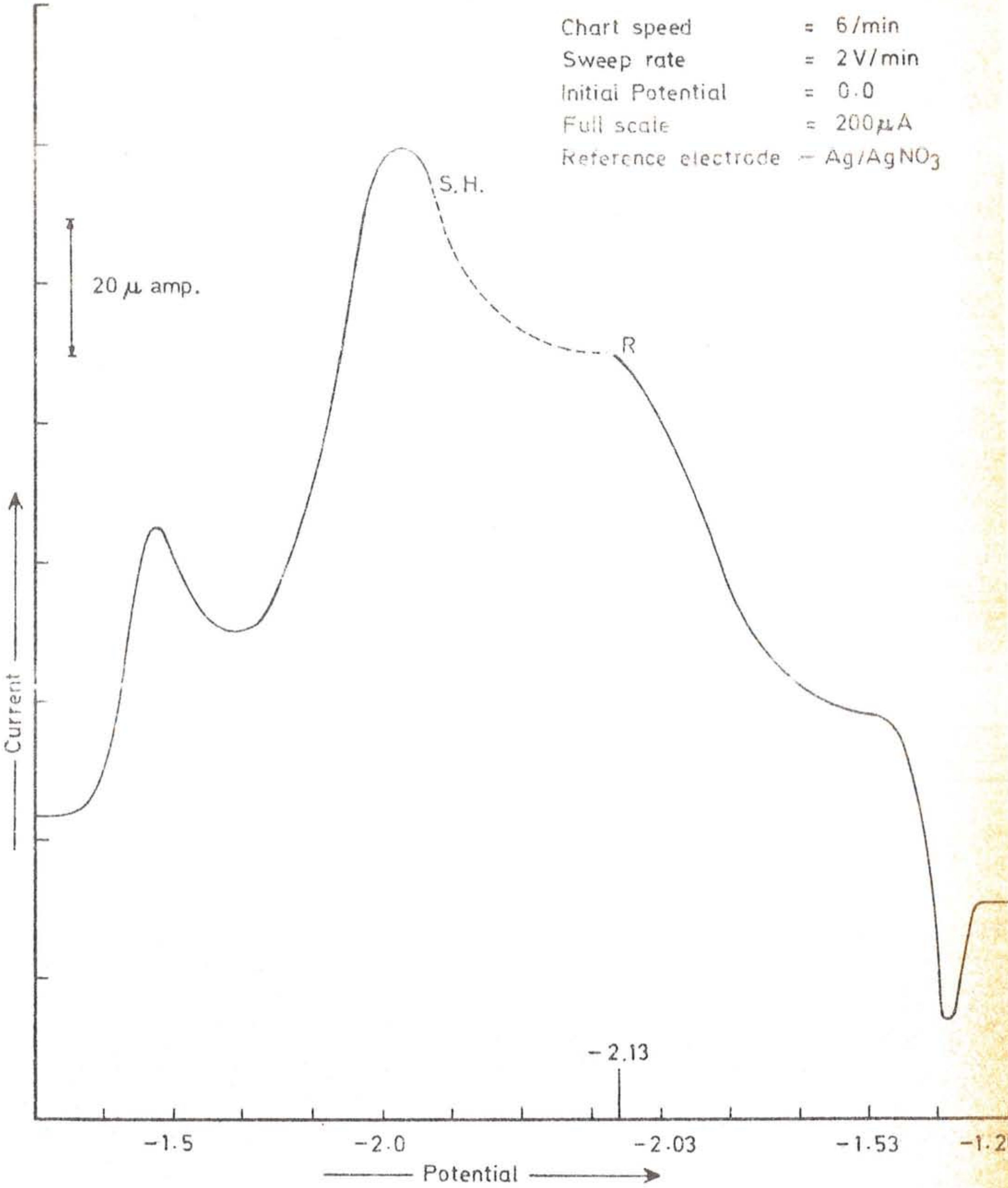

FIG. 8 3-Nitroaniline

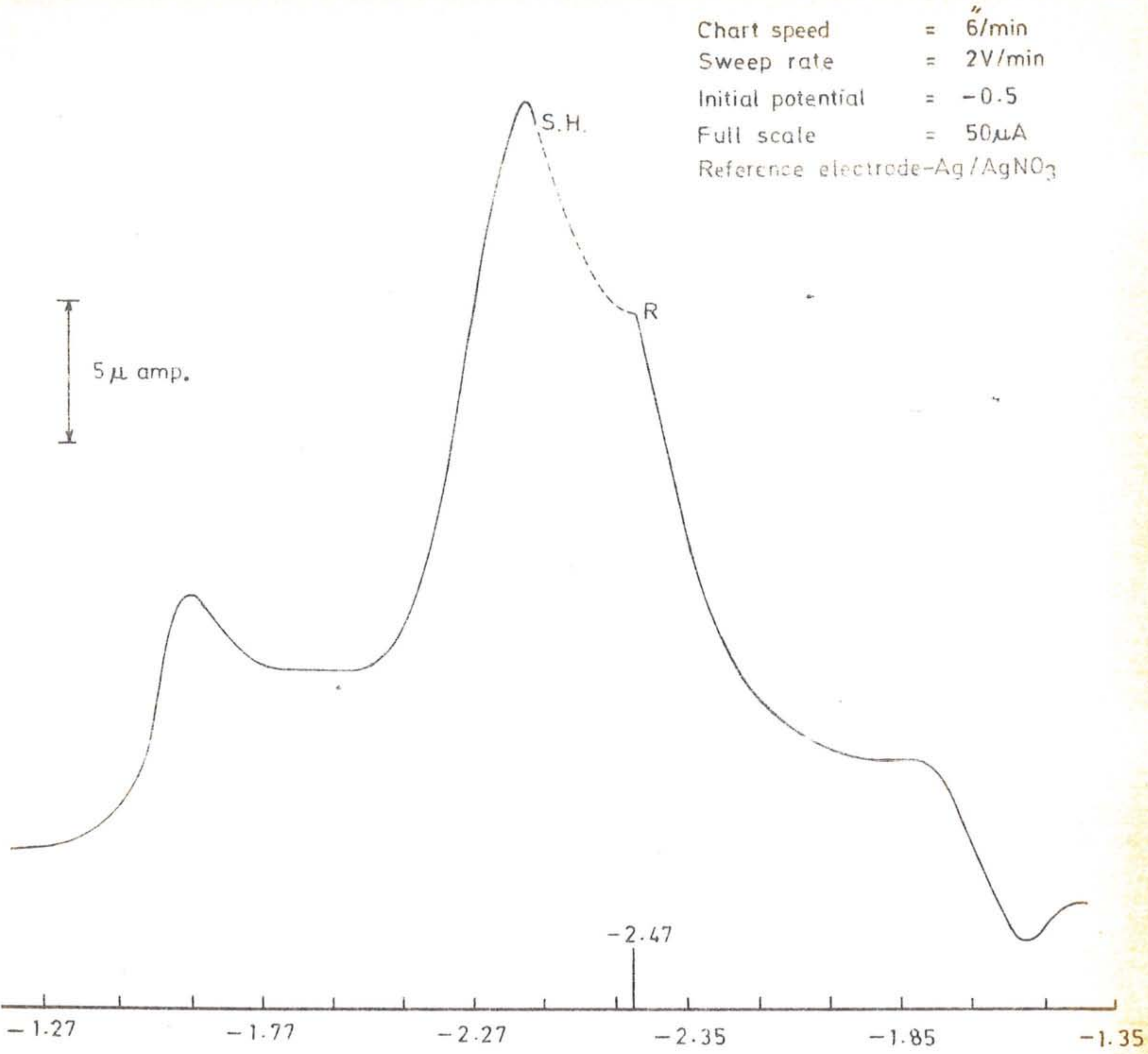

FIG. 9
4-Nitroaniline

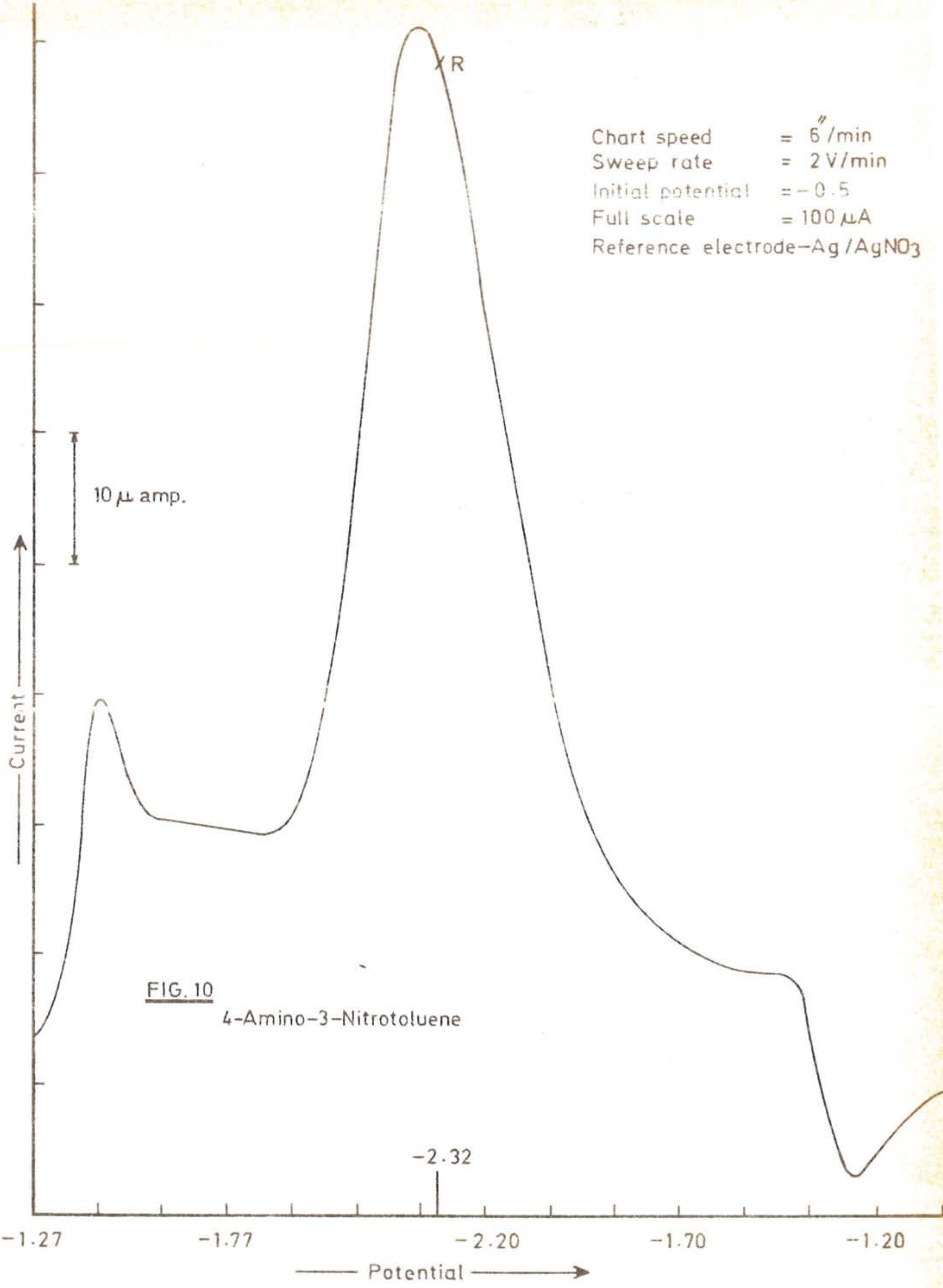

Chart speed = 6″/min
Sweep rate = 2 V/min
Initial potential = -0.5
Full scale = 100 μA
Reference electrode-Ag/AgNO$_3$

FIG. 10
4-Amino-3-Nitrotoluene

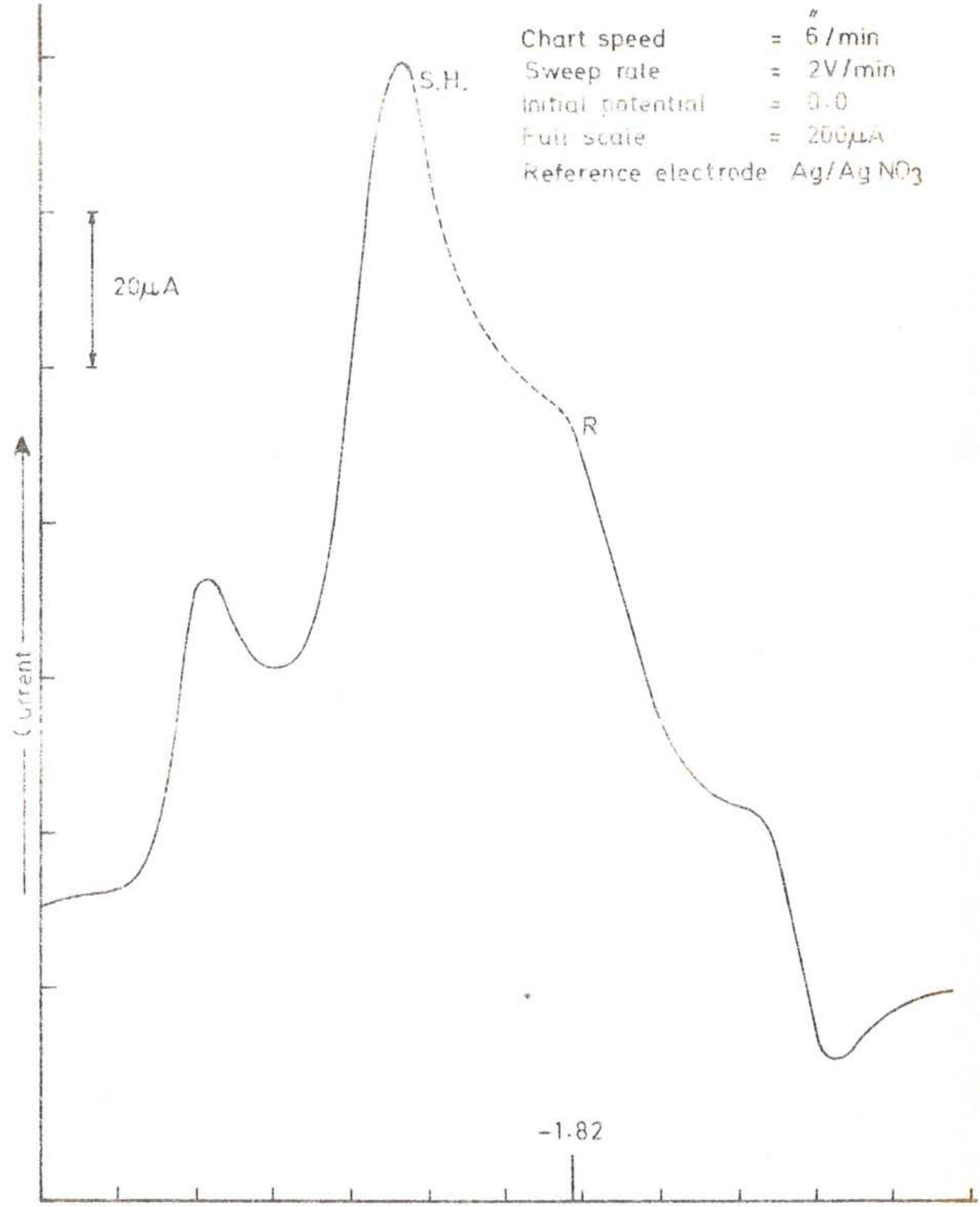

FIG. 11
1-Nitronaphthalene

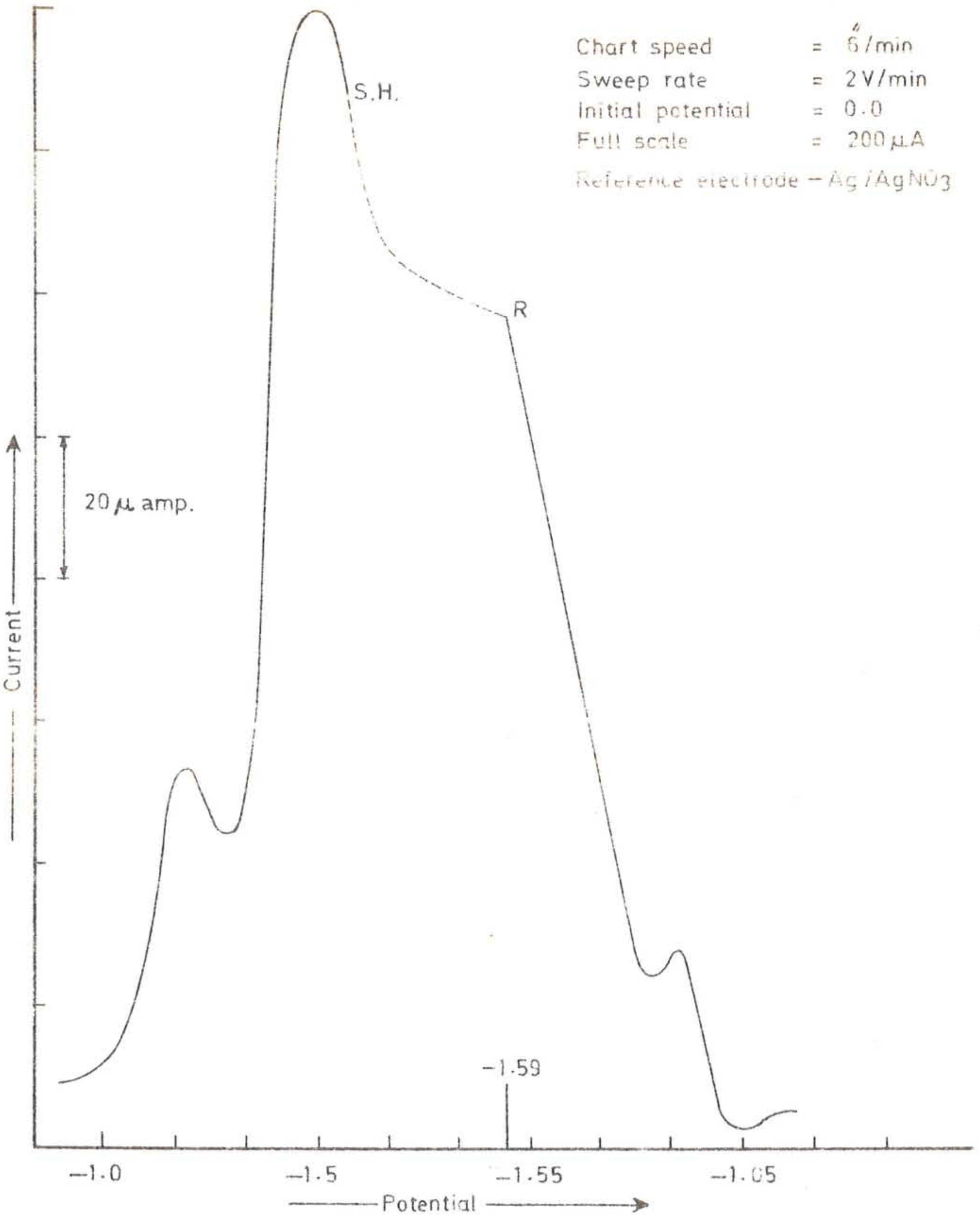

FIG. 12 1,3-Dinitrobenzene

rate -determining step can be found from the effective slope of the peak voltammogram

$$E_p - E_{p/2} = \frac{47.7}{\alpha n} \qquad mV$$

It is apparent from the equation that as (αn) decreases, the peak polarogram becomes more spread out. Also the peaks tend to be rounded rather than sharp. In other words we may say that when αn is unity the corresponding peak or reduction potential will be reversible and when it is much less than unity then the corresponding reduction potential will be irreversible. We have calculated the αn values for all the five compounds. As it can be seen from the table (3) the value of αn for m-dinitrobenzene is approximately equal to one which has reversible IInd reduction potential. Now for the remaining four compounds 3-Nitroamiline, 4-Nitroaniline and 4-Amino-3-Nitrotoluene the value of αn is approximately equal to 0.3, which proves that second reduction potentials of these compounds are completely irreversible. The value of αn for 1-nitronaphthalene is a little higher i.e; approximately equal to 0.4, which suggests that it is also irreversible. At the same time it may be possible that it is reversible for a very short time, which we were unable to see experimentally. Anodic peaks corresponding to second cathodic peak could not be observed. The signal for faster scan rate (e.g. 0.500 V and 5.00 V per second etc.) were fed into oscilloscope and steady state (for faster scan rates) signal as well as single sweep (slower scan rate) both showed absence of anodic peak corresponding to the second cathodic peak at these scan rates. For m-Dinitrobenzene the anodic peak corresponding to second cathodic peak were observed both by single scan as well as for fast scan rates and the remaining compounds 3-NA, 4-NA, 4-ANT, I-NN did not shown the anodic peak corresponding to second cathodic peak.

There are two possibilities which may be the cause of absence of anodic peak corresponding to the second cathodic peak. These could be due to either irreversible electron transfer or coupled chemical reation. The case of multistep charge transfer in which an electron transfer is followed by an irreversible process

$$R + e \rightleftharpoons R^- \qquad (2)$$

$$\bar{R} + e \longrightarrow R^* \qquad (3)$$

This type of multistep electron transfer process has been discussed by Polcyn and Shain (7). The cyclic voltammograms for 3-Nitroaniline, 4-Nitroaniline, 4-Amino-3-Nitrotoluene and 1-Nitronaphthalene differ from the (ideal) cyclic voltammogram shown in fig. 2- The height of the second peak in the ideal case (irreversible heterogeneous electron transfer) is not much larger than the Ist one. But the height of the second peak in the cyclic voltammograms of the above mentioned four compounds is much larger than the Ist one. This leads us to suspect a process like (4)

$$R + e \rightleftharpoons R^-$$

$$R^- + n_e + nH^+ \longrightarrow \text{Products} \qquad (4\text{-a})$$

Or

$$\bar{R} + n_e \rightleftharpoons R^{-(n+1)e}$$

$$R^{-(n+1)e} + (n+1)H \longrightarrow \text{Products} \qquad (4\text{-b})$$

to occur. The nature of the product was not investigated. It was observed on the oscilloscope that with the increase in the scan rate the second peak shifted cathodically (while the first peak did not shift). For a reversible electron transfer process followed by chemical reaction the E_p shifts cathodically (37). Thus we may conclude that in our case the Ist peak or Ist reduction potential is reversible followed by a process given in the equation4(b) above The possibility given in4(a) can not be ruled out. No theoretical study has been done about the effect of scan rate on peak potential for process4(a). We suspect the conversion of NO_2 group to NO (nitroso) or NH_2 group.

Thus the overall picture emerges as a reversible electron transfer (first peak) followed by an irreversible electron transfer involving simultaneously protonation (second peak).

TABLE- I.

Table-I:- 3-Nitroamiline

No	$(E_{1/2})_c^{i}$	$(E_{1/2})_a^{ii}$	$(E_p)_c^{iii}$	$(E_p)_a^{iv}$	$(I_p)_c/(I_p)_a^{v}$	$(E_{p/2})_c^{vi}$	$(E_{p/2})_a^{vii}$	Red Potential	Ref.electrode
1.	-1.11	-1.065	-1.15	-1.032	about 1	-1.075	-1.085	Ist	Gold-wire
	-1.65		-1.76			-1.58		IInd	"
2	-1.13	-1.08	-1.17	-1.037	about 1	-1.09	-1.10	Ist	"
	-1.677		-1.77			-1.585		IInd	"
3	-1.10	-1.075	-1.16	-1.035	about I	-1.08	-1.09	Ist	"
	-1.652		-1.765			-1.583		IInd	"

Continued ......

Table-1:- 4 -Nitroaniline

No	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	$(I_p)_c/(I_p)_a$	Red.Pot.	Ref.electrode
1.	-1.283	-1.273	-1.333	-1.266	-1.256	-1.293	about I	Ist	Gold-wire
	-2.044		-2.12		-1.97			IInd	"
2.	-1.292	-1.282	-1.343	-1.270	-1.268	-1.30	about I	Ist	"
	-2.046	-	-2.125	-	-1.975			IInd	"
3.	-1.285	-1.275	-1.338	-1.260	-1.244	-1.304	about I	Ist	"
	-2.092		-2.16		-1.99			IInd	"

Continued ....

Table 1:- 4-Amino-3-Nitrotoluene

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	$(I_p)_c/(I_p)_a$	Red Pot.	Ref.electrode
1.	-1.131	-1.134	-1.152	-1.09	-1.11	-1.167	about I	Ist	gold-wire
	-1.942		-2.0		-1.84		-	IInd	"
2.	-1.135	-1.132	-1.160	-1.10	-1.115	-1.166	about I	Ist	"
	-1.950		-2.0		-1.835			IInd	"
3.	-1.140	-1.136	-1.163	-1.10	-1.116	-1.168	about I	Ist	"
	-1.952		-2.01		-1.84			IInd	"

Continued........

Table-1:- I-Nitronaphthalene

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(I_p)_c/(I_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	Red.Pot	Ref.electrode
1.	-0.95	-0.93	-0.986	-0.902	about I	-0.91	-0.952	Ist	Gold-wire
	-1.33		-1.395			-1.29		IInd	"
2.	-0.955	-0.928	-0.99	-0.908	about I	-0.916	-0.949	Ist	"
	-1.334		-1.405			-1.305		IInd	"
3.	-0.945	-0.925	-0.984	-0.905	about I	-0.914	-0.960	Ist	"
	-1.328		-1.40			-1.295		IInd	"

Note:- Table-I:-

(i) $(E_{1/2})_c$ is the cathodic half-wave potential (ii) $(E_{1/2})_a$ is the anodic half-wave potential.

(iii) $(E_p)_c$ is the cathodic peak potential. (iv) $(E_p)_a$ is the anodic peak potential

(v) $(I_p)_c$ represents the cathodic peak current and $(I_p)_a$ represents the anodic peak current (vi) $(E_{p/2})_c$ is the cathodic half peak potential (vii) $(E_{p/2})_a$ represents the anodic half-peak potential.

TABLE-2.

3- Nitroaniline

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(I_p)_c$	$(I_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	Red. Pot.	Ref.electrode
1.	-1.410	-1.365	-1.45	-1.332	31 μA	28 μ A	-1.375	-1.385	Ist	Ag/$AgNO_3$
	-1.950		-2.06		62 "		-1.88		IInd	"
2.	-1.42	-1.37	-1.46	-1.337	30 "	28 "	-1.38	-1.39	Ist	"
	-1.967		-2.06		68 "		-1.87		IInd	"
3.	-1.41	-1.36	-1.445	-1.327	32 "	28 "	-1.37	-1.385	Ist	"
	-1.94		-2.04		63 "		-1.863		IInd	"
4.	-1.43	-1.38	-1.6	-1.346	33 "	29 "	-1.385	-1.395	Ist	"
	-2.00		-2.09		72 "		-1.92		IInd	"
5.	-1.43	-1.38	-1.6	-1.348	33 "	29 "	-1.39	-1.40	Ist	"
	-2.00		-2.115		70 "		-1.94		IInd	"
6.	-1.431	-1.38	-1.6	-1.348	33 "	29 "	-1.39	-1.40	Ist	"
	-2.00		-2.115		70 "		-1.94		IInd	"
7.	-1.40	-1.365	-1.45	-1.332	31 "	28 "	-1.37	-1.385	Ist	"
	-1.94		-2.06		60 "		-1.88		IInd	"

Continued......

Table-2:- 4-Nitroaniline

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(I_p)_c$	$(I_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	Red.Pot	Ref.electrode
1.	-1.553	-1.543	-1.603	-1.536	14 µA	12 µA	-1.526	-1.563	Ist	Ag/AgNO$_3$
	-2.314		-2.39		39 "		-2.24		IInd	"
2.	-1.562	-1.552	-1.613	-1.54	15 "	12 "	-1.538	-1.57	Ist	"
	-2.316		-2.395		42 "		-2.245		IInd	"
3.	-1.555	-1.545	-1.608	-1.53	16 "	13 "	-1.514	-1.574	Ist	"
	-2.362		-2.43		45 "		-2.26		IInd	"

Continued.......

Table-2:- 4-Amino-3-Nitrotoluene

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	$(I_p)_c$	$(I_p)_a$	Red.Potential	Ref.electrode
1.	-1.40	-1.394	-1.412	-1.35	-1.37	-1.427	18 µA	16 µA	Ist	A $Ag/AgNO_3$
	-2.202		-2.26		-2.10		60 "		IInd	"
2.	-1.395	-1.392	-1.420	-1.360	-1.375	-1.426	-19	17 "	Ist	"
	-2.210		-2.26		-2.095		58 "		IInd	"
3.	-1.40	-1.396	-1.423	-1.36	-1.376	-1.428	19 "	16 "	Ist	"
	-2.212		-2.27		-2.10		59 "		IInd	"

Continued......

Table-2:- I-Nitronaphthalene:-

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(I_p)_c$	$(I_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	Red.Pot	Ref.electrode
1.	-1.328	-1.305	-1.366	-1.28	33 μA	30 μA	-1.29	-1.33	Ist	$Ag/AgNO_3$
	-1.715		-1.78		76 "		-1.67		IInd	"
2.	-1.329	-1.305	-1.366	-1.27	34 "	30 "	-1.295	-1.325	Ist	"
	-1.72		-1.78		80 "		-1.66		IInd	"
3.	-1.333	-1.31	-1.368	-1.29	36 "	32 "	-1.305	-1.335	Ist	"
	-1.73		-1.79		74 "		-1.67		IInd	"
4.	-1.330	-1.315	-1.367	-1.285	34 "	30 "	-1.295	-1.33	Ist	"
	-1.73		-1.80		80 "		-1.68		IInd	"
5.	-1.328	-1.31	-1.367	-1.28	35 "	31 "	-1.30	-1.338	Ist	"
	-1.73		-1.81		74 "		-1.68		IInd	"
6.	-1.333	-1.32	-1.370	-1.29	35 "	32 "	-1.305	-1.340	Ist	"
	-1.734		-1.82		76 "		-1.69		IInd	"

Continued......

Table-2:- 1,3-Dinitrobenzene

No.	$(E_{1/2})_c$	$(E_{1/2})_a$	$(E_p)_c$	$(E_p)_a$	$(I_p)_c$	$(I_p)_a$	$(E_{p/2})_c$	$(E_{p/2})_a$	Red. Pot.	Ref. electrode
1.	-1.16	-1.12	-1.20	-1.10	26 µA.	22 µA	-1.133	-1.15	Ist	$Ag/AgNO_3$
	-1.41	-1.38	-1.442	-1.30	104 "	95 "	-1.385	-1.405	IInd	"
2.	-1.15	-1.12	-1.19	-1.09	27 "	25 "	-1.130	-1.14	Ist	"
	-1.405	-1.38	-1.435	-1.29	106 "	92 "	-1.38	-1.395	IInd	"
3.	-1.16	-1.11	-1.195	-1.095	24 "	20 "	-1.131	-1.14	Ist	"
	-1.40	-1.37	-1.43	-1.28	108 "	90 "	-1.375	-1.39	IInd	"
4.	-1.15	-1.11	-1.19	-1.09	25 "	20.5 "	-1.130	-1.14	Ist	"
	-1.40	-1.365	-1.427	-1.26	104 "	88 "	-1.37	-1.385	IInd	"

Note: $(E_{1/2})_c$, $(E_{1/2})_a$, $(E_p)_c$, $(E_p)_a$, $(I_p)_c$, $(I_p)_a$, $(E_{p/2})_c$ and $(E_{p/2})_a$ have the same meaning as explained in Table -I.

TABLE -3.

Table -3:- 3-Nitroaniline

No.	$(E_p)_c$	$(E_{p/2})_c$	$E_p - E_{p/2}$	$\alpha n = p/2$	Red. pot	Ref. electrode
1.	-2.06	-1.88	- 0.18	0.266	IInd	$Ag/AgNO_3$
2.	-2.06	-1.87	-0.19	0.251	"	"
3.	-2.04	-1.863	0.177	0.269	"	"
4.	-2.09	-1.920	0.17	0.28	"	"
5.	-2.10	-1.930	0.17	0.28	"	"
6.	-2.115	-1.940	-0.175	0.27	"	"
7.	-2.06	-1.88	-0.18	0.266	"	"

Continued.......

Table-3:- 4- Nitroaniline

No.	$(E_p)_c$	$(E_{p/2})_c$	$(E_p - E_{p/2})$	αn	Red. Pot	Ref.electrode
1.	-2.39	-2.24	+0.15	0.318	IInd	Ag/$AgNO_3$
2.	-2.395	-2.245	0.15	0.318	IInd	"
3.	-2.43	-2.26	0.17	0.28	IInd	"

Continuted.......

Table-3:- 4- Amino-3- Nitrotoluene.

No.	$(E_p)_c$	$(E_{p/2})_c$	$(E_p - E_{p/2})$	αn	Red. Pot.	Ref. electrode
1.	-2.26	-2.10	0.16	0.298	IInd	$Ag/AgNO_3$
2.	-2.26	-2.095	0.165	0.29	"	"
3.	-2.27	-2.10	0-17	0.28	"	"

Continued.......

Table-3:- I-Nitronaphthalene

No.	$(E_p)_c$	$(E_{p/2})_c$	$E_p - E_{p/2}$	αn	Red. Pot	Ref.electrode
1.	-1.78	-1.67	0.11	0.434	IInd	$Ag/AgNO_3$
2.	-1.78	-1.66	+0.12	0.397	"	"
3.	-1.79	-1.67	0.12	0.397	"	"
4.	-1.8	-1.68	0.12	0.397	"	"
5.	-1.81	-1.68	0.13	0.367	"	"
6.	-1.82	-1.69	0.13	0.367	"	"

Continued......

Table-3:- I,3- Dinitrobenzene

No.	$(E_p)_c$	$(E_{p/2})_c$	$E_p - E_{p/2}$	αn	Red. Pot.	Ref. electrode
1.	-1.435	-1.38	0-055	0.87	IInd	$Ag/AgNO_3$
2.	-1.442	-1.385	0.057	0.8	"	"
3.	-1.43	-1.375	0.055	0.87	"	"
4.	-1.427	-1.37	0.057	0.8	"	"

Note:. (i) αn was calculated from the relation $E_p - E_{p/2} = \frac{47.7}{\alpha n}$

$(E_p)_c$ and $(E_{p/2})_c$ has the same meaning as explained in table-1.

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