Some Theoretical Aspects of Polarography

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Abstract

Voltammetry comprises a group of electranalytical procedures that are based upon the potential-current behavior of a small, easily polarized electrode in the solution being analyzed. The dropping mercury electrode may be applied over the range + 0.4 to about - 2.0 V with reference to the S.C.E. With all the other factors remaining constant, the diffusion current is directly proportional to the concentration of the depolarizer. This is of great importance in quantitative polarographic analysis. It is necessary to remove any dissolved oxygen from the electrolytic solution whenever cathodic regions are being investigated in which oxygen interferes. Equation of the polarogrpahic wave can be represented by $E_{d.e} = E_{1/2} + \frac{0.0591}{2} \log \frac{i_d - i}{i}$ *at* 25^0*C, Where* $E_{d.e}$ *is the potential at any point of the polarogrphaic wave,* $E_{1/2}$ *is the half-wave potential, n is number of electrons involved in the reaction,* i_d *is diffusion current and i is current at any point on the polarographic wave minus the residual current. When* $\log \frac{i_d - i}{i}$ *is plotted against the corresponding potential of the micro-electrode, a straight line should be obtained with a slope of 0.0591/n for a reversible reaction; the intercept of line on Y-axis gives the half-wave potential. Hence n, the number of electrons taking part in the reversible reaction, may be determined. The processes are described as polargraphically irreversible when the mixture of oxidized and reduced forms shows a separated cathodic and anodic wave, when the half-wave potentials of the oxidized and reduced form differ. A straight line may still result (plot of* $\log \frac{i_d - i}{i}$ *vs E) but the slope of the log plot will differ from the theoretical value, hence the value of n calculated from the slope has no significance. Present work was undertaken to investigate some theoretical aspects of polarography such as types of electrode, types of current, interference of oxygen and its removal, redox reaction and reversibility, Polarographic diffusion coefficient etc.*

Keywords: Dropping Mercury Electrode, Diffusion Current, Migration Current, Polarographic Maxima.

Introduction

Voltammetry comprises a group of electranalytical procedures that are based upon the potential-current behavior of a small, easily polarized electrode in the solution being analyzed. The micro-electrode (working electrode) is usually constructed of some inert, conducting material such as gold, platinum or carbon and in some circumstances a dropping mercury electrode (D.M.E.) may be used; for this special case the technique is referred to as polarogrpahy. The polarography is an electrochemical method, invented by Czechoslovakian chemist Jaroslav Heyrovsky in 1922 for which he won the Nobel prize in

1959 [1-6]. In polarography the changes of the current, resulting from the electrolysis of the solution under investigation, are followed by using a droping mercury electrode and a gradually increasing applied voltage. The dropping mercury electrode consists of a glass capillary from which mercury falls at the rate of about 20 drops / min. The second large, not readily polarized reference/auxiliary/counter electrode consists either of a mercury pool at the bottom of the electrolytic cell containing test solution, calomel electrode or mercurous sulphate electrode. The instrument which records current-voltage curves is known as polarograph and the curves obtained with it are known as polarograms. Qualitative information can also be determined from the half-wave potential of the polarogram (the current vs. potential plot in a polarographic experiment). The value of the half-wave potential is related to the standard potential for the redox reaction being studied. This technique and especially the DPASV one can be used for environmental analysis, and especially for marine study for characterisation of Organic matter and metals interactions [7]. Present work was undertaken to investigate some theoretical aspects of polarography such as types of electrode, types of current, interference of oxygen and its removal, redox reaction and reversibility, Polarographic diffusion coefficient etc.

Methodology

1. *Types of electrode*

In comparison to other electrodes the dropping mercury electrode possesses various advantages. Use of the dropping mercury electrode at the anodic side is more limited than that of platinum micro electrode. Various investigators have reported current-voltage curves that show limiting currents in electrolysis experiments using stationary electrodes in unstirred solutions. Instead of platinum wire micro- electrode, electrodes of silver, copper [8] and of amalgams of these metals [9] have been recommended.

2. *Types of current*

There are various types of polarographic currents such as Diffusion Current and Migration Current, Kinetic Currents, Adsorption Currents, Regeneration Catalytic Currents, Catalytic Currents, Residual Currents, Polarographic Maxima etc.

Diffusion Current and Migration Current A polarographic wave occurs on the current-voltage curve in the presence of a depolarizer which is reduced or oxidized at the dropping mercury electrode and which hinders the polarization of the electrode. In the most general case reducible or oxidizable ions are supplied to the depleted region at the electrode surface by two forces : a diffusive force, proportional to the concentration gradient at the electrode surface, and an electrical force, proportional to the electrical potential difference between the surface and the solution. Reducible or oxidizable ions are, therefore, supplied to the electrode surface partly by diffusion and partly by electrical migration, so that the limiting current can be regarded as the sum of a “diffusion current” and a “mirgration current”. When excess of an indifferent electrolyte (supporting electrolyte), that do not cause depolarization of the dropping mercury electrode in the widest possible potential range and do not react either with depolarizers in the solution or with metallic mercury, is added to a solution containing relatively small concentration of the reducible or oxidizable ions i.e. depolarizer, the current through the solution will be carried practically entirely by the excess of indifferent ions, i.e. the transference number of the reducible or oxidizable ions is reduced practically to zero. The supporting electrolytes increase the conductivity, i.e. decrease the resistance of the electrolyte and decrease also the potential drop iR in the solution thus the potential gradient is compressed or shortened to a region so very close to the electrode surface that it is no longer operative to attract electroreducible or oxidizable ions and they do not take part in migration and are transported towards the surface of the electrode only by diffusion thus the migration component of the limiting current is practically completely eliminated, and the limiting current becomes solely a diffusion current.

Kinetic Currents There are instances where polarographic limiting currents are controlled not only by the diffusion rate of the reactive species but also by the rate of some chemical reaction related to the electrode process. These currents (not shown in Ilkovic equation) are abnormally influenced by temperature, capillary characteristics, and solution composition; they are known as kinetic currents.

Adsorption Currents Adsorption currents are observed on the current-potential curves when the current is governed by the surface area of the electrode which is covered by an adsorbed depolarizer or by an adsorbed product of the electrode process. Adsorption processes are manifested by a separate wave at potentials either more positive or more negative than the wave for the reduction or oxidation of the non-adsorbed compounds. In some instances, the adsorbed layer hinders further electrode processes, which can take place in the unhindered way only after desorption of such a layer.

Regeneration Catalytic Currents In a reversible oxidation-reduction system in the presence of a substance which chemically oxidizes the product of electro-reduction or chemically reduces the electro-oxidation product, a wave is observed on polarographic curves at the same potential as is found for the oxidation-reduction system alone. The addition of an oxidizing or a reducing agent causes an increase in the limiting current. This increase is governed by the rate of the chemical reaction regenerating the depolarizer.

Catalytic Currents When a substance, acting as a catalyst, is added to the solution of a depolarizer and causes a shift in the reduction of the depolarizer to more positive potentials or in the oxidation to more negative values, the electrode process is termed catalytic and catalytic currents are obtained. During the catalytic reduction, which may also involve adsoption processes, the catalyst is often regenerated. Hence, a small concentration of the catalyst can cause high limiting currents. The most common wave type of these currents is due to catalytic hydrogen evolution, involving a catalytic lowering of the hydrogen overvoltage. These currents are observed with some substances that posses acid-base properties in buffered solutions in the oxidized or reduced form. Other types of substances, especially those with a thiol group (-SH), give catalytic waves in ammoniacal solutions of cobalt salts. The active form in these instances is a complex cobalt compound.

Residual Currents The residual current may be regarded as a sum of two components a small Faradac current resulting from reduction or oxidation of traces of reducible or oxidizable impurities in the solution and a condenser / capacity/non Faradac / charging current resulting from the charging of the electrical double layer at the surface of each growing mercury drop.

Polarographic Maxima In some instances an increase of current is observed on polarographic curves, followed by a decrease until at sufficiently negative potentials the value of the limiting current is reached. This shape of current-voltage curve, is called a polarographic maximum.

3. *Interference of oxygen and its removal*

In every solution open to the atmosphere the concentration of dissolved oxygen is about 0.001 M. Oxygen dissolved in electrolytic solutions is easily reduced polarographically and gives two waves of approximate equal heights that overlap with waves occurring over a wide potential range.

4. *Redox reaction and reversibility*

A typical current- applied voltage curve (polarogram) is shown in Fig. 1. The potential at the point on the polarogram where the current is equal to one-half the diffusion current is termed the half-wave potential and is designed by $E_{1/2}$.

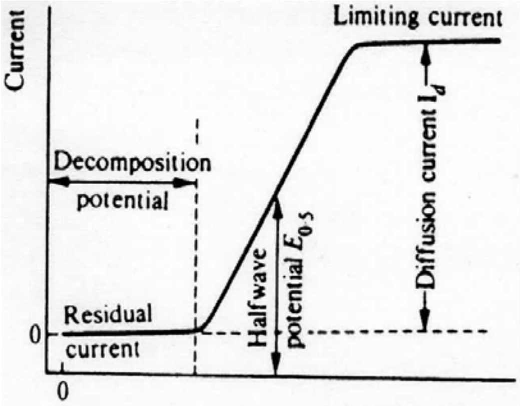


Fig. 1. Typical current-applied voltage curve

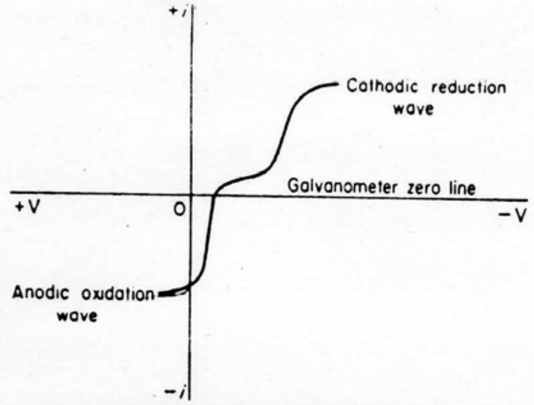


Fig. 2. Cathodic and anodic waves

When the depolarizer accepts electrons from the electrode, a reduction occurs in which the oxidation state of the depolarizer is lowered or a covalent bond is split. A reduction is manifested on the polarographic curve by the occurrence of a wave above the galvanometer zero line, called cathodic wave (Fig. 2) because in this instance the dropping mercury electrode function as a cathode. When the depolarizer donates electrons to the dropping electrode and the oxidation state of the depolarizer is increased, or the molecule is transformed by formation of a new covalent bond, then oxidation of the depolarizer takes place. The polarographic curve shows a wave beneath the galvanometer zero line, called an anodic wave, because the dropping electrode serves here as an anode.

Half wave potential is a characteristic constant for a reversible oxidation-reduction system and its value is independent of the depolarizer concentration, but depends on nature of depolarizer. It is essential basis for quantitative polarographic analysis. Equation of the polarogrpahic wave can be represented by following equation

$$E_{d.e.} = E_{1/2} + \frac{0.0591}{n} \log \frac{i_d - i}{i} \text{ at } 25^0C$$

Where $E_{d.e.}$ is the potential at any point of the polarogrphaic wave, $E_{1/2}$ is the half-wave potential, n is number of electrons involved in the reaction, i_d is diffusion current and i is current at any point on the polarographic wave minus the residual current.

When $\log \frac{i_d - i}{i}$ is plotted against the corresponding potential of the micro-electrode, a straight line should be obtained with a slope of 0.0591/n for a reversible reaction; the intercept of line on Y-axis gives the half-wave potential. Hence n, the number of electrons taking part in the reversible reaction, may be determined.

5. *Polarographic diffusion coefficient*

Diffusion coefficient is numerically equal to the number of moles of substance that diffuse across unit area in unit time when the concentration gradient is unity. The characteristic diffusion coefficient of an ion, salt and neutral molecule at infinite dilution is given by

$$D_i^o = \frac{RT}{zF^2}\lambda_i^0 \text{ or } D_i^o = 2.67\times10^{-7}\frac{\lambda}{z}, \text{ cm}^2 \text{ sec}^{-1} \text{ at } 25^0C$$

$$D_{salt}^0 = \frac{RT}{F^2}\left[\frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right]\left[\frac{1}{z_+} + \cdot\right] \text{ or } D_{salt}^0 = \frac{D_+^0 D_-^0 (z_+ + z_-)}{z_+ D_+^0 + z_- D_-^0}$$

$$D_0 = \frac{3.32\times10^{-3}}{(V_m)^{1/3}} cm^2 sec^{-1} at\ 25^0C$$

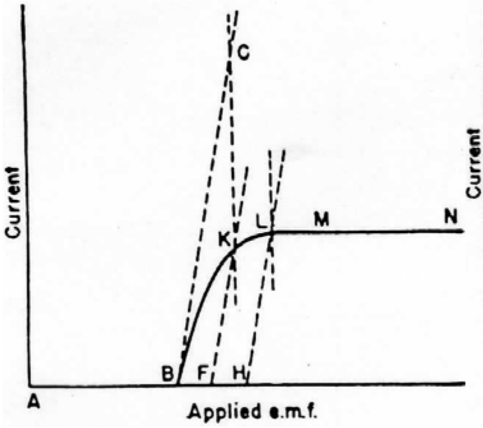
Result and Discussion

1. *Types of electrode*

Dropping Mercury Electrode The dropping mercury electrode may be applied over the range +0.4 to about -2.0 V with reference to the S.C.E.

Micro Electrodes Measurement with the stationary electrode involve the disadvantage that it is necessary to wait for at least two minutes at each value of the applied e.m.f. until a steady state of current is reached. Laitinen and Kolthoff [10] eliminated this disadvantage by working with a rotating micro electrode.

At the micro-electrode current density may be high, the electrode layer tends to become depleted of the ions being discharged at the electrode, and if the solution is not stirred, then the diffusion of ions across the resultant concentration gradient becomes an important factor in determining the magnitude of the current flowing. By constrast, at the large auxiliary electrode the current density will be very small, in consequence, the auxiliary electrode is not readily polarized, and when small currents flow through the cell, the concentration of the ions in the electrode layer (i.e. the layer of the solution immediately adjacent to the electrode) remains virtually equal to the concentration in the bulk solution, and the potential of the electrode is maintained at a constant value (Fig. 3 and 4).



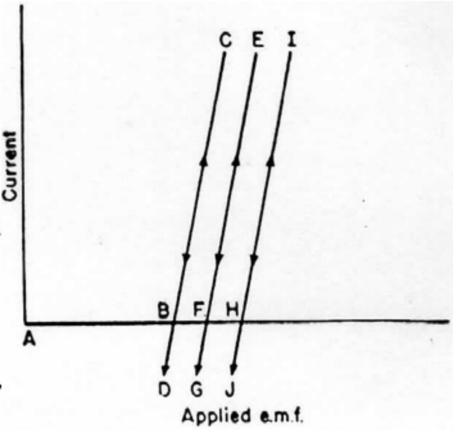


Fig. 3. Current-Voltage curves with concentration polarization.

Fig. 4. Current-Voltage curves without polarization.

2. *Types of current*

Diffusion Current and Migration Current Only in the presence of a sufficient concentration of the supporting electrolyte, a true diffusion current of the depolarizer ions occur. For the diffusion current, Ilkovic derived following equation:

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

Thus with all the other factors remaining constant, the diffusion current is directly proportional to the concentration of the depolarizer. This is of great importance in quantitative polarographic analysis.

Ilkovic equation neglects the curvature of the electrode surface therefore the following equation derived independently by Lingane and Loveridge [11] and by Strehlow and von Stackelberg [12] takes into account the curvature of the electrode surface (term in parenthesis).

$$id = 607nD^{1/2}Cm^{2/3}t^{1/6}\ (1 + AD^{1/2}t^{1/6}m^{-1/3})$$

where A is a constant and has a value of 39 according to Lingane and Loveridge while it is 17 as assigned by Strehlow and von Stackelberg.

Kinetic Currents Kinetic currents are usually proportional to the concentration of depolarizer; in most cases they increase markedly with rise in temperature and they are independent of the mercury pressure.

Adsorption Currents Adsorption currents are most frequently observed with organic substances of a high molecular weight and with substances that form compounds with mercury.

Regeneration Catalytic Currents Regeneration (catalytic) currents posses several properties typical of kinetic currents. Their height is dependent not only on the concentration of the depolarizer, but also on the concentration of the regenerating agent.

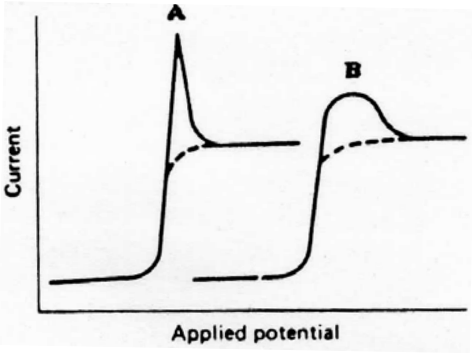
Catalytic Currents Catalytic waves are characterized by a non-linear dependence on the catalyst concentration. In buffered solutions, catalytic waves are often a function of pH (usually decreasing sharply with increasing pH value) and frequently increase with increasing buffer concentration. This dependence on buffer capacity distinguishes most markedly catalytic waves from other polarographic currents.

Residual Currents The condenser current is directly proportional to the height of the mercury column. It has not been used for practical purposes, and it can be observed only at very small concentrations of the depolarizer when higher sensitivities of the current-measuring device are employed.

Polarographic Maxima In a given supporting electrolyte, the height of the maxima depends on various factors such as the type and concentration of the electroactive substance; the height of the maxima increases with increasing concentration of electroactive substance; The potential at which the cathodic or anodic wave is observed; and the concentration of the supporting electrolyte.

Sufficient amount of the supporting electrolyte is added to eliminate migration component of the limiting current. The addition of the supporting electrolyte by decreasing the iR drop also decreases the inhomogeneity of the electric field around the dropping electrode. This inhomogeneity is the cause of the streaming of the solution which is manifested by the occurrence of sharp maxima, called maxima of the first type (Fig 5 A) at low concentrations of the supporting electrolyte on the increasing portion of the polarographic wave at the beginning of the limiting current, which do not depend in any characteristic manner on the mercury pressure. With increasing concentration of supporting electrolyte, maxima of the first type decreases. For their complete supperession surface active substances such as gelatin are added. On the other hand, total concentrations of supporting electrolytes above 0.3 M often give increasing of limiting current, which are also caused by streaming of the solution such rounded maxima are called maxima of the second kind (Fig. 5 B) which occurs over a wide potential range of the limiting current. The height of the maximum of the second kind increase with increasing height of the mercury column substantially more than diffusion current. At sufficiently low mercury pressures they do not appear at all. They are observed only when the out-flow velocity is greater than about 2 mg/sec. As with maxima of the first kind, maxima of the second kind are suppressed by various surface active agents such as gelatin.

In the potential region in which maxima occur the electroactive substance is brought to the surface of electrode by streaming or stirring or vigorous motion. At more positive potentials the solution streams towards the neck of the drop in other words streaming is directed from the top to the bottom of the mercury drop (Fig. 6 A) and at more negative potentials and at higher mercury columns, i.e. at a higher out-flow velocity of mercury, the direction of the streaming is changed. Under these conditions the streaming is directed toward the top of the mercury drop (sideward) (Fig 2 6).



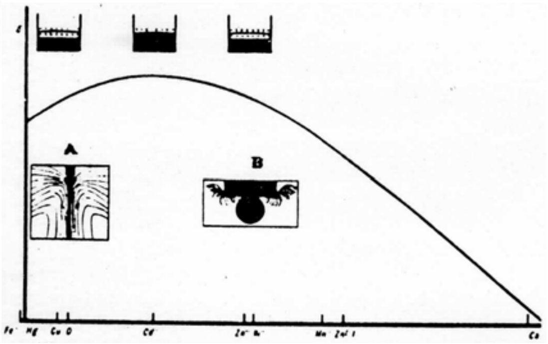


Fig.5. Typical Current Maxima. Fig. 6. Two main types of stirring as related to electrocapillary curve.

For the exact measurement of limiting currents and half wave potentials, when maxima are not required, a small amount of a surface active substance is added to eliminate the maximum completely. The function of any such maximum suppressor is probably to form an adsorbed layer on the aqueous side of the mercury-solution interface which resists compression; this prevents the streaming movement of the diffusion layer (which is believed to be responsible for the current maximum) at the interface.

3. *Interference of oxygen and its removal*

A typical polarogram for air-saturated M-Potassium chloride solution (in the presence of 0.01% methyl red) is given in Fig. 7 (curve A). Curve B in Fig. 7 was obtained after the removal of the oxygen by nitrogen.

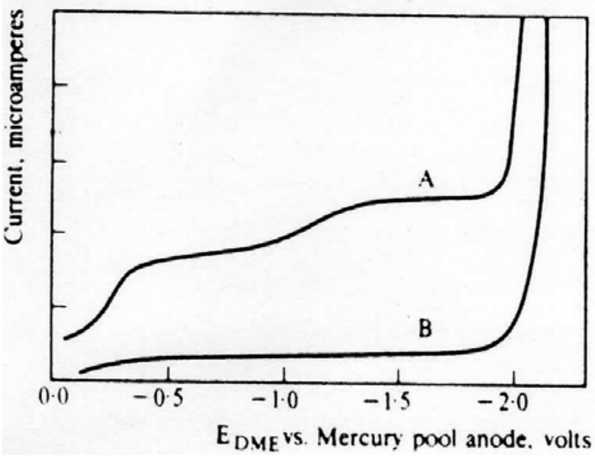


Fig. 7. Typical polarogram for air-saturated M-Potassium chloride solution . Before removal of the Oxygen (Curve A); After removal of the Oxygen (Curve B).

It has been stated that the first wave (starting at about -0.1 Volts relative to S.C.E.) is due to the reduction of oxygen to hydrogen peroxide:

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^- \text{ (neutral or alkaline solution)}$$

$$O_2 + 2H^+ + 2e = H_2O_2 \text{ (acid solution)}$$

The second wave is ascribed to the reduction of the hydrogen peroxide either to hydroxyl ions or to water :

$$H_2O_2 + 2e = OH^- \text{ (alkaline solution)}$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O \text{ (acid solution)}$$

It is therefore necessary to remove any dissolved oxygen from the electrolytic solution whenever cathodic regions are being investigated in which oxygen interferes. The removal of oxygen can be achieved either physically, by the **Introduction** of an inert gas (nitrogen or hydrogen) or by chemical reduction. **Introduction** of the inert gas result in a decrease in the partial pressure of oxygen in the gaseous phase. The decrease in the partial pressure above the solution in the vessel then causes a decrease in the oxygen concentration of the solution.

4. *Redox reaction and reversibility*

The processes are described as polargraphically irreversible when the mixture of oxidized and reduced forms shows a separated cathodic and anodic wave, when the half-wave potentials of the oxidized and reduced form differ. A straight line may still result (plot of $\log \frac{i_d - i}{i}$ vs E) but the slope of the log plot will differ from the theoretical value, hence the value of n calculated from the slope has no significance.

5. *Polarographic diffusion coefficient*

Diffusion currents obtained with either the D.M.E. or platinum micro-electrodes are proportional to the square root of the diffusion coefficient of the electroreducible or electrooxidizable substance. A knowledge of numerical values of diffusion coefficients of various substances is therefore essential for practical application of the diffusion current equations, e.g. for the evaluation of the n-value of an electrode reaction by use of the Ilkovic equation. Diffusion coefficient data will greatly facilitate the attainment of a systematized knowledge of the effect of complex formation, the nature of the solvent, etc. on diffusion coefficients.

Conclusion

The dropping mercury electrode may be applied over the range + 0.4 to about - 2.0 V with reference to the S.C.E. With all the other factors remaining constant, the diffusion current is directly proportional to the concentration of the depolarizer. This is of great importance in quantitative polarographic analysis. It is necessary to remove any dissolved oxygen from the electrolytic solution whenever cathodic regions are being investigated in which oxygen interferes. The removal of oxygen can be achieved either physically, by the **Introduction** of an inert gas (nitrogen or hydrogen) or by chemical reduction.

Equation of the polarogrpahic wave can be represented by following equation

$$E_{d.e.} = E_{1/2} + \frac{0.0591}{n} log \frac{i_d - i}{i} \, at \; 25^0 C$$

Where $E_{d.e.}$ is the potential at any point of the polarogrphaic wave, $E_{1/2}$ is the half-wave potential, n is number of electrons involved in the reaction, i_d is diffusion current and i is current at any point on the polarographic wave minus the residual current.

When $log \frac{i_d - i}{i}$ is plotted against the corresponding potential of the micro-electrode, a straight line should be obtained with a slope of 0.0591/n for a reversible reaction; the intercept of line on Y-axis gives the half-wave potential. Hence n, the number of electrons taking part in the reversible reaction, may be determined. The processes are described as polargraphically irreversible when the mixture of oxidized and reduced forms shows a separated cathodic and anodic wave, when the half-wave potentials of the oxidized and reduced form differ. A straight line may still result (plot of $log \frac{i_d - i}{i}$ vs E) but the slope of the log plot will differ from the theoretical value, hence the value of n calculated from the slope has no significance.

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