

CHAPTER II



POLAROGRAPHY AND PAPER CHROMATOGRAPHY

2.1 Principle of Polarography

Polarography is an electrochemical method based on the electrolysis with a dropping mercury electrode. The current flowing during this electrolytic process is recorded as a function of the applied potential. In the presence of a substance that can undergo reduction or oxidation at the surface of the mercury electrode, this current-voltage curve is called a polarogram. One of the characteristic features of a polarographic wave is the region in which the current levels off after a sharp rise and becomes essentially independent of the applied voltage; this is called a limiting current. The limiting current is the result of a restriction in the rate at which the participant in the electrode process can be brought to the surface of the microelectrode; with proper control over experimental conditions, this rate is determined almost exclusively by the velocity at which the depolarizer diffuses. Under these circumstances the limiting current is given a special name, the diffusion current (i_d). Ordinarily, the diffusion current is directly proportional to the concentration of the depolarizer (19). One other important term, the half-wave potential ($E_{\frac{1}{2}}$); this is the potential corresponding to a current that is equal to one-half the diffusion current. The half wave potential

is important for **qualitative** identification of the depolarizer (see Figure 1).

The rate of transport of the depolarizer to the surface of the electrode is determined by its diffusion and the current follows the Ilkovič derived equation (20).

$$i_d = 0.627 n F C D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} \quad (1)$$

where C = the concentration of the depolarizer in moles cm^{-3}

D = the diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$

F = the Faraday constant (96,484 coulombs)

m = the outflow velocity of mercury in g sec^{-1}

n = the number of electron transferred

t = drop time in sec

i_d = the diffusion current in ampere

The most important consequence of the Ilkovič derived equation for analytical applications is the linear relationship between the diffusion current and the square root of the height of the mercury column and the temperature (20).

In addition to the diffusion current there are also other types of polarographic current as follows .

1) Kinetic current (i_k) is the polarographic limiting current, caused by an electroactive species other than the substance present in bulk solution. It is limited by the rate of a chemical reaction when the reducible particle is formed in a chemical reaction in the neighborhood of the electrode and consequently undergoes reduction or oxidation at the dropping mercury electrode. In such instances,

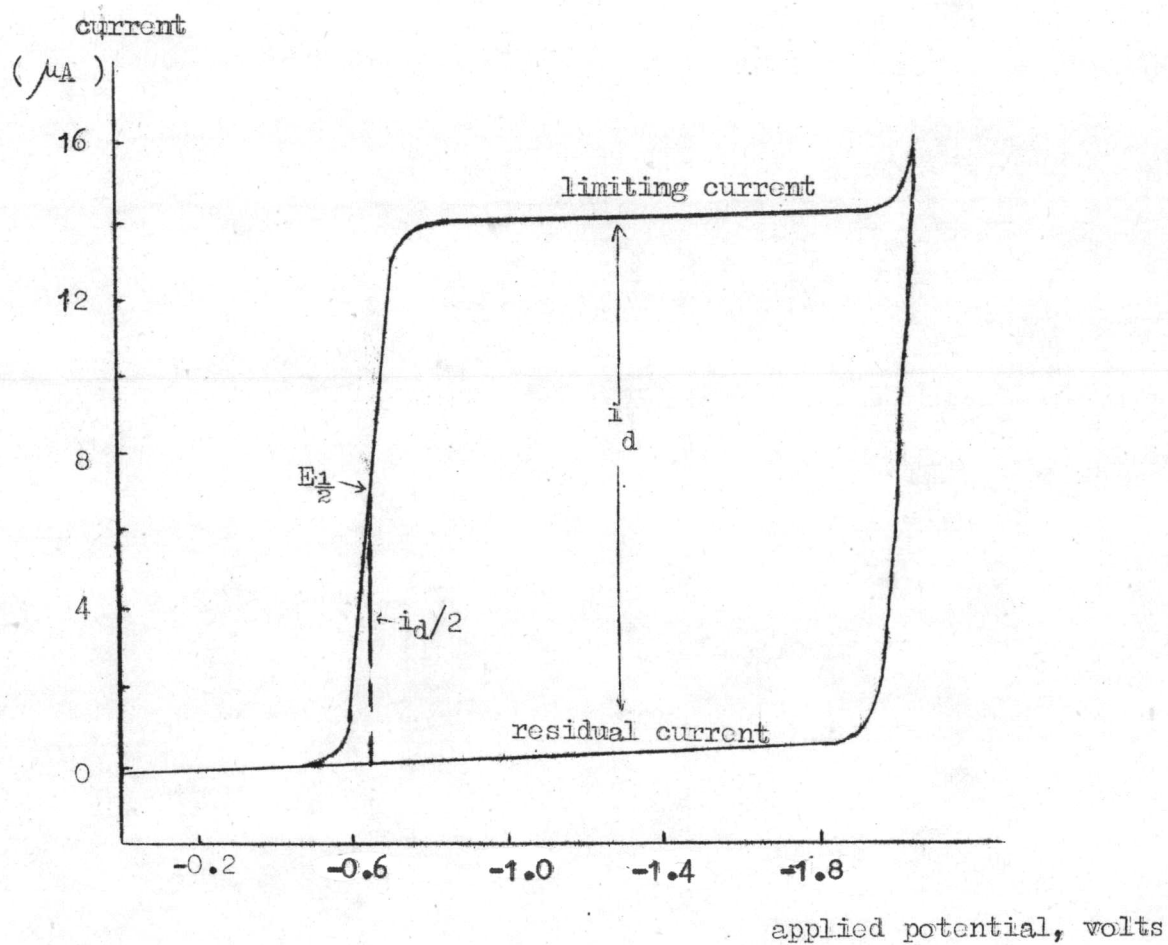


Figure 1 Polarogram for cadmium ion. The upper curve is for a solution that is 1×10^{-3} M with respect to Cd^{2+} ion and 1 M with respect to KCl. The lower curve is for a solution that is 1 M in KCl only.

the rate of a chemical process is slow enough to be the determining step of the electrode process. The equation,

$$i_k = 0.51 n F C D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{2}{3}} k_f K^{\frac{1}{2}} \quad (2)$$

where k_f = rate constant

K = equilibrium constant,

is obeyed for fast reaction, i.e. $(k_f K)^{\frac{1}{2}} < 0.05 \text{ sec}^{\frac{1}{2}}$. Kinetic currents are usually proportional to concentrations of the depolarizer; in most cases they increase markedly with rise in temperature and they are independent of the mercury pressure (20).

2) Catalytic current (i_c) is a limiting current, caused by the presence of a catalyst. The reduction of the depolarizer is shifted to more positive potential or the oxidation is shifted to more negative value. Catalytic waves are characterized by a non-linear dependence on the catalyst concentration. In buffered solutions, catalytic waves are often a function of pH and frequently increase with increasing buffer concentration. It also depends on the mercury pressure.

3) Adsorption current (i_a) is a polarographic limiting current, caused by the adsorption of the oxidized or reduced form of the depolarizer at the surface of the electrode. The current which is limited by the rate of the formation of the surface of the electrode covered by the adsorbed layer follows the equation

$$i_a = 0.85 n F Z m^{\frac{2}{3}} t^{\frac{1}{3}} \quad (3)$$

where Z = the number of moles of the substance adsorbed on 1 cm^2 of the surface of the electrode

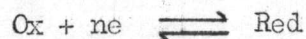
Adsorption process is manifested by separated wave at potentials either more positive or more negative than the wave for the reduction or oxidation of the non-adsorbed compound (21). Many organic compounds exhibit anomalous prewaves at potentials less negative than the main waves, which are observed at high concentrations. Adsorption currents are most frequently observed with organic substances of high molecular weights and with substances that form compounds with mercury. The limiting current reaches its maximum value, and the height of such wave is proportional directly to the height of the mercury and depends to various extents on temperature (21).

Other currents occurred during the polarographic process are the charging and migration currents (22). Current owing to the charging of the electrode to the respective potential is called the charging or condenser current. It is observed even in a pure supporting electrolyte. In the absence of any supporting electrolyte, if charged electroactive particles are present in the solution, the migrations of these charged particles in the electric field between the two electrodes take place, providing migration currents. In polarographic study, migration currents are undesired and are eliminated by an addition of a supporting electrolyte. Normally, the molar concentration of the supporting electrolyte is more than twenty times higher than that of the substance studied.

Another important characteristic of a polarogram is the reversibility of the electrode reaction. A reversible system is one in which both the rate of the reduction and that of the

oxidation process are fast. In irreversible processes, some of the steps of the total process are slow.

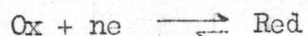
The reversible electrode process can be symbolized as:



For such system, if the value of D_{Ox} and D_{Red} are equal and f_{Ox} and f_{Red} (f is activity coefficient) are the same the half wave potential is proportional to the standard free energy change ΔG° (23).

$$\frac{E_1}{2} = \frac{-\Delta G^\circ}{nF} \quad (4)$$

An irreversible electrode process can be written as:



In this case the half wave potential is a function of the free energy of activation, ΔG^\ddagger , provided that the changes in \ln are known (23).

$$\frac{E_1}{2} \sim \frac{\Delta G^\ddagger}{\alpha nF} + \frac{RT}{\alpha nF} \ln 0.886 \sqrt{\frac{t}{D}} \quad (5)$$

where α = electron transfer coefficient

Whenever possible the polarographic waves of both the oxidized form and reduced form of a given system should be compared. For a reversible process, if the oxidized form alone is present in the solution, the cathodic half wave potential, at which the current is equal to one half of the diffusion current, is given by

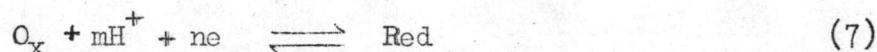
$$\frac{E_1}{2} = E^\circ - \frac{RT}{nF} \ln \sqrt{\frac{D_{\text{Ox}}}{D_{\text{Red}}}} \quad (6)$$

On the other hand, when only the reduced form is present in the solution, the half wave potential of the anodic wave is also given by equation (6). Finally, when both the oxidized and the reduced

form are present in the solution, the half wave potential is again given by equation (6). Since in all three cases the ratio $D_{\text{Ox}}/D_{\text{Red}}$ **does not** vary considerably from unity, the value of the second term on the right hand side of equation (6) is negligible and

$$\left(\frac{E_1}{2}\right)_{\text{Ox}} = \left(\frac{E_1}{2}\right)_{\text{Red}} \approx E^\circ$$

In the reduction or oxidation of an organic substance, hydrogen ion is usually involved in the electrode reaction (24). In a general case in which the oxidant and reductant are both uncharged molecules, the electrode reaction may be written



If the foregoing reaction is reversible at the dropping electrode, the potential of the electrode can be determined by

$$E_{\text{de}} = \frac{E_1}{2} - \frac{2.303RT}{nF} \log \frac{i - (i_d)_a}{(i_d)_c - i} \quad (8)$$

where $\frac{E_1}{2}$ = the half-wave potential (volt)

i = the current at any point on the wave (μA)

$(i_d)_a$ = the anodic diffusion current (μA)

$(i_d)_c$ = the cathodic diffusion current (μA).

Where the half-wave potential is given by

$$\frac{E_1}{2} = E^\circ - \frac{2.303RT}{nF} \log \sqrt{\frac{D_{\text{Ox}}}{D_{\text{Red}}}} - \frac{2.303RT}{nF} m\text{pH} \quad (9)$$

where m = number of protons consumed in the reaction.

When only the oxidized form is present in the solution, $(i_d)_a = 0$, and the equation (8) is simplified to

$$E_{\text{de}} = \frac{E_1}{2} - \frac{2.303RT}{nF} \log \frac{i}{(i_d)_c - i} \quad (10)$$

To prove that the system is reversible and that it follows one of the above equations, the diffusion current (i_d) is measured first. Then the current i is measured at each of several potentials E on the rising portion of the polarogram. The value of $\log i/(i_d - i)$ is computed for each point and plotted against the corresponding E . For a reversible system, a linear graph is given with the slope of $-2.303RT/nF$ which is $-59/n$ mV at 25°C and $-60/n$ mV at 30°C .

Another criterion of reversibility has already been employed, that is the value of $\frac{E_3}{4} - \frac{E_1}{4}$ which should be equal to $-56/n$ mV at 25°C and $-57/n$ mV at 30°C in the reduction (25, 26).

Equation (9) shows that the oxidation or reduction potential is a linear function of pH, even for a constant ratio of the oxidized and reduced forms. The equation is differentiated to

$$\frac{dE_{\frac{1}{2}}}{dpH} = 0.05915 \frac{m}{n} \text{ (volt/pH)} \quad (11)$$

From this slope of $\Delta E_{\frac{1}{2}}/\Delta pH$ the proton consumed in the reaction can be computed when n is known (25).

2.2 Principle of paper chromatography

Chromatography is a process in which species are separated by differential migration in a porous medium, the migration being caused by a flow of some mobile phase (27). Paper chromatography is a special field of liquid-liquid chromatography in which the stationary liquid is an adsorbed film of moisture on a paper (28). All one needs to do is to spot the sample near the edge of a piece of paper, and dip the edge of the paper into the eluting solvent. With sensitive developing reagents, it is particularly suited to

separating and identifying traces of components. The separation is accomplished by successive equilibrations of the sample components between two phases, one of which moves over the other. After location of the separated zones, a figure known as the R_f value is determined. This facilitated identification for the R_f value of an individual zone can be compared with the R_f value of the standard substance subjected to the same chromatographic treatment. The term R_f can be defined by the expression

$$R_f = \frac{\text{Distance travelled by zone or spot}}{\text{Distance travelled by solvent front}}$$

The determination of an R_f value thus involves measuring the distance from the initial point of application of the solute mixture to the center of an individual zone and to the edge of the solvent which flows along the support, solvent front. This is shown diagrammatically in Figure 2.

For the sample with impurity, the chromatogram will show spots of sample and impurity which have the difference R_f values or will show a tailing spot. But for the pure sample, the chromatogram will show a well-defined spot which the R_f value is constant for such solvent system.

2.3 Standard addition method.

In polarography it is desirable to perform quantitative measurement by a method of standard addition to compensate for matrix difference (29). The method is used when the peak height is proportional to concentration of the substance being determined. The concentration of the unknown solution can be achieved by

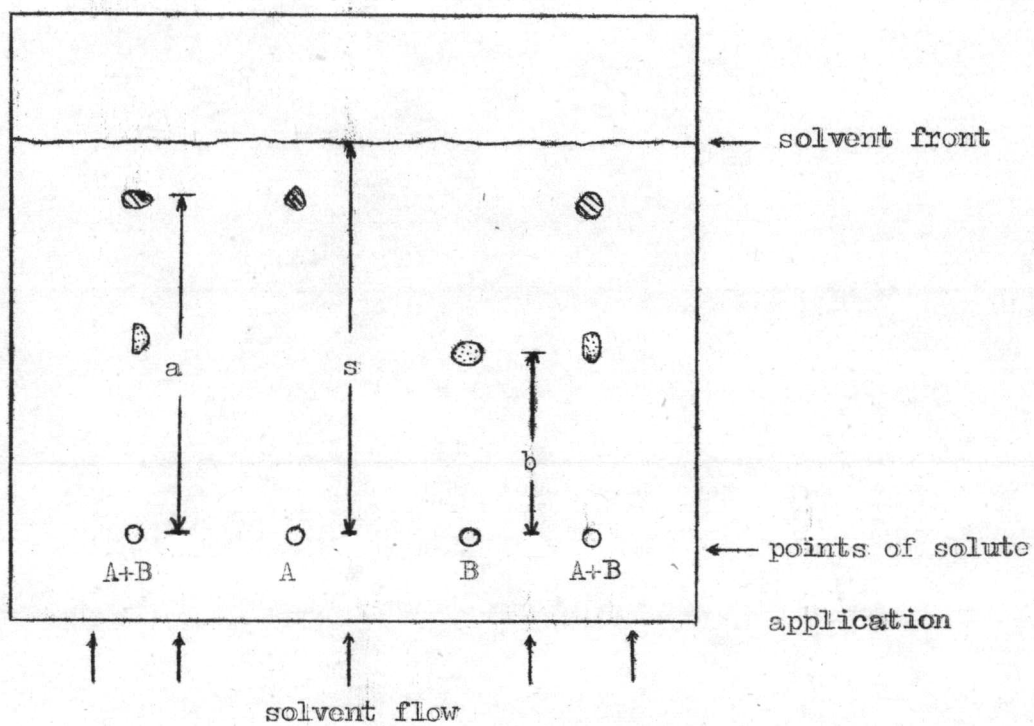


Figure 2 Paper chromatogram of two-component mixture

(A and B). R_f of A = a/s , R_f of B = b/s .

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calculation (30). If V is the volume of the unknown solution in cm^3 , C_x its concentration, i_1 its wave height; and if i_2 is the wave height resulted after adding $v \text{ cm}^3$ of a standard solution whose concentration is C_s , one has

$$i_1 = kC_x \quad (12)$$

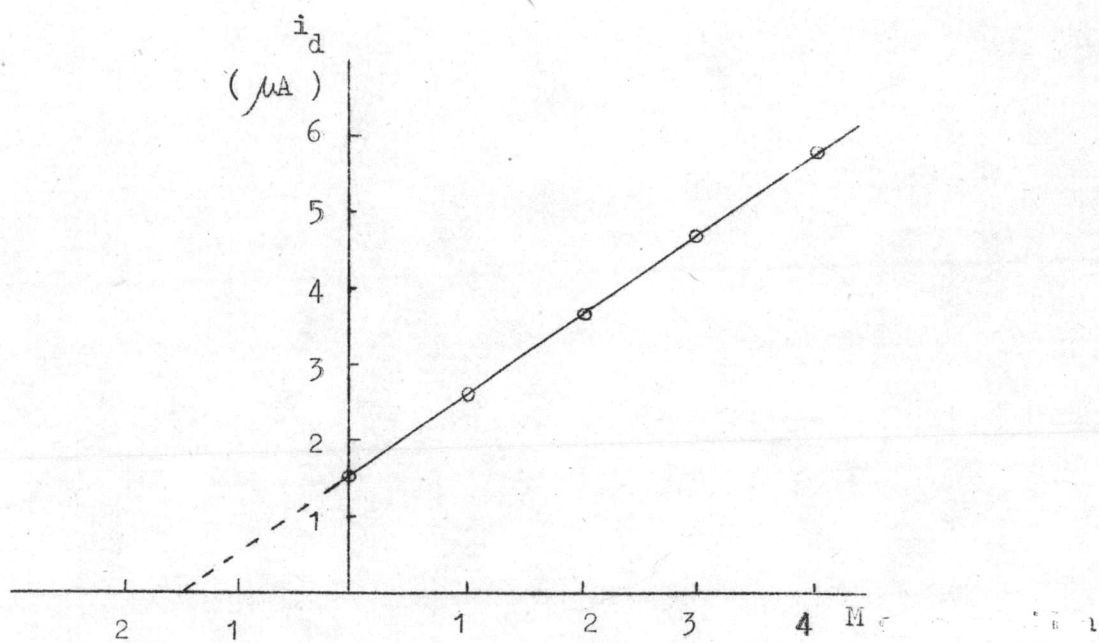
$$\text{and } i_2 = \frac{k(VC_x + vC_s)}{V+v} \quad (13)$$

Dividing equation (12) by equation (13) to eliminate the constant of proportionality k and rearranging the result yields

$$C_x = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V} \quad (14)$$

For the maximum precision the amount of standard solution added should be sufficient to about double the original wave height (30). Another method is a graphic representation of the standard addition method. The graph is plotted between the known concentration of standard added in unknown sample and the diffusion current. The point which is extrapolated to X-axis is the concentration of unknown sample (see Figure 3).

In the present investigation, purity of Amaranth, Ponceau 4R, Orange G, Orange RN and Sunset Yellow FCF are examined by paper chromatographic technique and ultraviolet-visible spectrophotometric technique. Then, polarographic behaviors of the dyes are studied in many electrolytes at various pH. The reversibility of every system at the DME is tested by the equation (10). The number of electron transferred in a system is determined from the slope of the plot of E_{de} versus $\log i/(i_d - i)$. For a reversible process the slope is



Concentration of the dye added to the unknown sample

Figure 3 Graphic representation of the standard addition method

$-2.303RT/nF$ and n is an integer (see equation 10). The proton which is consumed in the process is determined by equation (11). The calibration curve in the range interested is studied. The sensitivity is also determined. Qualitative and quantitative analyses of dyes in some beverages are determined by paper chromatographic and polarographic techniques.