CHAPTER II

POLAROGRAPHY AND PAPER CHROMATOGRAPHY

2.1 Polarography

Polarography is an electrochemical method in which the changes of currents are followed by increasing the applied voltage at a dropping mercury electrode (DME). The current-voltage curve is called the polarogram (usually S shaped) and the electrolytic current of the wave, which attains a constant value with increasing voltage, is called a limiting current (i_l) (see figure 1).

In most instances, the value of the limiting current is limited by the diffusion of the depolarizer. The diffusion current (i_d) is proportional to the concentration of the depolarizer and the half-wave potential ($E_{\frac{1}{2}}$) is the important qualitative characteristic of the substance. The diffusion current follows the Ilkovic equation:

$$i_d = 0.627 \ nFCD^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} \qquad (1)$$

where n = the number of electrons transferred in the reduction or oxidation of the depolarizer

F = the Faraday charge

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

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

m = the rate of flow of mercury in g sec^{-1}

t = the drop time in sec

i_d = **the diffusion current in ampere**

current

(μA)

16 ┤

limiting current

12 ┤

8 ┤

$E_{\frac{1}{2}}$

i_d

4 ┤

$i_d/2$

residual current

0 ┤

-0.2   -0.6   -1.0   -1.4   -1.8
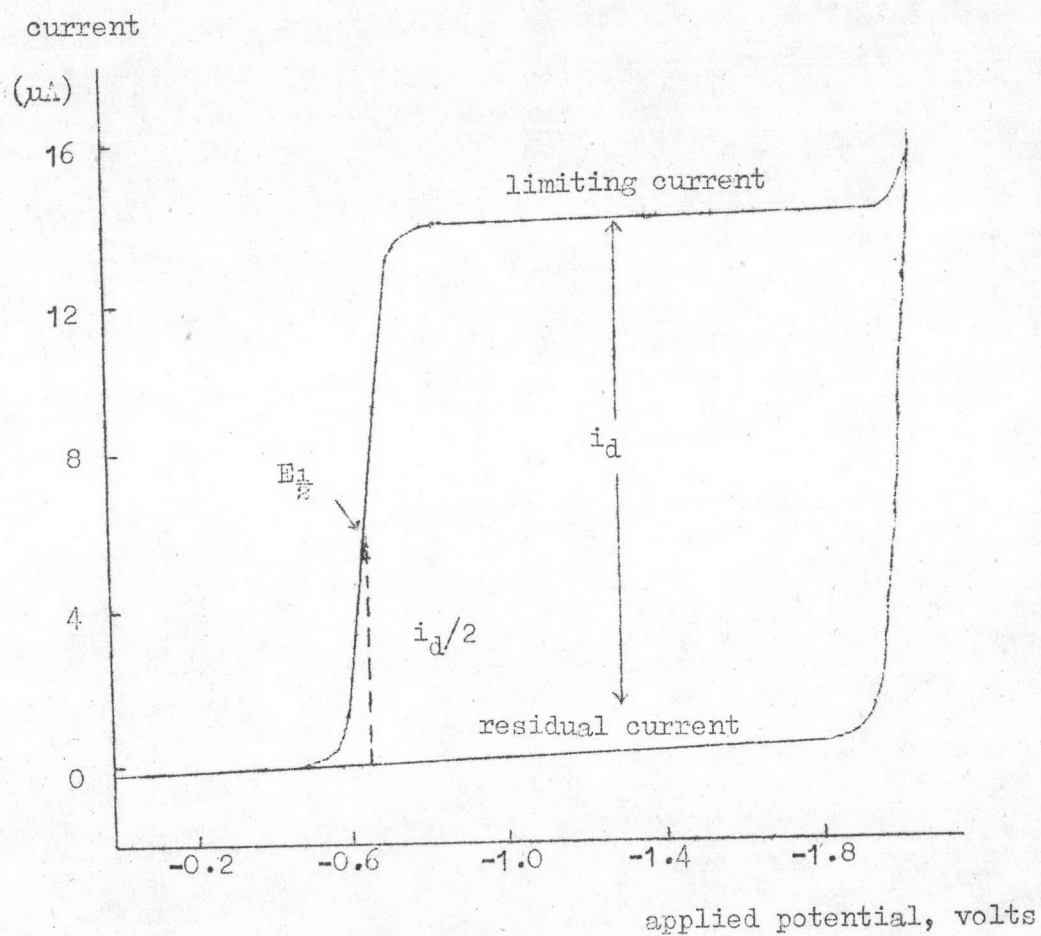
applied potential, volts

Figure 1 Polarogram for **cadmium(II)**. The upper curve is for
a solution that is 1×10^{-3} M with respect to **cadmium(II)**
and 1 M with respect to KCl. The lower curve is
for a solution that is 1 M KCl only.

and 0.627 is a numerical coefficient resulting from the combination of geometrical factors. The diffusion current is also proportional to the square root of the height of the mercury column (21), and increases about 1.3% for a one degree rises in temperature (22).

Another type of the polarographic limiting current is kinetic current (i_k). It is caused by an electroactive species other than the substance present in the bulk solution. It is limited by the rate of a chemical reaction when the reducible species is formed in a chemical reaction in the neighborhood of the electrode and consequently undergoes reduction and oxidation at the dropping mercury electrode. The rate of the chemical reaction is slow enough to be the determining step of the electode process. Kinetic current is expressed as

$$i_k = 0.51 \ nFCD^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{2}{3}} kf^{\frac{1}{2}} K^{\frac{1}{2}} \qquad (2)$$

where k_f is the rate constant and K is the equilibrium constant. This equation is obeyed for fast reaction, i.e. $(kfK)^{\frac{1}{2}} < 0.05 \ sec^{-1}$. Kinetic current is proportional to the concentration of the depolarizer, it is dependent with temperature and independent of the mercury pressure (21).

The catalytic current is another type of the limiting current, caused by the presence of a catalyst. The reduction of the depolarizer is shifted to more positive potential or in the oxidation it is shifted to more negative value (23). Catalytic wave is nonlinear dependence on the catalyst concentration and it increases with decreasing height of the mercury column (21).

The adsorption current (i_a) is another type of limiting currents, caused by the adsorbed depolarizer or adsorbed products **covered** the surface area of the drop. The height of the adsorption current is pH independent, but it depends on temperature and the height of the mercury column (21). The adsorption current follows the equation

$$i_a = 0.85 \ nFZm^{\frac{2}{3}}t^{-\frac{1}{3}} \qquad (3)$$

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

Other polarographic currents are migration current and condenser current or charging current. 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 solution of pure supporting electrolyte. The condenser current is directly proportional to the height of the mercury column. In the presence of the electroactive particles in the solution, if there is not a sufficient excess of the supporting electrolyte, these charged particles migrate between the electrodes in the electric field. The current which flows by the effect of electrostatic force is the migration current. In polarographic study this migration current is eliminated by adding excess of the supporting electrolyte.

Another important characteristic of the polarographic wave is the electrode reaction. The reversible process is one of the electrode processes in which the electron transferred reaction

proceeds at a rate fast enough to maintain the surface concentration of the reactant and the product very close to the equilibrium value.
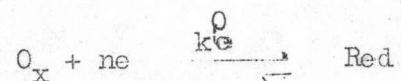
In irreversible process, the electron transferred reaction does not proceed rapidly enough to maintain equilibrium at the electrode surface. The reversible electrode process can be symbolized as

$$Ox + ne \rightleftharpoons Red$$

The half wave potential of a reversible process is expressed in the standard free energy, ΔG^{o}, (23) term as

$$-E_{\frac{1}{2}} = \Delta G^{o}/ nF \qquad (4)$$

An irreversible electrode process can be written as

$$O_x + ne \xrightarrow{k_e^o} Red$$

where k_e^o is the heterogeneous rate constant of the electrode process at the standard potential.

The half wave potential of an irreversible process depends on the activation free energy, $\Delta G^{\neq}$, (23).

$$E_{\frac{1}{2}} = E^{o} - (\Delta G^{\neq}/\alpha n) \log 0.886 (t_1/D)^{\frac{1}{2}} \qquad (5)$$

where α is the electron transferred coefficient and t_1 is the drop time. Whenever possible the polarographic wave of both oxidized and reduced forms of a given system should be compared. For reversible process, if the oxidized form is present alone in the solution, the

cathodic half wave potential, at which the current is equal to one half of the diffusion current, is given by (23)

$$E_{\frac{1}{2}} = E^0 - \frac{0.05915}{n} \log \frac{D_O^{\frac{1}{2}}}{D_R^{\frac{1}{2}}} \qquad (6)$$

The ratio $D_O^{\frac{1}{2}} / D_R^{\frac{1}{2}}$ is equal to the ratio of the cathodic and anodic diffusion current constants and can be evaluated experimentally. When the formal potential of the couple is known under the conditions of the experiment, the half wave potential can be calculated from the equation 6. If the cathodic wave agrees with the calculated one and the anodic wave has the same half wave potential, the couple must be reversible. If the half wave potential of the either wave disagrees with the calculated value, the couple is irreversible (22).

In the reduction or oxidation of an organic substance, hydrogen ion is usually involved in the electrode reaction (23). The general reaction is represented as

$$O + mH^+ + e \rightleftharpoons R \qquad (7)$$
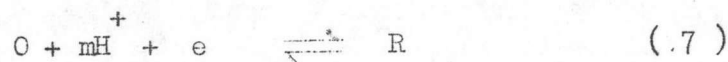
If the reaction is reversible at the DME, the potential of the electrode can be expressed by

$$E_{de} = E_{\frac{1}{2}} - 2.303 \frac{RT}{nF} \log \frac{i - (id)_a}{(id)_c - i} \qquad (8)$$

where 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)

The half wave potential is given by

$$E_{\frac{1}{2}} = E^{O} - 2.303 \frac{RT}{nF} \log \frac{D_{O}^{\frac{1}{2}}}{D_{R}^{\frac{1}{2}}} - 2.303 \frac{RT}{nF} mpH \quad (9)$$

where m is the 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

004519

$$E_{de} = E_{\frac{1}{2}} - 2.303 \frac{RT}{nF} \log \frac{i}{i_{d-i}} \quad (10)$$

To proof the system is reversible and that it follows one of the above equations (equation 8,10) the diffusion current (i_d) is measured. Then the current (i), in the rising part of the polarographic wave is measured at several potential, E. The value of $\log i / i_{d-i}$ is computed for each point and plotted against the corresponded E. For reversible process, the graph is linear with a slope of - 2.303 RT/ nF which is - 0.059/ n V at 25°C and - 0.060/ n V at 30°C (23), where n is an integer.

Another criterion of the **reversibility and irreversibility** is the measurement of $E_{\frac{1}{4}}$ and $E_{\frac{3}{4}}$ from polarogram, the value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ should equal - 56.4/ n mV at 25°C and -- 57/ n mV at 30°C for reversible process (22).

For irreversible process the relation of potential and diffusion current is expressed as (22)

$$E_{de} = E_{\frac{1}{2}} - \frac{0.05915}{\alpha n} \log \frac{i}{i_{d}-i} \quad (11)$$

From equation 9, a plot of the half wave potential versus pH gives a straight line with a slope of $\Delta E_{\frac{1}{2}}/\Delta pH$ which equals $0.05915\frac{m}{n}$ (volt/ pH) at 25° C and $-0.060\frac{m}{n}$ (volt/ pH) at 30° C. The proton consumed between oxidized and reduced forms can be computed from the slope when n is known (23).

2.2 Paper Chromatography

Chromatography is a process in which the flow of a mobile phase promotes the separation of substances by differential migration in the porous medium (24). Paper Chromatography is a special field of liquid-liquid chromatography in which the stationary liquid is an adsorbed film of substance on a paper and a mobile phase is allowed to flow over the spot to cause the separation. A spot of the sample is placed near the edge of the paper strip and the strip is immersed in the solvent chosen as the mobile phase. The solvent percolates through the fibers of the paper by capillary action, and moves the components of the mixture to different extents in the direction of flow. When the solvent front has moved to a suitable distance, the paper is removed from the apparatus, the position of the solvent front is marked, and the sheet is allowed to dry. If the substances are colored they are visible as spots. The distance of the spot from the base line is measured (see Figure 2) and the R_f value is determined. Identification of an individual zone or spot can be performed by comparison between its R_f value to the R_f value of the standard substance subjected to the same chromatographic treatment. The term
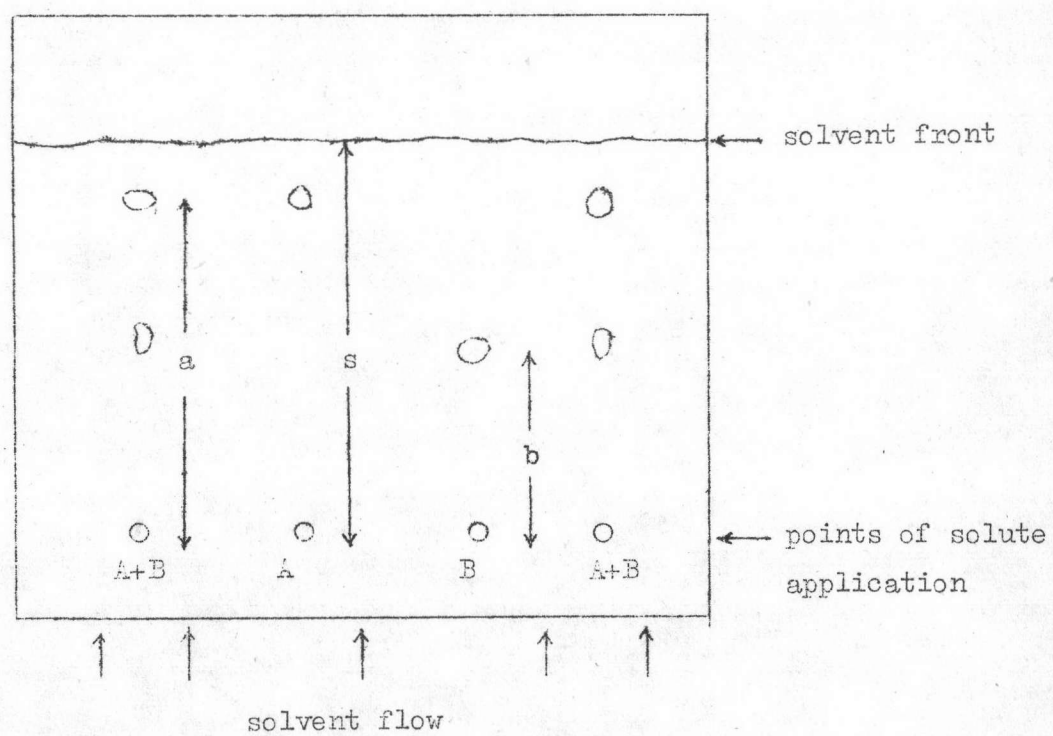
Figure 2 Paper chromatogram of two-component mixture

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

R_f value can be expressed as

$$R_f = \frac{\text{distance moved by solute zone}}{\text{distance moved by solvent front}}$$

The R_f values are reproducible as long as all conditions which affect them are held constant. The **conditions** include the solvent used, the paper used, the method of development, vapor equilibrium with the solvent and the temperature (25,26). For the sample with impurities, the chromatogram will show the separated spots of the sample and the impurities which have the difference R_f values or will show a tailing spot. However, the chromatogram of a pure component gives a well-defined spot which the R_f value is constant for such solvent system.

2.3 Standard addition method

In quantitative analysis of a sample by polarography, the method of standard addition is capable of accuracy. The method is based on the increase in wave height which results when a known amount of the substance being determined is added to the sample (27). If V is the volume of the unknown solution, C_u its concentration and i_1 its wave height and if i_2 is the wave height secured after the addition of v cm^3 of a standard solution whose concentration is C_s. The equation is modified as

$$i_1 = k\, C_u$$

and

$$i_2 = k(V\, C_u + v\, C_s / (V + v)$$

according by
$$k = i_2(V + v)/(VC_u + vC_s)$$

whence
$$C_u = i_1/k = i_1 vC_s / \left[i_2 v + (i_2 - i_1)V \right] \quad (12)$$

The accuracy of this method depends on the precision in which the two volumes of the solution and the corresponding diffusion currents are measured (28). Another method is a graphic representation of the standard addition method (29). The graph is plotted between the diffusion current and the known concentration of the standard added in the unknown sample. The point which is extrapolated to X-axis is the concentration of the unknown sample (See Figure 3).

In the present investigation, purity of Quinoline Yellow, Tartrazine and Brillant Blue FCF are examined by paper chromatographic and visible spectroscopic techniques. Then, polarographic behaviors of these dyes are studied in many electrolytes at various pH. The reversibility of every system at the DME. is tested by equation 10 and by the difference between $E_{3/4}$ and $E_{1/4}$. The number of electrons transferred in a system is computed from the slope of the plot of E_{de} versus log $i/i_d - i$. The proton consumed in the process is determined by equation 9. The sensitivity for every dye is also determined. In addition, qualitative and quantitative analyses of dyes in some beverages are determined by paper chromatographic, spectrophotometric and polarographic techniques.
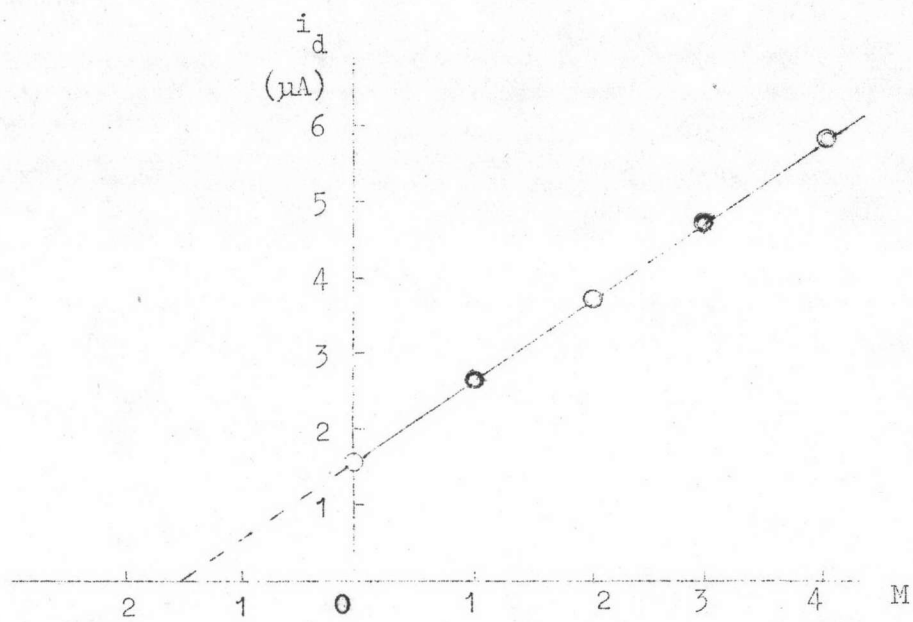
Concentration of the dye added to the unknown sample

Figure 3   Graphic representation of the standard addition method