

(a) Residual or condenser current : Mercury is unique in remaining electricity uncharged when it is dropping freely into a solution containing an indifferent electrolyte, such as KCl, KNO_3 etc. If a current-voltage curve is determined for a solution containing ions with a strongly negative reduction potential (e.g., potassium ions), a small current will flow before the decomposition of the solution begins. This current increases almost linearly with the applied voltage, and it is observed even when the purest air free solutions are used, so that it cannot be due to the reduction of impurities. It must, therefore, be considered a *non-faradic* or *condenser current*, made appreciable by the continual charging of new mercury drops to the applied potential. It is known that metals when submerged in an electrolyte, are covered with an electrical double layer with positively and negatively charged ions. The composition of the double layer and hence the charging current varies, depending upon the potential which is imposed upon the metal.

In practice one often finds that the indifferent electrolyte contains traces of impurities, so that small, almost imperceptible currents are super-imposed upon the condenser current. It is customary to include all these currents in the residual current. As will be shown later, in practical polarographic work, the residual current is automatically subtracted from the total observed current by proper extrapolation and placements of tangents to the wave.

(b) Migration current : Electro-active material reaches the surface of the electrode largely by two processes. One is the migration of charged particles in the electric field caused by the difference of potential existing between the surface of the electrode and the solution, the other is concerned with the diffusion of particles, and will be discussed in the succeeding paragraph. Heyrovsky (1934) showed that the migration current can be practically eliminated if an indifferent electrolyte is added to the solution in a concentration so large that its ions carry essentially all the current. (An indifferent electrolyte is one which conducts the current but does not react with the material under investigation, nor with the electrodes within the potential ranges under study). In practice, this means that the concentration of the added electrolyte (supporting electrolyte) must be at least 100-fold that of the electro-active material. An example of this supporting electrolyte will make it clear. Let us imagine an electrolytic solution containing potassium ions 0.10M and copper ions 0.005M. If we assume that the equivalent conductivities of each ion are approximately equal then it follows that 90% of the current will be transported to the cathode by the potassium ions and only 10% by the copper ions. Both ions will tend to diffuse towards any portion of the solution where a concentration gradient exists, but the rate of diffusion will be slow. If the concentration of the potassium ions be increased until it represents 99% of the total cations present, practically all the current passing through the cell will be transported by the potassium ions. Under such conditions, the electroactive material can reach the electrode surface only by diffusion. It must be emphasised that the supporting electrolyte must be composed of the ions which will discharge at the potentials which will not interfere or react chemically with the ions under investigation.

(c) Diffusion current : The effect of various factors on the diffusion current has been examined by Ilkovic (1948) who derived an equation by regarding the thickness of the cathode layer as small compared to the radius of the drop and thus using a relation for linear diffusion of the ionic species during electrolysis.

Strictly speaking, the linear diffusion of an ionic species during electrolysis will occur in the presence of a plane electrode forming one end of a cylindrical vessel, when the diffusion of the ions will be linear, parallel to the axis of the cylinder. Despite this approximation, the equation applies well to diffusion near spherical mercury drops, though for accurate determinations, some correction terms are necessary. The *Ilkovic equation* is given by,

$$I_d = 607 n D^{1/2} m^{2/3} t^{1/6} c$$

where I_d = diffusion current in microamperes, n = number of electrons involved in the reduction of one molecule of the reducible substance, D = diffusion coefficient of the substance in $\text{cm}^2/\text{sec.}$, m = weight of mercury in grams flowing through the capillary of the cathode per sec., t = time necessary for the formation of one drop of mercury, c = concentration of the substance in millimoles/litre.

The diffusion coefficient, D is dependent upon temperature T , viscosity of the medium η , ionic mobilities, u and ionic strength of the solution, μ . The value of t depends upon the pressure of mercury and the interfacial tension at the mercury solution interface. It follows that at constant values of D , t , n and m , the Ilkovic equation becomes :

$$I_d = Kc$$

i.e., diffusion current is directly proportional to the concentration of the reducible substance.

IV) Modification of Ilkovic Equation

Lingane and Loveridge derived an equation on the basis of the spherical diffusion of the ionic species, viz.,

$$I_d = 607n D^{1/2} m^{1/3} t^{1/6} (1 + 39D^{1/2} m^{-1/2} t^{1/6})$$

The term in bracket corresponds to the difference between linear and spherical diffusion. This correction term is not large, amounting to about 3-7% of the total current. This equation is taken for accurate work.

In order to obtain the true d.e. of a substance, a correction must be made for the residual current. The most reliable method for making the correction is to evaluate in a separate polarogram, the residual current of the supporting electrolyte alone. The value of the residual current at any particular potential of the dropping electrode is then subtracted from the total current observed, as illustrated in fig. (5). In practice, an adequate correction can be obtained by extrapolating the residual current portion of the polarogram immediately preceding the rising part of the polarogram, and taking as the diffusion current the difference between the extrapolated line and current-voltage wave. This method is useful when the polarogram consists of several waves. In

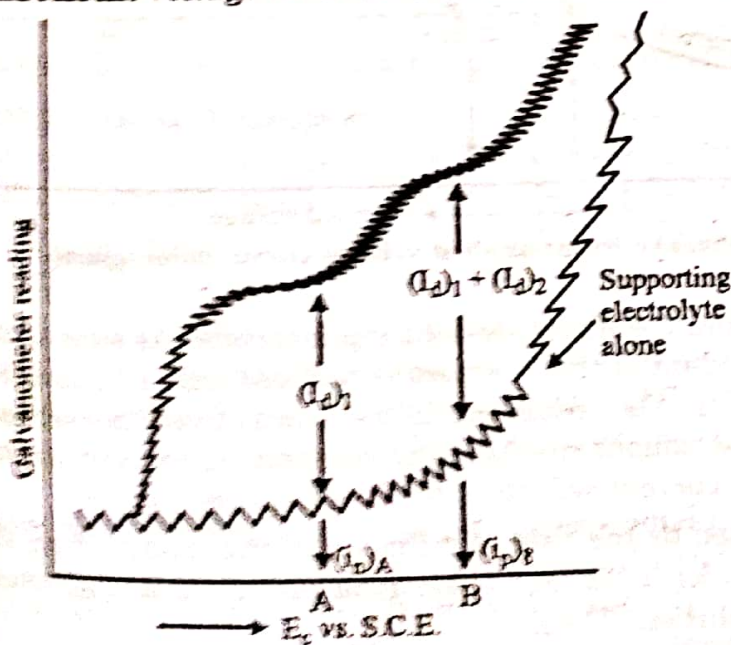


Fig. 5

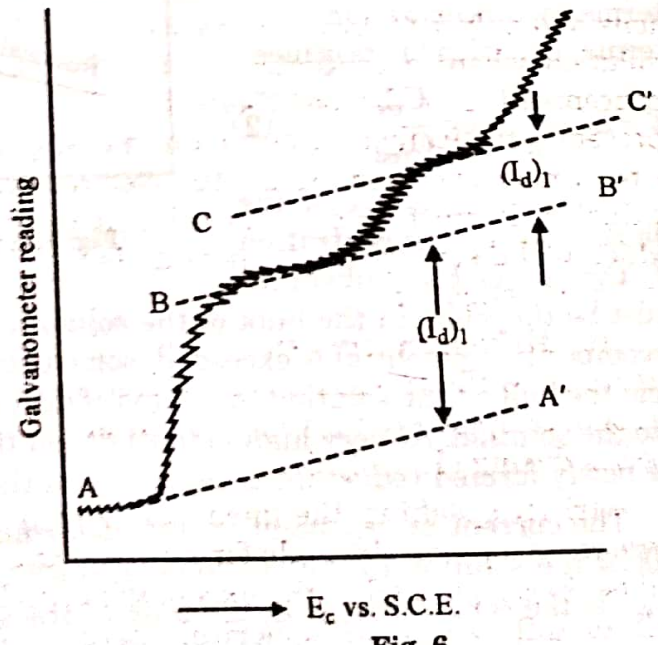


Fig. 6

this case, the diffusion current plateau of a preceding wave may be extrapolated. This method is shown in figure (5).