POLAROGRAPHY-Ilkovic equation

Chapter- ELECTROCHEMISTRY

Part-2

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Ilkovic equation for polarography :- Limiting current density is directly proportional to concentration of ions

Cottrell equation:- Time dependence of current under diffusion control at constant potential.

As the supply of charge carriers decreases the current slowly decreases. Cottrell equation is a consequence of Fick's laws of diffusion.

The diffusion current is proportional to concentration of reducible ions.

First law:- number of mols diffusing is proportional to concentration gradient.

Since diffusion in polarography is the rate controlling (determining) step, consequently the rate of diffusion is thus equal to the rate of electrode reaction and therefore the rate of the electrode reaction is proportional to the concentration gradient.

Number of mols of a substance that diffuse across a plane of area A per unit time is proportional to the concentration gradient (dc/dx) in the diffusion field.

$$\frac{dN}{Adt} = D\left(\frac{dc}{dx}\right)$$

The flow of current i across a plane during electrolysis is given by

$$i = \left(\frac{dN}{Adt}\right) A \times n \times F = nFAD\frac{dc}{dx}$$

Fick's first law is limited only for the cases where the diffusion layer is of constant thickness and where the conditions are stationary. In other cases when the diffusion layer thickness alters with time and concentration is varying with both time and distance, Fick's second law must be introduced.

Second law:- number of mols diffusing is proportional to concentration gradient.

According to Fick's second law, the rate of change of concentration with time, dc/dt as a result of diffusion of the substance across the plane, is proportional to the differential of the concentration gradient.

$$\frac{dc}{dt} = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$

In case of dropping mercury electrode, although spherical, at very low thickness linear diffusion can be assumed

$$\frac{\partial c}{\partial x} = \frac{c^0}{(D\pi t)^{1/2}}$$

where c0 is the concentration of ionic species in the bulk of the solution and t is the time elapsed since the onset of electrolysis.

Substituting in first law

$$i = \frac{nFAD^{1/2}c^0}{(\pi t)^{1/2}}$$

Now since the current is the diffusion current

$$i_d = \frac{nFAD^{1/2}c^0}{(\pi t)^{1/2}}$$

This is the Cottrell equation.

As time increases the diffusion current decreases due to broadening of the diffusion layer, and decrease in the diffusion rate.

The volume of mercury drop increases linearly with time.

Drop volume at time $t = \frac{4}{3}\pi r_t^3$

Mass of the drop at time t (mass = volume x density)

$$= \frac{4}{3}\pi r_t^3 \rho$$

If the flow rate of mercury is m, then the drop mass at time t will be mt

$$\frac{4}{3}\pi r_t^3 \rho = mt$$

$$r_t = \left(\frac{3mt}{4\pi\rho}\right)^{1/3}$$

Therefore area at time t

$$A_t = 4\pi r_t^2 = 4\pi\left(\frac{3mt}{4\pi\rho}\right)^{2/3}$$

$$A_t = 0.8515 m^{2/3} t^{2/3}$$

Substituting in Cottrell equation

$$i_d = \frac{nFAD^{1/2}c^0}{(\pi t)^{1/2}}$$

$$i_d = nFD^{1/2}\frac{c^0}{(\pi t)^{1/2}} \times 0.8515 m^{2/3} t^{2/3}$$

As mercury drop is continually growing the linear diffusion process is disturbed. The electrode surface moves in to a new area where the con of ions is more than near the stationary electrode surface. Ilkovic introduced a correction factor $(7/3)^{1/2}$

Thus $i_d = \left(\frac{7}{3}\right)^{\frac{1}{2}} nFD^{1/2}\frac{c^0}{(\pi t)^{1/2}} \times 0.8515 m^{2/3} t^{2/3}$

giving F = 96485 C mol^{-1}

$$i_d = 708 n m^{2/3} t^{1/6} c^0 D^{1/2}$$

m in milligrams per sec; co in millimols per dm^3 t in secs and D in $cm^2\ s^{-1}$

This is the maximum value of the current when the mercury drop falls

$$i_d(\max) = 708 n m^{2/3} t^{1/6} c^0 D^{1/2}$$

The average value of current is 6/7th of its maximum value.

$$i_d(aver) = 607 n m^{2/3} t^{1/6} c^0 D^{1/2}$$

Thus, the current is directly proportional to the bulk concentration C^0 of its reducible ions. The above equation is Ilkovic equation.