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$E_{1/2}$:- the half wave potential – the polarographic wave equation

The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E_{1/2}$ and its quantity is characteristic of a particular species under fixed experimental conditions. Thus $E_{1/2}$ value serves as finger-print for the species undergoing redox.

Consider the reversible and rapid half cell equation at the cathode

Ox + ne $\rightarrow$ Red

Ox = substance that get reduced or the reactant; Red = reduced substance or the product

If the electrode is reversible; equilibrium can be attained and Nernst equation gives the potential as

$$E_{cathode} = E^0 - \frac{0.0591}{n}\log\frac{[\mathrm{Re}\,d]_0}{[Ox]_0}$$

where $[Red]_0$ and $[Ox]_0$ represents the concentrations to the film surrounding the DME.

The applied potential is given by

$$E_{applied} = E_{cathode} + E_{anode}$$

Here E_{anode} is saturated calomel electrode E_{SCE}

$$E_{applied} = E^0 - \frac{0.0591}{n}\log\frac{[\mathrm{Re}\,d]_0}{[Ox]_0} + E_{SCE}$$

$$E_{applied} - E_{SCE} = E^0 - \frac{0.0591}{n}\log\frac{[\mathrm{Re}\,d]_0}{[Ox]_0}$$

In the beginning of the experiment the solution very near to DME consists only the reactant. When voltage is applied the reaction starts slowly and the concentration of reactant at electrode surface starts decreasing. The remaining reactants in the bulk solution start moving towards the electrode surface. Thus at intermediate voltage the current is given by

$$i = K([Ox] - [Ox]_0)$$

Where K = 708 n $D_o^{1/2}$ $m^{2/3}$ $t^{1/6}$

D_0 = diffusion coefficient of oxidant

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where K represents the constants of the Ilkovic equation. At the limiting diffusion current the concentration of the oxidant at the electrode surface is almost zero and the diffusion current is given by

$$i_d = K[Ox]$$

Substracting these two we get

$$[Ox]_0 = \frac{(i_d - i)}{K}$$

For the anodic processes occuring at the electrode surface

$$i = K^{!}[\mathrm{Re}\,d]_0$$

where K! is another constant (Ilkovic constant)

$K^! = 708\ n\ D_r^{\ 1/2}\ m^{\ 2/3}\ t^{\ 1/6}$

D_r = diffusion coefficient of reduced product

$$[\mathrm{Re}\,d]_0 = \frac{i}{K^!}$$

Substituting these two in above equation

$$E_{applied} - E_{SCE} = E^0 - \frac{0.0591}{n}\log\left[\frac{i}{i_d - i} \times \frac{K}{K^!}\right] \text{......................(1)}$$

$$E_{applied} = E_{SCE} + E^0 - \frac{0.0591}{n}\log\frac{K}{K^!} - \frac{0.0591}{n}\log\frac{i}{i_d - i} \text{ ....(2)}$$

When $i = i_d/2$; $E_{applied} = E_{1/2}$

$$E_{1/2} = E_{SCE} + E^0 - \frac{0.0591}{n}\log\frac{K}{K^!} \text{ ....(3)}$$

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Thus half wave potential is a constant independent of the concentration. It depends on the standard potential of the redox system.

Substituting in the equation ….(2)

$$E_{applied} = E_{1/2} - \frac{0.0591}{n}\log\frac{i}{i_d - i}$$

This equation is called as the polarographic wave equation

A plot of $E_{applied}$ Vs $\log i/(i_d - i)$ gives a straight line with slope equal to -0.0591/n . From the slope n; the no of electrons gained by reductant could be obtained. $E_{1/2}$ is the potential at which $\log i/(i_d - i) = 0$