

## Debye - Huckel Limiting Law for strong electrolyte

Debye - Huckel derived a mathematical expression to account for the deviation of mean activity coefficients of strong electrolyte from unity. The Debye - Huckel theory is based on the following assumptions: -

- (i) The solution is a dielectric continuum of dielectric constant of relative permittivity ( $\epsilon_r$ )
- (ii) The ions are hard spheres of diameter ( $a$ )
- (iii) The concentration of the electrolyte in solution is low.

Derivation of Debye - Huckel Limiting Law: -

Let us consider a uni-univalent electrolyte. From electrostatics it is known that there exists an average potential  $\psi$  at a distance  $r$  from a given ion. The potential energy of an ion under this potential is  $e\psi$ , where  $e$  is the electronic charge.

According to Boltzmann distribution law, the probability that a given positive ion is in a region of potential  $\psi$  around a particular ion having the same charge is given by

$$n_+ = n_+ e^{-e\psi/kT} \quad \text{--- (1)}$$

where  $n_+$  is the number of ions per unit volume. Similarly for a negative ion,

$$n_- = n_- e^{e\psi/kT} \quad \text{--- (2)}$$

Hence, the net charge density ( $\rho$ ) is given by

$$\rho = (n_+ - n_-)e = n_+ e \left( e^{-e\psi/kT} - e^{e\psi/kT} \right) \quad \text{--- (3)}$$

In a medium of dielectric constant  $\epsilon_r$ , the well-known Poisson's equation is given as  $\nabla^2 \psi = -\frac{4\pi\rho}{\epsilon_r}$ , where  $\nabla^2$  is the Laplacian operator.

In the terms of spherical polar co-ordinates, the Poisson equation is written as,

$$\nabla^2 \psi = \frac{1}{r^2} \times \frac{d}{dr} \left[ r^2 \frac{d\psi}{dr} \right] = -\frac{4\pi\rho}{\epsilon_r} \quad \text{--- (4)}$$

Substituting for charge density from equation (3) we have

$$\nabla^2 \psi = -\frac{4\pi n_+ e}{\epsilon_r} \left( e^{-e\psi/kT} - e^{e\psi/kT} \right) \quad \text{--- (5)}$$

If  $\psi$  is not large, then exponentials can be expanded to give

$$e^{-e\psi/kT} = 1 - \frac{e\psi}{kT} + \text{higher powers of } \frac{e\psi}{kT} \quad \text{--- (6)}$$

$$e^{e\psi/kT} = 1 + \frac{e\psi}{kT} + \text{higher powers of } \frac{e\psi}{kT} \quad \text{--- (7)}$$

Now from equation (5), (6) and (7). We get,

$$\nabla^2 \psi = \frac{4\pi n_+ e}{\epsilon_r} \left[ 1 - \frac{e\psi}{kT} - \left( 1 + \frac{e\psi}{kT} \right) \right]$$

$$\nabla^2 \psi = -\frac{4\pi n_+ e}{\epsilon_r} \left( \frac{-2e\psi}{kT} \right)$$