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 permitivity (ε_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 an uni-univalent electrolyte. From electrostatic it is known that there exists an average potential ψ 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 ψ around a particular ion having the same charge is given by

$$n_+ = n e^{-e\psi/KT} \qquad (1)$$

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

$$n_- = n e^{e\psi/KT} \qquad (2)$$

Hence, the net charge density (ρ) is given by

$$\rho = (n_+ - n_-)e = ne\left(e^{-e\psi/KT} - e^{e\psi/KT}\right) \qquad (3)$$

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

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

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

Substituting for charge density from equation (3) we have

$$\nabla^2\psi = -\frac{4\pi ne}{\varepsilon_r}\left(e^{-e\psi/KT} - e^{e\psi/KT}\right) \qquad (5)$$

If ψ is not large, then exponentials can be expanded to give

$$e^{e\psi/KT} = 1 + \frac{e\psi}{KT} + \text{higher powers of } \frac{e\psi}{KT} \cdots (6)$$

$$e^{-\frac{e\psi}{KT}} = 1 - \frac{e\psi}{KT} + \text{higher powers of } \frac{e\psi}{KT} \qquad (7)$$

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

$$\nabla^2\psi = \frac{4\pi ne}{\varepsilon_r}\left[1 - \frac{e\psi}{KT} - \left(1 + \frac{e\psi}{KT}\right)\right]$$

$$\nabla^2\psi = -\frac{4\pi ne}{\varepsilon_r}\left(-\frac{2e\psi}{KT}\right)$$