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 or 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 Operater.

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

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

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

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

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

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

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

or $\nabla^2\psi = \left[\frac{8\pi n e^2}{\epsilon_r KT}\right]\psi$ ——— (8)

Defining a quantity K by

$$K^2 = \frac{8\pi e^2}{\epsilon_r KT}\sum n_i Z_i^2 \quad \text{——— (9)}$$

Where Z_i is the charge on the ion, for uni-univalent electrolyte,

$$K^2 = \frac{8\pi n e^2}{\epsilon_r KT} \quad \text{——— (10)}$$

Thus equation (8) becomes,

$\nabla^2\psi = K^2\psi$, which has the solution

$$\psi = \frac{Ze}{\epsilon_r \cdot r}e^{-Kr} \quad \text{——— (11)}$$

The exponetial equation (11) can be expanded, retaining only the first two terms to give,

$$\psi(r) = \frac{Ze}{\epsilon_r r} - \frac{ZeK}{\epsilon_r} \quad \text{——— (12)}$$

In equation (12), the first term on the right hand side is the potential due to the charge on the ion itself, while the second term can be thought of as the potential due to charge $-Ze$ at a distance $\frac{1}{k}$. The quantity $\frac{1}{k}$, which has the dimension of length and it is known as effective radius of the ionic atmosphere or **Debye length**.

The free energy associated with the additional potential arising from the ionic atmosphere is equal to the reversible electrical work Wel, it is required to form the ionic atmosphere. This is obtained by integrating the second term in equation (12) from 0 to full charge Ze.

$$W_{el} = \int_0^{Ze}\left(-\frac{ZeK}{\epsilon_r}\right)d(Ze) = -\frac{K}{2\epsilon_r}(Ze)^2 \quad \text{——— (13)}$$

For dilute solution, Wel, can also be written as

$$W_{el} = kT\ln\gamma_i = -\frac{Z_i^2e^2K}{2\epsilon_r} \quad \text{——— (14)}$$

Where γ_i is the activity coefficient of the ith ion component.

Thus, $\ln\gamma_i = \frac{Z_i^2e^2K}{2\epsilon_r kT}$ ——— (15)

Since the mean ionic activity coefficient is defined as

$$\gamma_\pm^{\nu} = \gamma_+^{\nu_+}\gamma_-^{\nu_-} \quad \text{——— (16)}$$

Where V_+ and V_- are the number of positive and negative ions respectively and $V = V_+ + V_-$

Hence $$\ln\gamma_\pm = \frac{\nu_+}{\nu_-}\ln\gamma_+ + \frac{\nu_-}{\nu_+}\ln\gamma_- \qquad (17)$$

also $$\nu_+ z_+ = \nu_- z_- \qquad (18)$$

Hence from equation (15), (17) and (18) we have

$$\ln\gamma_\pm = -|z_+ z_-|\frac{e^2\kappa}{2\epsilon_r kT} \qquad (19)$$

Using the definition of ionic strength, μ as

$$\mu = \frac{1}{2}\sum c_i z_i^2 \qquad (20)$$

and $$n_i = \frac{c_i N_A}{1000}$$

Where N_A is Avagadro's number and $c_i = m_i\rho_0$ (where ρ_0 being the density of the solvent) we obtain,

$$\kappa^2 = \frac{8\pi N_A^2 e^2 \rho_0 \mu}{1000\,\epsilon_r kT}$$

$$\text{or, } \kappa = \left(\frac{8\pi N_A^2 e^2 \rho_0 \mu}{1000\,\epsilon_r kT}\right)^{1/2} \qquad (21)$$

Substituting for κ in equation (19) and setting $\rho_0 = 1\,g\,ml^{-1}$ for water, we get,

$$\log\gamma_\pm = -A\,|z_+ . z_-|\,\mu^{1/2}$$

Where A is a constant, expressed as.

$$A = \frac{N_A^2 e^3}{2.303\,\epsilon RT}\left(\frac{2\pi}{1000\,\epsilon_r RT}\right)^{1/2}$$

Substituting the value of N_A π and ρ, we get

$$A = \frac{1.8246\times10^6}{(\epsilon_r . T)^{3/2}}$$

At 25°C the dielectric constant (ϵ_r) for water is 78.54 so that the Debye-Huckel constant becomes equal to 0.509, Thus

$$\log\gamma_\pm = -0.509\,|z_+ . z_-|\,\mu^{1/2} \qquad (23)$$

This is Debye-Huckel limiting law equation relating the mean ionic activity coefficient to the ionic strength of solution.
The negative value for $\log\gamma_\pm$ in equation (23) indicates that the mean ionic activity coefficient ($\gamma_\pm$) is less than unity.
The limiting law equation holds good for dilute solution only.