

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

$$\text{or } \nabla^2 \psi = \left[\frac{8\pi n e^2}{\epsilon_r kT}\right] \psi \quad \text{--- (8)}$$

Defining a quantity K by

$$K^2 = \frac{8\pi n e^2}{\epsilon_r kT} \sum n_i z_i^2 \quad \text{--- (9)}$$

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,

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

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

The exponential 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 W_{el} , 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, W_{el}^0 can also be written as

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

where γ_i is the activity coefficient of the i th ion component.

$$\text{Thus, } \ln \gamma_i = \frac{z_i^2 e^2 k}{2\epsilon_r kT} \quad \text{--- (15)}$$

Since the mean ionic activity coefficient is defined as

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

where ν_+ and ν_- are the number of positive and negative ions respectively and $\nu = \nu_+ + \nu_-$

Hence

$$\ln \gamma_{\pm} = \frac{v_+}{v_-} \ln \gamma_+ + \frac{v_-}{v_+} \ln \gamma_- \quad (17)$$

also $v_+ z_+ = v_- z_-$

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

$$\ln \gamma_{\pm} = -|z_+ z_-| \frac{e^2 k}{2 \epsilon_r k T} \quad (19)$$

using the definition of ionic strength, μ as

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

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

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

$$k^2 = \frac{8 \pi N_A^2 e^2 \rho_0 \mu}{1000 \epsilon_r k T}$$

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

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

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

where A is a constant, expressed as.

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

Substituting the value of N_A , π and ρ , we get

$$A = \frac{1.8246 \times 10^6}{(\epsilon_r \cdot T)^{3/2}}$$

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

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

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 (γ_{\pm}) is less than unity. The limiting law equation holds good for dilute solution only.