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M.Sc. Sem I

CC-2 unite II

Debye-Huckel Theory.

Interionic attraction theory of electrolytic conductivity was developed by Debye and Huckel in 1923. and is known as Debye-Huckel Theory of strong electrolytes which can satisfactorily explain their behaviour in very dilute solution below 0.005M.

The postulates of Debye-Huckel Theory are:-

(i) Every strong electrolyte is completely ionized at all dilutions.

(ii) Two forces act on the mobile ions (a) electrical forces and (b) resistance due viscosity of the medium i.e viscous drag.

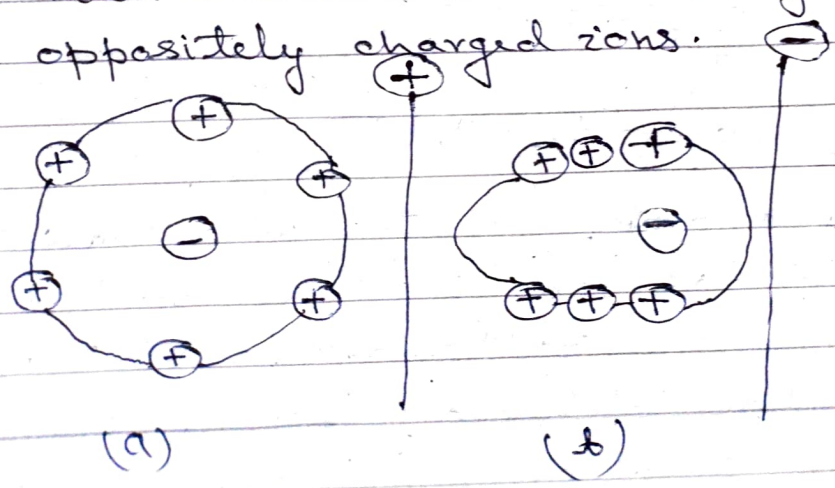
∴ Resultant force = Electrical force − Viscos drag.

(iii) The forces acting between the ions are electrostatic forces governed by coulomb's law.

$$F \propto \frac{q_1 q_2}{r^2}$$

where q_1 and q_2 = charges on the ion
r = distance between the two ions.

(iv) Each ion is surrounded by a number of oppositely charged ions.



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· The following two factors as shown in fig. tend to decrease the conductivity in concentrated solutions.

Mathematical Derivation of Debye-Huckel Equation

The electrical potential at any point is defined as the work done in bringing a unite charge from infinity to that paritcular point. Let ψ be the potential at any given point in the vicinity of a positive ion. then the work done in bringing a positive ion of velecy Z_+ i.e. carrying a charge $Z_+\varepsilon$ (ε is electronic charge) to that point is $Z_+\psi$. similary the work done required for a negative ion is $-Z_-\varepsilon\psi$ where Z_+ and Z_- are numerical values only and do not include the sign.

If the concentration of ions at a large distance from the given ion, where ψ may be taken as zero, are n_+^0 and n_-^0 per unite volume. Then by Maxwell Boltzmann's distribution law for particles in a field of varying potential, we have.

$$n_+ = n_+^0 e^{-(Z_+\varepsilon\psi/kT)}$$

$$n_- = n_-^0 e^{-(-Z_-\varepsilon\psi/kT)}$$

where n_+ and n_- are the concentrations of +ve and -ve ions at a given point under consideration. k = Boltzmann's constant.

The total charge density ρ_e (charge per c.c) at any point where the

potential is ψ is given by the excess of positive or negative electricity per unite volume at the point. i.e.

$$P_e = (n_+ z_+ \varepsilon) - (n_- z_- \varepsilon)$$

$$= \left[(n_+^0 e^{-(z_+ \varepsilon \psi / kT)} z_+ \varepsilon) \right] - \left[(n_-^0 e^{-(-z_- \varepsilon \psi / kT)} z_- \varepsilon) \right] \quad \text{——— (1)}$$

In simpler case of uni-univalent electrolyte. $z_+ = z_- = 1$ and $n_+^0 = n_-^0 = n$ where n is the number per c.c. of ions.

putting these value in equ (1)

$$P_e = n\varepsilon \left(e^{-\varepsilon\psi/kT} - e^{\varepsilon\psi/kT} \right)$$

It is assumed the $\varepsilon\psi/kT$ is small in comparision to unity and neglecting higher power of $\varepsilon\psi/kT$, we get.

$$P_e = -(\varepsilon^2 \psi / kT) 2n.$$

In general case $z_+ = z_- \neq 1$

Then equ (1) takes the form.

$$P_e = \sum n_i z_i e^{-z_i \varepsilon \psi / kT}$$

where n_i and z_i represents the number per c.c and valency. $z_i \varepsilon \psi / kT$ is very small as compared to unity then.

$$P_e = \sum n_i z_i \varepsilon - \sum n_i z_i^2 \varepsilon^2 \psi / kT \quad \text{——— (2)}$$

The first term cancles out by virtue of

the requirment of over all electrical neutrality, so the equ. (2) becomes

$$\rho_e = -(\varepsilon^2 \psi / kT) \sum n_i z_i^2$$

In electrostatics, poisson's equ. gives a relation between variation of electrical potential and charge density. It is given by,

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} = \frac{-4\pi \rho_e}{D} \quad \text{——— (3)}$$

x, y, z are rectangular co-ordinates
D = dielectric constant. converting to polar co-ordinates the term $\delta\psi/\delta\phi$ and $\delta\psi/\delta\theta$ will be zero. since the potential about any point in electrolyte is spherically symmetrical. so. equ. (3) becomes.

$$\frac{1}{r^2} \cdot \frac{\delta}{\delta r}\left(r^2 \frac{\delta \psi}{\delta r}\right) = -\frac{4\pi \rho_e}{D} \quad \text{——— (4)}$$

substituting the value of ρ_e in. (4)

$$\frac{1}{r^2} \frac{\delta}{\delta r}\left(r^2 \frac{\delta \psi}{\delta r}\right) = -\frac{4\pi}{D}\left[-\frac{\varepsilon^2 \psi}{KT} \sum n_i^2 z_i^2\right] \quad \text{———}$$

$$= \frac{4\pi}{D} \frac{\varepsilon^2 \psi}{KT} \sum n_i^2 z_i^2 \quad \text{——— (5)}$$

$$= K^2 \psi \qquad \left[\text{where } K = \frac{4\pi \varepsilon^2 \sum n_i z_i^2}{DKT}\right]^{1/2} \quad (5a)$$

The general solution of the equation (5) giving ψ as a function of distance r from the centre of the given ion is given by.