Ref. : ..... Date : .....

Conductance : 04

Debye - Huckel - Onsager Equation :

The strong electrolytes are considered as completely ionised in soln. which means that in a soln. of containing 1 gm equivalent the no. of ions would be same at all conc. Equivalent conductance (λ) increases with dilution. This is due to ionic speed, which alters with dilution. At ordinary conc. the ions are in close proximity and hence their interionic forces restrain them unable to move with a speed. With dilution, the interionic forces diminish and hence conductance increases.

Debye and Huckel (1923) treated the interionic effects of a soln. carrying an electric current quantitatively. This is known as Debye - Huckel theory of interionic attraction. This treatment has later modified in some respects by Onsager (1927). It is based on application of

Ref. : ..... Date : .....

Hydrodynamics → the mathematical Presentation is highly involve. It is evident that different forces are influence the speed of an ion in soln. moving under an applied electric field.

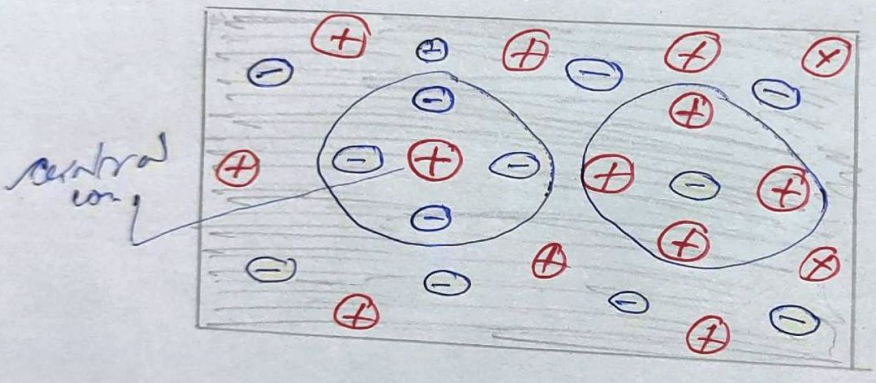

Fig. An ideal distribution of ions in soln. of strong electrolyte.

Let, an ion in a soln., a representative +ve ion (say) of certain charge (e) name as central ion. Let, E be the intensity of the external electric field which directs the ion to move in a direction of x axis. In such situation there are four different forces which play on the given ion → we may consider them separately -

Ref. : ..... Date : .....

i) There is the electric force (E_e) acting on the ion in the direction of x axis.

ii) As the ion move forward, there is a frictional force which retards the motion, this is actually viscous force. It expressed as ($K_1 v$)

iii) In the Debye-Huckel theory it is conceived that each ion is surrounded by an ionic atm. whose net charge is on average opposite to that of the central ion. Onsager calculated this force as $-K_1 E\sqrt{C}$.

iv) The fourth force is, which opposes the speed of an ion & it is responsible for lowering of conductivity. This is arises out of electrophoretic effect.

Debye and Huckel as also Onsager expressed this opposing force due to electrophoretic effect as $-K_2 E\sqrt{C}$

Date : .....

Under equb.^{m} Cond.^{n} the four forces may be equated as —

$$Ee = kv + K_1 E\sqrt{c} + K_2 E\sqrt{c}$$

$$\Rightarrow \quad v = \frac{Ee}{k} - \frac{K_1 + K_2}{k} \cdot E\sqrt{c}$$

It is easily seen that due to Presence of the ionic atmosphere ~~of~~ in consequence of the asymmatric, the electrophoretic ~~of~~ viscous effects the mobility of an ion in a sol^{n} of Conc. c would be less than that ~~of~~ in an infinitely dilute sol^{n}. At $c \to 0$.

The ultimate mathematical expression of Equivalent Conductance of a dilute sol^{n} of Conc. c is was given by

$$\lambda = \lambda_0 - b\sqrt{c}$$

This is known as Debye-Huckel-Onsager Equation. #