

Debye-Huckel theory of activity coefficients of strong electrolytes

Strong electrolytes:- X-ray analysis of crystals of ionic solid, such as NaF, KCl, Na_2SO_4 and NaOH showed that they exist as ion even in solid state. They are no molecules. Hence, as mentioned in Arrhenius theory there is an equilibrium between ionized and non-ionized state in ionic solid which is skipped in cases of strong electrolytes.

According to Coulomb's law, the electrostatic forces vary inversely as the dielectric constant of which is around 80 times greater than that of air. Therefore, the electrostatic force is considerably weakened and ions move much freely and conduct the electricity more strongly.

Debye Huckel Theory:-

According to this theory, strong electrolytes exist as ions even in solid state, they must be completely ionized in aqueous solution at all concentrations.

For the solvents with high dielectric constant, the force of attraction between the ions (electrostatic force) is very small.

For dilute solutions, the distance between ions is very large. Since, the electrostatic forces vary inversely as the square of the distance between the ions is more weakened. Under such conditions, the force of attraction (interionic forces) between the ions reduces and hence the ions lie far from one another.

For the solvents with low dielectric constant such as ethanol or the solution is at higher concentration even when water is used as solvent, the interionic forces will be appreciable. Under such conditions ions are not separated completely and they exist as ion-pair and known as ionic-doublets.

"The electrolytes are completely ionized in such cases but they are not completely dissociated."

On increasing the dilution, the molar conductance increases.

Arrhenius attributed this increase to the increase in the degree of ionization and this can be used to calculate degree of ionization of strong electrolyte.

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \quad \text{--- (1)}$$

$\Lambda_m \rightarrow$ molar conductance at certain concentration.

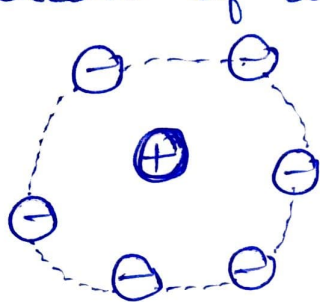
$\Lambda_m^\circ \rightarrow$ molar conductance at an infinite dilution.

According to the modern theory of strong electrolytes, the degree of ~~dissociation~~ ionization of strong electrolytes is unity even at moderate concentrations. This created a contradiction with the above theory.

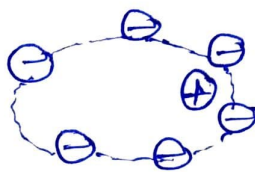
Debye Huckel suggested that increasing in molar conductance with dilution in case of strong electrolyte is due to the increase in ionic mobilities due to weaker interionic attraction rather than due to increase in the degree of ionization.

It can be proposed that the decrease in molar conductance with increase in concentration is not due to increase in the degree of ionization but ~~to~~ due to greater interionic effect.

- In case of strong electrolytes, interionic attraction and not partial dissociation is the cause of decrease of conductance with increase in concentration.



symmetric ionic atmosphere



Asymmetric ionic atmosphere.

Debye and Huckel derived an equation which enabled them to calculate the magnitude of the interionic effects.

It is considered that each ion is surrounded by ions of opposite charge giving rise to the ionic atmosphere.

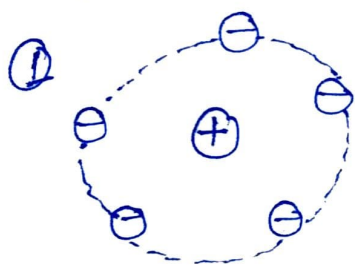
Formation of the ionic atmosphere can be explained in two ways:-

- (1) The Coulombic interaction which tends to arrange the ions in an ordered and organized structure.
- (2) The thermal collisions between the ions and solvent molecules which prevent the existence of organized structure in the solution.

→ At high temperature, the structure is less organized because of internal thermal collisions.

Due to the result of two opposing forces i.e. thermal collision and electrostatic attraction, a situation arises when negative ions end up as the nearest neighbours of given central positive ion and vice-versa.

Therefore a cation is surrounded by more number of anions as compared to the cations. This causes an ionic atmosphere where an anion is surrounded by group of cations and a cation is surrounded by a group of anions.

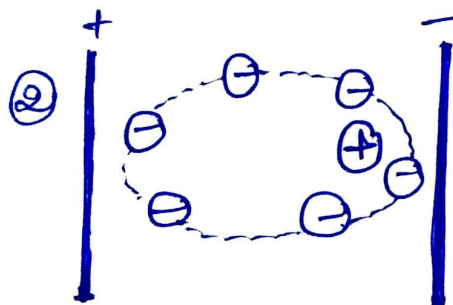


Symmetric ionic atmosphere

The central ion is positively charged and is surrounded by an atmosphere of negatively charged ions.

On the application of electric field the ions are set up in motion.

The central ion (positive) to move towards cathode on the opposite direction.



uniform in all

The symmetry of the ions is destroyed and the ionic atmosphere gets distorted. Force of attraction by ion atmosphere before the passage of electricity is uniform in all the directions and cancels out.

→ The ion experiences a retarding force, a force which tends to drag it backwards and the movements of ion is slowed.

1) Asymmetry effect: The drag on the central ion is known as the asymmetry effect because it arises from the lack of symmetry in the atmosphere of moving ion.

2) Electrophoretic Effect: The motion of ions is slowed down at higher concentrations arising from the tendency of ionic atmosphere associated with molecules of water of hydration to move in the direction opposite of movement of central ion.

Such counter currents slow down the ions in the same way as counter currents & known as electrophoretic effect.

3) Viscous effect: It arises from the viscous drag of the solvent on the movement of the ions. The ions tends to move in the direction of applied electric field. This force is opposed by frictional drag due to viscosity. Greater the viscosity of the solvent, greater is the viscosity viscous drag for a given ion and reduced ionic ~~mobility~~ mobility.

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