

(6)

field is known as interionic effect.
On dilution the ions will ^{move} go far apart - and the forces of attraction between the oppositely charged ions (i.e. the hindrance due to a surrounding ion) decreases and the mobility of ions increases.

The three main factors that effects the mobility as well as the conductance of an a strong electrolyte are

- (i) Asymmetry effect or relaxation effect.
- (ii) Electrophoretic effect.
- (iii) Viscous effect.

Asymmetry on relaxation effect :-

Due to coulombic attraction between the ions a particular ion is surrounded by the oppositely charged ions e.g. if we consider a particular (+) ion (or a reference ion), it will be surrounded by some (-) ions symmetrically around it [Fig I(a)]. It is called an ionic atmosphere. When an electric field is applied the cation (+ve ion) tries to move towards cathode and the anions try to move towards anode. The symmetry of the structure is destroyed, and the ionic atmosphere become distorted. In other words, ~~the force~~ in the symmetrical structure before the passage of electricity the forces of attraction exerted by the atmosphere on the central ion is uniform in all directions, and therefore, cancels out. On the passage of electricity the number of (-)ve charge will be greater behind the (+)ve ion than in front due to the movement of the ions [Fig I(b)].

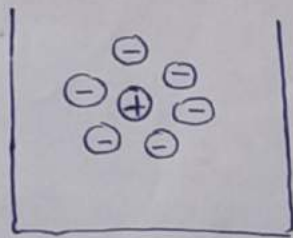
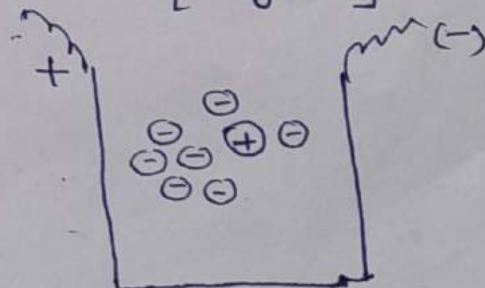


Fig I(a) - Symmetrical ionic atmosphere.



I(b) - Asymmetrical Ionic atmosphere under the influence of an electric field.

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As a result, the central ion (+ve ion) experiences a retarding force, a force which tends to drag it backward. The movement of the ion, therefore, is slowed down. It is called asymmetry effect as it arises due to the lack of symmetry of the ionic atmosphere.

This effect can be explained in another way also by considering that the (+ve) ion which leaves the ionic atmosphere of negative ions behind, has to rebuild a new ionic atmosphere ~~behind~~, around it. However, the process of building up a new and dying away of old ionic atmosphere do not take place at the same rate. The formation of the new ionic atmosphere does not take place at the same time at which the old ionic atmosphere dies out. There is a time lag between the two processes which is called as time of relaxation. During the time of relaxation the old ionic atmosphere drags the moving (+ve) ion backward, and thus retards the motion of the ion. For this reason this effect is also called relaxation effect.

Electrophoretic effect :- In a solution the ions are present in the solvated form. Each ion in the ionic atmosphere is associated with some molecules of solvent. Under the influence of electric field, the central ion moves in one direction and its oppositely charged ionic atmosphere along with the associated solvent molecule moves in opposite direction. As a result the central ion experiences a large amount of opposing force and its mobility decreases. This effect is called electrophoretic effect.

Viscous effect :- The third factor which affects the mobility of the ions is the viscous effect. It arises from the viscous drag of the solvent on the movement of the ions. The ion tends to move in the direction of the applied electric field. This electrical force is opposed by the frictional viscous drag exerted by the solvent. This force will depend

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upon the viscosity of the medium and its dielectric constant. For an ion with a given charge, size and shape, the greater the viscosity of the solvent, the greater is the viscous drag. Similarly the solvent with high dielectric constant ~~have~~ offer high frictional resistance.

The Debye-Hückel Onsager Equation:-

In 1926 Debye, Hückel and Onsager worked out + mathematically the magnitudes of asymmetry and electrophoretic effect in terms of valency of the ion, ionic concentration, dielectric constant and the viscosity of the medium. For uni-univalent electrolyte, like KCl, the following equation was derived.

$$\Lambda_m = \Lambda_m^0 - \left[\frac{82.4}{(\epsilon_r T)^{1/2} \eta} + \left(\frac{8.20 \times 10^5}{(\epsilon_r T)^{1/2}} \Lambda_m^0 \right) \right] \sqrt{C} \rightarrow \text{①}$$

which is known as Debye Hückel Onsager equation.

Here Λ_m = Molar conductance of the electrolyte at concentration C

Λ_m^0 = Molar conductance of the electrolyte at infinite dilution

ϵ_r = Dielectric constant of the medium,

η = Co-efficient of viscosity of the medium.

T = absolute temperature.

C = Concentration of the solution in moles per litre.

In the equation the first term within the bracket gives a measure of the electrophoretic effect - and the 2nd term is due to asymmetric effect. Sum of these effects multiplied by square root of molar concentration.

gives the decrease in Λ_m from the limiting value Λ_m^0

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validity of Onsager equation.

For a given solvent and at a given tempⁿ the eqnⁿ can be expressed as

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c} \rightarrow (2)$$

Where A and B are Debye Hückel constants and their value at 25°C is 60.2 and 0.229 respectively ↓

$$\Lambda_m = \Lambda_m^0 - (60.2 + 0.229\Lambda_m^0)\sqrt{c} \rightarrow (3)$$

This equation may also be written as

$$\Lambda_m = \Lambda_m^0 - b\sqrt{c}$$

$$A = \frac{82.4}{(\epsilon_r T)^{3/2} \eta}$$

$$B = \frac{8.20 \times 10^5}{(\epsilon_r T)^{1/2}}$$

This equation is valid, if

(i) Plot of molar conductance (Λ_m) against the square root of the concentration (\sqrt{c}) is a straight line.

(ii) The slope of the lines equal to $(60.2 + 0.229\Lambda_m^0)$, should be obtained.

This has been tested for different uni-univalent strong electrolytes and found to be true upto a concentration of 0.02M. At higher concentration it fails

indicating that certain approximation made in the derivation of the equation is not valid when the concentration is high.

At infinite dilution when $c \rightarrow 0$, the 2nd term of the equation (2) becomes negligible and Λ_m approaches Λ_m^0

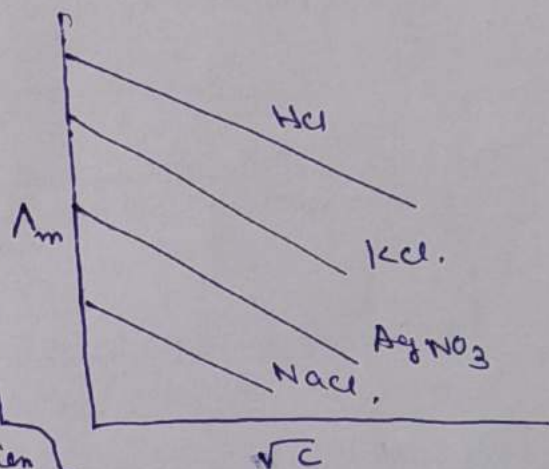


Fig I
Verification of Debye Hückel equation.

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