

Debye-Huckel Theory

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INTRODUCTION



- ❧ Equivalent conductance increases with dilution in the case of weak electrolytes.
- ❧ In case of weak electrolytes increase in conduction is due to increase of dissociation of weak electrolyte.
- ❧ But strong electrolytes are completely dissociated even at moderate concentration.
- ❧ In this theory we have to explore those factors which increase the conductance of strong electrolytes

Three major factors are:

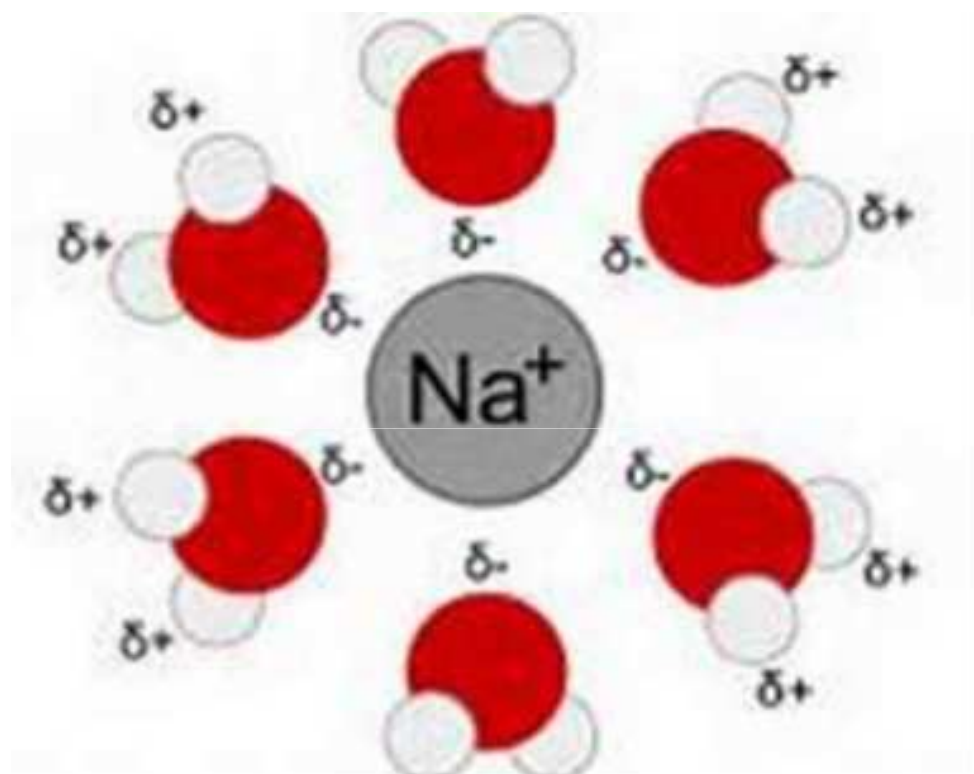


1. Relaxation effect or asymmetry effect.
2. Electrophoretic effect.
3. Frictional resistance of the medium.

RELAXATION EFFECT

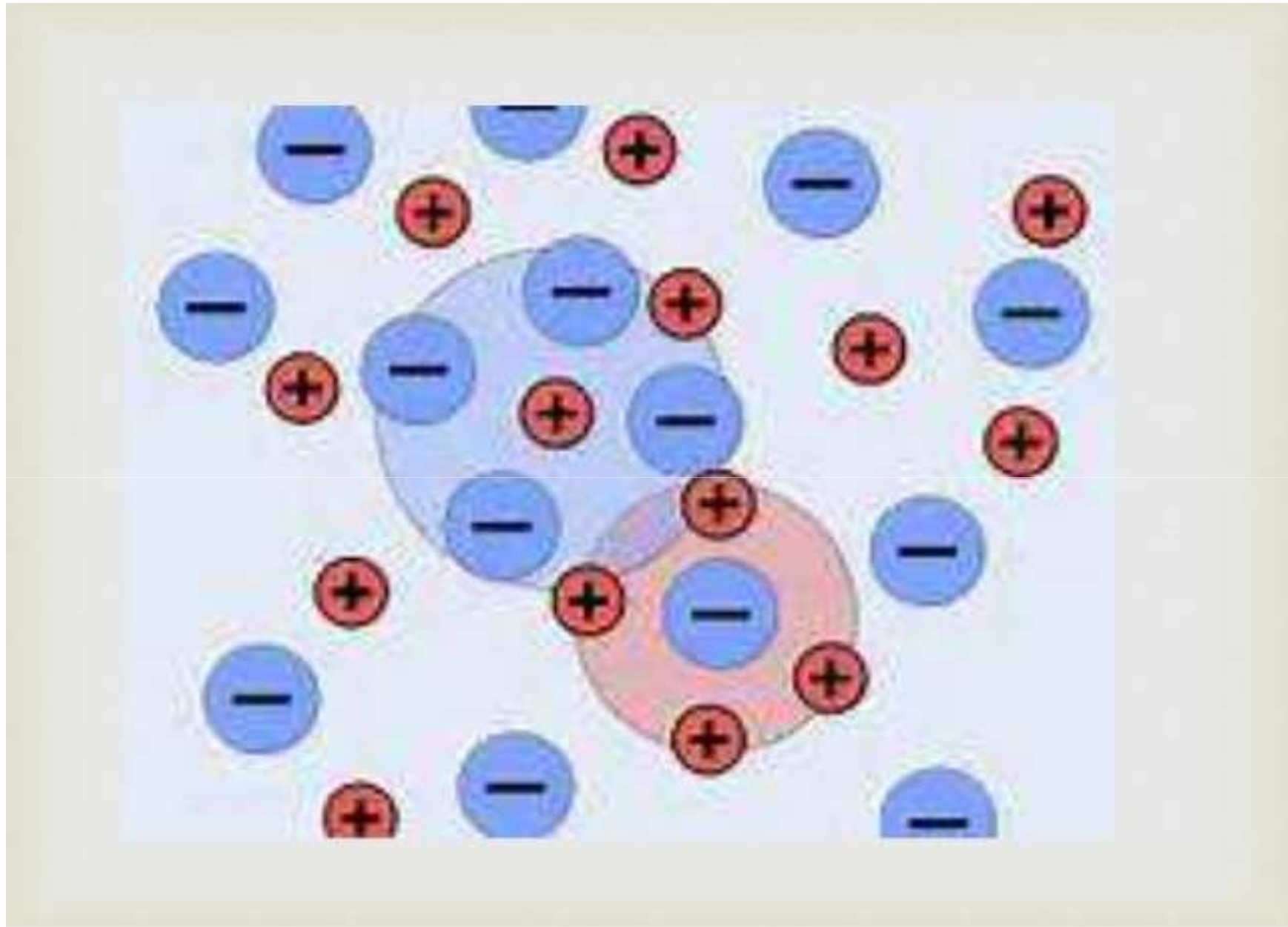


Electrolytes dissociate in solutions state to give positive and negative ions. Each ion is surrounded by an ionic atmosphere of opposite charge. This ionic atmosphere is spherically symmetrical. When a current is passed through the solution, the center of ion of the ionic atmosphere moves towards the oppositely charged electrode. During this movement it has to rebuild an ionic atmosphere of opposite charge around it. At this time the old ionic atmosphere dies out. These two processes do not take place simultaneously. There is a some time lag which is called time of relaxation. During this time, old ionic atmosphere pulls the moving ion backward and so motion is retarded. Due to this the effect is called relaxation effect.



ELECTROPHORETIC EFFECT

- ⌘ During the application of electromotive force, the central ions moves in one direction and the oppositely charged ions present in their ionic atmosphere move in opposite direction. Solvent molecules are also there in the ionic atmosphere. It means that the central ion is moving against the stream , hence the motion of the central ion is retarded. The effect is called electrophoretic effect.



FRictionAL RESISTANCE OF THE MEDIUM



Whenever an ion with its ionic atmosphere travels in the solution, then the medium of the solution offers the frictional resistance. This force depends upon viscosity of the medium and its dielectric constant.

MATHEMATICAL



EXPLANATION



- Debye and Huckle derived a mathematical expression in 1923.
- The equation derived by them was further improved by Osangar in 1926.
- The equation is called **DEBYE-HUCKLE-OSANGAR equation**.



$$\Lambda = \Lambda^\circ - \left[\frac{82.4}{(DT)^{1/2}} \eta + \frac{8.20 \times 10^5}{(DT)^{3/2}} \cdot \Lambda^\circ \right] \sqrt{C} \dots\dots(1)$$

Λ = Equivalent conductance at any concentration

Λ° = Equivalent conductance at infinite dilution

D = Dielectric constant of medium

η = Viscosity of the medium

T = Temperature of solution

C = Conc. Of solution



D, T and η are constant, so

$$82.4 / (DT)^{1/2} \eta = A \quad \dots\dots\dots(2)$$

$$8.20 \times 10^5 / (DT)^{3/2} = B \quad \dots\dots\dots(3)$$

So, eq(1) can be written as

$$\Lambda = \Lambda^\circ - (A + B \Lambda^\circ) \sqrt{C} \quad \dots\dots\dots(4)$$



$$\Lambda = (A + B \Lambda^{\circ})\sqrt{C} + \Lambda^{\circ}$$

$$\Lambda = \Lambda^{\circ} (-A\sqrt{C} - B\sqrt{C} \Lambda^{\circ})$$

$$\Lambda^{\circ} - \Lambda = (A\sqrt{C} - B\sqrt{C} \Lambda^{\circ}) \dots\dots\dots(5)$$

☞ When solution is infinitely dilute, then $C=0$ and

$$\Lambda = \Lambda^{\circ} \dots\dots\dots(6)$$

☞ Greater the value of A and B , lesser the value of Λ
and Λ°

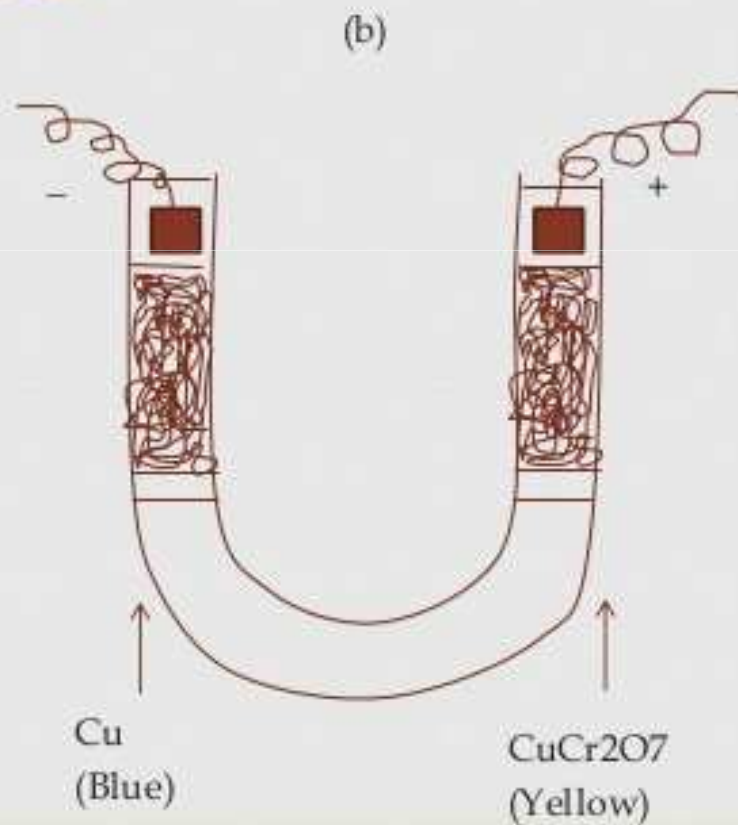
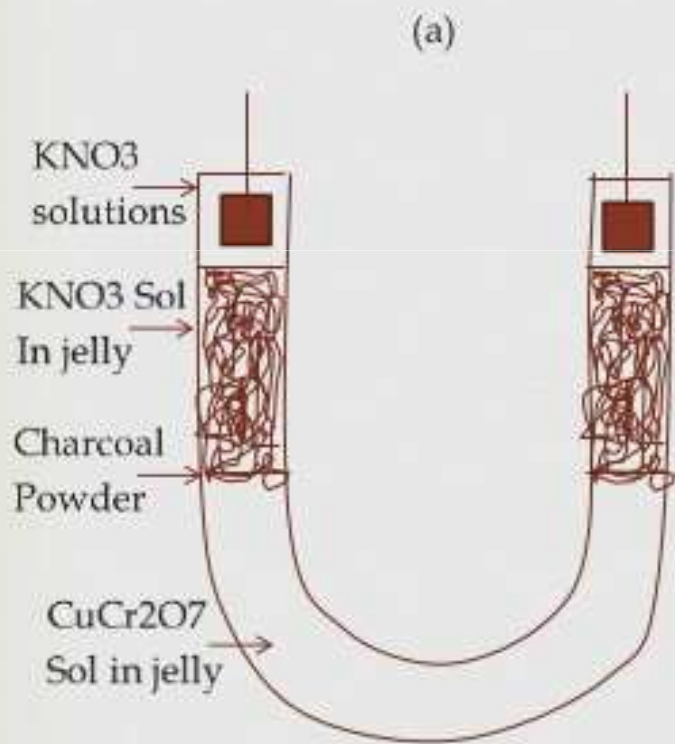
EXPEERIMENTAL



VERIFICATION

(a) Situation when current is not applied

(b) Situation when current is applied

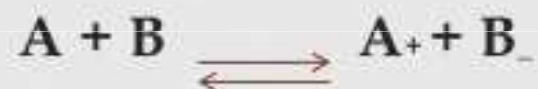


DEGREE OF
∞
DISSOCIATION

Definition



∞ The fraction of the amount of the electrolyte in solution present as free ions is called the degree of dissociation.



$$x = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}}$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

THE COMMON



ION EFFECT

Definition



☞ The reduction of the degree of dissociation of a salt by the addition of a common ion is called the Common ion effect.

FACTORS



Influencing the degree of
dissociation

The degree of dissociation of an electrolyte in solution depend on following factors



- (1) Nature of solute.
- (2) Nature of the solvent.
- (3) Concentration.
- (4) Temperature.

Nature of solute



- Strong acids , strong bases and salts obtained by their interaction are almost completely dissociated.
- Weak acids , weak bases and their salts are feebly dissociated.

Nature of solvent



∞ Dielectric constant:

The capacity of solvent to weaken the force of attraction between the electrical charges immersed in the solvent.

∞ The higher the value of dielectric constant the greater is the dissociation of the electrolyte dissolved in it.

Concentration



- ❧ Dissociation of an electrolyte is inversely proportional to the concentration of its solution.
- ❧ This is due to the fact that in a dilute solution the ratio of solvent molecules to the solute molecule is large and the greater number of solvent molecule will separate more molecules of the solute into ions

Temperature



- ∞ Higher the temperature greater is the dissociation.
- ∞ At high temperature the increased molecular velocities overcome the force of attraction between the ions and consequently the dissociation increases.