slow down a swimmer. For any dilute solution, the ionic atmosphere is almost non-existent, so asymmetric effect is zero. Similarly at infinite dilution, the electrophoertic effect is also negligible, but both effects have definite values in concentrated solutions. Debye and Huckel showed that both of these retarding effect on an ion produce a decrease in the equivalent conductance. These are the theoretical explanation for the decrease of equivalent conductance in case of solutions of strong electrolytes.

9.15 DEBYE-HUCKEL THEORY: THE IONIC ATMOSPHERE

The possibility that the attractive forces between ions might have some influence on the electrolytic conductance, especially with strong electrolytes, was considered by Noyes (1904), Sutherland (1906) Bijerum (1909) and Miller (1912) among others. But the modern quantitative treatment of this concept is due mainly to the work of Debye and Huckel and its extension chiefly by Onsager and Falkenhagen.

When an electrolyte is dissolved in a polar solvent, it gets dissociated into ions and the solutions may contain a large number of kinetically identifiable species in addition to the solvent molecules which are always in equilibrium with each other. A completely random distribution of ions around each other can not be physically possible. A positive ion will have a negative ion in its immediate vicinity, thereby resulting in an ordered arrangement, which is offset by thermal motions. Thus the resulting situation is a dynamic compromise between the electrostatic interactions and kinetic collisions. The net result is that in a small volume element of the solution around an ion, on time average, there is slightly greater concentration of the ions carrying opposite charge than those carrying similar charge. Thus, each ion has an ionic atmosphere of oppositely ions, whose net electrical charge is equal and opposite

to that of the central ion. This forms an essential postulate of the Debye-Huckel theory for dilute solutions of strong electrolytes.
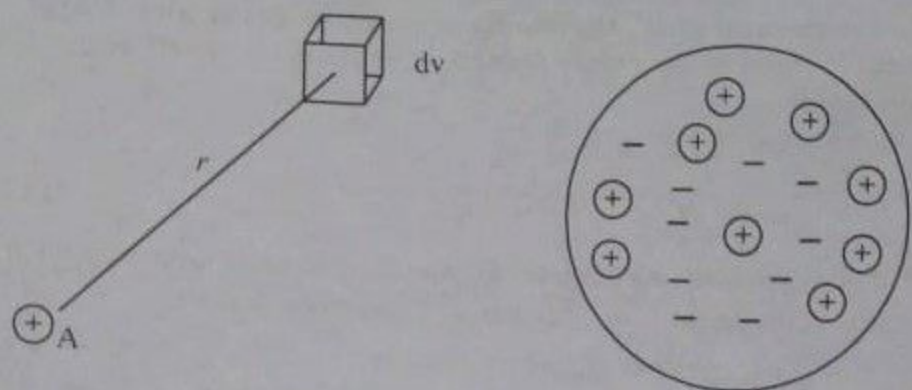

Fig. 9.5 The ionic atmosphere and time average distribution of ions around a reference ion

Let us consider a positive ion situated at A(Fig.9.5). Suppose there is small volume element dv at the end of radius vector r; the distance r is supposed to be of the order of less than about 100 times, as the diameter of the ion. Due to thermal movement of ions sometimes there occurs an excess of positive ions and sometimes an excess of negative ions in the volume dv. If a time average is taken, however, it will be found to have, as a consequence of electrostatic attractions by the positive charge at A, a negative charge density. In this way every ion may be assumed to have an ionic atmosphere of opposite sign. The net charge of the ionic atmosphere is equal in magnitude and opposite in sign to that of the central ion. It is possible to define the effective thickness of the ionic atmosphere.

Debye and Huckel took the interionic attraction into consideration and calculated the ratio of activity to the concentration of an ion in dilute solutions. Suppose the time average of the electrical potential in the center of the volume element dv in Fig.9.5 is Ψ. It is defined as the work done in bringing a unit charge from infinity to a particular point. The work done in bringing a positive ion of valence Z_+ and carrying a charge ϵ to that point is given by $(Z_+ \epsilon \Psi)$. Similarly the work done in bringing a negative ion is $(Z_- \epsilon \Psi)$. Z_+ and Z_- are numerical values only, and do not include the sign. If the concentrations of the ions at a considerable distance from the given ion, where Ψ may be taken as zero, are n_+^o and n_-^o per unit volume, then by the Boltzmann distribution law for particles in a filed of varying potential, the concentration of the positive and negative ions, i.e., n_+ and $n-$, at the point under consideration, are given by

$$n_+ = n_+^o \, e^{-(Z_+ \epsilon \Psi / kT)} \quad \quad (9.26)$$

$$n_- = n_-^o \, e^{-\left(Z_- \epsilon \Psi / kT\right)} \quad \quad (9.27)$$

and $\quad n_- = n_-^o \, e^{-(Z_- \epsilon \Psi / kT)}$

where k is the Boltzmann constant. Since Z_+ and Z_- are the numerical values only, it is clear that n_- is greater than n_+, and so there are on the average more negative ions than positive ions in the vicinity of any positive ion, the reverse will be true for

negative ion. It is seen, therefore, that every ion is surrounded by an oppositively charged ionic atmosphere.)

In the vicitinity of A^+, the density of electricity or electrical charge density (ρ) at any point is equal to the excess positive or negative electricity per unit volume at that point, that is,

$$\rho = n_+ Z_+ \epsilon - n_- Z_- \epsilon$$

$$\rho = \epsilon[n_+ Z_+ e^{-(Z_+ \epsilon \Psi/kT)} - n_- Z_- e^{-(-Z_- \epsilon \Psi/kT)}] \qquad (9.28)$$

For uni-univalent electrolyte, Z_+ and Z_- are unity and n_+ and n_- must be equal because of electrical neutrality hence, Eq.(9.28) reduces to

$$\rho = \epsilon(ne^{-\epsilon \Psi/kT} - ne^{\epsilon \Psi/kT})$$

or $\qquad \rho = \epsilon n(e^{-\epsilon \Psi/kT} - e^{\epsilon \Psi/kT}) \qquad (9.29)$

or $\qquad \rho = \epsilon n(e^{-x} - e^{x}) \qquad (9.30)$

where n is the number of either kind of ion in unit volume. Expanding the two exponential series and writing x in plane of $\epsilon \Psi/kT$, one gets,

$$e^x = 1 + \frac{X}{1!} + \frac{X^2}{2!} + \frac{X^3}{3!} + \dots$$

$$e^{-x} = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} + \dots$$

$$-e^x = -1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \dots$$

$$(e^{-x} - e^x) = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} \dots - 1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \dots \infty$$

$$(e^{-x} - e^x) = -\frac{2X}{1!} - \frac{2X^3}{3!} - \frac{2X^5}{5!} - \dots \infty$$

$$(e^{-x} - e^x) = \frac{-2X}{1!}\left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \dots\right)$$

$$\rho = \epsilon n\left(-\frac{2\epsilon\Psi}{kT}\right)\left[1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \dots\right]$$

or $\qquad \rho = -\frac{\epsilon^2 \Psi}{kT} 2n\left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \dots\right) \qquad (9.31)$

If it is assumed that X is small in comparison with unity, all terms beyond the first in the parenthesis may be neglected

$$\rho = -\frac{\epsilon^2 \Psi}{kT} 2n \qquad (9.32)$$

where $2n = Z_+^2 n + Z_-^2 n$

$$2n = n_+ Z_+^2 + n_- Z_-^2$$

This is only true for $1:1$ electrolyte. Hence Eq.(9.32) may be written as

$$\rho = -\frac{\epsilon^2 \Psi}{kT}(n_+ Z_+^2 + n_- Z_-^2)$$

(9.33)

In the general case where $Z+$ and $Z-$ are not necessarily unity and if the solution may contain several kinds of the ions, Eq.(9.33) may take the following form.

$$\rho = -\frac{\epsilon^2 \Psi}{kT} \sum_i n_i Z_i^2$$

(9.34)

Where n_i and Z_i represent the number per unit volume and valence of the ions of ith kind. The summation is taken over all kinds of ions present in the solution and Eq.(9.34) is applicable irrespective of the number of different kinds of ions.

In order to solve for Ψ it is necessary to have another relationship between ρ and Ψ and this may be obtained by intorducing Poisson's equation and this equation in rectangular coordinates is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = -\frac{4\pi\rho}{D}$$

(9.35)

Where x, y and z are the coordinates of the point in the given volume element and D is the dielectric constant of the medium. Converting to polar coordinates, and making use of the fact that the terms containing $\partial \Psi/\partial \theta$ and $\partial \Psi/\partial \phi$ will be zero, since the distribution of the potential about any point in the electrolyte must be spherically symmetrical and consequently, independent of the angles θ and ϕ, Eq.(9.35) becomes

$$\frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \frac{d\Psi}{dr}\right) = -\frac{4\pi\rho}{D}$$

(9.36)

Substituting the value of ρ from Eq.(9.34) in Eq.(9.36) we get

$$\frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \frac{d\Psi}{dr}\right) = -\frac{4\pi}{D}\left(-\frac{\epsilon^2 \Psi}{kT}\sum n_i Z_i^2\right)$$

$$\left.\begin{array}{l}\dfrac{1}{r^2} \cdot \dfrac{d}{dr}\left(r^2 \dfrac{d\Psi}{dr}\right) = \dfrac{4\pi\epsilon^2 \Psi}{DkT}\sum_i n_i Z_i^2 \cdot \\[3mm] \dfrac{1}{r^2} \cdot \dfrac{d}{dr}\left(r^2 \dfrac{d\Psi}{dr}\right) = k^2 \Psi \qquad .\end{array}\right\}$$

$k^2 \Psi = \dfrac{4\pi\epsilon^2 \Psi \cdot \sum_i n_i}{DkT}$

(9.37)

where the quantity k(not to be confused with specific conduction) is defined by

$$k^2 = \frac{4\pi\epsilon^2 \sum_i n_i Z_i^2}{DkT}$$

or $\qquad k = \left(\dfrac{4\pi \epsilon^2 \underset{i}{\Sigma} n_i Z_i^2}{DkT} \right)^{1/2}$ $\qquad\qquad$ (9.38)

where r denotes the distance from the central ion to the point where Ψ is determined. and $\dfrac{1}{k}$ has the dimensions of length. It is called Debye-Huckel reciprocal length. It is the distance over which electrostatic field of an ion extends with appreciable strength. k^{-1} is a measure of the thickness of the ionic atmosphere.

The differential equation Eq.(9.37) can be solved, and the solution has the general form

$$\Psi = \frac{Ae^{-kr}}{r} + \frac{Be^{kr}}{r} \qquad\qquad (9.39)$$

Where A and B are integration constants, whose values are determined by applying the boundary conditions. Since Ψ must approach zero as r increases, because the potential at infinite distance from the given point in the solution must be zero

$$0 = \frac{Ae^{-\infty}}{\infty} + \frac{Be^{\infty}}{\infty}$$

$$0 = 0 + \frac{Be^{\infty}}{\infty}$$

$$\left|\begin{array}{l} e^{\infty} = \infty \\[4pt] e^{-\infty} = 0 \\[4pt] \dfrac{1}{e^{\infty}} = 0 \end{array}\right.$$

This can be only true if $B = 0$, since $\dfrac{e^{\infty}}{\infty} \neq 0$, hence Eq.(9.39) becomes

$$\Psi = \frac{Ae^{-kr}}{r} \qquad\qquad (9.40)$$

The value of A can be calculated by the fact that for very dilute solution $\underset{i}{\Sigma} n_i Z_i^2$ is almost zero and hence k is also zero. The value of potential Ψ_i at the point under consideration will be

$$\Psi_i = \frac{A}{r} \qquad\qquad (9.41)$$

In case of dilute solutions the potential in the neighbourhood of an ion will be due to that ion alone, since other ions are too far away to have any influence. If the ion is being regarded as being a point charge, the potential at small distance will be

$$\Psi_i = \frac{Z_i \epsilon}{Dr} \qquad\qquad (9.42)$$

Eliminating Ψ_i between Eq.(9.41) and Eq.(9.42), we get

$$\frac{A}{r} = \frac{Z_i \epsilon}{Dr}$$

or $\qquad A = \dfrac{Z_i \in}{D}$

(9.43)

Substituting the value of A into Eq. (9.40), we get

$$\Psi = \dfrac{Z_i \in}{Dr} e^{-kr}$$

(9.44)

The value of Ψ represented by Eq.(9.44) is the mean value of the potential at point r produced by the ionic atmosphere and the central ion. Real solutions are characterized by the potential of the ionic atmosphere which is found as the difference between Ψ and Ψ_i

$$\Psi_{ia} = \Psi - \Psi_i$$

$$\Psi_{ia} = \dfrac{Z_i \in}{Dr} e^{-kr} - \dfrac{Z_i \in}{Dr} \qquad\qquad \therefore \quad e^{-kr} = 1 - kr$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 1 - e^{-kr} = [1 - ka] = kr$$

$$\Psi_{ia} = \dfrac{Z_i \in}{Dr} (e^{-kr} - 1) \qquad\qquad e^{-kr} - 1 = 1 - kr - 1 = -kr$$

$$\Psi_{ia} = \dfrac{Z_i \in}{Dr} (-kr)$$

$$\Psi_{ia} = -\dfrac{Z_i \in k}{Dr}$$

(9.45)

The Eq.(9.45) is independent of r and hence it may be assumed to hold even when r is zero, so that the potential on the ion itself, due to ionic atmosphere is given by above equation. The net charge of the ionic atmosphere is $-Z_i \in$, because it is equal in magnitude and opposite in sign to that of the central ion itself. If this charge was placed at a distance 1/k from the ion, the potential produced at it, would be $-Z_i \in k/D$, which is identical with the value given by equation (9.45). The quantity 1/k can thus be regarded as a measure of the thickness of the ionic atmosphere in a given solution. According to the definition of k, the thickness of the ionic atmosphere will depend on the number of ions of each kind present in unit volume and on their valence. If C_i is the concentration of the ions of the ith kind expressed in moles (gram-ions) per liter, then

$$n_i = C_i \dfrac{N}{1000}$$

where N is the Avogadro number, hence from Eq.(9.38)

$$\dfrac{1}{k} = \left(\dfrac{DT}{\Sigma C_i Z_i^2} \dfrac{1000\, k}{4\pi \in^2 N} \right)^{1/2}$$

The value of universal constants are as follows: k is 1.38×10^{-16} erg per degree, $\in$ is 4.80×10^{-10} esu and N is 6.025×10^{23}, hence

$$\frac{1}{k} = 2.81 \times 10^{-10} \left(\frac{DT}{\Sigma C_i Z_i^2} \right)^{1/2} \text{cm}$$

For water as solvent at 25°C, D is 78.6 and T is 298, so that

$$\frac{1}{k} = \frac{4.31 \times 10^{-8}}{(\Sigma C_i Z_i^2)^{1/2}} \text{cm}$$

The thickness of the ionic atmosphere is thus seen to be of the order of 10^{-8} cm or 10^{-10} m. It decreases with increasing concentration and valence of the ions present in the electrolyte, and increases with increasing dielectric constant of the solvent and with increasing temperature.

9.16 DEBEY-HUCKEL-ONSAGER'S EQUATION

According to Debye-Huckel theory of strong electrolytes each ion is surrounded by an ionic atmosphere of opposite charge. A moving ion under the influence of applied electrical field is un-symmetrically surrounded by the ionic atmosphere of opposite charge. The charge density is greater in the rear than in the front of ion. As the ionic atmosphere is not symmetrical, it results in the retardation of the ion moving under the influence of applied field. This influence on the speed of ion is called asymmetric or relaxation effect. A viscous resistance of the solvent also acts on the moving ion. It is similar to the resistance acting against the movement of the colloidal particles in an electric field. It is called electrophoretic effect Both asymmetric and electrophoretic effects retard the speed of the central moving ions and ultimately decrease the conductance.

Debye and Huckel made an attempt to calculate the magnitude of the process which oppose the motion of the ions in solution. They supposed the ions to travel

$$\Lambda_o \eta_o = 0.70$$

The above rule of Walden does not apply to water and glycol as solvents. For water $\Lambda_o \eta_o = 1$ and the value of constant was observed to vary with the nature of solute. A particular ion does not have the same effective radius in different solvents. It is probable that the ions are solvated in the solution. Since the extent of solvation as well as the size of solvating molecules, varies with the nature of the solvent, the effective radius will not be constant. The ions have different effective radii in different solvents due to difference in the extent of solvation. As the solvation effects are quite prominent for smaller ions (particular small cations), the deviation from the Walden's rule would be quite severe for smaller cations. Larger cations do not undergo solvation to an appreciable extent, and hence the Walden's product for such ions remains constant even in different types of solvents.

9.12 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the behavior of solutions of electrolytes, Arrhenius (1887) put forward the theory of electrolytic dissociation in aqueous solutions. The main points of this theory in this modern form may be summed up as follows:

(i)   The electrolytes in solution are dissociated into electrically charged particles called ions. The positively charged particles are called cations and the negatively charged particles are known as anions. A dynamic equilibrium exists in the solution between the undissociated molecules and the ions which dissociate from the electrolytes, that is

$$MA \rightleftharpoons M^+ + A^-$$
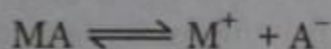
(ii)   The ions are free to move independently under the influence of an applied electric field. Cations move towards the negative electrode or cathode and the anions move towards the positive electrodes or anode.

(iii)   The number of positively charged cations and negatively charged anions may be different. However, the total charge carried by cations is equal to the total charge carried by anions. The net result is that the solution as a whole is electrically neutral in spite of the presence of charged particles.

(iv)   The extent of dissociation is different for different electrolytes and depends on the concentration of electrolyte, temperature and nature of electrolyte.

The amount of electrolyte which dissociates into ions varies with its concentration. It may then be anticipated from the law of chemical equilibrium that the extent of dissociation increases with the decrease in concentration and attains a limiting value at very high dilution. At extreme dilutions, all the electrolytes are completely dissociated into ions. The fraction of the total number of molecules dissociated, is called the degree of dissociation (α). Thus

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total numbr of molecules}}$$

Calculation of the degree of dissociation for various electrolytes in aqueous solutions show that practically all salts, and strong acids and bass are highly ionized in water. These are known as strong electrolytes. Aqueous solutions of these electrolytes are therefore good conductors of electricity. On the other hand, there are many substances whose aqueous solutions are poor conductor of electricity. These include many organic acids and bases (such as acetic acid, benzoic acid, methyl amine, aniline etc.), inorganic acids and bases (such as carbonic acid, hydrocyanic acid, ammonium hydroxide etc.). These are called weak electrolytes. This division into strong and weak electrolytes is a qualitative one. There are some electrolytes such as $BaCl_2$ etc. which exhibit an intermediate behaviour.

Limitations of the Arrhenius Theory

Arrhenius theory is satisfactory for weak electrolytes. However, when applied to strong electrolytes many anomalies have been observed which seriously question the validity of some of the postulates of theory. Some of the important discrepancies are:

(i)   The degree of dissociation obtained from conductivity measurement and from colligative properties are in good agreement for weak electrolytes. But for the strong electrolyte the agreement is very poor.

(ii)   The Ostwald's dilution law is obeyed by weak electrolytes but not all by strong electrolytes.

(iii) Arrhenius theory assumes the existence of ions but does not take into account the electrostatic attraction between ions. The effect of interionic attractions is quite small in solutions of weak electrolytes, but in case of strong electrolytes, this effect is quite pronounced.

These points conclude that Arrhenius theory is essentially valid for weak electrolytes but does not describe the behavior of strong electrolytes.

THE OSTWALD'S DILUTION LAW