

CHAPTER II

THEORY



2.1 Basic Theory

The equivalent conductance Λ of completely dissociated electrolytes at low concentrations is found to be a decreasing linear function of the square root of concentration. Extrapolation to zero concentration yields the limiting equivalent conductance Λ° . Thus,

$$\Lambda = \Lambda^\circ - A\sqrt{M} \quad (1)$$

as was first observed by Kohlrausch. Most of the uni - univalent electrolytes and certain bi and tri - univalent electrolytes in aqueous solution were found to exhibit the linear relation (1). The theoretical prediction of the constant A was made by Onsager, from which he found that

$$\Lambda = \Lambda^\circ - \left(B_1 \Lambda^\circ + B_2 \right) \sqrt{M} \quad (2)$$

known as the Onsager limiting law. In the equation (2)

$$B_1 = \frac{|z_A z_B|^3 e^3}{3(DkT)^{3/2}} \cdot \frac{q}{1+q} \cdot \beta$$

and

$$B_2 = \frac{|z_A| + |z_B|}{(DkT)^{1/2}} \cdot \frac{F e^2}{6\pi\eta} \cdot \beta$$

where

$$\beta = \left[\frac{8\pi N}{1000} \right]^{1/2} \frac{\sqrt{I}}{\sqrt{M}} \quad \text{and } z_A \text{ and } z_B \text{ are valencies}$$

of the cation and anion, respectively.

For data at higher concentration, Onsager's limiting form is no longer adequate. Shedlovsky observed that for completely dissociated 1:1 electrolytes with $M \leq 0.1$ the deviation of the conductance from the Onsager prediction is a linear function of the concentration, with the intercept equal to Λ° . That is

$$\Lambda^\circ - \Lambda' = BM \quad (3)$$

where B is a constant

Rearranging (2),

$$\Lambda^{\circ} = (\Lambda + \frac{B_1}{M}) / (1 - \frac{B_2}{M})$$

Substitution into (3) and rearrange, hence

$$\Lambda^{\circ'} = \frac{\Lambda + B_2 \sqrt{M}}{1 + B_1 \sqrt{M}} - BM \quad (4)$$

where $\Lambda^{\circ'}$ is known as Shedlovsky extrapolation function. For highly valent or unsymmetrical electrolytes, certain deviations from equation (4) are expected. To account for the deviation, explicit interpretation of these constants becomes essential. The ion size parameter was introduced into the conductance equation, initially to fit the calculated and the observed conductances. Considerable improvement was achieved, however the equations are still restricted to a dilute concentration range and are mostly successful for simple electrolytes.

The complete representation of the transport properties of electrolytes involves the limiting value of the transport properties at infinite dilution, the electrophoretic part, and the relaxation contribution.

The two main effects causing interaction between ions are the electrophoretic effect, and the relaxation effect.

The 'electrophoretic effect' arises from the viscous drag of the medium in the vicinity of any given ion j in the solution. The effect will therefore be the retardation of the motion at the other ions which have opposite charge to that of the ion i . The effect is clearly concentration dependent. The computation of this effect requires the use of the distribution function and the equation of electrostatic theory. For solutions in equilibrium, the 'ionic atmosphere' (the whole assemblage of ions outside the central one chosen) is on a time average distributed with spherical symmetry. In electrical conduction experiments, the motion of ions under the influence of external forces will disturb this symmetrical distribution of ions. The central ion j may then move to an off-centre position and experiences a restoring force due to dissymmetry of the ionic atmosphere. The average restoring force experienced by the central ion is called the 'relaxation effect'. This effect

also tend to decrease the velocity of the central ion. If X is the intensity of the applied field in x -direction, the relaxation field ΔX will act in the same direction but in opposite sense. The computation of ΔX involves a combination of the interionic interaction theory with the equation of hydrodynamic continuity, and is mathematically the most difficult part of electrolyte theory.

The evaluation of the terms involved in conductance equations (relaxation and electrophoretic terms) follows the general procedure summarised as follows

Appropriate expressions for charge density (ρ_{ji}), potential (ψ_j), pair distribution function (f_{ji}), force (X) etc., are derived according to the model and the situation (equilibrium or non-equilibrium) considered. The electrical forces and potentials are integrated over all space using spherical polar coordinates. The total pair distribution function is the summation of the pair distribution function of all the species in solution. Using an iteration procedure, the pair distribution function and forces are expressed in terms of a correlation function (G). These equations are then rearranged to the form that can be solved by the Laplace transform. This gives the solution of the correlation function (G), which is normally in terms of integral functions. Certain boundary conditions are then imposed on the limit of the values of f_{ji} , ρ_{ji} , and thus G with respect to a distance of approach between ions, r . This allows the integration constants (A) of the integration functions to be evaluated. Substitution of G and A into the former equations of f_{ji} , ρ_{ji} and X gives the explicit expressions of these terms which contribute to the complete conductance equations. The system is firstly considered under an equilibrium situation in the absence of external field. The equilibrium expressions of the time average functions such as n_{ji} , f_{ji} , ρ_{ji} and thus G_{ji} are then obtained by the general procedure outlined above.

A non-equilibrium situation is then considered when an external field X is applied to the system. A perturbation method of solving the Onsager continuity equation (5) is used.

$$\text{div}_1 (f_{ji} \cdot v_{ji}) + \text{div}_2 (f_{ji} \cdot v_{ji}) = 0 \quad (5)$$

where v_{ji} is the average velocity of an ion i at dr_2 in the vicinity of an ion j at dr_1 with respect to the external frame of reference (see Fig. 2.5). For example, the pair distribution function f_{ji} in the perturbed case then,

$$f_{ji} = f_{ji}^{\circ} + f'_{ji}$$

where $f_{ji}^{\circ} = n_{ji}^{\circ} n_{ji}^{\circ}$ in the equilibrium case and $f'_{ji}(r, \theta)$ is the perturbation of f_{ji}° due to the applied field X .

2.2 Ion in Solution and Ion Association

The organisation of ions and solvent molecules in electrolyte solutions is dependent upon interactions of four types; dipole-dipole, ion-dipole, ion-ion and ion-dipole-ion forces. These interactions arise from coulombic forces which depend on the molecular and electrostatic nature of the ion and solvent. On this basis, the system of ions in polar solvent is generally understood as follows.

For a given isolated ion in very dilute solution, the organisation of the solvent surrounding it will vary with distance, being dependent on the relative strengths of two opposing forces, ion-dipole and dipole-dipole. Ion-dipole interactions will cause solvent molecules in direct contact with the ion to be strongly aligned and polarised by the intense electric field at its surface and some or all of these molecules will move with the ion as it travel through the solution. At large distances from the central ion, dipole-dipole forces will predominate and the solvent molecules will remain part of the bulk solvent structure. An intermediate "disorganised" region will exist in which neither force is predominant and hence solvent molecules will be partially aligned by the field of the ion, but will not move with it through the solution; they will not, however, be part of the bulk solvent structure. Random translational motion of the solvated ion can arise from the thermal energy of the ion. This motion changes the strength of the ion-solvent and solvent-solvent forces between the solvent molecules in the intermediate region behind and ahead of it. The three solvent regions about an ion are shown in Fig. 2.1

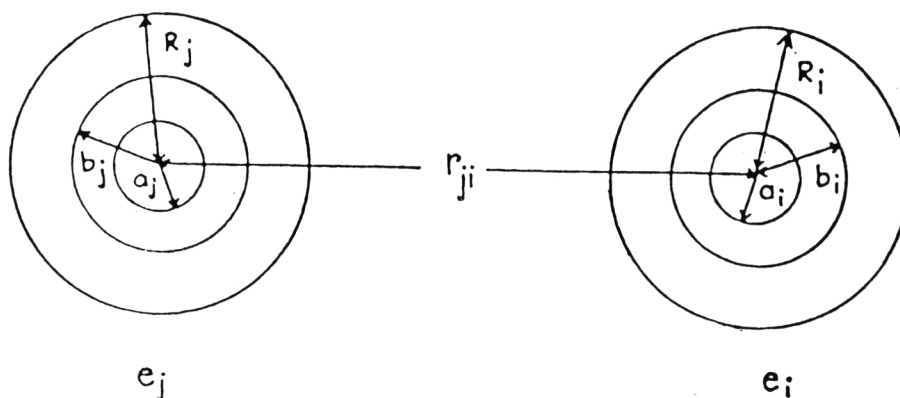


Fig 2.1 Organisation of solvent at site of an ion.

In a more concentrated solution. ion-ion interactions become significant. Two types of interactions are involved (5, 6, 7)

(1) Long-range Coulombic Forces:

when two ions are far apart they interact as though they are two point charges in a dielectric continuum. Thus the coulombic force exerted between the ions i and j of charges e_i and e_j separated by a distance r in solvent with a dielectric constant D , is

$$F = e_i e_j / Dr^2 = e_i \psi_j^0(r) = V_{ji}(r)$$

where $\psi_j^0 = e_j / Dr^2$ an electrostatic potential produced by ion j .

(2) Short-range Forces:

As two ions approach, various short-range interactions become significant. They arise from the effects of size and structure of ion and solvent molecules.

(2.1) Polarisation Effects: Two ions in close proximity tend to polarise each other, giving rise to an extra attractive force between the two ions ($\propto 1/r^5$). This may give rise to a contact ion-pair (CIP).

(2.2) Effects due to Dielectric Saturation about the Ions: The solvent molecules in the region of the dielectric saturation about an ion will interact with those of the nearby ion, giving rise to extra repulsive forces between ions ($\propto 1/r^5$).

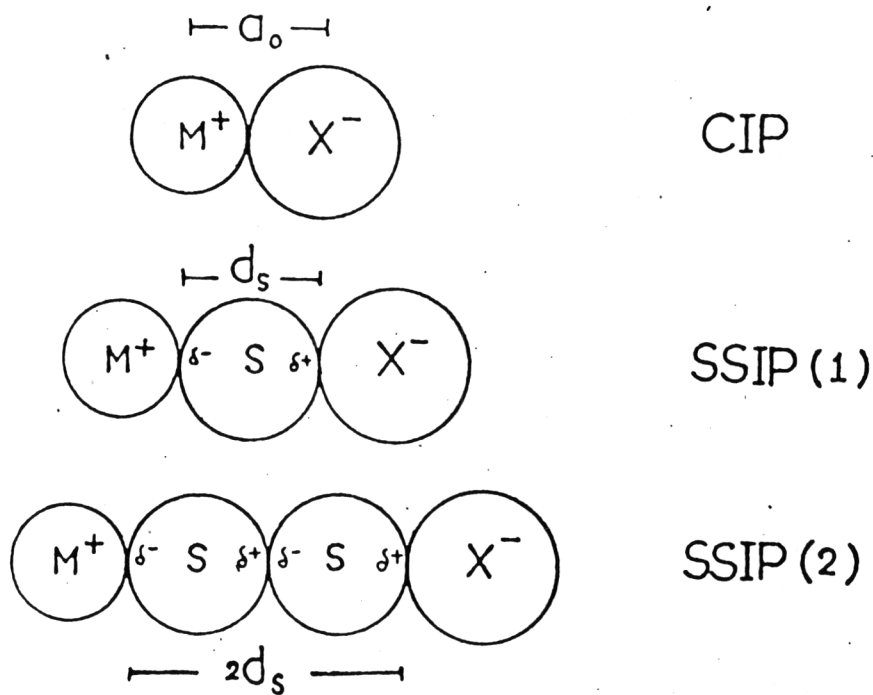
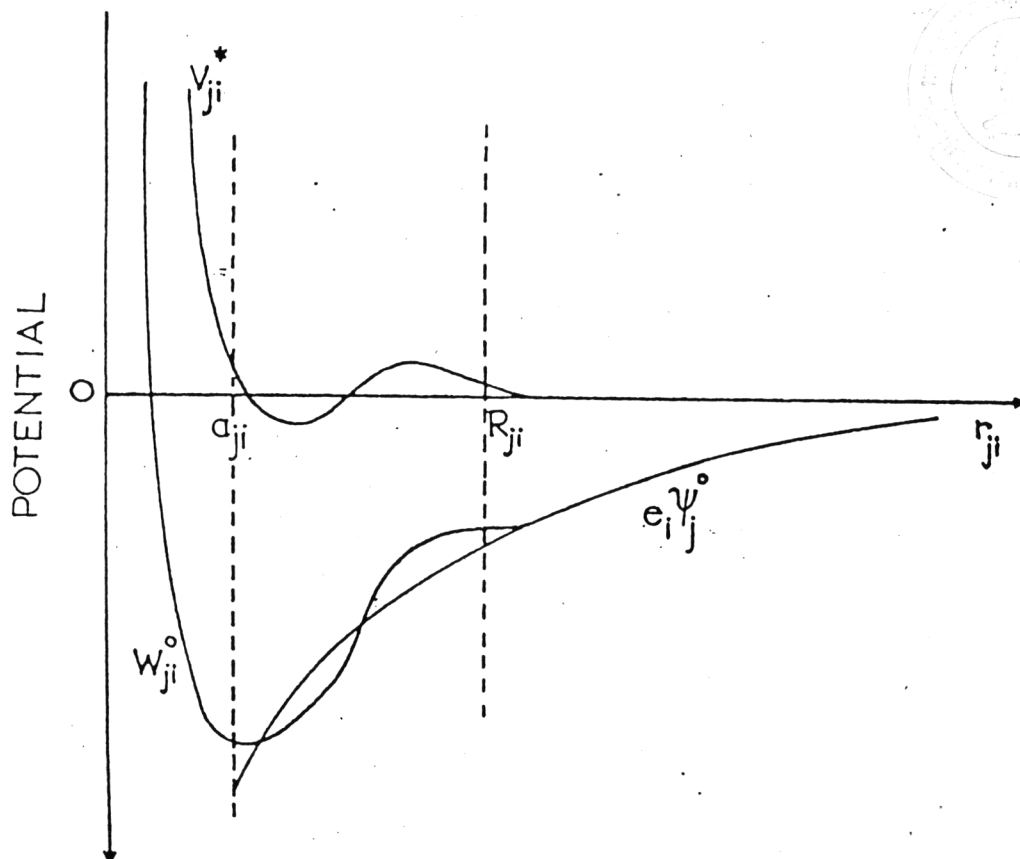


Fig 2.2 Ion-pair Formation

Fig 2.3 Potential of Forces vs. Distance r curves for a pair of oppositely charged ions i and j .

(2.3) Hard Core Interaction: This is due to interelectronic repulsive forces ($\propto 1/r^n$, $n = 8-10$).

(2.4) Ion-induced Dipole-ion Forces: When ions are only 2-3 solvent molecules apart, the discrete molecular structure of the solvent becomes important, and attractive forces due to mutual polarisation of ions occur. This gives rise to a solvent separated ion pair (SSIP).

The potential of average forces between two oppositely charged ion is therefore (5)

$$W_{ji}^0(r) = e_i \psi_j^0(r) + V_{ji}^*(r)$$

where V_{ji}^* is the short range potential arising from short range interactions mentioned above. Plots of these potentials as a function of a distance r are given in Fig 2.3 as a general case. The behaviour of V_{ji}^* is system specific, mainly due to the ion-solvent-ion component of V_{ji}^* . The formation of SSIP between two oppositely charged ions may be considered to give rise to species 1 or 2 shown in Fig 2.2, with one or two solvent molecules separating the two ions. These formations may be kinetically and spectroscopically evident. The stability of these SSIP depends on the polarising power of M^{n+} and X^{n-} ions and on the polarisability of solvent molecules. Small or highly charged ions have the greatest polarising power. Solvents of low dielectric constant reinforce the formation of SSIP type 2. The relative stability of these SSIP'S and the contact ion pair (CIP), thus, results in a discontinuous function of $W_{ji}^0(r)$ shown in Fig 2.4. The relative depths and heights of the potential wells A, B and C depend on the relative stability of CIP, SSIP type 1 and SSIP type 2, respectively.

In ion association, a similar situation applies (7). When the ions are small or highly charged and the solvent molecules are readily polarisable, a semistable SSIP of type 2 will be formed. Depending on the balance of coulombic, thermal, and solvation forces, the SSIP type 2 may break up or one of the solvent molecules may be forced out, and SSIP type 1 is formed. The relative probability of either alternative depends on the depth of the potential well C and the heights of the potential barriers on either side of it. In many cases C will be shallow and SSIP type 1 will be the first stable species to be formed.

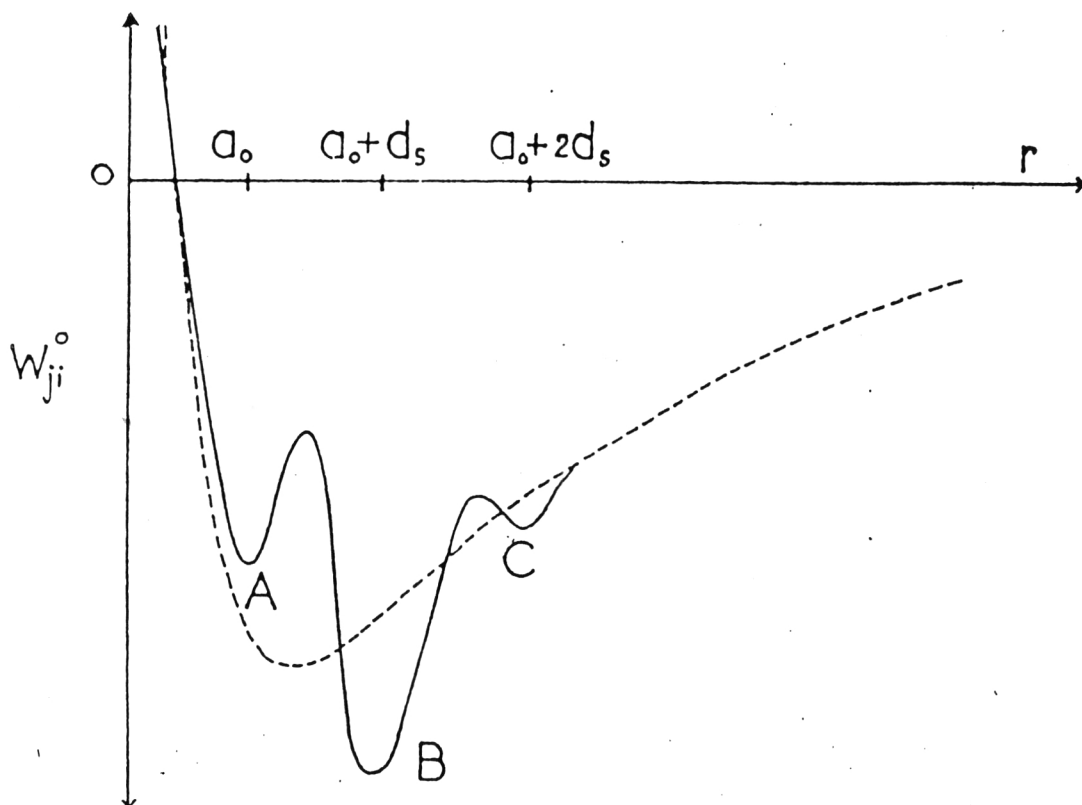


Fig 2.4 Potential of Average Force W_{j1} vs. distance r for ion-pairing.

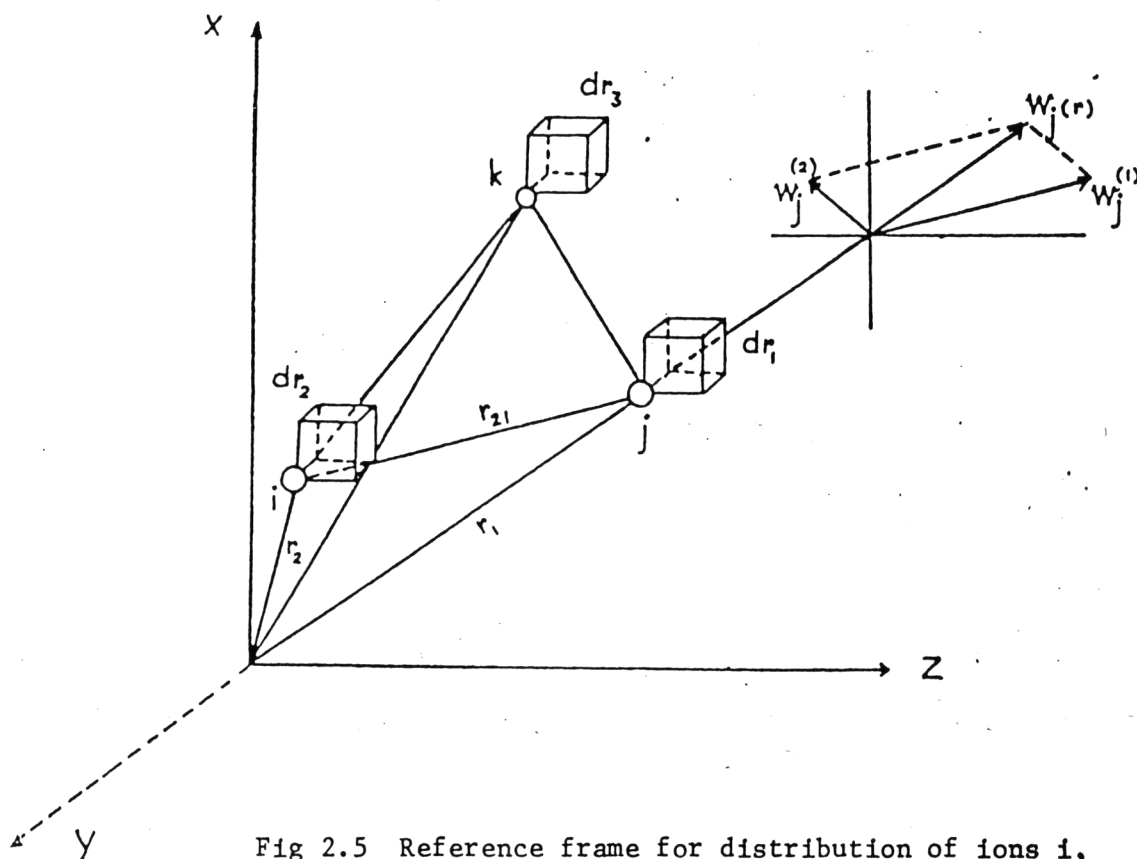


Fig 2.5 Reference frame for distribution of ions i , j and k with respect to solvent in solution.

The distribution of ion in solution may be considered with reference to Fig. 2.5, where ion j in the volume element dr_1 and ion i in the volume element dr_2 are at a distance r_{21} ($= r$). Since each ion in solution will attract ions of opposite charge and repel those of like charge, the time average charge density about a given ion will be of opposite sign to that of the central ion itself. A general plot of the pair distribution function f_{ji} with r is given in Fig 2.6. f_{ji} gives the probability of finding an ion of species i in volume element dr_2 (see Fig. 2.5) and an ion of species j in dr_1 simultaneously where dr_1 and dr_2 are at a distance r_{21} ($= r$) apart, and $f_{ji} = n_j n_{ji}$ where n_{ji} is the local concentration (in ion cm^{-3}) of ionic species i in volume element dr_2 . The initial increase in f_{ji} with decreasing r_{21} is due to the attractive coulombic force between the two ions. As r_{21} is less than the sum of the anionic and cationic crystal radii, f_{ji} decreases rapidly to zero because of the hard core repulsion. When only long-range coulombic and hard core interactions are considered f_{ji} will be represented by plot 1. When there is a possible formation ofSSIP's, a plot type 2 is to be expected.

Although many features of complex models of electrolyte solutions have been identified, there still remains the difficulty in representing these features in mathematically solvable expressions in electrolyte theories. Early electrolyte theories (2, 16) were therefore based on a simple model of ions in solutions whereby certain approximations were made, and the mathematical expressions were simplified. Their application was therefore limited to systems where the assumptions applied. Certain modifications of the models and theories have recently (5, 6, 7) been made to provide a more realistic representation of the system.

2.3 Lee and Wheaton Conductance Equation

A summary of the derivation of the conductance equations based on a chemical model developed by Lee and Wheaton is given here.

A chemical model (5, 6, 7)

The model is developed to represent the picture of ions in solutions close to the physical reality. The concept of Gurney's cosphere

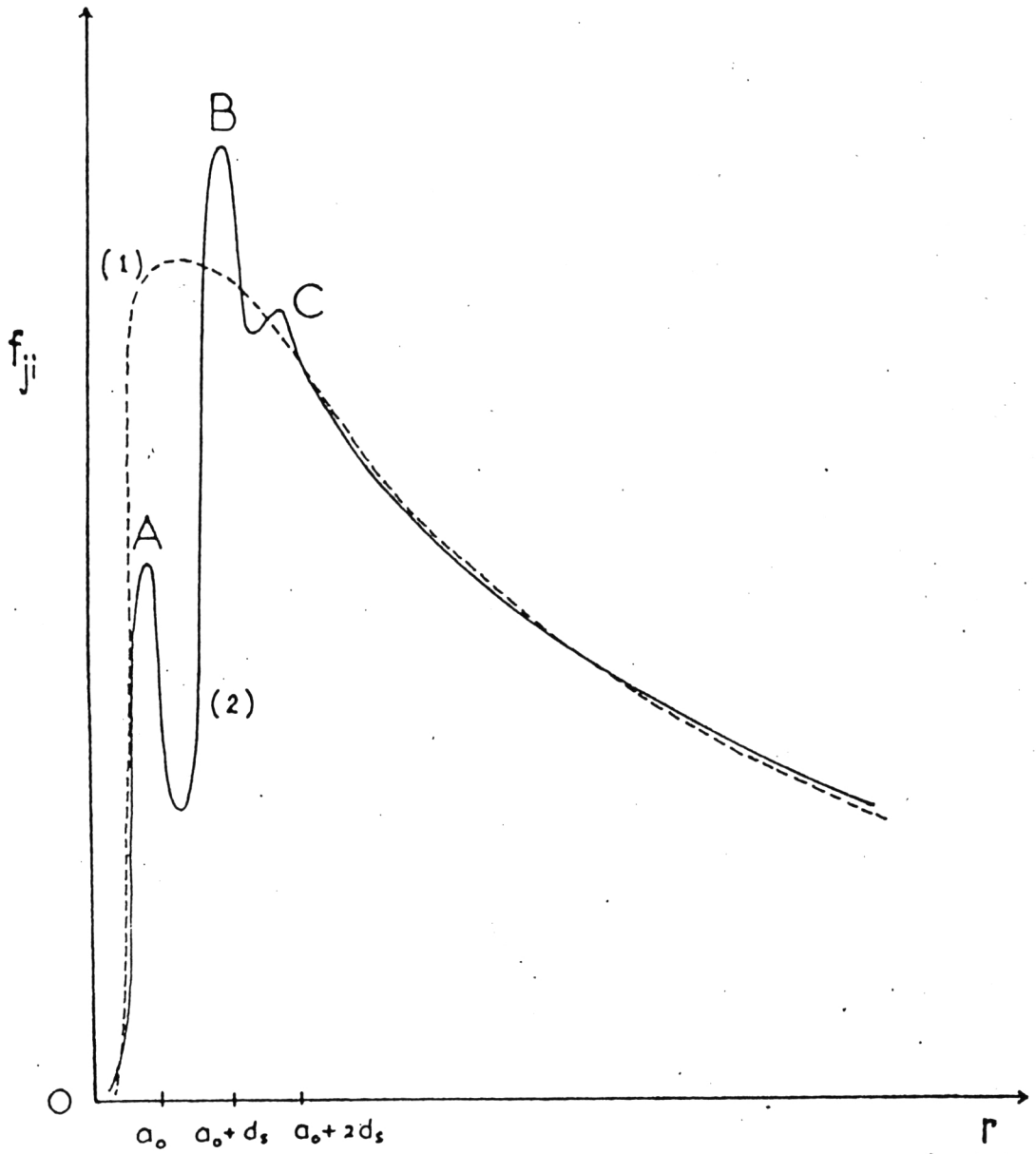


Fig 2.6 Pair distribution function f_{ji} vs. distance r for ion-pairing.

used by Fuoss for the treatment of simple electrolytes was extended to a general case.

As shown in Fig 2.1, an ion is assumed to be a rigid symmetrical sphere of a radius a_j and charge e_j surrounded by a solvent shell of width $(b_j - a_j)$ and very low dielectric constant. Such an assembly moves in solution as a single entity with a hydrodynamic radius b_j . In this region solvent molecules are strongly aligned and polarised by ion-dipole forces. This solvated ion is further surrounded by another solvent shell of width $(R_j - b_j)$ referred to as the domain of the ion. In this region modification of the dielectric constant is assumed, and the solvent molecules are partially aligned. R_j is the radius of the Gurney cosphere of the ion j . Outside R_j , the solvent is considered as a structureless dielectric continuum and only long range coulombic interaction are significant. All oppositely charged pairs of ions whose domains/cospheres overlap or contact are defined as associated.

Therefore, the model consists of a system of spherically symmetric ionic cospheres of radius R_j moving in a dielectric continuum and interacting through long range coulombic forces only. A parameter R_{ji} is the distance of closest approach between the cospheres/domains of two ions of species i and j i.e. $R_{ji} = R_j + R_i$. When this occurs, two ions are considered to reach a stable or semistable configuration (contact ion-pair (CIP) or solvent separated ion pair (SSIP) and form a new species. As a consequence of this imposed model, the following condition of charge density (ρ_{ji}^o), pair distribution function (f_{ji}^o), forces (V_{ji}) and potential of average forces between ions (W_{ji}) hold.

$$\begin{aligned} \text{(i)} \quad \rho_{ji}^o(r) &= 0 \quad \text{for } r < R \quad (R = R_{ji}) \\ \text{(ii)} \quad f_{ji}^o(r) &= \bar{o} \quad \text{for } r < R \\ \text{(iii)} \quad V_{ji}^*(r) &\approx 0 \quad \text{for } r < R \end{aligned}$$

That is for $r > R$, all short range forces rapidly become zero, mainly due to ion-dipole-ion forces. It follows that

$$W_{ji}^o(r) \approx V_{ji}(r) \quad \text{for } r > R$$

(iv) Since the formation of a stable ion-pair of $r = R$ requires a minimum in the potential energy curve (see Fig. 2.4), thus

$$dW_{ji}^o(r) / dr = 0 \quad \text{at } r = R$$

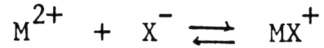
01127i

It follows that

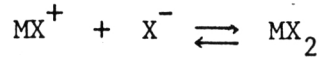
$$df_{ji}^{\circ}(r) / dr = 0 \quad r = R$$

since the existence of minimum in $W_{ji}^{\circ}(r)$ at R gives rise to a maximum in $f_{ji}^{\circ}(r)$ at this point (see Fig. 2.6).

For unsymmetrical electrolyte i.e. $|e_i| \neq |e_j|$, where there are possible association equilibria such as



and



a newly formed MX^{+} is therefore counted separately as another conducting entity, and thus the above conditions still apply. A simplifying assumption that, all the cation cospheres have the same radius, and all the anion cospheres have the same radius, is made where more than two species are present.

Using the boundary conditions (i), (ii) (iii) above and the assumption that V_{ji}^* becomes infinite at some point $r = a_j$, i.e.

$$(v) \quad V_{ji}^*(r) = \infty \quad \text{when } r \leq a_j$$

With the new model, $f_{ji}^{\circ} = 0$ for $r \leq R$ and R is the distance at which the effect of the short range interaction becomes significant enough to cause a maximum to occur in f_{ji}° . They, thus proposed a boundary condition,

$$(vi) \quad df_{ji}^{\circ}/dr = 0 \quad \text{at } r = R$$

In deriving the relaxation field ΔX acting on an ionic species j in a solution containing s species, the Onsager continuity equation (5), is used in the region $r > R$.

$$\text{If} \quad v_{ji} = w_i + \omega_i H_{ji}$$

where w_i = the time average solvent velocity at the site of the i -ion, ω_i is the mobility of the i -ion, and H_{ji} is the force acting on the i -ion, then

$$v_{ji} = w_i + \omega_i \left[X e_i \hat{i} - \frac{\nabla_2 \phi_{ji}}{2} - kT \nabla_2 \ln(f_{ji}) \right]$$

where

$X e_i \hat{i}$ is the force due to the external field (along x-axis).

$\nabla_2 \phi_{ji}$ is the force due to the local electrostatic field at dr_2 ,

containing two parts; (i) due to the action of the field of the j-ion, (ii) due to the total ion atmosphere about the i-j pair.

$kt\nabla_2 \ln(f_{ji})$ is the force due to thermal motion.

The relaxation field is then considered as $\Delta X_j = \sum_{t=0}^2 \Delta X_j^{(t)}$ ($t = 0, 1, 2$)
The correlation function $G_p^{(t)}$ is solved using Laplace transforms. The boundary conditions (vi) and $f_{ji} \rightarrow 0$ as $r \rightarrow \infty$ are used to obtain the limit in $G_p^{(t)}$ with r , and the integration constants are then evaluated. The general expression of the relaxation field term $\Delta X_j^{(t)}$ is therefore obtained in terms of a constant C, an integration constant $A_p^{(t)}$. Individual relaxation terms are then determined separately, whereby

$\Delta X_j^{(0)}$ is the term arising from external field effects

$\Delta X_j^{(1)}$ is the hydrodynamic relaxation term

and $\Delta X_j^{(2)}$ is the local electrostatic term.

The hydrodynamic part of the relaxation term, $\Delta X_j^{(1)}$, however, requires knowledge of solvent velocities. The hydrodynamic velocity field about a given ion is therefore examined to obtain expressions for $\Delta X_j^{(1)}$, and the electrophoretic retarding velocity, u_{je} . Lee and Wheaton have derived the time averaged velocity of the solvent at a distance r relative to the j-ion $w_j(r)$ from the effects of (i) the motion of the i- and j-ions through the solvent, and (ii) the volume forces, and found that in the limit of $r \rightarrow \infty$ used to derive $w_i(r)$, the term due to the motion of the j-ion through the solvent rapidly approaches zero in this limit. Hence the expression of $w_i(r)$ is reduced to the electrophoretic retarding velocity arising from volume forces. Following the general procedure, $\Delta X_j^{(1)}$ is finally obtained.

The drift velocity of the central ion u_j consists of 3 components,

$$\bar{u}_j = u_{js} + u_{je} + u_{jR} \quad (6)$$

where u_{js} is the drift velocity of the j-ion in the absence of the interionic effects.

u_{je} is the electrophoretic velocity,

and u_{jR} is the velocity due to the relaxation field.

In the calculation of the electrophoretic velocity, u_{je} , the force F per unit volume acting on the solvent at r from the central j -ion is considered, where

$$F = \sum_{i=1}^s n_{ji} F_i$$

where n_{ji} = the local concentration (ion cm^{-3}) of i -ions at r

and F_i = average force on a single i -ion at r .

Similar to the derivation of ΔX_j ,

$$F_i = X e_i \hat{i} - e_i \nabla_2 \psi_j(r) - k \nabla_2 \ln(f_{ji})$$

where ψ_j = the potential due to the j -ion and its atmosphere ($\psi_j = \psi_j^0 + \psi_j'$). Neglecting all terms $\propto X^2$ and those not giving rise to directed motion and letting

$$F = F^{(0)} + F^{(1)} + F^{(2)}$$

the expression for $F^{(0)}$, $F^{(1)}$ and $F^{(2)}$ are obtained, which are assigned to the corresponding $u_{je}^{(0)}$, $u_{je}^{(1)}$ and $u_{je}^{(2)}$ where

$$u_{je} = u_{je}^{(0)} + u_{je}^{(1)} + u_{je}^{(2)}$$

and $u_{je}^{(0)}$ is the leading term arising from the external field effect.

$u_{je}^{(1)}$ is the asymmetric electrophoretic term arising from the potential due to the j -ion and its atmosphere

and $u_{je}^{(2)}$ is the diffusion term due to thermal motion.

These terms are evaluated separately from each force term, following the general procedure. The terms u_{js} and u_{jR} are derived to be

$$|u_{js}| = X |e_j| w_j \quad (7)$$

$$|u_{jR}| = \Delta X |e_j| w_j \quad (8)$$

In deriving the relaxation field and the electrophoretic velocity, Lee and Wheaton initially used only the first four terms in f_{ji}^0 , which has its full expression as,

$$f_{ji}^0 = n_i n_j \exp \left[- \frac{e_i e_j}{\mu D k T} - \frac{e}{r} \right] \left\{ 1 + \frac{s}{1} (kr) (\beta k)^2 + \mathcal{O}(\beta k)^4 \right\}$$

where $\mu = e^{-\kappa R} (1+\kappa R)$ and $S_1(\kappa r)$ is the function of the integrals of the exponential in κr . Evaluation of the final term in f_{ji}^0 gives additional contributions to ΔX_j and u_{je} which consist of a term $\propto (\beta \kappa)^3$ and another term $\propto (\beta \kappa)^2$ and $K(b_{ji})$ (b_{ji} is Bjerrum parameter). The factor $K(b_{ji})$ which is a power series in $b_{ji}/(1+\kappa r)$ rapidly predominates when b_{ji} is large whereby ion association is to be expected (This term is referred to as the pseudo ion association term by Fuoss). The inclusion of this term makes the explicit introduction of the concept of ion-pairing unnecessary. In the new model the distribution function f_{ji}^0 in its full exponential form implicitly allows for the effects of ion pairing by a sharp increase at a distance close to the j -ion when b_{ji} is large. Therefore, to avoid counting the same effect twice, Lee and Wheaton exclude the terms with $K(b_{ji})$'s from the final conductance equation (6, 7).

The complete conductance equation is then assembled by collecting terms in the relaxation and electrophoretic effects. By definition, the equivalent conductance of a given ion j is

$$\lambda_j = F u_j$$

where u_j is the electrical mobility of the j -ion under unit applied field,

$$\text{i.e. } u_j = |\bar{u}_j| / X$$

From equation (6) thus

$$\lambda_j = F |u_{je} + u_{jR} + u_{js}| / X$$

substitution gives

$$\lambda_j = F \xi |e_j| w_j (1 + \Delta X_j / X) + F \xi u_{je} |e_j| / X e_j$$

where ξ is the conversion factor ($v \rightarrow$ e.s.u.) and $= 1/299.7925$.

$$\text{Since } \lambda_j^0 = F \xi |e_j| w_j$$

$$\text{therefore } \lambda_j = \lambda_j^0 (1 + \Delta X_j / X) + \lambda_{el,j} \quad (9)$$

where $\lambda_{el,j} = F \xi u_{je} |e_j| / X e_j$, the electrophoretic contribution,

$$\text{and } \Delta X / X = \left\{ \sum_{n=1}^5 \Delta X^{(0,n)} + \sum_{n=1}^2 \Delta X_j^{(2,n)} + \Delta X^{(1)} \right\} \frac{1}{X} \quad (10)$$

where n is the number of iterations used in the detailed derivation. For all ions in solution, thus

$$\Lambda = \sum_{i=1}^s |Z_j| M_j \lambda_j / C$$

where M_j is the molar concentration of a given free ion j and C is the stoichiometric equivalent concentration of the solution.

Correction for some errors in the Lee and Wheaton equations have been made, and are given in Appendix B