CHAPTER II

THEORETICAL BACKGROUND

As is well known, there are many substances which behave as a strong electrolyte when dissolved in one solvent, but as a weak electrolyte when dissolved in another solvent. In any solvent the Debye - Huckel interionic attraction theory(5) with some further improvement by Onsager(6) predicts how the ions of a solute should behave in an applied electric field, if the solute is completely dissociated into free ions. As a result of electrostatic forces and thermal motion, any selected ion in a solution, a positive one for instance, has on a time average more negative ions near it than if the distribution were purely random. This is known as the "ion atmosphere" of the selected ion. From the thermodynamic point of view, the present of ion atmosphere reduces the activity coefficients of the ions. It influences the electrolyte conductance by the so-called "electrophoretic effect" and "time of relaxation effect" both of these tend to decrease the ionic mobilities with increasing ionic concentration.

When an electric potential is supplied, the ion atmosphere, which has a net charge equal but opposite in sign to that of the central ion, tends to move with its associated solvent molecules in a direction opposite to that of this ion. This retards the central ion, which in effect moves against counter current of solvent amounting to an increase of viscous drag. Because of its analogy to the retarding effect of the solvent on the motion of colloidal particles in an electric field, this phenomenon has been called the electrophoretic effect.

When no external electric field is applied on a solution, the ion atmosphere is spherically symmetrical with its electrical center of gravity at the central ion. If, however, the ion is made to move by an external field, the ion atmosphere must also move to adjust for this change. This takes place rapidly (during the short time of relaxation) but not instantaneously, so that the ion atmosphere is distorted, it's electrical center of gravity is shifted to a point behind the central ion, and its motion is slowed up by an electrostatic retarding force. This phenominon is called the time of relaxation effect.

In very dilute solutions the "thickness" of ion atmosphere, $\frac{1}{\kappa}$, decreases with the square root of the ionic concentration and with the first power of ionic charge or, more precisely, with the square root of the ionic strength. The retarding effect on ionic mobility attributable to both the electrophoretic effect and time of relaxation effect turns out to inversely proportional to this thickness, which is usually of the order of angstroms. Moreover, the former is proportional to the ionic mobility at infinite dilution, and the latter to the fluidity of the solvent

The quantitative equation for conductivity of a very dilute solution according to Debye - Huckel – Onsager treatments are

$$\Lambda = \mathring{\Lambda} - \left[\frac{2.801\times10^{6}|Z_1 Z_2| q \Lambda^{\circ}}{(\varepsilon T)^{3/2}(1+\sqrt{q})} + \frac{41.25(|Z_1|+|Z_2|)}{\eta\ (\varepsilon T)^{1/2}} \right] \sqrt{I} \ldots\ldots.(2.1)$$

which is called "limiting law". It is infact of the form $\Lambda = \overset{o}{\Lambda} - A\sqrt{c}$ which was found empirically by Kohlrausch to describe the variation of equivalent conductance with concentration in dilute solution. For moderate concentration with a suitable choice of "a" (vide infra), especially for 1:1 electrolytes the term "$1 + \kappa a$" is included as the denominator of $\sqrt{I}$ in equation (2.1). These equations give a straight line with $\overset{o}{\Lambda}$ is an intercept and values in the parenthesis is a slope for Λ vs. $\sqrt{I}$ plot.

In the case that solutes behave as a weak electrolyte, Debye-Huckel-Onsager proposed that at any moment a certain fraction of the solute fails to contribute to the conductivity. In the Debye-Huckel-Onsager theory, it was pointed out that even in a very dilute solution containing uncharged solute particles a few pairs of solute particles in contact or near contact may be found.

If this idea is correct, the number of ions will not be proportional to the concentration of the solute, since at higher concentration more pairs of ions are united to form neutral molecules. If the conductivity is plotted against the concentration, the relation will not be linear; the conductivity will increase less rapidly, due to the progressive increase in the number of neutral molecules which play no part in carrying the current. For all electrolytes the conductivity is, in fact, found to behave in this way. Further, in most of non-aqueous solutions, owing to low dielectric constants, one would expect the presence of neutral molecules to be more marked, and it is found that the equivalent conductance of non-aqueous solutions falls off even more rapidly than that of aqueous solutions.

In 1926, the idea was put forward by Bjerrum(7) that when discussing the solute particles of a weak electrolyte, we do not have to choose between free ions and neutral molecules but that there is a kind of intermediate state. Bjerrum gave the name associated ion pair to this third state. An associated ion pair is a pair of oppositely charged ion caught in each other's field in the manner described above; one or more solvent molecules may separate the two ions, between which only the usual long range electrostatic forces are operation. A solute will behave as a completely dissociated electrolyte only provided that associated ion pairs are not formed; in addition short range forces of attraction must be absent. The problem is to decide under what concentrations associated ion pairs will be present. In the solution of a uni-univalent or of a divalent substance an associated ion pair will be electrically neutral and in important respects will behave like a neutral molecule. This can be regarded as the first ion-association or ion-pair theory that even proposed.

All measurements on and theories of ion-pair involved one ion-size parameter the "contact distance", a, i.e., the distance between the negative and positive centers of charge when the ions are in contact. This distance has been obtained from two kinds of measurements; dipole moment and conductance. One of the methods that ion-size parameter can be yielded is from various equations which relate the ion pair dissociation constant, K , the dielectric constant, ε , of the medium and "a". The procedure for the calculation of dissociation constant from conductivity data is itself a complex process. Hence the calculation of "a" from K and ε is by no means straight forward. The "a" obtained seems to depend on the method of calculation. Some of the methods or equations which are widely used are discussed inturn below.

By assuming Maxwell - Boltzmann distribution for the ions Bjerrum shows that for a distance $q = \frac{|z_1 z_2| e^2}{2 \varepsilon k T}$ the probability of ion-pair formation has a minimum. For distances $a \leq r \leq q$, Bjerrum considers the ion associated. Hence if the density of i-ions around the selected j-ion is given by the Boltzmann expression and the number in a shell of thickness dr at the distance r is

$$n_i \exp\left(\frac{-z_i e \psi_j}{kT}\right) 4\pi r^2 dr$$

When r is small, Bjerrum neglects the effect of interionic forces on the reasonable ground that the potential of the central ion will be dominant and writes:

$$\psi_j = \frac{z_j e}{\varepsilon r}$$

so that the number of i-ions in the shell is:

$$4\pi n_i \exp\left(\frac{-z_i z_j e^2}{\varepsilon k T r}\right) r^2 dr$$

The degree of association $(1-\alpha)$ is obtained by integrating the number of ions in all the shells from the distance of closest approach up to the critical Bjerrum distance:

$$(1-\alpha) = 4\pi n \int_a^q \exp\left(\frac{-z_1 z_2 e^2}{\varepsilon k T r}\right) r^2 dr$$

$$\text{put } x = -\frac{z_1 z_2}{\varepsilon k T r} e^2$$

so that the integral becomes:

$$-\left(\frac{|z_1 z_2| e^2}{\varepsilon k T}\right)^3 \int_b^2 \frac{e^x}{x^4}\, dx$$

where $\dfrac{|z_1 z_2|\, e^2}{\varepsilon k T a} = b$

and $\dfrac{|z_1 z_2| e^2}{\varepsilon k T q} = 2$

thus $(1-\alpha) = \dfrac{4\pi N c}{1000}\left(\dfrac{|z_1 z_2| e^2}{\varepsilon k T}\right)^3 Q(b)$

where $Q(b) = \displaystyle\int_2^b x^{-4} e^x dx$

Values of the integral, Q(b), have been tabulated$^{(7,8)}$ in Table 2.1.

Table 2.1

Values of Definite Integral Q(b)

b	Q(b)	b	Q(b)	b	log Q(b)
2.0	0	5	0.771	15	1.97
2.1	0.0440	6	1.041	17	2.59
2.2	0.0843	7	1.420	20	3.59
2.4	0.1560	8	2.000	25	5.35
2.6	0.2180	9	2.950	30	7.19
2.8	0.2740	10	4.630	40	11.01
3.0	0.3260	12	13.410	50	14.96
3.5	0.4420	14	47.000	60	18.98
4.0	0.5500	15	93.000	70	23.05

The dissociation constant, K , of the ion-pair, is given by the law of mass action, here thallous acetate is taken as an example:

$$K = \frac{\alpha^2 c}{(1-\alpha)} f_{\pm}^2 \qquad \ldots\ldots\ldots\ldots\ldots (2.2)$$

assuming that the activity coefficient of the ion-pair is unity. K can be evaluated by two methods, first by substituting numerical values into equation (2.2) and second by taking logarithmic for both sides of equation (2.2). The latter method yield a straight line equation of the form

$$\log K = \log \left\{ \frac{\alpha^2 c}{(1-\alpha)} \cdot f_{\pm}^2 \right\}$$

$$\text{or} \quad \log K = \log K' + 2 \log f_{\pm}$$

$$\text{Hence} \quad \log K' = \log K - 2 \log f_{\pm}$$

$$\text{where} \quad K' = \frac{\alpha^2 c}{1-\alpha}$$

By plotting $\log K'$ vs. $\log f_{\pm}$, $\log K$ becomes an intercept of the straight line.

The calculation now proceeds in three parts:

1. In very dilute solutions, $\alpha \approx 1$, $f_{\pm} \approx 1$ and

$$\frac{1}{K} \approx \frac{1-\alpha}{c} \approx \frac{4\pi N}{1000} \left(\frac{|Z_1 Z_2| e^2}{\varepsilon k T} \right)^3 Q(b).$$

For any value of $a(<q)$ there are corresponding values of b and Q(b) (Table 2.1) and hence of $\frac{1}{K}$ so that K is a function of the closest distance of approach of the ions.

2. The degree of association $(1-\alpha)$ at any value of c can be calculated by successive approximations of the two following equations:

$$\frac{\alpha^2 c}{(1-\alpha)} f_{\pm}^2 = K$$

and $$-\log f_{\pm} = \frac{A\sqrt{(\alpha c)}}{1 + Ba\sqrt{(\alpha c)}}.$$

3. From the equation

$$f_{\pm} \cdot \alpha c = f_{obs} \cdot c$$

knowing α and $f_{\pm}$ from the second computation, one can calculate f_{obs}, the activity coefficient which should result from experimental measurements, assuming complete dissociation, on an electrolyte processing the value of "a" adopted at the commencement of the calculations.

It is worth pointed out here that in the Debye model$^{(5)}$ the solvent is a continuum of uniform ε and the ions are rigid spheres with spherically symmetrical charges which do not change the ε of the solution, and all of which have the same diameter. The central ion is assigned a radious equal to this diameter and the other ions are treated as point charges. To calculate the free energy Debye - Hückel charged all the ions together, keeping the charge of every ion the same fraction of its final charge. On the other hand, Bjerrum charged a single ion or just enough ions to keep the net charge of the solution zero and obtained the chemical potential of the ion directly. The two methods agree for the Debye - Huckel approximation and for the terms proportional to $c \ln c$ and to c for the complete Boltzmann exponential, which can be considered to be correct for this model.

The simple electrostatic model of Bjerrum has enjoyed success in the prediction of "a" for quite a number of cases.$^{(9)}$ It seems likely that the cases most favorable for the validity of this model, with negligible interactions of a chemical nature will be those where one or both partners are already stable complex ions. However, this model gives too large value of the association for high valence ions in water. The possible causes of deviation from the prediction of Bjerrum's model is that it neglects covalent interactions and the charge distribution is polyatomic ions. The effects of specific free ion-solvent or complex ion-solvent interactions are also ignored.

Apart from Bjerrum's equation there are many more equations devised for the purpose of the computation of "a" from conductivity data, for example the Denison - Ramsay equation,(10) the Gilkerson equation,(11) the Fuoss - Kraus equation,(12) the Shedlovsky equation,(13) the Fuoss - Kraus theory.(14) A number of experimental papers dealing with the Fuoss - Onsager conductivity theory(15) have appeared and this theory deserves some attention. The theory is basically an application of the interionic attraction theory to charged spheres in a solvent continuum and has been developed for unassociated symmetrical 1:1 electrolytes. The conductivity equation has the limiting form of:

$$\Lambda = \Lambda^{o} - (\alpha\Lambda^{o} + \beta)c^{\frac{1}{2}} + \varepsilon c \ln c + (J_1 c - J_2 c^{3/2})(1 - \alpha c^{1/2})$$

in which the constant J_1 and J_2 are explicit functions of ion size "a" and Λ^{o} and properties of the solvent; ε is independent of ion size. This equation is capable theoretically of describing the concentration dependence of the equivalent conductance up to a concentration corresponding to $\kappa a = 0.2$. In 1959, Fuoss(16) has collected the revisions of the original Fuoss - Onsager equation, including is an outline of the methods of analysing conductivity data for unassociated electrolytes and electrolytes associating into ion-pairs and higher aggregates. Kay(17) has applied the equation to conductivity studies of solutions of the alkali halides, nitrate, bromates and perchlorates in water-methanol 50 mole percent methanol water, ethanol, n-propanol and liquid ammonia at several temperatures. He found that in many cases the values were substantially lower than the crystallographic radii. Kay attributed this to a result of a small amount of association. Sadek and Fuoss(18) has tested the above equation by measuring the conductivity of Bu_4NBr in nitrobenzene-methanol mixtures, and found that Bu_4NBr appears to be significantly associated in each of the pure solvents but undissociated in the mixture.

The conductivity in other salt-solvent systems have also received considerable interest both in the high ε and low ϵ solvents and also in the solvent mixtures. Few examples only will be cited here. The conductivity of the tetraphenylarsenium chloride in tetramethylene sulphone (sulphonate) has been measured by Burwell and Langford(19) in 1959. The conductivity appeared to be independent of concentration in the range between 5 X 10^{-3} and 1.25 X 10^{-2}M.

Brewster, Schmidt, and Schaap,(20) made the conductivity studies of thirteen alkali metal chlorides, bromides, iodides, nitrate and thiocyanates as well as silver nitrate and Bu_4NI in ethanolamine ($\varepsilon = 37.7$, $\eta = 0.19346$ poise) at 25°C. Data were analysed by the Shedlovsky's method.(13) Ion association constant for $AgNO_3$ and Bu_4NI were virtually the same, $\frac{1}{K}$ being 6.5 and 6.6 respectively. The sodium salts have uniformly lower association constant than the potassium salts.

From the inspection of the literatures; the interest in this field of research seems to be at the peak around 1959 - 1962 and from the publications appeared in the literatures up to present though numerous in number none has mentioned conductivity studies of thallous salt nor thallic salt in acetic acid which is the topic of interest of the author with reasons given in chapter I.

It should be noted also that Walden's rule: $\Lambda^{\circ}\eta^{\circ}$ = constant enable the limiting equivalent conductance of electrolytes to be found. Generally speaking, however, Walden's rule gives a useful guide to the conductivity to be expected, but it cannot be considered quantitatively reliable.

Another method of studying the incomplete dissociation of electrolytes depends on measuring the solubility of a sparingly soluble electrolyte in the presence of another electrolyte. Example cited here as an illustration is the case of the solubility of manganous oxalate in the presence of added electrolytes, dilute sodium or potassium oxalate, which can form complexes with manganous oxalate. For the simple system, the solubility would decrease because the product of $f_{\pm}^{2}\left[Mn^{2+}\right]\left[Ox^{2-}\right]$ is constant, the addition of oxalate ion would reduce the concentration of manganese in solution.

$$\mathrm{Mn\ Ox\ (solution)} \rightleftharpoons Mn^{2+} + Ox^{2-} \quad \ldots\ldots\ldots\ldots\ldots \; (2.3)$$

$$K_{sp} = f_{\pm}^{2}\left[Mn^{2+}\right]\left[Ox^{2-}\right] \quad \ldots\ldots\ldots\ldots\ldots \; (2.4)$$

$$\mathrm{K_2Ox\ (solution)} \rightleftharpoons 2K^{+} + Ox^{2-}$$

(Na_2Ox)

The increase of solubility indicates that the concentration of manganese increase because it can form complexes or a new species, $\mathrm{Mn\,Ox_2^{2-}}$, with the added oxalate.

$$\mathrm{MnOx} + \mathrm{Ox}^{2-} \rightleftharpoons \mathrm{MnOx}_2^{2-} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

On this basis the manganese content in the saturated solution is the sum of the concentrations of complex ion, MnOx_2^{2-}, the ion-pair, MnOx, and the Mn^{2+} ion.

From equation (2.5);

$$K_2 = \frac{\{\mathrm{MnOx}\}\{\mathrm{Ox}^{2-}\}}{\{\mathrm{MnOx}_2^{2-}\}}$$

$$\text{or } K_2 = \frac{[\mathrm{MnOx}][\mathrm{Ox}^{2-}]}{[\mathrm{MnOx}_2^{2-}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

$$\text{or } [\mathrm{MnOx}_2^{2-}] = [\mathrm{MnOx}][\mathrm{Ox}^{2-}] \Big/ K_2$$

$[\ K_2 = \text{instability constant of the complex ion}\ ]$

When the activity coefficient of the two bivalent ions are assumed that approximate equal.

One also has

$$[\mathrm{MnOx}_2^{2-}] = S - [\mathrm{MnOx}]$$

where S = measured solubility

$$[\mathrm{Ox}^{2-}] = A + S - [\mathrm{MnOx}] - 2\left\{\mathrm{MnOx}_2^{2-}\right]$$

$$= A - S + [\mathrm{MnOx}]$$

where A = concentration of added salt (assumed complete dissociate)

$$S - [\mathrm{MnOx}] = \frac{[\mathrm{MnOx}](A - S + [\mathrm{MnOx}])}{K_2}$$

$$\text{or } A = \left(S - [\mathrm{MnOx}]\right)\left(1 + \frac{K_2}{[\mathrm{MnOx}]}\right) \quad \ldots\ldots\ldots\ldots\ldots (2.7)$$

$$\text{where} \quad A = 0, \quad S = [\text{MnOx}]$$

$$S = 0, \quad -A = [\text{MnOx}] + K_2$$

The intercept on the ordinate gives the concentration of ion-pair in the saturated solution, and the extrapolation of the straight line gives the K_2. K_1, the dissociation constant of the ion-pair, can also be obtained from the measurements.

A value for $K_1 = \frac{[\text{Mn}^{2+}][\text{Ox}^{2-}]}{[\text{MnOx}]} \cdot f_{\pm}^{2}$ can be calculated by use of Debye-Huckel limiting equation. The value calculated in this way needs a correction for the small amount of complex ion present in the saturated solution, and this can be estimated from the K_2 value.