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MEAN-FIELD APPROACHES TO THE IONIC SOLUTIONS

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CONTENTS

FIGURE LISTS

SYMBOL LISTS

$\mathbf{a}$	:	Ion-size parameter
q_i	:	Ionic charge
$\mathbf{T}$	:	Temperature
k_B	:	Boltzmann's constant
$\mathbf{E}$	:	Electric field
ε	:	Dielectric constant of solvent
η_s	:	Viscosity constant of solvent
ρ	:	Counter charge density
κ	:	Screening parameter
κ_D	:	Debye parameter
Λ	:	Ionic equivalent conductivity
Φ	:	Osmotic pressure
$\gamma_{\pm}$	:	Mean activity coefficient
w_i	:	Mobility of i'th kind ion
τ_i	:	Relaxation time of i'th kind ion

MEAN-FIELD APPROACHES TO IONIC SOLUTIONS

SUMMARY

The main objective of this thesis is to obtain analytically dynamic and thermodynamic equations of electrolyte solutions to explain experimental data of electrolytes over a large concentration range as rigorously as possible in mean-field manner. Of course, from a complete statistical physics perspective, the mean field approaches may have some shortcoming from outset. However, in the rigorous statistical mechanical treatment, there is a big obstacle to treat the ionic solutions due to the very strong and very long Coulomb interaction between ions since the virial coefficient expansions encounter special convergence difficulties in this case. That is why, the only available picture to treat the problem analytically seems to be the mean-field type approaches.

In mean field type theories, the main concern is to express the radial correlation functions of the system with mean field ideas, namely the potential of mean force and counter charge density profile (or ionic atmosphere). Since there is an exact relation between the radial correlation functions and potential of mean forces in mean-field sense, making assumptions on the potential of mean forces leads to obtain the correlation functions of the system.

Thus, the properties of electrolytes can be treated in the correlation function formalism of statistical mechanics.

The most famous approximate mean field theory of electrolyte solution known as the Debye-Hückel theory which assumes the potential of mean force is equal to $q_i\Psi_j$, where q_i is the point charge of the test ion and Ψ_j in the time average mean potential around an j'th kind ion. DH assumes that $q_i\Psi_j/k_BT$ is a lot smaller than the unity which does not only facilitate the solution of mean potential but also ensures the satisfaction of linear superposition principle. This assumption is quite true for electrolytes at very low concentration ranges. But it turns out to be invalid at higher concentrations. This is also well true for extended DH type theories which considers finite ion radius instead of zero ion-size. Therefore, the introduction of ion-size parameter into DH picture improve the agreement of the theory with the experimental results .But, of course the ion-size are only considered as nothing but fitting parameters of the system from purely theoretical point of view. In addition, the ion-size introduces further difficulties to treat dynamic properties of electrolytes since solution of Onsager's relaxation field equation is not an easy task as in the case of zero ion size.

In this thesis, therefore, three different mean-field considerations have been taken into account to introduce plausible mean field pictures, each has its own uniqueness. In section two and three, the physical emphasis are same as the extended DH picture but correlation function is mapped into linearized form with two unknown parameters. One of them has been obtained from the charge neutrality condition. The second parameter has been obtained from the Stillinger second moment condition in section two. In section three, however, it is obtained from the comparison with the experimental data of equivalent conductivity. The parameters obtained from the equivalent conductivity in all these sections have also used for thermodynamic properties of electrolytes in order to satisfy the internal consistence of the treatment. In addition, the relaxation field has been solved by different considerations

in these sections. More importantly, in section three and four, ion-size parameter are assumed as equal to the sum of crystallographic ionic radii.

In section four, a unique mean field picture has been proposed based on a strong assumption on the counter charge density profile including two unknown parameters. The correlation functions have been obtained from this charge density by assuming $w_{ij} = -w_{ji}, i \neq j$ for symmetric electrolytes. The dynamic and thermodynamic properties have been treated in a manner as in section three.

İYONİK ÇÖZELTİLERE ORTALAMA ALAN YAKLAŞIMLARI

ÖZET

Bu tez çalışmasının amacı elektrolitlerin yüksek konsantrasyonlardaki davranışlarını açıklayacak dinamik ve termodinamik denklemleri ortalama alan yaklaşımıyla mümkün olduğu kadar açık bir şekilde belirlemektir. Tabiiki, tam bir istatistik fizik bakışıyla, ortalama alan yaklaşımının bazı eksikleri olacağı açıktır. Bununla beraber, temel istatistik mekanik yaklaşımında, virial açılımının Coulomb etkileşmesinin çok güçlü ve uzun erişimli olmasından dolayı ıraksaması, büyük bir güçlüğe neden olmaktadır. Bu yüzden bu problemi analitik olarak çözmek için ortalama alan yaklaşımı mümkün olan tek yol olarak gözükmektedir.

Ortalama alan teorilerinde önemli olan şey, korelasyon fonksiyonlarının ortalama alan kavramları olan ortalama kuvvetlerin yarattığı potansiyel ve iyonik atmosfer yardımıyla formüle edilmeleridir. Ortalama alan anlamında, korelasyon fonksiyonuyla ortalama kuvvetlerin yarattığı potansiyel arasında tam bir ilişki olmasından dolayı, ortalama kuvvetlerin yarattığı potansiyelin yaklaşık olarak belirlenmesi, korelasyon fonksiyonun belirlenmesine neden olmaktadır. Böylece, elektrolitlerin özellikleri istatistik mekaniğin korelasyon fonksiyonu formalizmiyle çözümlenebilir hale dönüşmektedir.

En ünlü elektrolit çözelti ortalama alan teorisi, ortalama kuvvetlerin neden olduğu potansiyeli $q_i\Psi_j$ olarak kabul eden Debye-Hückel teorisi olarak bilinir. Burada, q_i test iyonunun nokta yüküdür ve Ψ_j de j türü bir iyon

etrafındaki zaman üzerinden ortalama potansiyeldir. DH teorisi $q_i\Psi_j$ yi birden küçük olduğunu kabul eder. Bu durum ortalama potansiyelin çözümünü mümkün kılmakla beraber aynı zamanda süperpozisyon ilkesini de sağlar. Bu kabul düşük konsantrasyonlarda oldukça doğrudur. Fakat, yüksek konsantrasyonlarda geçersizdir. Bu durum iyon büyüklüğünü sıfırdan farklı kabul eden genişletilmiş DH teorisi için de geçerlidir. Bu yüzden iyon büyüklüğünün teoride yer alması teoriyle deneylerin uyumunu iyileştirmesine rağmen yalnızca bir ayarlama parametresi olarak görülür. Buna ek olarak iyon büyüklüğü Onsager releksasyon alanının çözümünü nokta yük durumundan daha zor hale getirdiğinden elektrolitlerin dinamik özeliklerini incelemek de daha fazla zorluklara neden olmaktadır.

Bu yüzden, bu tezde, her birinin kendi özgün özellikleri olan üç farklı ortalama alan yaklaşımı göz önüne alınmıştır. Bölüm iki ve üçde, fiziksel vurgulama DH teorisine benzemektedir fakat korelasyon fonksiyonları bilinmeyen iki parametreyle lineer forma indirgenmiştir. Bunlardan bir tanesi elektrik yük nötralliğinde bulunmuştur. İkinci parametre bölüm ikide Stillinger'in ikinci moment koşulundan ve bölüm üçde deneyle karşılaştırılarak bulunmuştur. Eşdeğer iletkenlikten bulunan parametreler teorinin içsel tutarlılığını sağlamak için termodinamik özellikler de aynen kullanılmıştır. Buna ek olarak relaksasyon alanı her bölümde farklı yaklaşımlar altında çözülmüştür. Daha önemlisi, bölüm üç ve dörtde, iyon büyüklüğü parametresi kristalografik iyonik yarıçapların toplamına eşit olduğu varsayılmıştır.

Bölüm dörtde özgün bir ortalama alan teorisi iki bilinmeyen parametresi olan iyonik atmosfer üzerinde yapılan güçlü bir kabulle önerilmiştir. Korelasyon fonksiyonları bu iyonik atmosferden $w_{ij} = -w_{ji}$, $i \neq j$ yaklaşımıyla belirlenmiştir. Dinamik ve termodinamik özelikler bölüm üçdekine benzer bir yöntemle hesaplanmıştır.

1 INTRODUCTION

Ionic solutions are mixture of solvent and solute molecules which disassociate into their ions. Since the Coulomb interactions between ions are of very long range and very strong, a complete theoretical treatment from statistical physics perspective is cumbersome, if not hopeless. Thus, complete rigorous statistical theory of electrolytes still remains an outstanding challenge for statistical physics. The problem, however, can be handled by some inevitable physical simplifications.

The first profound and useful simplification is the primitive model, in which solvent is assumed as a continuum dielectric, and the solute subsumed spherical ions in this dielectric bear a simple charge at their center and have some short range repulsion (usual a hard core). This simplification leaded to many theories constructed with different considerations: **i** mean field type theories [1-6], **ii** virial expansions calculations [7-10], **iii** integral equation methods [11-20], **iiii** semiempirical methods [21,22]. Although, in this thesis, ionic solutions of strong electrolytes are going to be only treated theoretically from the point of view of mean-field approach, We think that it is proper to give a brief review of those different theoretical frames.

In mean field type teories, the main concern is to express the radial correlation functions of the system with mean-field ideas, namely the potential of mean force and ionic atmosphere. The potential of mean force is interpreted as the multiplication of the bare charge of the test particle and the mean electrostatic potential. The above conventional approach is called as

Debye-Hückel (DH) theory of electrolytes which is going to be revisited so often in this thesis wherever it is necessary.

The virial coefficient expansions calculation is the fundamental frame in which the problem can be treated rigorously, the cluster expansions, however, encounter special convergence difficulties in the case of long range and very strong interactions between ions. The mathematical procedure introduced by Mayer [7], which leads to (DH) limiting laws, has been overcome the difficulties with a number of approximations and assumptions. Later, the range of accuracy of Mayer theory has been extended by Anderson and Chandler up to $0.1 mol/l$.

Onstain-Zernik equation based theories have been called integral equation method. Under certain approximations it leads to numerical solution for correlation functions. The method is considered the most accurate and trustable. Understanding and perception, however, are usually derived from approximate analytical theories.

In semiemprical representation of the properties of electrolyte solutions, the main objective is the prediction of the properties from the quantities which can not be measured directly but related to those measured. From this perspective, the more acceptable theory has been developed by Pitzer [21] in a way that the excess Helmoltz free energy has been represented by just keeping (DH) term and the terms coming from the rearrangement of Mayer series.

Of course, the above review is by no means exhaustive, however, We hope that it will serve as unique and representative samples which have been developed for almost one century. Nevertheless, One might still inquire to what extent the available theories physically transparent and understandable. So thus, one of the purpose of the thesis will be to provide an answer to this

question for mean-field approach.

These theories are, although, differing in the use of various assumptions and approximations as one can see from the above brief review, the introduction of distance of closed approach (or ion-size) is the only common consideration of all these theories. Of course, this introduction is plausible and maybe inevitable. Nevertheless, the parameter turns out to be a fitting parameter of the theories eventually. That is why, the available theories are rather good at predicting properties of electrolytes within the range of interested concentrations. Clearly, it is equally evident that there are discrepancies between obtained ion-size parameters of different theories. Consequently, these discrepancies lead to appreciable confusion to assess the quality of those theories. Thus, in an effort to obtain a physically transparent description, using well-defined ion-size parameter seems to be a crucial objective. Thus in the realm of this thesis, the ion-size parameter is considered in a rigorous manner as much as possible. Besides, the equilibrium and dynamic properties are going to be formulated with the same theoretical considerations in order to augment the quality and consistency of the theory.

Since the aim of this thesis is going to be to formulate a new quantitative mean field description of electrolytes, the reversible work theorem [23] is going to be used to obtain the ionic correlation functions in the primitive model point of view. The ion-solvent interaction which is crucial to explain the properties of electrolyte is going to be introduced by either continuum dielectric constant or semiquantitative manner.

In the second section, the potential of mean force is going to be assumed different from (DH) potential of mean force $q_i < \psi_j >$, where q_i is the charge of the $i'th$ ion in the atmosphere and $< \psi_j >$ is the time average potential around $j'th$ kind central ion. Although, current theories show for single component liquid that the radial correlation function is equivalent to Boltzman factor at low concentration, that is, the potential of mean force can

be considered as (DH) picture, at higher concentration extension of the theory may be introduced by quantitative potential of mean force. Thus, in the first section, the potential of mean force is assumed equal to $\eta q_i < \psi_j >$ and linear relation between the mean ionic electrostatic potential and the mean ionic counter charge density is going to be assumed. The unknown parameter η is going to be determined via Stillinger second moment condition. Under this consideration, the potential of mean force and radial correlation functions are going to be obtained. The ion-size parameter is going to be considered as a fitting parameter but the ion-size parameters evaluated from dynamic properties of electrolyte are going to be used for thermodynamic properties of electrolyte as well in order to satisfy at least internal consistence of the theory.

In the third section, although the similar consideration is going to be employed, the relaxation field is going to be solved by Green function method and the unknown parameter is going to be determined via comparison of the resulting equivalent conductivity relation with Onsager limiting law at low concentrations. In addition, the sum of crystollographic ionic radii are considered as the ion-size parameter. Thus, the ion-size parameters in this section are well-defined since it can be measured in independent experiment. Thus, the screening parameter κ turns out to be a well-defined parameter of the system.

In the fourth section, the basic assumption of (DH) type theories, namely the ratio of potential of mean force to thermal energy is a lot smaller than unity is going to be investigated. For this purpose, a counter charge density profile is going to be assumed based [11,15,18] on numerical theories and assumptions [13]. The radial correlation functions of the system are going to be derived for symmetric electrolytes under the assumption that $w_{jj} = -w_{ij}$, where $i \neq j$.

Since the ultimate justification of a physical theory is the comparison of

the theoretical result to the available experimental data, comparisons of the derived theoretical results to the experimental data are going to be considered in those sections. The theoretical results are going to be also compared some other mean field type theories. The last but not the least, the thermodynamic properties are going to be treated by available theories which have different theoretical considerations.

There are number of reasons why the mean field approach in this thesis can be fruitful and trustworthy. First, the correlation functions are expressed in terms of well-defined parameters of the system in section three and four. In section two, at least the internal consistence of the theory are satisfied by using same ion-size parameters for both dynamic and thermodynamic properties. That means, one can assess the quality of the theory rigorously. Second, the correlation functions are analytical, and consequently lead to analytical derivation of properties of electrolyte. Thus, the analysis may help to interpret certain results, which can be obscured in a numerical treatment. Third, in section three and four, the relaxation field have been obtained without any further assumption on the form of the field. In addition, the resultant field satisfy the Onsager limiting law at proper limits. Fourth, in the last section a unique mean field theory is introduced without using the Poissons equation.

1.1 Correlation Functions In Mean-Field Approach

The potential of mean force w_{ji} between two charged particles, types j and i, at a given relative configuration, let say $\mathbf{r_1}$ and $\mathbf{r_2}$, can be related to mean average forces as,

$$< \vec{\nabla}_{r_1} U >_{r_1,r_2} = \vec{\nabla}_{r_1} w_{ji}. \qquad (1.\ 1)$$

Where $U(\mathbf{r^N}) = U(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N})$ is the potential of the system. So thus the average force between these two particles can be written as

$$-\vec{\nabla}_{r_1} w_{ji} = \frac{\int d\mathbf{r_3} \cdots \mathbf{dr_N} (\vec{\nabla}_{r_1} e^{-\beta U})}{\int d\mathbf{r_3} \cdots \mathbf{r_N} e^{-\beta U}}. \tag{1. 2}$$

with a little bit algebra, one can readily see the following relation

$$-\frac{1}{\beta}\vec{\nabla}_{r_1} e^{-\beta U} = e^{-\beta U}\vec{\nabla}_{r_1} U. \tag{1. 3}$$

Substituting this relation into Eq.(1.1) leads to the following result

$$\beta\vec{\nabla}_{r_1} w_{ji} = -\frac{\vec{\nabla}_{r_1}[\int d\mathbf{r_3} \cdots \mathbf{dr_N} e^{-\beta U}]}{\int d\mathbf{r_3} \cdots \mathbf{r_N} e^{-\beta U}}. \tag{1. 4}$$

If the following simple mathematical relation

$$\frac{f'}{f} = \frac{d[ln(f)]}{dx} \tag{1. 5}$$

is considered, the above equation can be rewritten as

$$\beta\vec{\nabla}_{r_1} w_{ji} = -\vec{\nabla}_{r_1}[ln \int d\mathbf{r_3} \cdots \mathbf{r_N} e^{-\beta U}]. \tag{1. 6}$$

Since the correlation functions defined as

$$g_{ji}(\mathbf{r_1}, \mathbf{r_2}) = \int d\mathbf{r_3} \cdots \mathbf{r_N} e^{-\beta U}. \qquad (1.\ 7)$$

If this definition is substituted in Eq.(1.5), it can be expressed as

$$-\beta \vec{\nabla}_{r_1} w_{ji} = \vec{\nabla}_{r_1} ln g_{ji}(\mathbf{r_1}, \mathbf{r_2}). \qquad (1.\ 8)$$

If the correlation functions are also assumed as spherical symmetric, i.e., $g_{ji}(\mathbf{r_1}, \mathbf{r_2}) = g_{ji}(|\mathbf{r_1} - \mathbf{r_2}|) = g_{ji}(r)$, the solution of the simple equation obtained as

$$g_{ji} = e^{-\beta w_{ji}}. \qquad (1.\ 9)$$

At this point it is reasonable to inquire whether the exact relation (in mean-field sense) between the correlation function and the potential of mean force can serve as a basis for the exact treatment of the problem. The answer, of course, is no due to the complications of the system. Thus, in some sense, the picture has the same complications as in the rigorous statistical treatment. But, it merely provide a physical picture in which the ion-ion correlation functions turn out to be treatable since it is easier to make assumptions on the potential of mean force in the mean-field picture than making assumptions from outset, i.e., from definition of correlation function. All through this thesis, this point is going to be appreciated and exploited.

Before proceeding further in the discussion of the mean field theory sub-

ject of this section, it is worthwhile to begin with a brief review of highly regarded Debye-Hückel (DH) theory. The (DH) theory obtains ion-ion correlation functions by the following manner. First, an ion j defined as central ion which are embedded in a sea of other ions i, positive and negative, distributed about it at a distance r according to Boltzmann factor $g_{ji} = e^{-\beta q_i \psi_j(r)}$, where ψ_j is the time average local electrostatic potential around the ion j. Due to the definition of counter (or atmospheric) charge density, it leads directly to the Poisson-Boltzmann (PB) equation for ψ_j. Linearizing the (PB) equation facilitates its solution, but also ensures the satisfaction of the linear superposition principle. Consequently, it leads to the crucial (DH) screening of the bare Coulomb interaction by the factor $e^{-\kappa r}$. With this prediction, (DH) provides a general understanding of the unique aspect of the thermodynamic properties of solution of electrolyes at infinitely dilute concentration ranges by its limiting laws (DHLL) [23-25]. In addition, it also leads to equivalent conductivity formula called Onsager limiting law (OLL) [26,27]. The ion-size parameter **a** which can be considered as a fitting parameter of the theory [2,6] enters via a natural boundary condition which merely states that any screening charge vanish for $r < a$ and called modified (DH) theory.

Despite its modest accuracy, the usual (DH) theory continues to be a corner stone of the understanding of electrolytes. This is because of its introduction of mean field type theory with a unique conceptual description in the treatment of the problem, namely the concept of time average ionic charge density. Physically, this means that there is a tendency towards local charge neutrality beside the overall charge neutrality in nature. The concept has been also applied to other many body charged particle systems and interpreted as screening of the potential.

Therefore, the theoretical style and physical emphasis of this section is going to be same as (DH) theory due to its outstanding conceptual frame. But, of course, clarifying the ambiguities and over simplification of the modified (DH) treatments is going to be main objective of this work since extented

(DH) has several shortcomings which deteriorate the quality of mean field type treatments.

The first of them is the assumption of the $q_i < \Psi_j > /k_BT$ is a lot smaller than unity [28]. The condition might be true for the usual and extended DH treatment within very low concentration range ($< 0.01 mol/l$). But it is invalid beyond this concentration ranges. This point is considered in section four and further explanation is going to given there. In sections two and three, however, the definition of potential of mean forces in (DH) picture have been extended with a quantitative mean field manner as

$$w_{ji} = \eta q_i < \Psi_j > . \qquad (1.\ 10)$$

Although, there are number of ways to explain why the above definition of potential of mean force can be considered as a plausible one, for purely phenomonological manner, it can be justified as follows. Since the validity of DH treatment is valid only for very low concentrations, the unknown parameter, η in w_{ji}, may extent the validity of the DH assumptions if it is properly determined from some physical considerations. Therefore, determination of η turns out to be a crucial problem in our mean-field treatments.

For this purpose, one can find the Stillinger second moment condition [29] might be fruitful since it has leading role, together with DH theory, in the case of Coulombic phase transition [30,31]. So thus, one can hope intuitively that it may also lead to more accurate prediction of the properties of strong electrolyte. Thus the following mean field theory is going to be introduced with this hope in section two. In section three, however, the unknown parameter is going to be obtained as cited.

2 MEAN-FIELD TREATMENT OF IONIC SOLUTIONS

The ionic atmosphere charge density around a particular ion, let say j is related to the reduced distribution function as

$$< \rho_j(r) >= \sum_i n_i q_i e^{-\beta w_{ji}(r)} \qquad (2.\ 1)$$

where β is equal to $1/k_B T$, k_B and T are Boltzmann's constant and temperature respectively. Eq.(2.1) is valid by definition of the reduced distribution functions $g_{ji}(r)$, which are so defined that $n_i g_{ji}(r)$ is the average particle density of the ion type i at a distance r from an ion type j.

Since Poisson equation is going to be employed to find the time average potential $< \Psi_j >$, one has to consider the linear superposition principle of Possion equation since the definition of atmospheric charge density and Poisson equation are going to be used simultaneously. For this purpose one has no way but linearize the correlation function as

$$g_{ji} = 1 - \beta w_{ji}. \qquad (2.\ 2)$$

In an effort to obtain a physically transparent explanation of the above linearization, one can find the discussions presented by Kirkwood [32,33] is

very convincing and appears somewhat unique. The discussions simply states that the relation between the counter charge density profile and the potential is linear. The same conclusion can be also reached by the linear superposition principle of the Poisson's equation, which merely states that multiplying the charge density by a given factor multiplies the potential by the same factor. So thus, the charge density can be readily related to the potential without violating superposition principle.

Substituting Eq.(2.2) into this approximation leads to

$$g_{ji} = 1 - \beta\eta q_i < \Psi_j > . \tag{2. 3}$$

So thus the charge density can be written as

$$\rho_j = \sum_i n_i q_i (1 - \beta\eta q_i < \Psi_j >). \tag{2. 4}$$

Due to electroneutrality condition, $\sum_i n_i q_i = 0$, it can also be expressed as

$$\rho_j = -\varepsilon\kappa_D^2 \eta < \Psi_j > \tag{2. 5}$$

where κ_D is the well known Debye screening parameter which is defined as

$$\kappa_D^2 = \sum_i \frac{\beta}{\varepsilon} n_i q_i^2. \tag{2. 6}$$

If κ^2 is defined as equal to $\eta\kappa_D^2$, the charge density can be expressed as

$$\rho_j = -\varepsilon\kappa^2 < \Psi_j > \qquad (2.\ 7)$$

where ε is the dielectric constant of solvent and κ is just a parameter in the unit of m^{-1}. Thus, if a short range hard core repulsion part is assumed for $r < a$, the total charge density can be obtained as

$$< \rho_j >= \begin{cases} q_j\delta^{(3)}(r) & r < a \\ -\varepsilon\kappa^2 < \Psi_j > & r > a \end{cases} \qquad (2.\ 8)$$

where the parameter a is just analogous to the distance of closed approach (or ion-size) parameter in extented (DH) type theories.

In order to find a solution for the time averaged potential $< \Psi_j >$, Poisson's equation is going to be used by keeping the source term in total charge density (usually the Poisson's equation is written without the source term $q_j\delta^3(r)$), i.e.,

$$\nabla^2 < \Psi_j >= -\frac{1}{\varepsilon}(q_j\delta^3(r) - \varepsilon\kappa^2 < \Psi_j >). \qquad (2.\ 9)$$

The superposition of field is considered, $< \Psi_j >$ can be written as

$$< \psi_j >=< \psi_j^{(1)} > + < \psi_j^{(2)} > . \qquad (2.\ 10)$$

The potential due to the source therm $< \psi_j^{(1)} >$ can be readily obtained as

$$< \psi_j^1 >= \frac{q_j}{4\pi\epsilon r}. \qquad (2.\ 11)$$

Thus, the equation takes the following form

$$\nabla^2 < \psi_j^{(2)} >= \kappa^2 \frac{q_j}{4\pi\epsilon r} + \kappa^2 < \psi_j^{(2)} > \qquad (2.\ 12)$$

since $< \psi_j^{(2)} >$ is assumed as spherical symmetric, the equation can be written as

$$\frac{1}{r^2}\frac{d}{dr}(r^2 \frac{d}{dr} < \psi_j^{(2)} >) - \kappa^2 < \psi_j^2 >= \kappa^2 \frac{q_j}{4\pi\epsilon r}.\kappa^2 < \psi_j^{(2)} > \qquad (2.\ 13)$$

Now, if $< \psi_j^{(2)} >$ is defined as

$$< \psi_j^{(2)}(r) >= \frac{f(r)}{r} \qquad (2.\ 14)$$

where $f(r)$ is a function. If this definition is substituted into the above equation, it takes the following form

$$\frac{d^2 f}{dr^2} - \kappa^2 f = \kappa^2 \frac{q_j}{4\pi\epsilon}. \qquad (2.\ 15)$$

If $f(r)$ is defined as

$$f(r) = u - \frac{q_j}{4\pi\epsilon}. \tag{2. 16}$$

Finally, the equation can be written as

$$\frac{d^2u}{dr^2} - \kappa^2 u = 0. \tag{2. 17}$$

The solution of the equation can be readily obtained as

$$u(r) = Ae^{-\kappa r} + Be^{\kappa r}. \tag{2. 18}$$

If the definions f and u are considered, $< \psi_j^{(2)} >$ can be written as

$$< \psi_j^{(2)} >= -\frac{q_j}{4\pi\epsilon r} + A\frac{e^{-\kappa r}}{r} + B\frac{e^{\kappa r}}{r}. \tag{2. 19}$$

So thus the solution for $< \psi_j >$ can be expressed as

$$< \psi_j >= A\frac{e^{-\kappa r}}{r}r + B\frac{e^{\kappa r}}{r}. \tag{2. 20}$$

Since in the limit of $r \to \infty$, $< \psi_j >$ also goes to infinity. Physically this is

not possible and B must be zero. Thus the potential can be obtained as

$$< \psi_j >= A\frac{e^{-\kappa r}}{r}. \tag{2. 21}$$

The constant A can be obtained from the zeroth moment condition by the calculation of the following integral

$$-q_j = -\varepsilon\kappa^2 A\int_a^\infty \frac{e^{-\kappa r}}{r}4\pi r^2 dr. \tag{2. 22}$$

Evaluation of the integral leads to the following relation

$$-q_j = -\varepsilon\kappa^2 A4\pi\frac{e^{-\kappa r}}{r}(\frac{r}{-\kappa} - \frac{1}{\kappa^2})|_a^\infty. \tag{2. 23}$$

Thus, A can be obtained from the above relation as

$$A = \frac{q_j e^{\kappa a}}{4\pi\varepsilon(1+\kappa a)}. \tag{2. 24}$$

Substituting A into $< \psi_j >$ relation, it can be rewritten as

$$< \psi_j(r) >= \frac{q_j e^{\kappa a}}{4\pi\varepsilon(1+\kappa a)}\frac{e^{-\kappa r}}{r}. \tag{2. 25}$$

The form of the potential expression seems to imply that if the parameter κ or η is presented in a rigorous manner then the potential turns out to be

useful expression to determine the correlation functions. For this purpose, we will find Stillinger second moment condition [29] profitable as already mentioned. For 1:1 electrolytes second moment condition can be expressed in terms of the correlation functions as

$$-\frac{6}{\kappa_D^2} = 4\pi n \int_a^\infty r^4 [g_{++}^{(2)} - g_{+-}^{(2)}] dr. \tag{2. 26}$$

If the potential expression is substituted into Eq.(2.3), it becomes

$$g_{ji} = 1 - \frac{\kappa^2}{\kappa_D^2} \beta q_i \frac{q_j e^{\kappa a}}{4\pi\varepsilon(1+\kappa a)} \frac{e^{-\kappa r}}{r}. \tag{2. 27}$$

Substituting this expression into the second moment condition leads to

$$-\frac{6}{\kappa_D^2} = -4\pi 2nq^2\beta \frac{\kappa^2}{\kappa_D^2} \int_a^\infty r^4 \frac{e^{\kappa a}}{4\pi\varepsilon(1+\kappa a)} \frac{e^{-\kappa r}}{r} dr. \tag{2. 28}$$

Since $2nq^2\frac{\beta}{\varepsilon}$ is equal to κ_D^2, for 1:1 electrolytes, the integration leads to

$$\kappa_D^2 = \frac{\kappa^2(1+\kappa \mathbf{a})}{1+\kappa \mathbf{a} + (\kappa \mathbf{a})^2/2 + (\kappa \mathbf{a})^3/6}. \tag{2. 29}$$

Multiplying both side of Eq.(2.29) by $\mathbf{a}^2$, $\kappa\mathbf{a}$ can be solved in terms of $\kappa_D\mathbf{a}$. Numerical solution of $\kappa\mathbf{a}$ shows that it has real and positive roots up to $\kappa_D\mathbf{a} = 2.44$, beyond that value it has purely complex roots. The real roots of $\kappa\mathbf{a}$ corresponding to $\kappa_D\mathbf{a}$ are plotted in Fig.2.1 and it can be expressed

analytically as

$$\kappa \mathbf{a} = \kappa_D \mathbf{a} + 0.04(\kappa_D \mathbf{a})^2 + 0.16(\kappa_D \mathbf{a})^4. \qquad (2.\ 30)$$

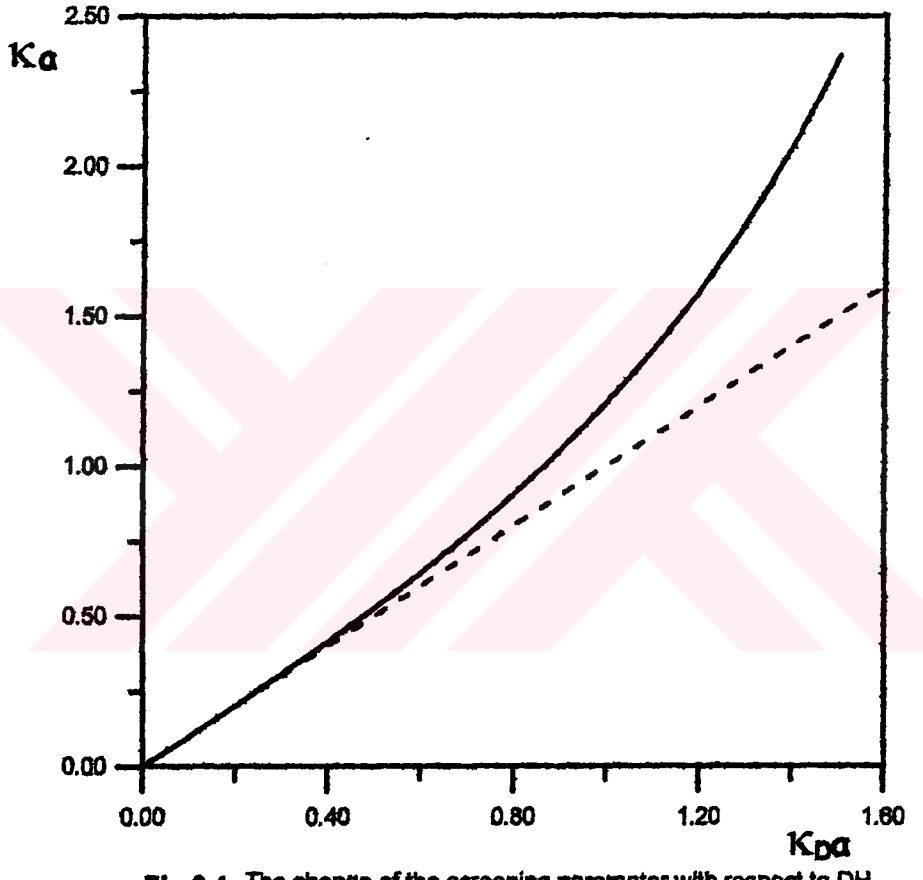

Fig.2.1 The change of the screening parameter with respect to DH screening parameter.

Since $\kappa \mathbf{a}$ is expressed in terms of a well defined parameter κ_D and **a** fitting parameter (or ion-size parameter) **a**, the distribution function becomes well defined function except for the ion-size parameter. Thus, the distribution function turns out to be a single parameter equation and this implies some modification of the measured properties of electrolyte solutions.

Now, we are ready to the applications of the correlation functions since they merely provide a way to treat the properties of electrolyte in correlation function construction of statistical mechanics. Although, only the thermodynamic properties of electrolyte have been considered even in the recent works [30-35], the dynamic property (or ionic conductivity) is also going to be treat in this thesis in order to satisfy the self-consistency of the treatment. Since the ultimate justification of a physical theory must be based on its comparison to the experiment, the theoretical results are also going to be compared with experimental data of electrolyte which are tabulated in several hand books.

2.1 Ionic Conductivity

A special branch of the theory of strong electrolytes deals with the dependence of electrical conductivity of electrolytes on concentration. Conventionally, the measure of conductivity is the equivalent conductivity Λ which is defined as the conductivity divided by the equivalent molar concentration C^*,

$$\Lambda = \frac{\sigma}{C^*} \tag{2. 31}$$

where C^* is equal to $|z_i \nu_i C|$ and $\sigma = \sum_i \sigma_i$, here σ_i is the conductivity due to $i'th$ kind ion. q_i and n_i are defined in terms of z_i and ν_i as $q_i = z_i e$ and

$n_i = \nu_i C$. Physically, the conductivity σ is defined as the proportionality constant between the electric field $\vec{E}$ and the current density $\vec{J}$ it induces

$$\vec{J} = \sigma \vec{E}. \tag{2. 32}$$

In terms of average velocity v_i, it can also be expressed as

$$\vec{J} = \sum_i n_i q_i v_i. \tag{2. 33}$$

Comparing these two equations, σ_i can be obtained as

$$\sigma_i = \frac{n_i q_i}{|\vec{E}|} v_i. \tag{2. 34}$$

With the equation, the problem of obtaining an equivalent conductivity expression turns out to be obtaining the average ionic velocity. Of course, this is not an easy task since it requires an intimate knowledge of ions in motion. In other words, the movement of any particular ions does not seem to be independent of the existence and motions of the other ions and solvent molecules. But, the interactions between any particular ion and the rest of the particles of the system turns out to be treatable if the interactios are reduced to the ion and its ionic atmosphere (or counter charge density). Actually, this approach was applied to the theoretical calculation of equivalent conductivity by Onsager. In addition, he also introduced two meaningful physical effects to obtain the average ionic velocity: relaxation and electrophoretic. Then, he calculated these effects in (DH) picture and ended up with the unique formula what is known as Onsager's limiting law (OLL) which can only explain

the experimental data at infinitely dilute concentration range.

In this work, it is assumed that the limitation of OLL result to infinitily dilute concentration is not due to the physical treatment introduced by Onsager but is due to the the limitation of the (DH) theory. Therefore, the theoretical style and physical emphasis in the derivation of equivalent conductivity are going to be same as Onsager's theory but instead of the DH distribution function, the distribution functions derived in above are going to be used. Since its derivation include the second moment condition, one can hope that it leads to more accurate results in the predictions of equivalent conductivities of electrolytes.

Thus, following Onsager's discussion, the average velocity can be expressed as

$$\vec{v_i} = \vec{v_i}^0 + \vec{v_i}^r + \vec{v_i}^e. \qquad (2.\ 35)$$

$\vec{v_i}^0$ is the average velocity of $i'th$ kind ion in infinitely dilute solution, $\vec{v_i}^r$ and $\vec{v_i}^e$ are the change of the average velocity due to relaxation and electrophoretic effects respectively. In infinitely dilute solution, it is reasonable to suppose that the migration of each ion, and hence its contribution to equivalent conductivity, is independent of all the other ions since the ion atmosphere is so tenuous that its effect on the movement of ions can be neglected.

In this limiting case, one can express the equivalent conductivity as, $\Lambda(C \to 0) = \Lambda_0$. This means, in this limiting case, ionic mobilities are just only affected by the solvent molecules. Since the limiting equivalent conductivity Λ_0 can only determined from extrapolation of experimental data, the ion-solvent interaction which is the cumbersome part of the conventional electrolyte theory is considered inside the experimental parameter Λ_0 implicitly. Thus, in the treatment of ionic conductivity, ion-solvent interaction is

presented with the continuum dielectric constant ε as far as the parameters of the system, for example, the dielectric constant ε does not depend on concentration strongly. Luckily, there are experimental implications which show that the continuum parameters of the system, that is, dielectric and viscosity constants do not change appreciable, up to $1 mol/l$.

From now on, we do not worry about additional ion-solvent interaction as far as the above interpretion is valid. Thus, v_0 can be obtained in the following manner which was initially introduced by Drude [34,35]. If a typical ion is considered at time zero and if t is the time elapsed since its last collision, its velocity at time zero will be its velocity $\vec{v_c}$ immediately after that collision plus the additional velocity $q_i\vec{E}t/m_i$ it has subsequently acquired. Since one can assume that an ion emerges from a collision in a random direction, there will be no contribution from $\vec{v_c}$ to the average ionic velocity, which must therefore be given entirely by the average of $q_i\vec{E}t/m_i$. However, the average of t is the relaxation time τ_i. Therefore,

$$\vec{v_i}^0 = q_i\vec{E}\tau_i/m_i. \qquad (2.\ 36)$$

The second major contribution to the average velocity is relaxation effect. Physically, it is the additional electric field $\vec{E'}$ created by the distortion in ionic charge density due to the applied external electric field $\vec{E}$. Thus, if the discussion given to calculate $\vec{v_i}^0$ is applied, it can be expressed as

$$\vec{v_i}^r = q_i\vec{E'}\tau_i/m_i. \qquad (2.\ 37)$$

The third major contribution to the average velocity is $\vec{v_i}^e$. It is the result of the simultaneous movement of the ion in the direction of the applied field

and of the ionic atmosphere in the opposite direction. Both the central ion and its ionic atmosphere take the neighbouring solvent molecules with them, which result in a retardation of the movement of the central ion. Thus, substituting these velocities into Eq.(2.35) and assuming that the external field is along the x direction, Eq.(2.34) can be expressed as

$$\sigma_i = \frac{n_i q_i}{|\vec{E}|}(q_i|\vec{E}|\frac{\tau_i}{m_i} - q_i|\vec{E'}|\frac{\tau_i}{m_i} - |\vec{v}_i^{\,e}|). \qquad (2.\ 38)$$

Thus, if $|\vec{E'}|$ and $|\vec{v}_i^{\,e}|$ are both calculated in terms of well-defined parameters of the system, Eq.(2.34) together with Eq.(2.31) lead to an equivalent conductivity relation. Calculation of $|\vec{E'}|$ which is the most involved part of the electrolytes is based on interionic iteraction and Onsager's hydrodynamic equation of continuity. At this point, it would be reasonable if the basic assumptions of Onsager's equation of continuity are summarized briefly.

Considering an ionic solution in the absence of external forces, the distribution function can be obtained in a simpler manner than in the presence of external forces. This is due to intimate physical relation between two factors; namely the distribution functions, and the presence of the force acting on themselves and the external force. These factors are not mutually exclusive since the factor effects the distribution of ions and the distribution of ions determines the forces. As one can readily imagine that he or she needs more general treatment of an ionic solution in a perturbed state (in the presence of external forces) than in equilibrium.

While the familiar transport equations are employed to concern with the evaluation of velocity-dependent distribution functions and thus lead ultimately to expressions for conductivity through the evaluation of instantaneous particle velocities, the contribution to the average drift velocity due to the distortion of ionic atmosphere in the presence of external electric field

is going to be dealt with here as already outlined. To do so, one only needs to know the perturbed electric field E'. One might think that the picture is greatly oversimplified; however, a more refined treatment can be more complicated to have a feasible picture.

If $F_{ji}(\vec{r}_1, \vec{r}_{21})$ is defined as a distribution function in an external field, then the Onsager's equation of continuity in steady state can be written as

$$\nabla_{r_{12}} F_{ij}(r_2, r_{12}) \vec{v}_{ij}(r_2, r_{12}) + \nabla_{r_{21}} F_{ji}(r_1, r_{21}) \vec{v}_{ji}(r_1, r_{21}) = 0. \qquad (2.\ 39)$$

Here the gradient operators $\nabla_{r_{12}}$ and $\nabla_{r_{21}}$ are taken with respect to $\vec{r}_1$ and $\vec{r}_2$ respectively. $\vec{r}_{21} = \vec{r}_1 - \vec{r}_2$. Following Onsager and Fuoss [26], it is assumed that, in general, the average velocity of a particle is directly proportional to the total force acting on it. In electrolyte system, there are two components of $\vec{v}_{ji}(\vec{r}_1, \vec{r}_{12})$ due to the total force acting on the ion i and the density gradient. Thus one may write

$$\vec{v}_{ji}(\vec{r}_1, \vec{r}_{12}) = w_i(\vec{K}_{ji} - kT\vec{\nabla} ln F_{ji}) \qquad (2.\ 40)$$

where w_i is the proportionality constant known as mobility and K_{ji} is the total force acting on i ion which will be given by

$$\vec{K}_{ji} = \vec{k}_i - q_i \vec{\nabla}_{r_{21}} \Phi_j(\vec{r}_1, \vec{r}_{12}). \qquad (2.\ 41)$$

In this equation, k_i is the applied external force $q_i E$. The second term is the force acting on the i ion due to the potential of the j ion and its

atmosphere. Thus the velocity relation turns out to be

$$\vec{v_{ji}}(r_1, r_{12}) = w_i(\vec{k_i} - q_i\vec{\nabla}_{r_{21}}\Phi_j(\vec{r_1}, \vec{r_{12}}) - k_BT\vec{\nabla}_{r_{21}}lnF_{ij}(r_1, r_{r_{21}})). \quad (2.\ 42)$$

Substitutig this relation in to $\nabla F_{ij}v_{ij}$, it can be expressed as

$$\nabla_{r_{12}}[w_i((\vec{k_i}F_{ij} - q_iF_{ij}\vec{\nabla}_{r_{21}}\Phi_j(\vec{r_1}, \vec{r_{12}}) - k_BTF_{ij}\vec{\nabla}_{r_{21}}lnF_{ij}(r_1, r_{r_{21}})). \quad (2.\ 43)$$

In the case of external electric field is maintained constant, and therefore, $\nabla_{r_{21}}\vec{k_i} = 0$. And also if the expression $q_iF_{ij}\nabla_{r_{21}}\Phi_j$ is replaced by $n_in_j\nabla\Phi_j$, Under these reductions Eq.(43) becomes

$$\vec{\nabla}_{r_{12}}F_{ij}\vec{v}_{ij} = w_j\vec{k}_j.\vec{\nabla}_{r_{12}}F_{ij} - q_jw_jn_in_j\nabla^2_{r_{12}}\Phi_i - w_jk_BT\nabla^2_{r_{12}}F_{ij} \quad (2.\ 44)$$

The correlation functions in the presence of external field, F_{ji}, may be related to the unperturbed distribution functions by the following manner

$$F_{ji} = f_{ji} + f'_{ji}. \quad (2.\ 45)$$

Here $f_{ji} = n_in_jg_{ji}$ is the distribution functions in equilibrium and the primed term represents the effect of the perturbation . Due to this perturbation, the

potential around the central ion is also become asymmetric, and it can be expressed as

$$\Phi_j = \Psi_j + \Psi_j'. \tag{2. 46}$$

In the absence of external field E, $\vec{k}_i = 0$, so thus the drift velocity $\vec{v}_{ij} = 0$. Under this condition, one can readily obtain that

$$q_i \nabla_{r_{21}} \Psi_j(r) = -k_B T \nabla_{r_{21}} ln f_{ij}(r). \tag{2. 47}$$

Rewriting Eq.(2.44) as

$$\nabla_{r_{12}} F_{ij} \vec{v}_{ij} = w_j \vec{k}_j . \vec{\nabla}_{r_{12}} (f_{ij} + f_{ij}')$$

$$- q_j w_j n_i n_j \nabla^2_{r_{12}} (\Psi_i + \Psi_i') - w_j k_B T \nabla^2_{r_{12}} (f_{ij} + f_{ij}') \tag{2. 48}$$

Approximating the following term as

$$f_{ji} \vec{\nabla}_{r_{21}} \Psi_j = n_j n_i \vec{\nabla}_{r_{12}} \Psi_j. \tag{2. 49}$$

And also using the following approximation

$$\nabla_{r_{12}} F_{ij} = \nabla_{r_{21}} f_{ij}(r). \tag{2. 50}$$

Substituting these relations into Onsager continuity equation, it becomes

$$w_i\vec{k}_i\vec{\nabla}_{r_{21}}f_{ji} + w_j\vec{k}_jT\vec{\nabla}_{r_{12}}f_{ij} - q_in_in_jw_iT\nabla^2_{r_{21}}\Psi'_j$$

$$- q_jn_in_jw_j\nabla^2_{r_{12}}\Psi'_i - w_ik_B\nabla^2_{r_{21}}f'_{ji} - w_jk_B\nabla^2_{r_{12}}f'_{ij} = 0. \qquad (2.\ 51)$$

Since $\vec{r}_{12} = -\vec{r}_{21}$, the following equalities can be helpful to simplify the equation

$$\vec{\nabla}_{r_{12}} = -\vec{\nabla}_{r_{21}} = \vec{\nabla} \qquad (2.\ 52)$$

$$\nabla^2_{r_{12}} = \nabla^2_{r_{21}} = \nabla^2. \qquad (2.\ 53)$$

Using these relations and assuming $\vec{E}$ is along the x direction, the equation can be expressed as

$$(w_ik_i - w_jk_j)\frac{\partial f_{ji}(r)}{\partial x} - q_iw_in_in_j\nabla^2\Psi'_j$$

$$- q_jw_jn_in_j\nabla^2\Psi'_i(-r) - w_ik_BT\nabla^2f'_{ij} - w_jk_BT\nabla^2f'_{ji}(-r) = 0. \qquad (2.\ 54)$$

By consideration of following symmetry relations

$$f'_{ji}(r) = -f'_{ji}(-r) = f'_{ij}(r) \qquad (2.\ 55)$$

$$\Psi'_i(r) = -\Psi'_i(-r) \qquad (2.\ 56)$$

the above equation becomes

$$(w_i k_i - w_j k_j)\frac{\partial f_{ji}(r)}{\partial x} - q_i w_i n_i n_j \nabla^2 \Psi_j^{'}$$

$$+ q_j w_j n_i n_j \nabla^2 \Psi_i^{'}(r) - (w_i - w_j) k_B T \nabla^2 f_{ji}^{'} = 0. \qquad (2.\ 57)$$

By means of Poisson equation

$$\nabla^2 \Psi_j^{'} = -\frac{1}{\varepsilon}\sum_i \frac{q_i}{n_j} f_{ji}^{'} \qquad (2.\ 58)$$

$f_{ji}^{'}$ may be eliminated from this equation. Using the Poisson equation and multiplying differential equation by $\sum_i \frac{q_i}{\varepsilon n_j k_B T(w_i+w_j)}$ leads to

$$\sum_i \frac{q_i(w_i k_i - w_j k_j)}{\varepsilon n_j k_B T(w_i + w_j)} \frac{\partial f_{ji}}{\partial x} - \sum_i \frac{q_i^2 w_i n_i \nabla^2 \Psi_j^{'}}{\varepsilon k_B T(w_i + w_j)}$$

$$- \sum_i \frac{q_i q_j w_j n_i \nabla^2 \Psi_i^{'}}{\varepsilon k_B T(w_i + w_j)} + \nabla^4 \Psi_j^{'} = 0. \qquad (2.\ 59)$$

If the equation is written for $j = 1$ and $k_i = q_i E$, it becomes

$$\frac{q_2^2 w_2 - q_1 q_2 w_1}{\varepsilon n_1 k_B T(w_1 + w_2)} \frac{\partial f_{12}}{\partial x} - \frac{q_2^2 w_2 n_2 \nabla^2 \Psi_1^{'}}{\varepsilon k_B T(w_1 + w_2)} - \frac{q_1 q_2 w_1 n_2 \nabla^2 \Psi_2^{'}}{\varepsilon k_B T(w_1 + w_2)} + \nabla^4 \Psi_1^{'} = 0. \qquad (2.\ 60)$$

Further, the condition

$$\Psi_1' = \Psi_2' \tag{2. 61}$$

can be true due to the symmetry of the problem. Thus, under this condition, the equation becomes

$$\nabla^2[\nabla^2 - \frac{q_2^2 n_2 w_2 + q_1^2 n_1 w_1}{\varepsilon n_1 k_B T(w_1 + w_2)}]\Psi_1' = -\frac{(q_2^2 w_2 - q_1 q_2 w_1)E}{\varepsilon n_1 k_B T(w_1 + w_2)}\frac{\partial f_{12}}{\partial x}. \tag{2. 62}$$

For 1:1 electrolytes $n_1 = n_2$, $q_1 = -q_2$ and $f_{12} = n_1 n_2 g_{12}$, the equation can be expressed as

$$\nabla^2(\nabla^2 - \kappa_1^2)\Psi_1' = -\kappa_1^2\frac{\partial g_{12}}{\partial x} \tag{2. 63}$$

here $\kappa_1^2 = \frac{1}{2}\kappa_D^2$. Since the correlation function g_{12} was obtained as

$$g_{12} = [1 - \frac{q_1 q_2}{4\pi\varepsilon k_B T(1 + \kappa a)}\frac{\kappa^2}{\kappa_D^2}\frac{e^{-\kappa(r-a)}}{r}] \tag{2. 64}$$

the equation becomes

$$\nabla^2(\nabla^2 - \kappa_1^2)\Psi_1' = \Omega\gamma\frac{\partial}{\partial x}\frac{e^{-\kappa r}}{r}. \tag{2. 65}$$

Where, Ω and γ are defined as

$$\Omega = \frac{q_1 q_2 E \kappa_1^2}{\varepsilon k_B T} \tag{2. 66}$$

$$\gamma = \frac{\kappa^2 e^{\kappa a}}{4\pi(1+\kappa a)\kappa_D^2}. \tag{2. 67}$$

The differential equation indicates that the perturbed potential has the following property

$$\psi'(-x,y,z) = -\psi'(x,y,z). \tag{2. 68}$$

Thus for the solution of the above differential equation, the following form is going to be assumed from the outset

$$\psi'(x,y,z) = xP(x,y,z). \tag{2. 69}$$

If the terms of the above equation are evaluated for this form, one can readily obtain the following relations

$$\nabla^2 = 2\frac{dP}{dx} + x\nabla^2 P(r) \tag{2. 70}$$

$$\nabla^4 = 4\frac{d}{dx}\nabla^2 P + x\nabla^4 P(r). \tag{2. 71}$$

If $\frac{d}{dx}$ is also written in terms of the spherical coordinate, it takes the following form

$$\frac{d}{dx}\frac{e^{-\kappa r}}{r} = \frac{x}{r}\frac{d}{dr}\frac{e^{-\kappa r}}{r}. \qquad (2.\ 72)$$

Substitutions of all these relations in the above differential equation leads to the following equation

$$\frac{4}{r}\frac{d}{dr}\nabla^2 P_i(r) + \nabla^4 P_i(r) - \kappa_1^2[\frac{1}{r}P_i(r) + \nabla^2 P_i(r)] = \Omega\gamma\frac{1}{r}\frac{d}{dr}(\frac{e^{-\kappa r}}{r}). \qquad (2.\ 73)$$

Integration of the above differential equation with respect to r yields

$$r^2\frac{d^3P_i}{dr^3} + 7r\frac{d^2P_i}{dr^2} + (8 - r^2\kappa_1^2)\frac{dP_i}{dr} - 2r\kappa_1^2 P_i = \Omega\gamma e^{-\kappa r}. \qquad (2.\ 74)$$

If it is assumed that $P_i(r)$ has a solution of the form $P_i(r) = f(r)e^{-\kappa r}$, the above differential equation can be written as

$$r^2[(\kappa^2\tfrac{df}{dr} - 2\kappa\tfrac{d^2f}{dr^2} + \tfrac{d^3f}{dr^3}) - \kappa(\kappa^2 f - 2\kappa\tfrac{df}{dr} + \tfrac{d^2f}{dr^2})]$$

$$+ 7r(\kappa^2 f * 2\kappa\frac{df}{dr} + \frac{d^2f}{dr^2}) + (8 - r^2\kappa_1^2)(\frac{df}{dr} - \kappa f) - 2r\kappa_1^2 f = \Omega\gamma. \qquad (2.\ 75)$$

One can solve the above differential equation under the assumption that $f(r)$ has a series solution as

$$f(r) = \sum_{n=0}^{\infty} a_n r^n,$$

where $\{a_n\}_{n=0}^{\infty}$ are coefficients restricted by the differential equation. The relations among the coefficient are evaluated from the differential equation as

$$8a_1 - 8a_0 = \Omega\gamma \tag{2. 76}$$

$$(7\kappa^2 - 2\kappa_1^2)a_0 - 10\kappa a_1 - 10a_2 = 0 \tag{2. 77}$$

$$a_{n+3} = ([(n+2)(3n+5)\kappa + 8\kappa]a_{n+2} - [(n+1)(3\kappa^2 - \kappa_1^2)$$

$$+ (7\kappa^2 - 2\kappa_1^2)]a_{n+1} - [\kappa_1^2\kappa - \kappa^3]a_n)/(n+3)(n+2)^2 \tag{2. 78}$$

where $n = 0, 1, 2...$. The first four coefficients are

$$a_0 = -\frac{\Omega\gamma}{3(\kappa + \kappa_1)}; a_1 = a_0\frac{5\kappa - 3\kappa_1}{8}$$

$$a_2 = a_0\frac{16\kappa_1^2 - 30\kappa_1\kappa - 6\kappa^2}{4}; a_3 = a_0\frac{-2\kappa^2 + \kappa_1^2\kappa}{4} \tag{2. 79}$$

The additional electric field E_a in the x direction is found as

$$E_x' = -\frac{d\Psi'(x,y,z)}{dx} = -\frac{d(xre^{-\kappa r})}{dx},$$

$$E_{ax} = -[f(r) + \frac{x^2}{r}(\frac{df}{dr} - \kappa f)]e^{-\kappa r}.$$

At $x = 0$ and $r = a$, E_x' can be written as

$$E_x'(x = 0) = -[a_0 + a_1\mathbf{a} + a_2\mathbf{a}^2 + \cdots]e^{-\kappa\mathbf{a}}. \quad (2.\ 80)$$

In the above relation for E_x', only the first six terms contribute appreciable within the range $\kappa\mathbf{a} < 1$ and the higher order terms can be omitted. Thus, the additional electric field can be approximately expressed as

$$E_x'(x = 0) = -a_0\xi e^{-\kappa\mathbf{a}} \quad (2.\ 81)$$

where ξ is equal to

$$\xi = [1 + 3\kappa_D\mathbf{a}/8 - (\kappa_D\mathbf{a})^2/8 - 3(\kappa_D\mathbf{a})^3/8 - (\kappa_D\mathbf{a})^4/4 - (\kappa_D\mathbf{a})^5/6]. \quad (2.\ 82)$$

Substituting a_0 into ξ, Eq.(2.81) can be written as

$$E_x'(x = 0) = -\frac{q_1 q_2 E\kappa^2}{3(\kappa + \kappa_1)2(4\pi)(1 + \kappa\mathbf{a})}\xi \quad (2.\ 83)$$

The additional electric field relation has some similarities with the derivations of Falkenhagen [38] and Pitts [39]. For instance, as far as the first power of $(\kappa_D\mathbf{a})$ in Falkenhagen's derivation is considered, it becomes exactly the same as his result but Eq.(2.83) differs from both Falkenhagen's and Pitts' derivations if higher powers of $(\kappa_D\mathbf{a})$ are taken into account. Furthermore,

in the limit of $\mathbf{a} \rightarrow 0$, it turns into Onsager's [26] additional electric field at low ionic concentration.

Electrophoretic effect

Due to the external electric field, the central ion and its atmosphere tend to move in opposite direction as mentioned above. Consequently, the central ion drags its own atmosphere along with it which changes its drift velocity. Thus, the contribution of the ionic atmosphere velocity moving in a viscous medium defined by the solvent viscosity coefficient of the medium η_s also needs to be considered. The mathematical calculation can be treated by the help of Stokes' law since it is assumed that it reaches a limiting velocity. Infinitesimal change of velocity for each shell of ionic atmosphere due to Stokes' force F is written as

$$dv_j^e = \frac{dF}{6\pi\eta_s r} \tag{2. 84}$$

where $dF = \rho_j E dV$, where ρ_j is given by Eq(2.7). Thus dF can be expressed as

$$dF = -\kappa^2 \frac{q_j e^{-\kappa(r-a)}}{4\pi(1+\kappa\mathbf{a})r} 4\pi r^2 E dr. \tag{2. 85}$$

The whole increment v_j^e, is obtained by integration over all shells from the ion size parameter $\mathbf{a}$ to infinity.

$$v_j^e = \frac{q_j \kappa E}{6\pi\eta_s(1+\kappa\mathbf{a})}. \tag{2. 86}$$

The net conductivity of $i'th$ kind ion is then expressed as

$$\sigma_i = \frac{q_i n_i}{|E|}(q_i|E|\frac{\tau_i}{m_i} - q_i|E'|\frac{\tau_i}{m_i} - v_i^e). \tag{2. 87}$$

Since equivalent conductivity is going to be used so often in this thesis it is going to be derived for general purpose. Thus σ_1 and σ_2 can be written from the above equation as

$$\sigma_1 = \frac{v_1 z_1^2 e^2 E w_1 N_A c}{E} - \frac{v_1 z_1 E' w_1 N_A c}{E} - \frac{v_1 |z_1| e^2 N_A c v_1^e}{E} \tag{2. 88}$$

$$\sigma_2 = \frac{v_2 z_2^2 e^2 E w_2 N_A c}{E} - \frac{v_2 z_2 E' w_1 N_A c}{E} - \frac{v_2 |z_2| e^2 N_A c v_2^e}{E}. \tag{2. 89}$$

Defining $\lambda_i = \frac{\sigma_i}{|v_i z_i| c}$, the equivalent conductivity $\Lambda = \lambda_1 + \lambda_2$ can be expressed as

$$\lambda_1 = |z_1| e^2 w_1 N_A - \frac{|z_1| e^2 E' w_1 N_A}{E} - \frac{e^2 N_A}{E} v_1^e \tag{2. 90}$$

$$\lambda_2 = |z_2| e^2 w_2 N_A - \frac{|z_2| e^2 E' w_2 N_A}{E} - \frac{e^2 N_A}{E} v_2^e. \tag{2. 91}$$

If limiting equivalent conductivity Λ^0 is defined as

$$\Lambda^0 = \lambda_1^0 + \lambda_2^0. \tag{2. 92}$$

Where λ_1^0 and λ_2^0 are defined as

$$\lambda_1^0 = |z_1|e^2 w_1 N_A \tag{2. 93}$$

$$\lambda_2^0 = |z_2|e^2 w_2 N_A. \tag{2. 94}$$

Finally, using the above relations, one can obtain a equivalent conductivity expression as

$$\Lambda = \Lambda^0[1 - [\frac{|E'|}{|E|} + \frac{eN_A}{|E|\Lambda^0}(|v_1^e| + |v_2^e|)]]. \tag{2. 95}$$

If E_x' and v_1^e and v_2^e are substituted in the above equation they lead to

$$\Lambda = \Lambda^0[1 - (\frac{e^2\kappa}{4\pi 6\epsilon k_B T(\kappa + \sqrt{0.5}\kappa_D)}\xi + \frac{Fe}{3\pi\eta_s\Lambda^0})\frac{\kappa}{1+\kappa\mathbf{a}}]. \tag{2. 96}$$

In the above equation $\kappa/(1+\kappa\mathbf{a})$ can be approximately expressed as

$$\frac{\kappa}{1+\kappa\mathbf{a}} = \frac{1}{\mathbf{a}}[\kappa_D\mathbf{a} - 0.9(\kappa_D\mathbf{a})^2 + 0.5(\kappa_D\mathbf{a})^3 - 0.11(\kappa_D\mathbf{a})^4]. \tag{2. 97}$$

Substituting this approximate relation into the equivalent conductance rela-

tion Eq.(2.96), it can be expressed as

$$\Lambda = \Lambda^0[1 - (0.71\xi + \frac{186.3}{\mathbf{a}\Lambda^0})[\kappa_D\mathbf{a} - 0.9(\kappa_D\mathbf{a})^2 + 0.5(\kappa_D\mathbf{a})^3 - 0.11(\kappa_D\mathbf{a})^4]]. \quad (2.\ 98)$$

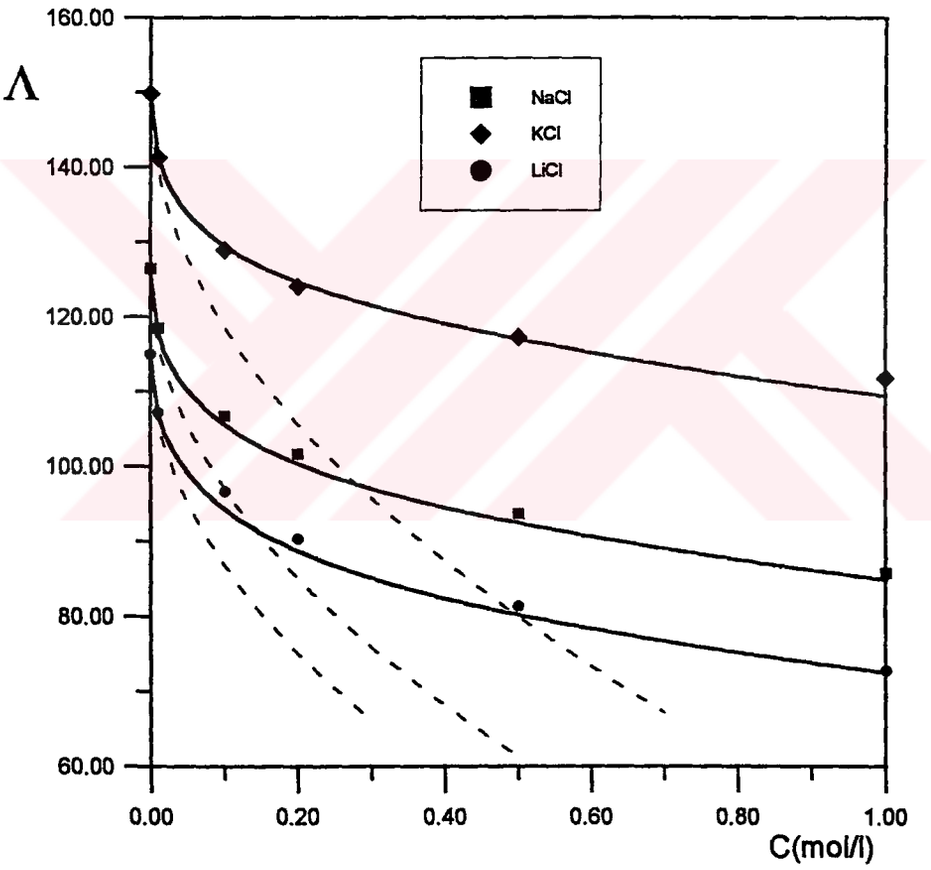

Fig.2.2 The equivalent conductivities versus concentration at T=293K. The dashed lines show the Onsager limiting law results.

In this equation Λ^0 is in the unit of $Ohmcm^{-2}/mol$ and **a** is in the unit of angstrom. Using $\kappa_D = 0.33\ C^{1/2}\ \mathring{A}^{-1}$, where C is ionic concentration in the unit of mol/l, the equivalent conductance relation can be compared with experimental data. The result is plotted in Fig.2.2 for NaCl, LiCl, KCl and the agreements all of these three aqueous solutions are excellent. The ion size parameters of NaCl, LiCl, KCl are found as 3.55 $\mathring{A}$, 3.4 $\mathring{A}$ and 4.5 $\mathring{A}$, respectively.

At infinite dilution, $\kappa \to \kappa_D$ and $\mathbf{a} \to 0$, Λ obeys the Onsager limiting law[26]. Satisfying Onsager limiting law is a test of the above equivalent conductance relation at least at the very low ionic concentration range. Besides that, as seen from Fig.2.2, the equivalent conductivity relation is valid not only at low ionic concentration, but also at very high ionic concentration range, up to 1 mol/l.

2.2 Osmotic And Activity Coefficient

Osmotic and activity coefficients of electrolyte solutions are the main thermodynamic quantities of solution of electrolytes. Osmotic pressure of the electrolyte solution equals [40-43]

$$P = k_B T n - \frac{1}{6}\sum_{i,j} n_i n_j \int 4\pi r^3 \frac{du_{ij}}{dr} g_{ij}(r) dr \qquad (2.\ 99)$$

where $k_B T n$ is the ideal pressure, P_{ideal}. The osmotic coefficient is defined as $\Phi = P/P_{ideal}$. Thus, dividing both side of Eq.(110) by P_{ideal}, osmotic coefficient can be expressed as

$$\Phi = 1 - \frac{1}{6k_B T n}\sum_{i,j} n_i n_j \int 4\pi r^3 \frac{du_{ij}}{dr} g_{ij}(r) dr \qquad (2.\ 100)$$

where u_{ij} is the pair potential which has discontinuity at ion size parameter **a**. The abrupt change in the potential u_{ij} at a hard sphere diameter **a** may be expressed as

$$\frac{du_{ij}}{dr} = -k_B T \delta(r - \mathbf{a})$$

[36]. Thus, it can be written for $r \geq \mathbf{a}$ as

$$\frac{du}{dr} = \begin{cases} -k_B T \delta(r) & r = a \\ -\frac{q_i q_j}{4\pi\varepsilon r^2} & r > a \end{cases} \qquad (2.\ 101)$$

Following this discussion osmotic coefficient can be written as

$$\Phi = 1 + \frac{4\pi d^3}{6 k_B T n} \sum_{ij} n_i n_j g_{ij}(a) + \frac{U^{ex}}{3 k_B T}. \qquad (2.\ 102)$$

If the derived correlation function is recalled,

$$g_{ij}(a) = 1 - \frac{\kappa^2}{\kappa_D^2} \frac{q_i q_j}{4\pi\varepsilon k_B T (1 + \kappa \mathbf{a})} \qquad (2.\ 103)$$

the first term of the expression can be calculated readly as

$$\sum_{ij} n_i n_j g_{ij}(a) = \sum_{i} n_i n_1 (1 - \frac{\kappa^2}{\kappa_D^2} \frac{q_i q_1}{4\pi\varepsilon k_B T (1 + \kappa)}) + n_i n_2 (1 - \frac{\kappa^2}{\kappa_D^2} \frac{q_i q_2}{4\pi\varepsilon k_B T (1 + \kappa \mathbf{a})}) \qquad (2.\ 104)$$

If charge neutrality condition , $n_1 q_1 = -n_2 q_2$, is used, it can be expressed as

$$\sum_{ij} n_i n_j g_{ij}(a) = \sum_i n_i (n_1 + n_2) = (n_1 + n_2)^2 = n^2. \qquad (2.\ 105)$$

The sum in excess free energy U^{ex} can be easily calculated as

$$\sum_{ij} n_i n_j q_i q_j g_{ij} = \sum_i n_i q_i \rho_i. \qquad (2.\ 106)$$

If the expression, $\rho_i = -\varepsilon\kappa^2 < \Psi_i >$, is substituted into the sum

$$\sum_{ij} n_i n_j q_i q_j g_{ij} = -\varepsilon\kappa^2 \sum_i n_i q_i < \Psi_i > \qquad (2.\ 107)$$

where Ψ_i is equal to

$$< \Psi_i >= \frac{q_i e^{-\kappa(r-\mathbf{a})}}{4\pi\varepsilon(1+\kappa\mathbf{a})r}. \qquad (2.\ 108)$$

So thus the sum turns out to be

$$\sum_{ij} n_i n_j q_i q_j g_{ij} = -\frac{\varepsilon\kappa^2\kappa_D^2}{4\pi\beta(1+\kappa\mathbf{a})} \frac{e^{-\kappa(r-\mathbf{a})}}{r} \qquad (2.\ 109)$$

$$U^{ex} = -\frac{1}{6k_B T n} \frac{\varepsilon\kappa^2\kappa_D^2 e^{\kappa\mathbf{a}}}{4\pi(1+\kappa\mathbf{a})\beta} \int_a^\infty 4\pi r^3 \left(\frac{1}{4\pi\varepsilon r^2}\right) \frac{e^{-\kappa r}}{r} dr. \qquad (2.\ 110)$$

Evaluation of the integral leads to an expression for the excess free energy

$$U^{ex} = -\frac{\kappa\kappa_D^2}{24\pi n\beta(1+\kappa \mathbf{a})}. \qquad (2.\ 111)$$

Substituting this terms into the osmotic coefficient expression it can be obtained as

$$\Phi = 1 + \frac{2\pi n \mathbf{a}^3}{3} - \frac{\kappa\kappa_D^2}{24\pi n\beta(1+\kappa \mathbf{a})}. \qquad (2.\ 112)$$

For 1:1 electrolytes can be expresed as

$$\Phi = 1 + \frac{2\pi n \mathbf{a}^3}{3} - \frac{e^2}{24\pi\varepsilon k_B T}\frac{\kappa}{1+\kappa \mathbf{a}}. \qquad (2.\ 113)$$

Substituting Eq.(2.98) into Eq.(2.115), it can be expressed as

$$\Phi = 1 + \frac{4\pi N 10^3 c\mathbf{a}^3}{3} - \frac{e^2}{24\pi\varepsilon \mathbf{a} k_B T}[0.33dc^{1/2}$$

$$- 0.098\mathbf{a}^2 c + 0.0179\mathbf{a}^3 c^{3/2} - 0.0013\mathbf{a}^4 c^2] \qquad (2.\ 114)$$

where N_A is the Avogadro constant, **a** is in the unit of Angstrom. In Fig.2.3, this osmotic coefficient relation is compared with experimental data of NaCl

for a = 3.55 $\mathring{A}$, which is the ion-size or (fitting) parameter calculated from the equivalent conductance equation.

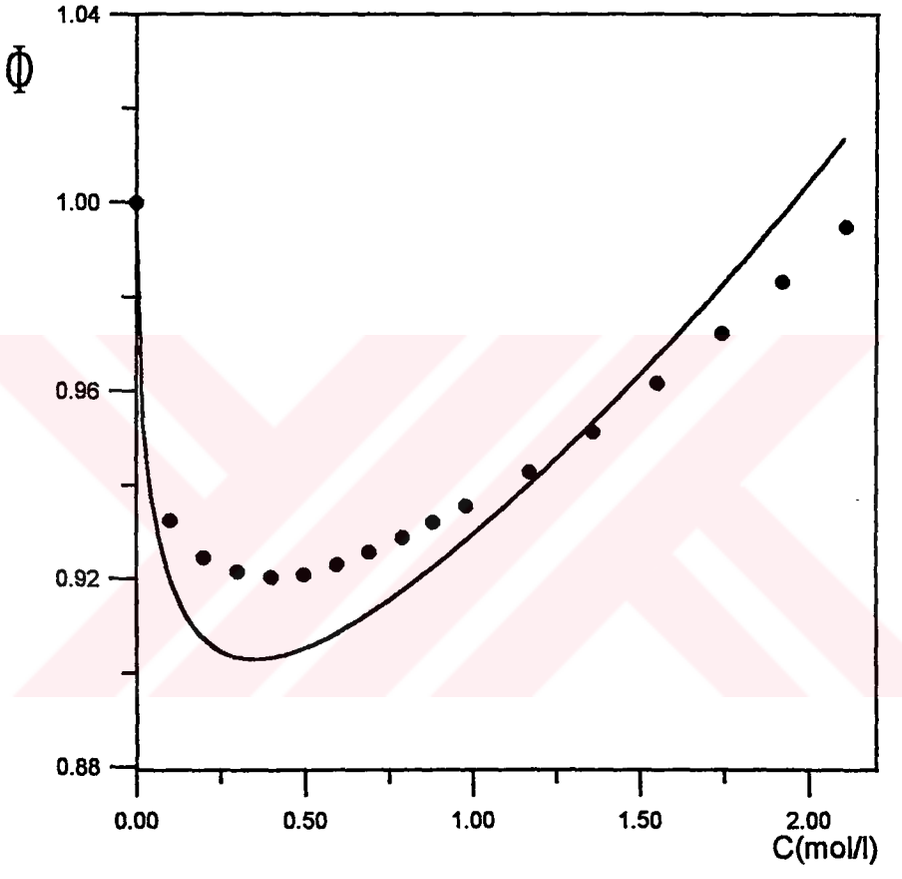

Fig.2.3 The osmotic coefficient of NaCl versus concentration at T=293K.

To calculate mean activity coefficient of 1:1 electrolytes, the relation between the mean activity coefficient and the osmotic coefficient given by

Eq.(2.115) is going to be used [37],

$$\mathbf{d}[C(1-\Phi)] + C\mathbf{d}\ln\gamma_{\pm} = 0. \qquad (2.\ 115)$$

In the above differential equation, temperature T and solvent chemical potential μ are kept constant. The solution of above differential equation can be written as

$$\ln\gamma_{\pm} = -(1-\Phi) - \int \frac{1-\Phi}{C} dC. \qquad (2.\ 116)$$

Substituting osmotic coefficient relation into Eq.(2.116), $\ln\gamma_{\pm}$ can be expressed in terms of concentration C as

$$\ln\gamma_{\pm} = \frac{q^2}{24\pi\varepsilon dk_B T}[0.99\mathbf{a}c^{1/2} - 0.196\mathbf{a}^2 c + 0.298\mathbf{a}^3 c^{3/2}$$

$$- 0.00195a^4c^2] + \frac{4N_A 10^3 \mathbf{a}^3 2\pi}{3} c. \qquad (2.\ 117)$$

This activity coefficient relation is compared with experimental data of NaCl

for the same fitting parameter **a** = 3.55 $\mathring{A}$ and plotted in Fig.2.4.

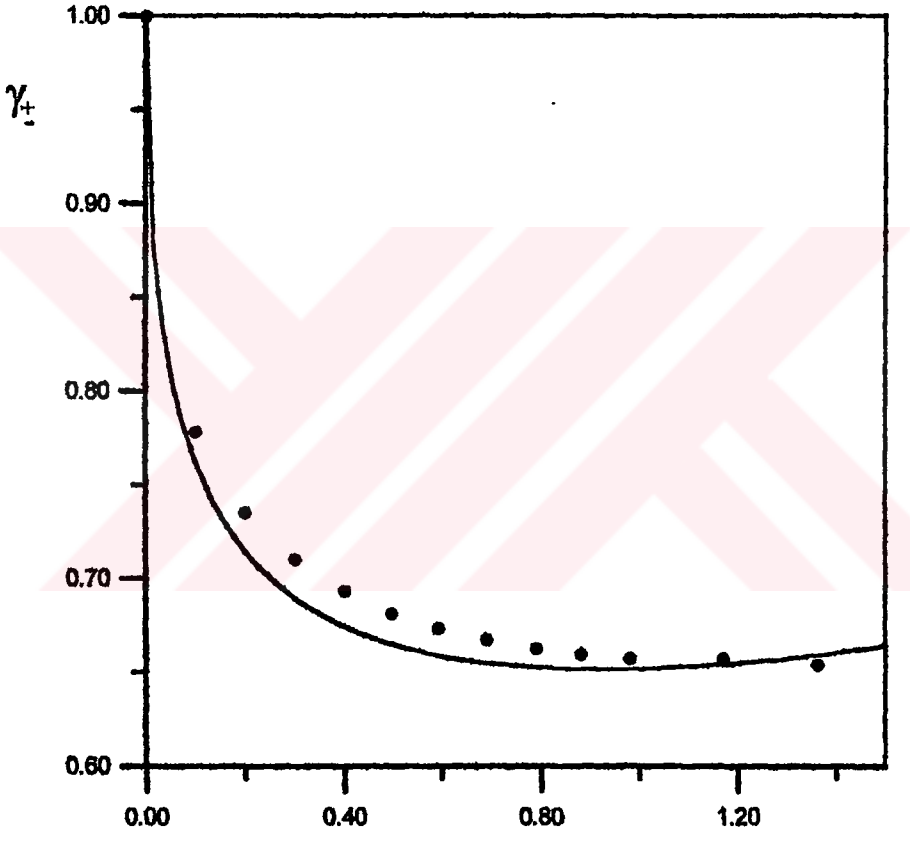

Fig.2.4 The activity coefficient of NaCl versus concentration at T=293K.

3 SEMIQUANTITATIVE MEAN-FIELD APPROACH

In the second section Stillinger second moment condition based mean-field theory in the restricted primitive model of electrolytes (hard sphere of diameter **a** carrying electric charge $\pm q$) was developed in the sense of (DH) approach. From purely experimental point of view, it may simple interpreted as a mean field theory which predicts experimental data of 1:1 electrolytes within a satisfactory accuracy up to $1 mol/l$. From purely theoretical point of view, however, it may be either claimed that it is second moment condition supplemented mean field theory, and it may have some merits, or it is just a modified (DH) theory carrying the same merits and ambiguities as in the other modified (DH) type theories. As it is going to be shown in the fourth section, further specific physical consideration must be introduced in the outset of treatment in order to find a fully reasonable account for the correction of the ambiguities. This means a major change of the conventional mean-field treatment of electrolytes. In this section, however, the same mean- field approach introduced in the second section is going to be employed to explain the properties of electrolytes in terms of fully well-defined parameters of the system. In addition, the relaxation field, which is the most involved part of the theory of electrolytes, is going to be calculated by the Green's function method since the series solution has some inevitable deficiency which may

obscure the quality of the mean field treatment in section one.

3.1 Solution Of Relaxation Field By Green's Function Method

In section two a general differential equation was derived to solve the relaxation field from Onsager equation of continuity as

$$\nabla^2[\nabla^2 - \frac{q_2^2 n_2 w_2 + q_1^2 n_1 w_1}{\varepsilon n_1 k_B T(w_1 + w_2)}]\Psi_1' = -\frac{(q_2^2 w_2 - q_1 q_2 w_1)E}{\varepsilon n_1 k_B T(w_1 + w_2)}\frac{\partial f_{12}}{\partial x}. \qquad (3.\ 1)$$

If the definition of $f_{12} = n_1 n_2 g_{12}$ is recalled and the expression of g_{12} is cited from section two

$$g_{12} = 1 - \frac{q_1 q_2}{4\pi\varepsilon k_B T(1+\kappa a)}\frac{\kappa^2}{\kappa_D^2}\frac{e^{-\kappa(r-a)}}{r}. \qquad (3.\ 2)$$

Eq.(3.1) turns out to be

$$\nabla^2[\nabla^2 - \frac{q_2^2 n_2 w_2 + q_1^2 n_1 w_1}{\varepsilon n_1 k_B T(w_1 + w_2)}]\Psi_1' = \frac{(q_2^2 w_2 - q_1 q_2 w_1)E}{\varepsilon n_1 k_B T(w_1 + w_2)}\frac{\partial}{\partial x}\frac{e^{-\kappa r}}{r}. \qquad (3.\ 3)$$

Since our purpose to solve this equation for the two component electrolytes in general case it may be useful to redefine the parameters of the equation by the following manner

$$\kappa_1^2 = \frac{q_2^2 n_2 w_2 + q_1^2 n_1 w_1}{\varepsilon k_B T(w_1 + w_2)}. \qquad (3.\ 4)$$

If this expression is divided and multiplied by $(q_1 - q_2)$ and also if the charge neutrality condition is recalled it can be written as

$$\kappa_1^2 = \frac{(q_1 w_1 - q_2 w_2)}{(q_1 - q_2)(w_1 + w_2)} \kappa_D^2. \tag{3. 5}$$

If κ_1^2 is redefined as $\kappa_1^2 = R\kappa_D$, where R is equal to

$$R = \frac{(q_1 w_1 - q_2 w_2)}{(q_1 - q_2)(w_1 + w_2)} \tag{3. 6}$$

the parameters in the right of the equation can also be simplified as

$$\frac{(q_2^2 w_2 - q_2 q_1 w_1) n_2 q_1 q_2}{(\varepsilon k_B T)^2 (w_1 + w_2)} = \frac{q_1 q_2}{\varepsilon k_B T} \kappa_1^2. \tag{3. 7}$$

So thus the differential equation can be expressed as

$$\nabla^2 [\nabla^2 - \kappa_1^2] \Psi_1' = \Gamma \frac{\partial}{\partial x} \frac{e^{-\kappa r}}{r} \tag{3. 8}$$

where Γ is equal to

$$\Gamma = \frac{q_1 q_2 \kappa_1^2}{\varepsilon k_B T} \frac{\kappa^2 e^{\kappa \mathbf{a}} E}{4\pi (1 + \kappa \mathbf{a}) \kappa_D^2}. \tag{3. 9}$$

The differential equation can also written as

$$\nabla^2[\nabla^2 + (i\kappa_1)^2]\psi_1' = \Gamma\frac{\partial}{\partial x}\frac{e^{-\kappa r}}{r}. \qquad (3.\ 10)$$

If a Green's function is obtained for the above differential equation, then it may lead to more rigorous solution than the series method used in section two.

The Green's function must satify the following equation

$$\nabla^2[\nabla^2 + (i\kappa_1)^2]G(\vec{r_1}, \vec{r_2}) = -\delta(\vec{r_1}, \vec{r_2}). \qquad (3.\ 11)$$

If a solution of the equation is obtained, then it also leads to the solution of Ψ_1' as

$$\Psi_1'(r) = -\int G(\vec{r}, \vec{r_1})\Gamma\frac{\partial}{\partial x_1}\frac{e^{-\kappa r_1}}{r_1}dr_1. \qquad (3.\ 12)$$

Since ∇^2 and $(\nabla^2 + (i\kappa_1)^2)$ are commute then Eq.(3.11) can also be written as

$$[\nabla^2 + (i\kappa_1)^2]\nabla^2 G(\vec{r_1}, \vec{r_2}) = -\delta(\vec{r_1}, \vec{r_2}). \qquad (3.\ 13)$$

If f is defined as

$$\nabla^2 G(\vec{r_1}, \vec{r_2}) = f(\vec{r_1}, \vec{r_2}) \qquad (3.\ 14)$$

then the equation can be written as

$$[\nabla^2 + (i\kappa_1)^2] f(\vec{r}_1, \vec{r}_2) = -\delta(\vec{r}_1, \vec{r}_2). \tag{3. 15}$$

The solution of the equation can readily be obtained [40]

$$f(\vec{r}_1, \vec{r}_2) = \frac{e^{-\kappa_1 |\vec{r}_1 - \vec{r}_2|}}{4\pi |\vec{r}_1 - \vec{r}_2|}. \tag{3. 16}$$

Thus Eq.(3.14) becomes

$$\nabla^2 G(\vec{r}_1, \vec{r}_2) = \frac{e^{-\kappa_1 |\vec{r}_1 - \vec{r}_2|}}{4\pi |\vec{r}_1 - \vec{r}_2|}. \tag{3. 17}$$

If $|\vec{r}_1 - \vec{r}_2| = r$ defined and $G(\vec{r}_1, \vec{r}_2) = G(r)$ is assumed due to the symmetry of the problem then divergence theorem can be a useful consideration to find the Green's function. So thus defining $\vec{A} = \nabla G$

$$\int \vec{A} d\vec{S} = \int div \vec{A} dV = \int \nabla^2 G dV \tag{3. 18}$$

leads to the following equation

$$\int \vec{A} d\vec{S} = \int_0^r \frac{e^{-\kappa_1 r'}}{4\pi r'} 4\pi (r')^2 dr'. \tag{3. 19}$$

Due to the spherical symmetry the above equation can be solved as

$$4\pi A r^2 = -e^{\kappa_1 r'}(\frac{r'}{\kappa_1} + \frac{1}{\kappa_1^2})|_0^r. \tag{3. 20}$$

Thus A can be obtained as

$$A = \frac{1}{4\pi r^2}[e^{\kappa_1 r}(\frac{r}{\kappa_1} + \frac{1}{\kappa_1^2}) - \frac{1}{\kappa_1^2}]. \tag{3. 21}$$

From the definition of A, G can be written as

$$G(r) = \int A dr. \tag{3. 22}$$

If the result for A is substituted in this integral, one can readily obtain the following relation

$$G(r) = \int \frac{1}{4\pi r^2}[e^{\kappa_1 r}(\frac{r}{\kappa_1} + \frac{1}{\kappa_1^2}) - \frac{1}{\kappa_1^2}]dr. \tag{3. 23}$$

If separate terms of the integral are evaluated as

$$\int \frac{dr}{r} e^{-\kappa_1 r} = Ei(-\kappa_1 r) \tag{3. 24}$$

$$\int \frac{dr}{r^2} e^{-\kappa_1 r} = -\frac{e^{-\kappa_1 r}}{r} - \kappa Ei(-\kappa_1 r). \tag{3. 25}$$

$G(R)$ can be obtained as

$$G(r) = \frac{1}{4\pi\kappa_1^2}(\frac{1}{r} - \frac{e^{-\kappa_1 r}}{r}). \tag{3. 26}$$

Thus $G(\vec{r}, \vec{r}_1)$ can be expressed as

$$G(\vec{r}, \vec{r}_1) = \frac{1}{4\pi\kappa_1^2}[\frac{1}{|\vec{r} - \vec{r}_1|} - \frac{e^{-\kappa_1|\vec{r}-\vec{r}_1|}}{|\vec{r} - \vec{r}_1|}]. \tag{3. 27}$$

Using this relation leads to a solution for Ψ_1' as

$$\Psi_1' = \Gamma \int G(\vec{r}, \vec{r}_1)\frac{\partial}{\partial x_1}(\frac{e^{-\kappa r_1}}{r_1})d\vec{r}_1. \tag{3. 28}$$

Substituting the Green's function in this integral leads to

$$\Psi_1' = \Gamma' \int [\frac{1}{|\vec{r} - \vec{r}_1|} - \frac{e^{-\kappa_1|\vec{r}-\vec{r}_1|}}{|\vec{r} - \vec{r}_1|}]\frac{\partial}{\partial x_1}(\frac{e^{-\kappa r_1}}{r_1})d\vec{r}_1 \tag{3. 29}$$

where Γ' is equal to

$$\Gamma' = \frac{1}{4\pi\kappa_1^2}\Gamma. \tag{3. 30}$$

Our aim to find a solution for $r < \mathbf{a}$. Since we know that $r < \mathbf{a} < r_1$, the

term $|\vec{r}-\vec{r}_1|$ can be approximated to the following relation.

$$|\vec{r}-\vec{r}_1| = r_1[1+(\frac{r}{r_1})^2 - \frac{2r}{r_1}Cos\gamma]^{1/2} \simeq r_1(1-\frac{r}{r_1}Cos\gamma) \qquad (3.\ 31)$$

where $Cos\gamma$ is equal to

$$Cos\gamma = Cos\theta Cos\theta_1 + Sin\theta Sin\theta_1 Cos(\phi-\phi_1). \qquad (3.\ 32)$$

Using the relation $x_1 = r_1 Sin\theta_1 Cos\phi_1$, then the derivative can be expressed as

$$\frac{d}{dx_1} = Sin\theta_1 Cos\phi_1 \frac{d}{dr_1}. \qquad (3.\ 33)$$

Using this relation in the above integral leads to

$$\Psi_1' = -\Gamma' \int \frac{1}{r_1(1-\frac{r}{r_1}Cos\gamma)}[1-e^{-\kappa_1 r_1(1-\frac{r}{r_1}Cos\gamma)}]Sin\theta_1 Cos\phi_1$$

$$[\frac{(1+\kappa r_1)}{r_1^2}e^{-\kappa r_1}]r_1^2 Sin\theta_1 d\theta_1 d\phi_1 dr_1. \qquad (3.\ 34)$$

Since the solution of the integral around $r << \mathbf{a}$ is sufficient to obtain the relaxation field around $r = 0$, the integral is going to be evaluated under this condition. Thus the integral can be written as

$$\Psi_1' = -\Gamma' \int \frac{(1+\frac{r}{r_1}Cos\gamma)}{\kappa_1^2 r_1}[1-e^{-\kappa_1 r_1}(1+\kappa_1 r Cos\gamma)]$$

$$(1+\kappa r_1)e^{-\kappa r_1}Sin^2\theta_1 Cos\phi_1 d\theta_1 d\phi_1 dr_1. \qquad (3.\ 35)$$

Keeping only the terms order of r, the following expression can be approximated as

$$(1+\frac{r}{r_1}Cos\gamma)[1-e^{-\kappa_1 r_1}(1+\kappa_1 r Cos\gamma)](1+\kappa r_1)e^{-\kappa r_1}$$

$$\simeq [(1-e^{-\kappa_1 r_1}(1+\kappa_1 r Cos\gamma)+\frac{r}{r_1}Cos\gamma-\frac{r}{r_1}e^{-\kappa_1 r_1}Cos\gamma](1+\kappa r_1) \qquad (3.\ 36)$$

$$=(1-e^{-\kappa_1 r_1})(1+\kappa r_1)+(1+\kappa r_1)Cos\gamma[\frac{r}{r_1}(1-e^{-\kappa_1 r_1})-\kappa_1 r e^{-\kappa_1 r_1}].$$

Substituting this final form into the integral, it becomes

$$\Psi_1' = \Gamma' \int \frac{1}{r_1}[(1-e^{-\kappa_1 r_1})(1+\kappa r_1)+(1+\kappa r_1)Cos\gamma$$

$$[\frac{r}{r_1}(1-e^{-\kappa_1 r_1})-\kappa_1 r e^{-\kappa_1 r_1}]Sin^2\theta_1 Cos\phi_1 d\theta_1 d\phi_1 dr_1. \qquad (3.\ 37)$$

The integration over θ and ϕ can be evaluated as follows

$$I_1 = \int Sin^2\theta_1 Cos\phi_1 d\theta_1 d\phi_1 = 0 \qquad (3.\ 38)$$

$$I_2 = \int Sin^2\theta_1 Cos\phi_1 Cos\gamma d\theta_1 d\phi_1 \qquad (3.\ 39)$$

where $Cos\gamma$ is equal to

$$Cos\gamma = Cos\theta Cos\theta_1 + Sin\theta Sin\theta_1(Cos\phi Cos\phi_1 + Sin\phi Sin\phi_1). \quad (3.\ 40)$$

Thus I_2 can be written as

$$I_2 = \int Sin^3\theta_1 Cos\phi_1 Sin\theta(Cos\phi Cos\phi_1 + Sin\phi Sin\phi_1)d\theta_1 d\phi_1. \quad (3.\ 41)$$

Rearranging the integral leads to

$$I_2 = Sin\theta Cos\phi \int Sin^3\theta_1 Cos^2\phi_1 d\theta_1 d\phi_1$$

$$+ Sin\theta Sin\phi \int Sin^3\theta_1 Cos\phi_1 Sin\phi_1 d\theta_1 d\phi_1. \quad (3.\ 42)$$

Evaluation of the following integral

$$\int_0^{\pi} Sin^3\theta_1 d\theta_1 = \frac{4}{3} \quad (3.\ 43)$$

$$\int_0^{2\pi} Cos^2\phi_1 d\phi_1 = \pi \quad (3.\ 44)$$

leads to

$$I_2 = \frac{4\pi}{3}. \quad (3.\ 45)$$

Thus Ψ_1' becomes

$$\Psi_1' = \frac{4\pi}{3}\Gamma' \int \frac{e^{-\kappa r_1}}{r_1^2}(1+\kappa r_1)[1-e^{-\kappa_1 r_1}-\kappa_1 r_1 e^{-\kappa_1 r_1}]dr_1. \qquad (3.\ 46)$$

Separating the integral as

$$I_1 = \int_a^\infty \frac{e^{-\kappa_1 r_1}}{r_1^2}[1-e^{-\kappa_1 r_1}-\kappa_1 r_1 e^{-\kappa_1 r_1}]dr_1 \qquad (3.\ 47)$$

$$I_2 = \kappa \int_a^\infty \frac{e^{-\kappa_1 r_1}}{r_1}[1-e^{-\kappa_1 r_1}-\kappa_1 r_1 e^{-\kappa_1 r_1}]dr_1. \qquad (3.\ 48)$$

The solution of the integrals in terms of exponential integral functions as

$$I_1 = \frac{e^{-\kappa \mathbf{a}}}{\mathbf{a}} + \kappa Ei(-\kappa \mathbf{a}) - \frac{e^{-(\kappa-\kappa_1)\mathbf{a}}}{\mathbf{a}} - (\kappa+\kappa_1)Ei(-(\kappa+\kappa_1)\mathbf{a}) + \kappa_1 Ei(-(\kappa+\kappa_1)\mathbf{a}) \qquad (3.\ 49)$$

$$I_2 = -\kappa Ei(-\kappa \mathbf{a}) + \kappa Ei(-(\kappa+\kappa_1)\mathbf{a}) - \frac{\kappa\kappa_1}{\kappa+\kappa_1}e^{-(\kappa+\kappa_1)\mathbf{a}}. \qquad (3.\ 50)$$

Since the solution of Ψ_1' is equal to

$$\Psi_1' = \frac{4\pi}{3} r Sin\theta Cos\phi \Gamma'(I_1+I_2). \qquad (3.\ 51)$$

substituting I_1 and I_2 in this relation leads to

$$\Psi_1' = \frac{4\pi}{3}\Gamma' r Sin\theta Cos\phi[\frac{e^{-\kappa \mathbf{a}}}{\mathbf{a}} - \frac{e^{-(\kappa+\kappa_1)\mathbf{a}}}{\mathbf{a}} - \frac{\kappa\kappa_1}{\kappa+\kappa_1}e^{-(\kappa+\kappa_1)\mathbf{a}}] \qquad (3.\ 52)$$

Derivation of Ψ_1' with respect to x leads to an expression for the relaxation field $E'(0)$. Since $x = rSin\theta Cos\phi$, the derivation can be taken readily and the result can be expressed as

$$E'(0) = \frac{4\pi}{3}\Gamma'[\frac{e^{-\kappa \mathbf{a}}}{\mathbf{a}} - \frac{e^{-(\kappa+\kappa_1)\mathbf{a}}}{\mathbf{a}} - \frac{\kappa\kappa_1}{\kappa+\kappa_1}e^{-(\kappa+\kappa_1)\mathbf{a}}]. \qquad (3.\ 53)$$

Substituting Γ' in this relation leads to

$$E'(0) = \frac{|z_1||z_2|e^2E}{12\pi\varepsilon k_B T(1+\kappa \mathbf{a})}\frac{\kappa^2}{\kappa_D^2}[\frac{1}{\mathbf{a}} - \frac{e^{-\kappa_1 \mathbf{a}}}{\mathbf{a}} - \frac{\kappa_1\kappa}{\kappa+\kappa_1}e^{-\kappa_1 \mathbf{a}}]. \qquad (3.\ 54)$$

Substituting this result into the equivalent conductivity formula, Eq.(2.95) together with Eq.(2.86), derived in the second section leads to

$$\Lambda = \Lambda^0[1 - [\frac{|z_1||z_2|e^2}{12\pi\varepsilon k_B T(1+\kappa \mathbf{a})}\frac{\kappa^2}{\kappa_D^2}(\frac{1}{\mathbf{a}} - \frac{e^{-\kappa_1 \mathbf{a}}}{\mathbf{a}} - \frac{\kappa_1\kappa}{\kappa+\kappa_1}e^{-\kappa_1 \mathbf{a}})$$

$$+ \frac{e^2 N_A \kappa}{\Lambda^0 6\pi\eta_s(1+\kappa \mathbf{a})}(|z_1|+|z_2|)]]. \qquad (3.\ 55)$$

The series solution treatment of the second section have produced the relaxation field in the form of infinite series, of which only the first few terms

have been kept in the equivalent conductivity formula, within the interested concentration range. That is why, without giving any further physical justification the series solution seems somewhat ambigous. The Green's function solution, however, produced a compact relaxation field expression. This compactness may be considered as a significant contribution to the theory of electrolytes if it is compared to the others works [38,39]. In addition, the differential equation has been solved without introducing any further assumption on the form of relaxation potential. Thus, if the unknown parameter η is obtained, one can compare the agreement of the formula with the experimental equivalent conductivity data. For this purpose, the following procedure is going to be taken.

If the obtained equivalent conductivity written for $\kappa \mathbf{a} << 1$, it can be expressed as

$$\Lambda = \Lambda^0[1 - [\frac{|z_1||z_2|e^2}{12\pi\epsilon k_B T}\frac{\kappa^2}{\kappa_D^2}(\frac{\kappa_1^2}{\kappa+\kappa_1} + \kappa\kappa_1\mathbf{a}) + \frac{e^2 N_A \kappa}{\Lambda^0 6\pi\eta_s}(|z_1| + |z_2|)]]. \quad (3.\ 56)$$

At very extremely low concentration the term $\kappa\kappa_1\mathbf{a}$ can also omitted without loosing the generality. Thus, in this case its form turns out to be exactly the same as Onsager equivalent conductivity formula. Thus the equivalent conductivity relation derived in this section satisfy the most important criterion.

At this point I think it is worth to mention that the only difference between the Onsager's equivalent conductivity and our result is the replacement of κ_D by κ at this limiting case. Thus, since we know that the usual DH theory is excellent at very low concentrations one can readily see that $\kappa \rightarrow \kappa_D$

at very dilute concentration.

Since the main concern of this section is to formulate a mean field theory with well-defined parameters of the system, the distance of closed approach parameter **a** is going to be interpreted as the sum of the crystollagraphic ionic radii, manifested by X ray diffraction, instead of assigning arbitrary values.

With those consideration one can readily obtain the η by just comparing the equivalent conductivity expression with experiment. For this purpose, one has to propose an expression for η. From the above discussion, one can only expect that η depends on ionic concentration and the values of ionic charges of the system. If the limiting behaviour of κ, that is, $\kappa \rightarrow \kappa_D$ at very low concentrations, is also considered, one might find the following expression for κ as a plausible form

$$\kappa = \kappa_D e^{-b(\kappa_D)^{(1/4)}}. \qquad (3.\ 57)$$

From experiments, the values of b have been obtained as 0.2 for all 1:1 electrolytes and 0.75 for all 2:1 electrolytes. With these values κ are also turned out to be well-defined expressions for the electrolytes systems.

From purely theoretical point of view, although the determination of κ from the experiments might be considered as a somewhat ambigous approach, there is no fundamental theoretical consideration to calculate κ from the theory in this section but just comparisons with experiment. This approach have also used in many works with two or three adjustable parameters[41-43]. Notice that, in section two, however, κ was determined by the use of Stillinger's second moment condition. That is why, the theoretical treatment restricted to the 1:1 electrolyte systems with a adjustable ion-size parameter.

The most interesting difference between these two different approaches is that the κ determined from Stillinger second moment condition increases faster than κ_D with increasing concentration while determination of κ from the experiments shows that κ increases slower than κ_D with increasing concentration. These two opposite predictions might be, of course, due to the different physical consideration employed in the derivation of Stillinger second moment condition, namely total associations of the ions. Apparently, the total association consideration does not work for dynamic properties of strong electrolyte sytem as it was thought to be for thermodynamic properties of electrolyte systems [13,14].

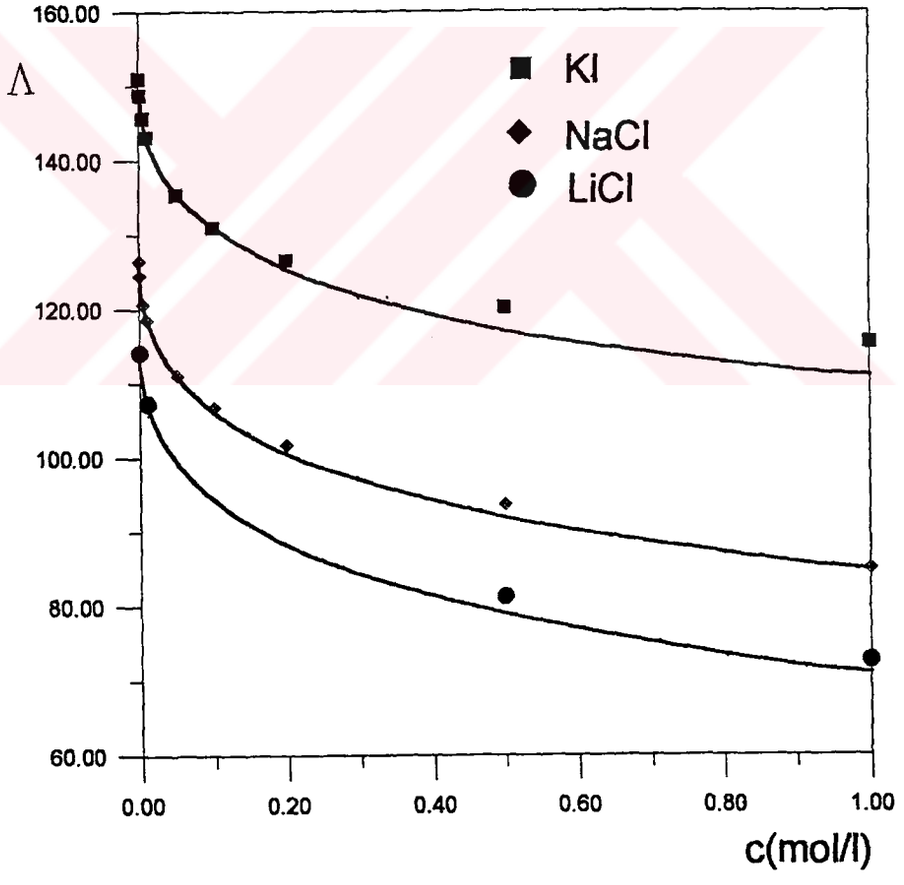

Fig.3.1 The equivalent conductivities of NaCl, KI, LiCl versus concentration at T=293K for ion-sizes equal to 2.89, 3.36, 2.41 respectively.

With these experimentally determined κ, the equivalent conductivity formula can be compared with experimental data. The results are plotted in Fig.3.1 for 1:1 electrolytes and in Fig.3.2 for 1:2 electrolytes. As seen from the figures the agreement are quite good. One may not expect better agreement from any mean field theory formulated with a single adjustable parameters [41-43]. In addition, the parameter are same for all the elements of the electrolyte system. That is, it just depends on electrolyte system such as 1:1 and 2:1. This property can also considered as an precious result if the cited works are considered [41-43].

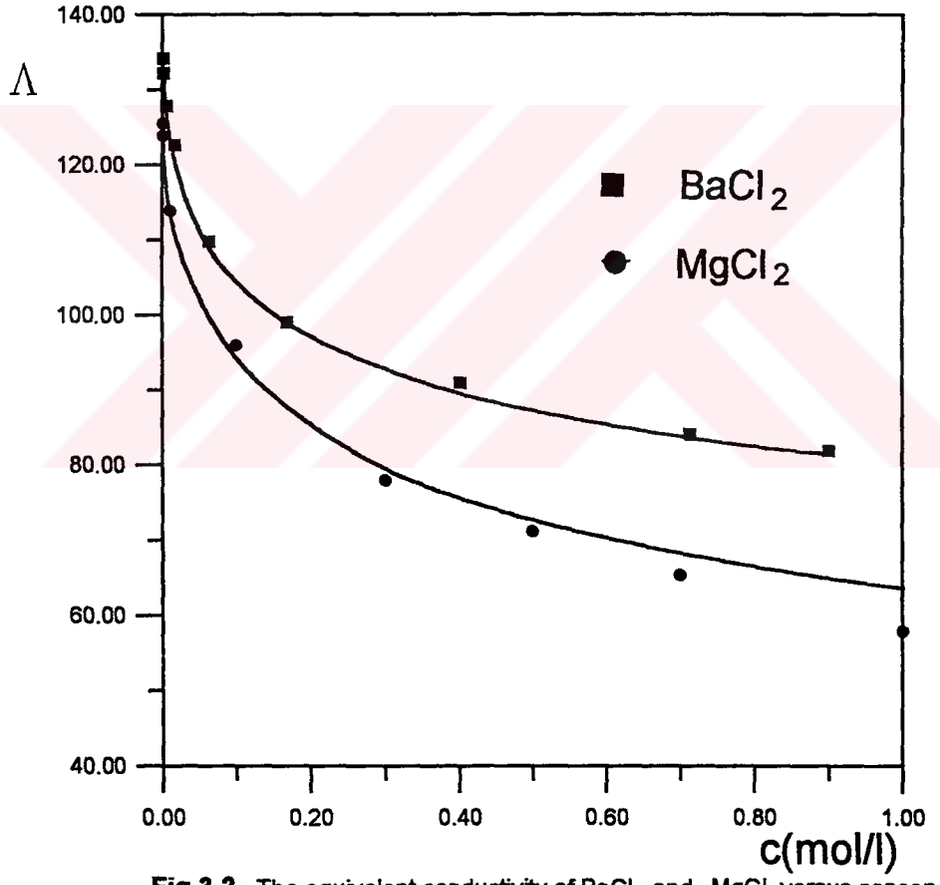

Fig.3.2 The equivelent conductivity of $BaCl_2$ and $MgCl_2$versus concentration for ion-sizes 3.16 and 2.46 in angstroms respectively

3.2 Application To The Thermodynamic Properties

In the treatment of thermodynamic properties of electrolytes in this section, we also use the pressure equation (or the virial equation) as in the first section due to its applicational simplicity since we already know the radial correlation functions in mean-field sense. Of course, without lack of the knowledge of the correlation functions, the simplification would be only apparent, because the difficulty would have been shifted to that of determining the correlation function. It would not be, however, an easy task to perform analytically. So thus the analytical treatment of properties of electrolytes would be imposssible. The problem would have been even more complicated if the pair potential was not assumed as spherically symmetric Coulomb potential. Luckily, the mean field treatment produces spherically symmetric correlation functions from outset in a simple manner. Thus the only thing, one has to worry about is the calculation of the following pressure expression

$$P = k_B T n - \frac{1}{6}\sum_{i,j} n_i n_j \int 4\pi r^3 \frac{du_{ij}}{dr} g_{ij}(r) dr. \qquad (3.\ 58)$$

This osmotic pressure formula leads to the same osmotic coefficient expression as in the first section since the form of the correlation functions are same. Thus the osmotic pressure expression can be written as

$$\Phi = 1 + \frac{2\pi n \mathbf{a}^3}{3} - \frac{e^2}{24\pi\epsilon k_B T}\frac{\kappa}{1+\kappa\mathbf{a}}. \qquad (3.\ 59)$$

As far as the treatment of thermodynamic properties is concerned, the only difference between the osmotic pressure expression of this section and that of the last section is the replacement of the κ_D by $\kappa^2 = \eta\kappa_D^2$. Making use

of the values of b obtained from in the treatment of equivalent conductivity, the expression has been compared with experimental data. In Fig.3.3, some 1:1 electrolytes are compared with experimental data.

The activity coefficient in this chapter is also going to be calculated from the interrelation between osmotic pressure coefficient and activity coefficient. From the section two, it can be written as

$$ln\gamma\pm = -(1-\Phi) - \int \frac{1-\Phi}{c} dc. \qquad (3.\ 60)$$

If the obtained κ is substituted into osmotic coefficient expression it can be written for 1:1 electrolyte solutions as

$$\Phi = 1 + \frac{4\pi N_A c a^3}{3} - \frac{e^2}{24\pi\varepsilon k_B T} \frac{\kappa_D e^{-0.2\kappa_D^{1/4}}}{1 + a\kappa_D e^{-0.2\kappa_D^{1/4}}}. \qquad (3.\ 61)$$

For the sake of simplicity, the last term is going to be approximated so that the integral can be evaluated without further complications. The following approximation can be considered as a fairly good for this purpose

$$\frac{\kappa_D e^{-0.2\kappa_D^{1/4}}}{1 + a\kappa_D e^{-0.2\kappa_D^{1/4}}} \simeq \frac{\kappa_D(1 - 0.2\kappa_D^{1/4})}{1 + a\kappa_D(1 - 0.2\kappa_D^{1/4})} \simeq 0.33c^{1/2}(1 - 0.17ac^{1/4}). \qquad (3.\ 62)$$

Now, the integral can be calculated readily. The result for the activity coefficient can then obtained as

$$ln\gamma\pm = 2\frac{4\pi N_A c a^3}{3} - \frac{e^2}{24\pi\varepsilon k_B T}[0.33c^{-1/2}(1 - 0.17ac^{1/4}) + 0.66c^{1/2} - 0.06ac^{3/4}] \qquad (3.\ 63)$$

The above activity coefficient expression can also be compared with the experimental data. The result have been plotted in fig.3.4.

In the treatment of thermodynamics, κ can be considered as a well-defined parameter since the values of b were obtained from independent experiment, that is, from equivalent conductivity. Since the values of ion-size parameter were also taken from X ray diffraction experiments, the osmatic pressure expression can also considered as well-defined. With this property, the agreement of the osmotic coefficient expression to the experimental data can be considered as a fairly good.

Since for many years, discussion of the thermodynamic properties of electrolyte solution has been dominated by the conventional treatment of DH theory and by the modification of it instead of virial coefficient expansions method, it can be worthwhile if our mean field treatment are considered with the theoretical approaches of the conventional treatment of the electrolyte solutions.

3.3 Conventional Treatment Of Thermodynamic Properties

Conventionally, the thermodynamics of ionic solution are handled by imaginary charging processes from which the energy of creating an ion in the solvent can be calculated. The most common of them is generally known as the Guntelberg charging process in recognition of its originator. In this process, the central ion j is assumed to be in a hypothetical condition and the rest of the ions, fully charged, constitute an ionic atmosphere enveloping the charge introduced in the position of the central ion. Thus, the potential is created by the rest of the ions in the ionic atmosphere when the charge $\xi_i q$

is at the center can be expressed as

$$\Phi_j^{atm} = \frac{\xi z_j e}{4\pi\varepsilon r}[\frac{e^{-\kappa(r-a)}}{1+\kappa a} - 1] \tag{3. 64}$$

where ξ is the fractional charge on ion j. The potential for $r < a$ can then be written as

$$\Phi_j^{atm} = -\frac{\xi z_j e}{4\pi\varepsilon}\frac{\kappa}{1+\kappa a}. \tag{3. 65}$$

To bring up an amount of charge $z_j e d\xi_j$ to the ion j, the work done is just the product of the charge and the ion atmosphere potential, $\Phi_j^{atm}(r=0) z_j e d\xi_j$. Therefore, we obtain the work done as

$$W_j = -\int_0^1 \frac{\xi z_j^2 e^2}{4\pi\varepsilon}\frac{\kappa}{1+\kappa a} d\xi = -\frac{z_j^2 e^2}{8\pi\varepsilon}\frac{\kappa}{1+\kappa a}. \tag{3. 66}$$

By definition, the activity coefficient γ_j of the ion j is related to the work done as

$$k_B T ln\gamma_j = W_j. \tag{3. 67}$$

The individual ionic activity coefficient are, however, experimentally inaccessible. Thus, it is necessary to relate the individual ionic activity coefficient to the experimentally accessible mean ionic activity coefficient $\gamma_\pm$ so that the model can be tested. The mean ionic activity coefficient can be expressed as

a combination of the single ion activity coefficients. The result is,

$$ln\gamma_{\pm} = -|z_1 z_2| \frac{e^2 \kappa}{8\pi\varepsilon k_B T(1+\kappa a)}. \quad (3.\ 68)$$

In the limit of zero ion-size, one can readily obtains the following result

$$ln\gamma_{\pm} = -|z_1 z_2| \frac{e^2 \kappa}{8\pi\varepsilon k_B T}. \quad (3.\ 69)$$

Eq.(3.68) is also plotted in Fig.3.4.

In order to obtain an osmotic coefficient expression, the Gibbs-Duhem equation can also considered as a useful frame in conventional treatment. Thus, if water activity is omitted in the Gibbs-Duhem equation it can be solved alternatively [23] as

$$\Phi = 1 + \frac{1}{c}\int c d(ln\gamma_{\pm}). \quad (3.\ 70)$$

If the above approximation, that is,

$$\frac{\kappa}{1+a\kappa} = 0.33c^{1/2}(1 - 0.17ac^{1/4}) \quad (3.\ 71)$$

is also used here, then the term $ln\gamma_{\pm}$ can be calculated as

$$ln\gamma_{\pm} = -\frac{e^2}{8\pi\varepsilon k_B T}[0.165c^{-1/2} - 0.032c^{-1/4}]. \quad (3.\ 72)$$

Thus, the evaluation of the integral leads to the following expression for Φ

$$\Phi = 1 - \frac{e^2}{8\pi\varepsilon k_B T}[0.12c^{1/2} - 0.051c^{3/4}]. \qquad (3.\ 73)$$

The above conventionally derived expression have been compared with experimental data in Fig.3.3.

Since at very small concentrations, $\kappa \rightarrow \kappa_D$ the above expressions, at very small concentration, turn out to be DH limiting laws for mean activity coefficient and Osmotic presure coefficient, which are the outstanding achievement of DH ionic solution theory. As seen from Fig.3.3 and Fig.3.4, in spite of the excellent agreement between the prediction of DH picture and experimental values of corresponding physical properties at sufficiently low concentrations, there is a sharp disagreement at higher concentrations (e.g., $> 0.1 mol/l$). Of course, as seen from the figures, the most sharp disagreement at concentrations around $1 mol/l$, when the activity coefficients and osmotic coefficients begin to increase back toward the value they had in limitingly dilute solution. This sharp disagreement is, however, in agreement with the theoretical expectation of DH picture since only at infinite dilution are the cited assumption of DH theory valid.

In our picture, the behavior of experimental mean activity coefficient have been handled by the discontinuity at hard core potential and mapping the correlation function into linearized picture by the cited assumption. In conventional treatment, however, this apparently anomalous behavior of the activity coefficient has been argued by introducing ion-solvent interaction into the DH theory.

Introducing ion-solvent interaction into the treatment of the problem might be considered as a reasonable approach since, at least, from purely

intuitive point of view, one can imagine that the primitive model might have some short coming to present ion-solvent interaction with a continuum dielectric constant. The primitive model, particularly, may not be true for the short range interaction between ion and solvent. This reasonable consideration, however, have not been introduced rigorously, but the concept of hydration presented by a adjustable parameter, namely the hydration number. The concept of hydration eventually leads to the following expression for activity coefficient

$$ln\gamma_{\pm}^{exp} = ln\gamma_{\pm} - \frac{h}{n} ln a_w - ln[\frac{n_w + \nu - h}{n_w + \nu}]. \qquad (3.\ 74)$$

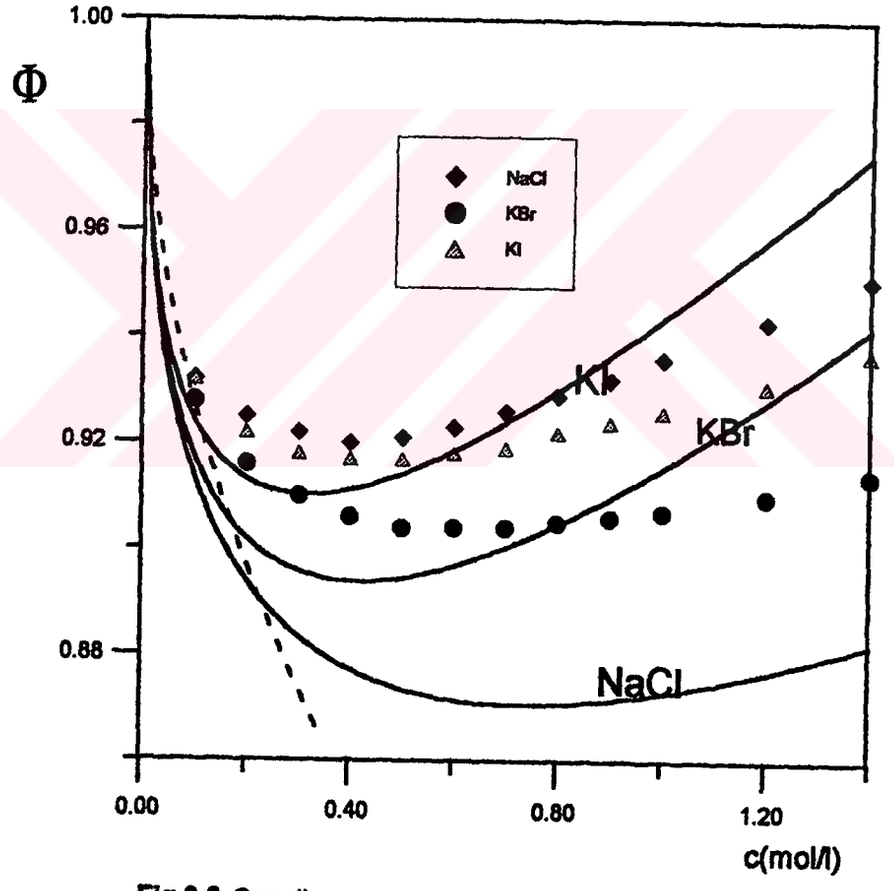

Fig.3.3 Osmatic pressure versus concentration at T=293K.The dashed line shows the (DH) limitin law result.

Here a_w is activity coefficient of water, n_w is mol number of water, n is mol number of the ions. Since the activity coefficient of water can be obtained from independent experiments, the quantity of hydration numbers of electrolytes can be determined from Eq.(3.74) as a adjustable parameter if the ion-size parameter is known. Mostly an experimentally calibrated value of the ion-size parameters are used in conventional treatments. The sum of the crstallographic ionic radii were taken as a ion-size parameter in our treatment as cited a few times.

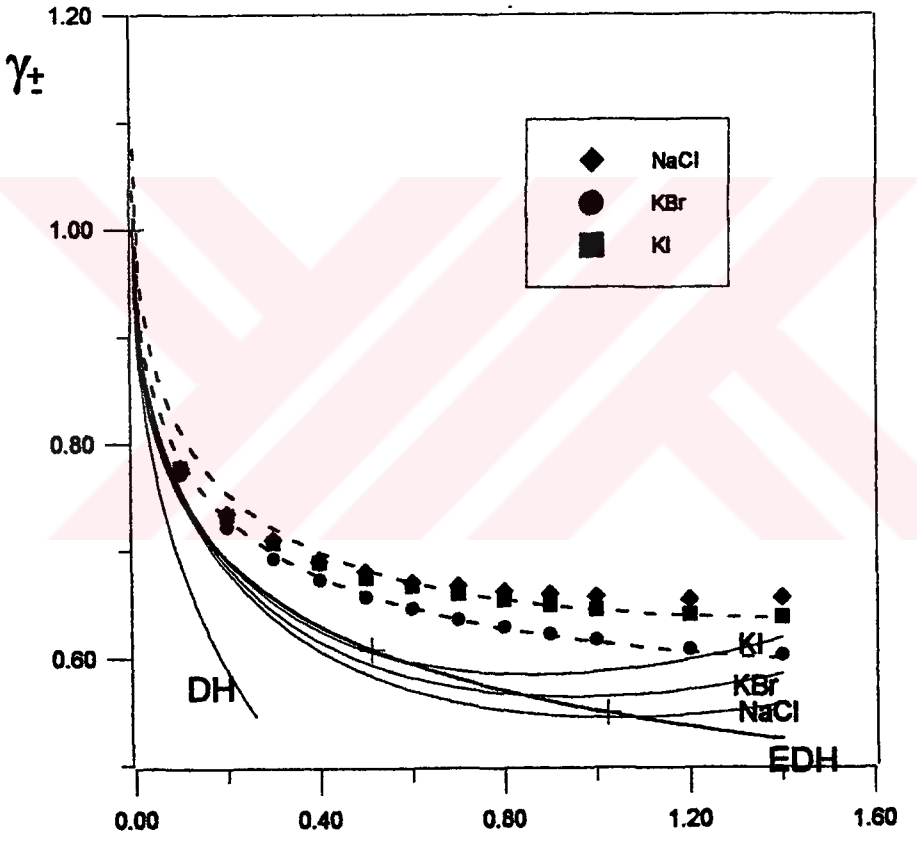

Fig.3.4 The activity coefficients versus concentration at T=293K
The solid lines show the result of Eq.(3.63) and the dashed lines show the results of Eq.(3.74) with hydration numbers 3.8, 1.8, 2.3 for NaCl, KBr and KI respectively.

4 COUNTER CHARGE DENSITY FORMALISM

4.1 Introduction To The Section

Before discussing the alternative mean field theoretical approach which is going to be subject of this section, questioning what really the linearized mean-field approach means seems to be a crucial point. Thus, the following argument can found important. In the mean-field treatment, from the definition of the counter charge density introduced by correlation functions leads to an exponential relation between the counter charge density and potential. However, the principle of the linear superposition of fields merely states that the potential due to two systems of charges in specified position is the sum of the potential due to each system separately. Thus, if all the ionic charges and therefore the counter charge density were multiplied by a factor α, the potential at any chosen point would according to this principle be multiplied by the same factor also. Since the counter charge density depends on the potential exponentially, it is imposible to satisfy the linear superposition principle. In order to satisfy the principle, therefore, the correlation function linearized as

$$g_{ji} = e^{-\beta w_{ji}} = 1 - \beta w_{ji} \qquad (4.\ 1)$$

by simple assuming that $\beta w_{ji} << 1$. Then, one can inquire the validity of

the assumption, that is, wheather βw_{ji} is a lot less than unity or not.

As an example, in usual DH case, the condition is well true at very low concentrations, let say up to $0.01 mol/l$ since the large portion of the counter charge density is laid beyond the average ionic spacing corresponding to $\beta q_i \Psi_j << 1$. As one can easily see, the validity of this condition gets worse if the concentration gets higher. Therefore, the DH theory can be considered as a fundamental law of nature at the very dilute concentration ranges. Thus, the mean field theories constructed by adjustable parameters in order to extend the validity of DH and Onsager limiting laws can be only considered as rounding out character rather than an investigative one.

In our treatments, in section two and three, we take into account this point by just simply introducing the linearizetion process via mapping or modifying DH correlation functions by different physical consideretions. Yet the dilemma is still there and one has to find to a way to treat the ionic solution problem from a more rigorous physical point of view. For this purpose one may find the following discussion more reasonable than the conventional linearized mean field approach.

The mean-field treatment of this section is going to be formulated by assumption that the counter charge density around a particular ion j can be expressed as

$$\rho_j = A\frac{e^{-\kappa r}}{r} \qquad (4.\ 2)$$

up to moderate concentration in the structureless dielectric solvent. Although, it is considered as a strong assumption at first sight, it has already been used in the work of Attard [13-14]. In addition, the works based on numerical solution of integral equation method [18,44-46] supports the form of the counter charge density. One can also see readily from the first two

sections that the form is fully in agreement with the linearized mean-field treatments. Thus, it seems that it is a promising assumption and may have some merits in it.

The parameter A can be easily calculated from the electroneutrality condition as

$$-q_j = 4\pi A \int_a^\infty \frac{e^{-\kappa r}}{r} r^2 dr. \tag{4. 3}$$

The evaluation of the above integral leads to

$$A = -q_j \frac{\kappa^2 e^{\kappa a}}{4\pi(1+\kappa a)}. \tag{4. 4}$$

Substituting A into the charge density relation leads to the following expression

$$\rho_j = -q_j \frac{\kappa^2 e^{\kappa a}}{4\pi(1+\kappa a)} \frac{e^{\kappa r}}{r}. \tag{4. 5}$$

Now, from the definition of the charge density

$$\rho_j = \sum_i n_i q_i g_{ji} \tag{4. 6}$$

one may obtain the correlation functions for using them in the treatment of properties of electrolytes. Writing the charge density for $j = 1$ and $j = 2$,

one can easily obtain the following equations

$$\rho_1 = n_1 q_1 [e^{-\beta w_{11}} - e^{-\beta w_{12}}]. \quad (4.\ 7)$$

$$\rho_2 = n_1 q_1 [e^{-\beta w_{21}} - e^{-\beta w_{22}}]. \quad (4.\ 8)$$

For symmetric electrolytes ($q_1 = -q_2$), These equations lead to $w_{11} = w_{22}$ and $w_{12} = w_{21}$. Due to the symmetry of the problem, one can readily assume that $w_{11} = -w_{12}$ at least for symmetric electrolytes. Making use of these relation leads to

$$\rho_1 = n_1 q_1 [e^{-\beta w_{11}} - e^{\beta w_{11}}]. \quad (4.\ 9)$$

Thus, the following relation can be easily obtained

$$\beta w_{11} = ArcSinh(\frac{\rho_1}{-2n_1 q_1}). \quad (4.\ 10)$$

Since the relation

$$ArcSinh(x) = ln(x + (1 + x^2)^{1/2}) \quad (4.\ 11)$$

is true for all x, one can readily obtain g_{11} as

$$g_{11} = e^{-\beta w_{11}} = e^{-ln[\frac{-\rho_1}{2n_1 q_1} + (1 + (\frac{-\rho_1}{2n_1 q_1})^2)^{1/2}]}. \quad (4.\ 12)$$

It can also be written as

$$g_{11} = [\frac{-\rho_1}{2n_1q_1} + (1 + (\frac{-\rho_1}{2n_1q_1})^2)^{1/2}]^{-1}. \quad (4.\ 13)$$

Since $g_{12} = e^{-\beta w_{12}} = e^{\beta w_{11}}$, g_{12} can easily obtained as

$$g_{12} = [\frac{-\rho_1}{2n_1q_1} + (1 + (\frac{-\rho_1}{2n_1q_1})^2)^{1/2}]. \quad (4.\ 14)$$

For the sake of simplicity, if B is defined as

$$B = \frac{\kappa^2 e^{\kappa a}}{8\pi n_1(1 + \kappa a)} \quad (4.\ 15)$$

then, the term $\frac{-\rho_1}{2n_1q_1}$ can be expressed as

$$\frac{-\rho_1}{2n_1q_1} = B\frac{e^{-\kappa r}}{r}. \quad (4.\ 16)$$

If the final expression is substituted into the g_{11} and g_{12}, they can be expressed as

$$g_{11} = [B\frac{e^{-\kappa r}}{r} + (1 + (B\frac{e^{-\kappa r}}{r})^2)^{1/2}]^{-1} \quad (4.\ 17)$$

$$g_{12} = [B\frac{e^{-\kappa r}}{r} + (1 + (B\frac{e^{-\kappa r}}{r})^2)^{1/2}]. \quad (4.\ 18)$$

Now, we are ready to calculate the properties of symmetric electrolytes in this picture. As in the first two section, we are going to calculate the relaxation field to obtain an equivalent conductivity formula then the thermodynamic properties are going to be presented.

4.2 Relaxation Field In This Formalism And Ionic Conductivity

The fundamental differential equation in the treatment of relaxation potential can be written for symmetric electrolytes as

$$\nabla^2[\nabla^2 - \kappa_1^2]\Psi_1' = -\kappa_1^2 E \frac{\partial}{\partial x} g_{12}. \qquad (4.\ 19)$$

Substituting g_{12} in the above equation, it becomes

$$\nabla^2[\nabla^2 - \kappa_1^2]\Psi_1' = -\kappa_1^2 E \frac{\partial}{\partial x}[B\frac{e^{-\kappa r}}{r} + (1 + (B\frac{e^{-\kappa r}}{r})^2)^{1/2}]. \qquad (4.\ 20)$$

In section two, a Green function have been obtained for the equation as

$$G(\vec{r}, \vec{r}_1) = \frac{1}{4\pi\kappa_1^2}(\frac{1}{|\vec{r} - \vec{r}_1|} - \frac{e^{-\kappa_1|\vec{r} - \vec{r}_1|}}{|\vec{r} - \vec{r}_1|}). \qquad (4.\ 21)$$

This Green function leads to a solution for Ψ_1' as

$$\Psi_1' = -\kappa_1^2 E \int G(\vec{r}, \vec{r}_1) \frac{\partial}{\partial x_1}[B\frac{e^{-\kappa r_1}}{r_1} + (1 + (B\frac{e^{-\kappa \vec{r}_1}}{\vec{r}_1})^2)^{1/2}] d^3 r_1. \qquad (4.\ 22)$$

x_1 is defined in spherical coordinate as

$$x_1 = r_1 Sin\theta_1 Cos\phi_1. \tag{4. 23}$$

So thus the derivative oparator is equal to

$$\frac{\partial}{\partial x_1} = Sin\theta_1 Cos\phi_1 \frac{d}{dr_1}. \tag{4. 24}$$

Since we are looking for a solution around $r << \mathbf{a}$, that is, $r << \mathbf{a} < r_1$, one can readily approximate the term $|\vec{r} - \vec{r}_1|$ as

$$|\vec{r} - \vec{r}_1| \simeq r_1(1 - \frac{r}{r_1} Cos\gamma) \tag{4. 25}$$

where $Cos\gamma$ is equal to

$$Cos\gamma = Cos\theta Cos\theta_1 + Sin\theta Sin\theta_1 Cos(\phi - \phi_1). \tag{4. 26}$$

Thus, under these approximations, the integral can be expressed as

$$\Psi_1' = -\frac{E}{4\pi} \int \frac{Sin\theta_1 Cos\phi_1}{r_1(1 - \frac{r}{r_1} Cos\gamma)} [1 - e^{-\kappa_1 r_1 (1 - \frac{r}{r_1}) Cos\gamma)}]$$

$$\frac{d}{dr_1}[B\frac{e^{-\kappa r_1}}{r_1} + (1 + B^2 \frac{e^{-2\kappa r_1^2}}{r_1})^{1/2}] r_1^2 Sin\theta_1 dr_1 d\theta_1 d\phi_1. \tag{4. 27}$$

The derivative can be taken easily as

$$\frac{d}{dr_1}[B\frac{e^{-\kappa r_1}}{r_1}+(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{1/2}]$$

$$=-B(1+\kappa_1 r_1)\frac{e^{-\kappa r_1}}{r_1^2}+\frac{1}{2}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2}(B^2\frac{2r_1+2\kappa r_1^2}{r_1^4}e^{-2\kappa r_1}) \quad (4.\ 28)$$

Substituting this relation and using $\kappa_1 r << 1$, Ψ_1' takes the following form

$$\Psi_1'=-\frac{E}{4\pi}\int\frac{(1+\frac{r}{r_1}Cos\gamma)}{r_1}[1-e^{-\kappa_1 r_1}(1+\kappa r_1 Cos\gamma)]$$

$$[-B(1+\kappa_1 r_1)\frac{e^{-\kappa r_1}}{r_1^2}+\frac{1}{2}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2}(B^2\frac{2r_1+2\kappa r_1^2}{r_1^4}e^{-2\kappa r_1})] \quad (4.\ 29)$$

$$r_1^2 Sin^2\theta_1 Cos\phi_1 dr_1 d\theta_1 d\phi_1.$$

Keeping only the terms order of r, the integral can be written as

$$\Psi_1'=-\frac{E}{4\pi}\int\frac{1}{r_1}[1-e^{-\kappa_1 r_1}(1+\kappa_1 r)+\frac{r}{r_1}Cos\gamma-\frac{r}{r_1}e^{-\kappa_1 r_1}Cos\gamma]$$

$$[B(1+\kappa r_1)e^{-\kappa r_1}+B^2\frac{(r_1+\kappa_1 r_1^2)e^{-2\kappa r_1}}{r_1^2}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2})] \quad (4.\ 30)$$

$$Sin^2\theta_1 Cos\phi_1 dr_1 d\theta_1 d\phi_1.$$

For the sake of simplicity, the integral has been arranged in the following form

$$\Psi_1^{'} = -\frac{E}{4\pi}\int \frac{1}{r_1}[(1-e^{-\kappa_1 r_1}) + Cos\gamma(\frac{r}{r_1}(1-e^{-\kappa_1 r_1} - \kappa_1 r e^{-\kappa r_1})]$$

$$[B(1+\kappa r_1)e^{-\kappa r_1} + B^2\frac{(r_1+\kappa_1 r_1^2)e^{-2\kappa r_1}}{r_1^2}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2})] \qquad (4.\ 31)$$

$$Sin^2\theta_1 Cos\phi_1 dr_1 d\theta_1 d\phi_1.$$

The integration over θ_1 and ϕ_1, as in the section three leads to $\frac{4\pi}{3}Sin\theta Cos\phi$. By substituting this result into the above integral, it becomes

$$\Psi_1^{'} = -\frac{ESin\theta Cos\phi}{3}\int \frac{1}{r_1}[-\kappa_1 r e^{-\kappa_1 r_1} + \frac{r}{r_1}(1-e^{-\kappa_1 r_1})]$$

$$[B(1+\kappa r_1)e^{-\kappa r_1} + B^2\frac{(r_1+\kappa_1 r_1^2)e^{-2\kappa r_1}}{r_1^2}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2})]dr_1 \qquad (4.\ 32)$$

With a little bit algebra, it can also expressed as

$$\Psi_1^{'} = -\frac{ErSin\theta Cos\phi}{3}\int \frac{1}{r_1^2}[-\kappa_1 r_1 e^{-\kappa_1 r_1} + 1 - e^{-\kappa_1 r_1})]$$

$$B(1+\kappa r_1)e^{-\kappa r_1}[1+\frac{B}{r_1}e^{-\kappa r_1}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2})]dr_1 \qquad (4.\ 33)$$

If the integral is divided into two parts as

$$I_1 = -\frac{ErSin\theta Cos\phi}{3}\int \frac{1}{r_1^2}[-\kappa_1 r_1 e^{-\kappa_1 r_1} + 1 - e^{-\kappa_1 r_1})]B(1+\kappa r_1)e^{-\kappa r_1}dr_1 \tag{4. 34}$$

$$I_2 = -\frac{ErSin\theta Cos\phi}{3}\int \frac{1}{r_1^2}[-\kappa_1 r_1 e^{-\kappa_1 r_1} + 1 - e^{-\kappa_1 r_1})]$$

$$B(1+\kappa r_1)e^{-\kappa r_1}\frac{B}{r_1}e^{-\kappa r_1}(1+B^2\frac{e^{-2\kappa r_1}}{r_1^2})^{-1/2})dr_1 \tag{4. 35}$$

one can readily see that I_1 is in the same form of the relaxation potential of the section three. Thus, the solution of it can simply expressed as

$$I_1 = -\frac{ErBSin\theta Cos\phi}{3}(\frac{e^{-\kappa \mathbf{a}}}{\mathbf{a}} - \frac{e^{-(\kappa+\kappa_1)\mathbf{a}}}{\mathbf{a}} - \frac{\kappa\kappa_1}{\kappa+\kappa_1}e^{-(\kappa+\kappa_1)\mathbf{a}}) \tag{4. 36}$$

The evaluation of I_2 is not an easy task due to the functional complication in the last term. It may be handled by the series expansion. The expansion, however, leads to infinite terms which is impossible to express meaningfully. Thus, it seems that replacing the term with a approximate one which leads to evaluation of the integral without loosing too much physics can be a plausiable way. Thus, if the term is written as

$$\frac{B}{r_1}e^{-\kappa r_1}[1+B^2\frac{e^{-2\kappa r_1}}{r_1^2}]^{-1/2} = [1+\frac{r_1^2}{B^2}e^{2\kappa r_1}]^{-1/2} \tag{4. 37}$$

one can easily see that the term is smaller than unity even close to ion-size parameter. For large spacing, that is $r_1 >> \mathbf{a}$, it is a lot smaller than unity.

Thus, taking these consideration into acount, one may replace it by $e^{-\kappa(r_1-a)}$. Thus, the evaluation of the integral can be performed easily as

$$I_2 = -\frac{ErBSin\theta Cos\phi}{3}\int \frac{1}{r_1^2}[-\kappa_1 r_1 e^{-\kappa_1 r_1}$$

$$+1-e^{-\kappa_1 r_1}](1+\kappa r_1)e^{\kappa a}e^{-2\kappa r_1}dr_1. \quad (4.\ 38)$$

For the sake of simplicity, I_2 is divided into two parts as

$$I_2 = -\frac{ErBSin\theta Cos\phi}{3}(I_{2,1}+I_{2,2}) \quad (4.\ 39)$$

where $I_{2,1}$ and $I_{2,2}$ are expressed as

$$I_{2,1} = e^{\kappa a}\int_a^\infty \frac{e^{-2\kappa r_1}}{r_1^2}[1-e^{-\kappa_1 r_1}-\kappa_1 r_1 e^{-\kappa_1 r_1}]dr_1 \quad (4.\ 40)$$

$$I_{2,2} = \kappa e^{\kappa a}\int_a^\infty \frac{e^{-2\kappa r_1}}{r_1}[1-e^{-\kappa_1 r_1}-\kappa_1 r_1 e^{-\kappa_1 r_1}]dr_1. \quad (4.\ 41)$$

In terms of exponential integral, they can be readily evaluated as

$$I_{2,1} = -e^{\kappa a}[-\frac{-2\kappa a}{a}-2\kappa Ei(-2\kappa a)+\frac{e^{-(2\kappa+\kappa_1)a}}{a}$$

$$+(2\kappa+\kappa_1)Ei(-(2\kappa+\kappa_1))] \quad (4.\ 42)$$

$$I_{2,2} = -\kappa e^{\kappa a}[Ei(-2\kappa a)-Ei(-(2\kappa+\kappa_1)a)+\frac{\kappa_1}{2\kappa+\kappa_1}e^{-(2\kappa+\kappa_1)a}] \quad (4.\ 43)$$

Thus, summation of these results lead to an expression for I_2 as

$$I_2 = -\frac{ErBSin\theta Cos\phi}{3} e^{\kappa a}[\frac{e^{-2\kappa a}}{a} - \frac{e^{-(2\kappa+\kappa_1)a}}{a}$$

$$- \frac{\kappa\kappa_1}{2\kappa+\kappa_1} e^{-2\kappa a} + \kappa Ei(-2\kappa a) - \kappa Ei(-(2\kappa+\kappa_1)a)]. \qquad (4.\ 44)$$

If the following expension for the exponential function

$$Ei(-x) = \gamma + lnx + \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{nn!} \qquad (4.\ 45)$$

is used, then I_2 can be written as

$$I_2 = -\frac{ErBSin\theta Cos\phi}{3} e^{\kappa a}[\frac{e^{-2\kappa a}}{a} - \frac{e^{-(2\kappa+\kappa_1)a}}{a} - \frac{\kappa\kappa_1}{2\kappa+\kappa_1} e^{-2\kappa a} +$$

$$\kappa ln(\frac{2\kappa}{2\kappa+\kappa_1}) + \kappa \sum_{n=1}^{\infty} \frac{(-1)^n}{nn!}((2\kappa a)^n - ((2\kappa+\kappa_1)a)^n)]. \qquad (4.\ 46)$$

If the open form of B is substituted into I_1 and I_2, Ψ_1' can be expressed as

$$\Psi_1' = -\frac{ErSin\theta Cos\phi\kappa^2}{24\pi n_1(1+\kappa a)}[(\frac{1}{a} - \frac{e^{-\kappa a}}{a} - \frac{\kappa\kappa_1}{\kappa+\kappa_1} e^{-\kappa_1 a})(1+e^{-2\kappa a})$$

$$+ \kappa ln(\frac{2\kappa}{2\kappa+\kappa_1}) + \kappa \sum_{n=1}^{\infty} \frac{(-1)^n}{nn!}((2\kappa a)^n - ((2\kappa+\kappa_1)a)^n)]. \qquad (4.\ 47)$$

Finally, the relaxation field along the x direction can be obtained as

$$E' = -\frac{E\kappa^2}{24\pi n_1(1+\kappa a)}[(\frac{1}{a} - \frac{e^{-\kappa a}}{a} - \frac{\kappa\kappa_1}{\kappa+\kappa_1}e^{-\kappa_1 a})(1+e^{-2\kappa a})$$

$$+ \kappa ln(\frac{2\kappa}{2\kappa+\kappa_1}) + \kappa\sum_{n=1}^{\infty}\frac{(-1)^n}{nn!}((2\kappa a)^n - ((2\kappa+\kappa_1)a)^n)]. \qquad (4.\ 48)$$

Substituting this expression into the equivalent conductivity formula leads to for 1:1 electrolytes

$$\Lambda = \Lambda^0[1 - \frac{e^2}{12\pi\varepsilon k_B T(1+\kappa \mathbf{a})}\frac{\kappa^2}{\kappa_D^2}[(\frac{1}{\mathbf{a}} - \frac{e^{-\kappa_1 \mathbf{a}}}{\mathbf{a}} - \frac{\kappa_1\kappa}{\kappa+\kappa_1}e^{-\kappa_1 \mathbf{a}})(1+e^{-2\kappa a})$$

$$+ \kappa ln(\frac{2\kappa}{\kappa+\kappa_1}) + \kappa\sum_{n=1}^{\infty}\frac{(-1)^n}{nn!}((2\kappa a)^n - ((2\kappa+\kappa_1)a)^n)] + \frac{e^2 N_A\kappa}{\Lambda^0 3\pi\eta_s(1+\kappa \mathbf{a})}] \qquad (4.\ 49)$$

If the parameter κ is obtained, then The equivalent conductivity formula can be used for 1:1 electrolytes generally. For this purpose, the equivalent conductivity formula is going to be compared with the OLL result at very low concentration, let say $0.001 mol/l$. Since we know that within this limiting concentration range OLL is exact and unambigous, the determination of κ from this comparison does not lead to any ambiguity at all at least at this concentration range. Thus, by recalling that κa is also a lot smaller than unity, the equivalent conductivity can be approximated as

$$\Lambda = \Lambda^0[1 - \frac{e^2}{12\pi\varepsilon k_B T(1+\kappa \mathbf{a})}\frac{\kappa^2}{\kappa_D^2}[(\frac{2\kappa_1^2}{\kappa+\kappa_1} + \kappa ln(\frac{2\kappa}{2\kappa+\kappa_1})]$$

$$+\frac{e^2 N_A \kappa}{\Lambda^0 3\pi\eta_s(1+\kappa \mathbf{a})}]. \qquad (4.\ 50)$$

Now, one should notice that the logarithmic term is equal to

$$\kappa ln(\frac{2\kappa}{2\kappa+\kappa_1}) = \kappa_D ln(\frac{2\kappa_D}{2\kappa_D+0.71\kappa_D}) = -\kappa_D ln(\frac{2}{2.71}) \qquad (4.\ 51)$$

at very low concentration. If this logarithmic term is equal to

$$-\kappa_D ln(\frac{2}{2.71}) = \frac{\kappa_1^2}{\kappa_D+\kappa_1} = \frac{0.5\kappa_D}{1.71} \qquad (4.\ 52)$$

then the above limiting form satisfy the Onsager limiting law which is also considered as a criterion for the equivalent conductivity expression derived in this section. Since $ln\frac{2}{2.71} = -0.2998$, one can readily concluded that the equivalent conductivity satisfies the Onsager limiting law. From the experience of section three, an expression for κ is going to be proposed as

$$\kappa = \kappa_D e^{-b(\kappa_D)^{1/4}}. \qquad (4.\ 53)$$

Comparison with experimental data produces a value for $b = 0.8$ for 1:1 electrolyte system. After determination of κ, the equivalent conductivity

relation can be compared with experimental data and the results of the comparison are plotted in Fig.4.1.

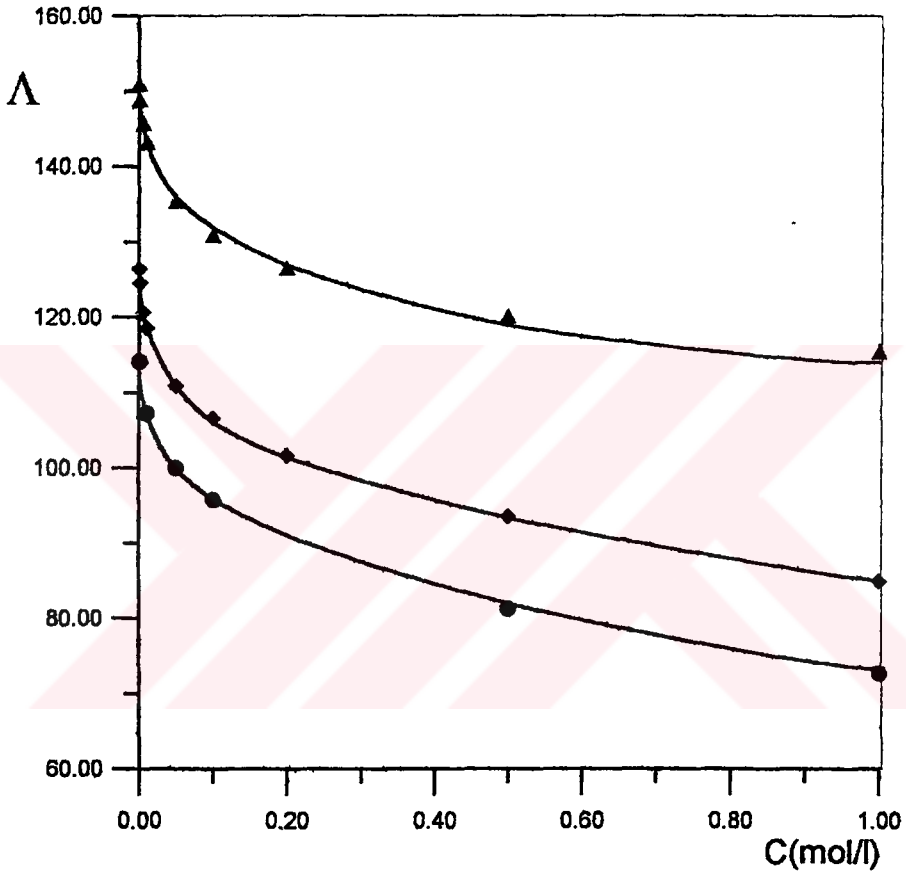

Fig.4.1 The equivalent conductivity versus consentration for ion-size parameters 2.87, 3.28, 3.49 in angstrom for NaCl, KBr, KI respectively.

4.3 Osmotic Coefficient In This Formalism

The osmotic coefficient formula obtained from the virial pressure in section one is going to be used to treat the thermodynamic properties of electrolyte in this section also. Since the form of the correlation function are different than those of the correlation function obtained in section two and three, one can expect that the form of the osmotic coefficient expression is different from those of the expressions derived in section one and two. That means, one has to calculate it for the correlation function derived above. Thus recalling the osmotic coefficient formula and the correlation functions which are given as,

$$\Phi = 1 + \frac{4\pi a^3}{6n}\sum_{i,j} n_i n_j g_{ji}(a) - \frac{1}{6k_B T n}\sum_{i,j}\int_a^\infty 4\pi r^3 (\frac{-q_i q_j}{4\pi\varepsilon r^2}) g_{ij} \qquad (4.\ 54)$$

$$g_{11} = [B\frac{e^{-\kappa r}}{r}(1 + (B\frac{e^{-\kappa r}}{r})^2)^{1/2}]^{-1} \qquad (4.\ 55)$$

$$g_{12} = [B\frac{e^{-\kappa r}}{r}(1 + (B\frac{e^{-\kappa r}}{r})^2)^{1/2}]. \qquad (4.\ 56)$$

One can calculate an osmotic coeffitient expression in this picture. For the sake of simplicity, the sums terms are going to be evaluated first

$$\sum_{i,j} n_i n_j g_{ji}(a) = 2n_1^2(g_{11}(a) + g_{12}(a)). \qquad (4.\ 57)$$

If the functions g_{11} and g_{12} are substituted into this expression leads to

$$\frac{4\pi a^3}{6n}\sum_{i,j} n_i n_j g_{ji}(a) = \frac{4\pi a^3 n}{6}F(a) \qquad (4.\ 58)$$

where $F(a)$ is equal to

$$F(a) = \frac{2f^2 + 2f(1+f^2)^{1/2} + 2}{f + (1+f^2)^{1/2}} \tag{4. 59}$$

where f is equal to

$$f = \frac{\kappa^2}{8\pi n_1(1+\kappa a)a}. \tag{4. 60}$$

The following sum was already calculate in section one as

$$\sum_{i,j} n_i n_j q_i q_j g_{ji} = \sum_j n_j q_j \rho_j. \tag{4. 61}$$

Substituting ρ_j into this sum leads to

$$\sum_j n_j q_j \rho_j = -\sum_j n_j q_j^2 \frac{\kappa^2 e^{\kappa a}}{4\pi(1+\kappa a)} \frac{e^{\kappa r}}{r}. \tag{4. 62}$$

For 1:1 electrolytes, it can be also written as

$$\sum_j n_j q_j \rho_j = -ne^2 \frac{\kappa^2 e^{\kappa a}}{4\pi(1+\kappa a)} \frac{e^{\kappa r}}{r}. \tag{4. 63}$$

Substituting this relation into the integral leads to

$$\frac{1}{6k_B T n} \sum_{i,j} n_i n_j \int_a^\infty 4\pi r^3 \left(\frac{-q_i q_j}{4\pi\varepsilon r^2}\right) g_{ij} dr = \frac{e^2\kappa}{24\pi k_B T \varepsilon(1+\kappa a)}. \tag{4. 64}$$

Thus, the osmotic pressure can be expressed as

$$\Phi = 1 + \frac{4\pi a^3 n}{6} F(a) - \frac{e^2 \kappa}{24\pi k_B T \varepsilon (1 + \kappa a)}. \qquad (4.\ 65)$$

This equation have been compared with the experimental data of NaCl solution at the temperature 293K in Fig.4.2.

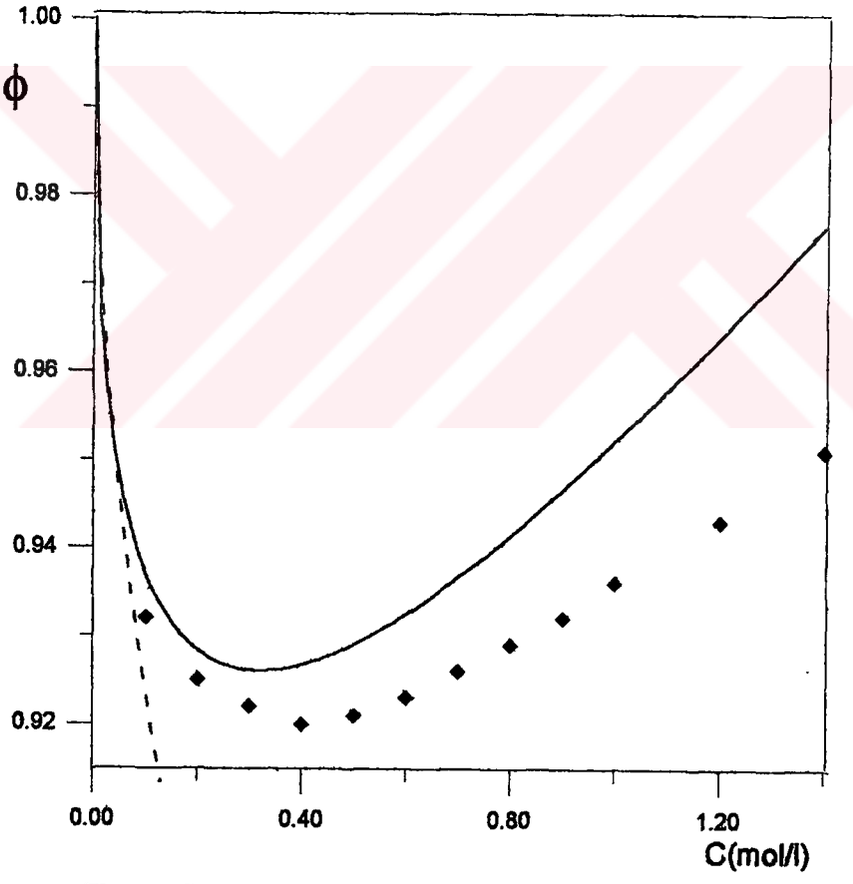

Fig.4.2 The osmatic coefficient of NaCl with 2.87 angstrom ion-size. The dashed line shows the DH limiting law result.

5 RESULTS AND DISCUSSION

The crucial remaining problem of ionic solutions which is the DH theory valid only at very low concentrations has been investigated by different considerations in order to extend the validity of the theory beyond this limiting concentrations in mean-field sense. The physical picture has been taken as the DH theory since conclusive proof of the validity of the theory at very low concentrations on both the experimental and theoretical levels has long been available. Therefore, the theory is considered as a fundamental law of nature. That is why, it has been used as an criterion all through this thesis. In addition the deviations from the DH theory have been interpreted due to the defects of the basic assumption of the theory at higher concentrations, rather then due to the non-Coulombic interactions of the system. Of course, introducing non-Coulombic interactions into the picture are plausible but the introduction turns out to be very ambiguous in mean-field type theories since determining which of these two factors, either Coulombic or non-Coulombic interactions, causes the deviation from the experiment is almost impossible.

On the other hand, one has to aware of that introducing non Coulombic-interactions with a continuum dielectric constant can cause theoretical deviations due to the striking difference between local and distant arrangements of the polar solvent molecules in the presence of ions. So thus, one can readily conclude that the continuum dielectric presentation may be true at low concentrations but it is evidently questionable at higher concentrations.

This point may explain that why the thermodynamic treatments of this thesis are not in a good agreement with the experiments, although, the equiv-

alent conductivity expressions are in a excellent agreement. We think this is due to the the limiting equivalent conductivity Λ^0 which keeps the effect of the ion-solvent interaction implicitly since it can only be determined by extrapolation. Therefore, introduction of non-Coulombic interaction in the treatment of thermodynamic properties of ionic solutions seems more important. But, it is equally evident that the introduction of non-Coulombic interaction in a rigorous manner is not an easy task in mean-field picture.

On the other hand, one might still inquire that whether the above mean field approaches can serve a fundamental basis for ionic solutions or not. A definite answer to this question can not be given easily since it necessitates a careful analysis of the mean-field pictures introduced all those sections. Of course, a careful analysis cannot be handled in the absence of an exact and rigorous theory of strong interacting particles. But, one can think that the present mean-field approaches may lead to a corresponding development in ionic dynamics since the relaxation field has been obtained in a rigorous manner in each sections for non-zero ion-size parameter. Since the rigorous solution of relaxation field is the most involved and cumbersome part of the ionic solutions theory, having a defined and rigorous result for the relaxation field can be considered as the most important production of this thesis.

In addition, in writing this thesis on strong electrolytic solution, I have tried to stress the importance of theory without neglecting empirical results. I have recognized this point by dealing with aqueous solutions since they are the commonest in nature and experimentally most easily accessible and also because of their great biological importance.

For future studing, I think one can extend the above mean field treatments by considering counter charge density oscillation which takes its toll at high concentration. Beside that, inserting the concentration dependence of continuum parameters, mainly dielectric constant and viscousity coefficient, into the mean field treaatments can also considered as a unique work.

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