



Studies on Ion-Solvent Interactions of Electrolyte Solutions – Part 3: Activity Coefficient Studies of 2-2 Electrolytes (Sulphates of Transition Metals)

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ABSTRACT

This paper presents the application of the evaluated dielectric data to the calculations of Activity coefficient and related parameters of the Pitzer's equations for 2-2 electrolytes namely Copper sulphate, Nickel sulphate, Manganese sulphate and Cobalt sulphate. Results are represented as plots between \sqrt{c} as abscissa and $[-\ln \gamma_{\pm}]$ as ordinate in set 1; and between \sqrt{c} as abscissa and A_{ϕ} as ordinate in set 2. The study of the slopes of the graphs reveals several details about the latent Eigen and Tamm's Ion-pair formation mechanism. Systematic analysis along with supporting findings from the literature is cited.

Keywords: Activity Coefficient, 2-2 Electrolytes, Pitzer's equations for the 2-2 electrolytes, Debye-Huckel theory, Debye-Huckel limiting law, Gibbs free energy, Thermodynamic Model of Electrolyte Solution.

1. INTRODUCTION

An activity coefficient [1] is a factor used in [thermodynamics](#) to account for deviations from ideal behavior in a [mixture of chemical substances](#). [Max Margules](#) [2-3] introduced a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture. After Lewis had introduced the concept of the activity coefficient, the model could be used to derive an expression for the [activity coefficients](#) ' γ_i ' of a compound i in a liquid. The activity coefficient is a measure for the deviation from ideal solubility. Activity coefficients may be measured experimentally or calculated theoretically, using the [Debye-Huckel equation](#) or extensions such as [Davies equation](#), [4], [Pitzer equations](#) [5] or TCPC model [6 to 9]. [Specific ion interaction theory](#) (SIT) [10], may also be used. Alternatively correlative methods such as [UNIQUAC](#) [11], [NRTL](#) model [12], [MOSCED](#) or [UNIFAC](#) may be employed, provided fitted component-specific or model parameters are available.

1.1 Debye-Huckel limiting law

The Debye-Huckel equation and Debye-Huckel limiting law were derived by [Peter Debye](#), M. Born and [Erlich Huckel](#) [13] who developed a [theory](#) with which we can calculate [activity coefficients](#) of [electrolyte](#) solutions. Taking into account the ion size parameter (expressed in angstroms), the original Debye-Huckel equation for the mean activity coefficient (γ), for a completely dissociated

binary electrolyte, consisting of ν ions mole of solute)⁻¹, with charges Z_+ and Z_- can be written as

$$\log \gamma_{\pm} = [Z_+ Z_- |A_{\gamma} I^{\frac{1}{2}}| / [1 + aB_{\gamma} I^{\frac{1}{2}}]]$$

where I is the ionic strength in molality (m) units of concentration. $I = (\nu/2) |Z_+ Z_-| m$, and A_{γ} and B_{γ} are parameters dependent on density and permittivity of the solvent and other symbols carry their usual meaning. It should be noted that according to Glueckauf's model [14] *the variation of the concentration of the electrolyte added to the solvent continuously alters the relative permittivity of the solvent when treated as a dielectric continuum*. This leads to a continuous change of the relative permittivity of the medium in which the ions of the electrolyte are located. Hence the two basic terms. A_{γ} and B_{γ} are the locations where we obtain information about the Eigen mechanism.

The Debye-Huckel equations also enable the determination of the activity coefficient of an ion in a dilute solution of known [ionic strength](#) I . The equation is given as:

$$\log(\gamma_i) = -\frac{z_i^2 q^2 \kappa}{8\pi \epsilon_r \epsilon_0 k_b T} = -\frac{z_i^2 q^2}{4\pi (\epsilon_r \epsilon_0 k_b T)^{3/2}} \sqrt{I} = -Az_i^2 \sqrt{I}$$

In which is the [charge number](#) of ion species I , q is the [elementary charge](#), κ is the [Debye screening length](#) defined below, ϵ_r is the [relative permittivity](#) of the

solvent, ϵ_0 is the [permittivity of free space](#), k_B is [Boltzmann's constant](#), T is the [temperature](#) of the solution, I is the [ionic strength](#) of the solution, and A is a constant that depends on the solvent. It is important to note that because the ions in the solution act together, the activity coefficient obtained from this equation is actually a mean activity coefficient.

This equation set remains to be the starting point for many models being developed for Activity Coefficient.

1.2 Recent Improvements over the Debye-Huckel Equation

The activity is proportional to the concentration by a factor known as the activity coefficient γ , and takes into account the [interaction energy](#) of ions in the solution. It is important to note that because the ions in the solution act together, the activity coefficient obtained from this equation is actually a mean activity coefficient. A number of approaches have been proposed [8 to 12]. The Non-Random Two-Liquid model [15] (short NRTL equation) is an activity coefficient model that correlates the [activity coefficients](#) γ_i of a compound i with its [mole fractions](#) x_i in the liquid phase concerned. The concept of NRTL is based on the hypothesis of Wilson that the local concentration around a molecule is different from the bulk concentration. The electrolyte Non-random two-liquid (NRTL) model of Chen et.al., combines a Debye-Huckel term with the NRTL local composition model. The local composition concept is modified for ions, and the model parameters are salt specific. This difference is due to a difference between the interaction energy of the central molecule with the molecules of its own kind U_{ii} and that with the molecules of the other kind U_{ij} . The energy difference also introduces non-randomness at the local molecular level. The NRTL model belongs to the so-called local-composition models. Other models of this type are the [Wilson](#) model, the [UNIQUAC](#) model, and the group contribution model [UNIFAC](#). These local-composition models are not thermodynamically consistent due to the assumption that the local composition around molecule 'i' is independent of the local composition around molecule 'j'. Flemmer [16] Established that this assumption is not true.

2. PITZER MODEL AS AN IMPROVEMENT OF RECENT PAST

Pitzer's model, being the best of the earlier models, was chosen by us to start our application of the earlier published dielectric data. K. Thomsen [17], developed, equations for the type of multi-phase flash calculations required for aqueous electrolyte process simulations in his doctoral work & multiple steady states were detected and analysed. Their equations are essentially similar to those of Nicolaisen et. al. [18]. They pointed out that in order to apply the Debye-Huckel theory, to non-ideal systems; it

has to be primarily combined with a term for short-range interactions. K. Thomsen et.al., [19] developed the extended UNIQUAC model in which the Debye-Huckel contribution to the excess Gibbs energy was deduced.

The Pitzer model was developed as an improvement upon an earlier model proposed by *Guggenheim* [20] involving some crude approximations about the concentration limit in connection with the osmotic coefficient of a reference salt which worked well at low electrolyte concentrations [21], but contained discrepancies at higher concentrations (>0.1M). *G. Scatchard* [22] suggested some modifications to these concepts, only to provide a compact summary of the experimental data but failed to cater to the desired requirements.

On the basis of the insight provided by the improvements of Friedman and collaborators [23], and those of *Card and Valteau* [24], the Pitzer model came to light and attempted to resolve these discrepancies, without resorting to excessive arrays of higher-order terms. Pitzer used A_ϕ , called the Debye-Huckel term, for simplification of the equations applicable to 2-2 electrolytes. The equations of Pitzer used in our calculations are given hereunder.

In the Pitzer model, the activity coefficient of each ion is described by two terms. The first one is due to long-range interactions (electrostatic or Debye-Huckel behaviour) and is given by f^γ . The second one is due to short-range interactions which are expressed in terms of second and third coefficients of a virial equation [25].

2.1 Omissions in Pitzer Model

As stated by Pitzer himself [26], some marked omissions are found in his model. Firstly: The model starts with the system proposed by *Guggenheim*. *Guggenheim* following *the principle of Specific interaction of Bronsted* [27] excluded terms related to short range forces between the like sign ions. The same is adopted in Pitzer's model. However mechanisms like the ion-pairing necessarily require cognizance of this.

The virial coefficients used in the equations even though are from the experimental origin, their statistical method of evaluation would not consider the ionic level happenings and their dependence on intricate properties like the relative permittivity on the concentration of the electrolyte in the solvent. Consequently the mechanisms that exist within Ionic atmosphere during solvation and the solute solvent interactions are not accounted in the statistical methods for the virial coefficients.

Also some assumptions about phenomena and concepts [26] like:

- The direct interactions of solute species at short distances and changes in solvation with concentration

which influence the effective inter ionic potential of average force are not distinguished,

- Apparently the distinction between molality and concentration is 'ignored', because mainly the statistical calculations are put to use based upon the molecular models, to develop empirical form of qualitative understanding. Especially molality is preferred by Pitzer since he presumes that the temperature variations influence the Activity and Osmotic coefficient to a lesser extent with molality.

However happenings around the proximity of the ion in the cosphere are not compatible with this approximation. Since the ion-pair formation around the central ion is sensitive to even the least potential contribution either in the proximity or at a reasonable distance from the site of mechanism.

Also as pointed out by *Guggenheim* and *Turgeon*, substantial discrepancies arise even at concentrations greater than 0.1M. Several authors made variety of attempts to accommodate for this, but to no avail [28]. For example *G.Scatchard* & his co-workers [29], extended and elaborated *Guggenheim* equations in several ways. First they subdivided the Debye-Huckel term in the expression for excess Gibbs Energy into a series of terms with different coefficients of $I^{1/2}$ in 'r' corresponding to different distances of closest approach for the solute components. Appropriate derivatives later yield very complex formulae for the coefficients γ and ϕ . Secondly the *Bronsted's principle of Specific interaction* is abandoned and terms are introduced for the short range interaction of ions of like sign. Arrays of third and fourth virial coefficients are added by *Lietzke* and *Stoughton*[28]. The Osmotic Coefficient data for 20 pure electrolytes was in a position to be represented by them to a fair accuracy. They treated several systems of mixed electrolytes also. Such a system of equations is unwieldy and raises other complications, because the physical interpretation of the involved terms and parameters becomes complex. These omissions during the development of the theoretical equations of the model were attempted to be approached in a pragmatic way, by making the equations simpler with more meaningful parameters introduced in the Pitzer's work.

The fundamental deficiency in the basic Debye-Huckel theory is the recognition of the parameter *the distance of closest approach*, 'a' in the calculation of the electrostatic energy in the distribution of ions. However the kinetic effect of hard core on γ and ϕ is ignored. *Kirkwood points* out [29] that the hard-core effects cannot be treated rigorously in the traditional way, by calculating the free energy. Terms were added [30] by *Van Rysselberghe* and *Eisenberg* to improve hard core effects, only for the feature of the particular interest to be lost by doing so. *Sengupta*, *Bagchi* & *Dutta* [31-32] attempted the application of new statistics and developed a new set of

distribution equations. *Dutta* & *Bagchi* deduced theoretically

$$n_{\pm,r} = \left[\frac{1}{b_{\pm}} \right] / \left[e^{V_{\pm} + (z_{\pm} \epsilon \phi_r / kT)} + 1 \right]$$

where (1) $n_{\pm,r}$ is the number density of positive or negative ions (2) b_{\pm} is the volume of the covering spheres (*Deckungssphären*) of positive or negative ions (3) V_{\pm}

parameters of distribution (4) z_{\pm} valence of the positive or negative ions and (5) ' ϵ , k and T ' have their usual significance. The formalism used in this equation has been developed by *Dutta* [33], and rests on the simple assumption that ions having characteristic volume of their own are under the influence of their mutual electrostatic field in solution. *Eigen* and *Wicke* [34] used a similar distribution formula in their theory of strong electrolytes in a slightly different form with slightly different explanation for the parameters involved.

Sengupta et.al. evaluated the available electric energy,

through the evaluation of λ where $\lambda = \left[\frac{\epsilon \phi}{kT} \right]$. The Poisson-Boltzmann equation was then solved. An expression for the Activity coefficient was then deduced. Using separate ionic radii for the ions. Our evaluation of Activity coefficient data with *Sengupta* model using our experimental dielectric data would appear shortly in a publication.

T. Hill [35] using Statistical mechanics proposed a convenient equation for hard core potential. This was used in the Pitzer's model for the Osmotic coefficient. However the equations of the statistical origin involve errors in the qualitative as well as quantitative understanding of happenings. This is to be accommodated at some juncture or other to make the Pitzer's model better. The attempts of other workers found in literature are not concentrating on these aspects. Consequently there will be marked deviations between the results of the application of the present theories and experimental findings. The explanation of the mechanisms like "*Eigen and Tamm Ion pair formation*" leave dissonance between theory and experiment as is found in some of our results, discussed below. We present below the application of Pitzer model [36], to our earlier published dielectric data in this paper. The basic equations for 2-2 electrolytes are summarized below:

2.2 A_{ϕ} Slope of Debye-Huckel Limiting Law

The Pitzer's model uses primarily the concepts of the Debye-Huckel model. A very important parameter that

appears in the Pitzer model is A_ϕ called the Debye-Huckel term.

$$A_\phi = \frac{1}{3} \sqrt{\frac{2\pi dN_0}{1000}} \left[\frac{e^2}{\epsilon kT} \right]^{3/2}$$

is the Debye-Huckel term.

This is the Debye-Huckel limiting law slope from the basic equation of the osmotic coefficient and is a function of temperature given by a polynomial correlation in 'T', used by Morteza Baghalha [37] (taken From D.G. Archer and P. Wang [38]). This parameter was very precisely obtained, from a careful evaluation of density and dielectric constant data by K.S. Pitzer, R. N. Roy and L.F. Sylvester [39] and H.F. Holmes and R.E. Mesmer [40]. As such this parameter coined originally by Debye - Huckel, and was later modified by a host of workers, considering the very accurate experimental data from more than one source, gives a comprehensive picture about the Ion pair formation mechanism that is discussed in this paper.

2.3 'B , α and β ' Relations used in the Model

Pitzer used a set of virial coefficients $B^\phi, \beta^{(0)}, \beta^{(1)}$ and $\beta^{(2)}$ which can be expressed in the form of an equation

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)} / \alpha_1^2 I) [I - (I + \alpha_1 I^{1/2} - \frac{1}{2} \alpha_1^2 I) e^{-\alpha_1 I^{1/2}}] + (2\beta_{MX}^{(2)} / \alpha_2^2 I) [I - (I + \alpha_2 I^{1/2} - \frac{1}{2} \alpha_2^2 I) e^{-\alpha_2 I^{1/2}}]$$

and $C_{MX}^\gamma = (3/2)C_{MX}^\phi$, all the parameters that are adjusted for each electrolyte are given in the subscript MX.

The symbols γ , (1), and (0) etc are labels but not exponents, and $b = 1.20$, as per the value assumed by Pitzer (1973), in his original paper. The data for 'The Four Parameters', $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ for the sulphates, and

C^γ were fitted by least squares adjustment. We used: α_1

$= 1.4$ and $\alpha_2 = 12.0$ in all the calculations of this paper. The values of these parameters used in our calculations are given in *Table 1*.

3. 'EIGEN AND TAMM' - ION PAIR FORMATION MECHANISM

The mechanism has been established on vigorous experimental data, obtained by several workers. However the fundamental concept of ion pairs has the origin from the basic Coulomb interaction. Therefore the dielectric continuum is responsible to organize the ion solvent interactions and the successive stages of the mechanism as envisaged from the fundamental equation of Bjerrum.

$$B^\phi = \beta^{(0)} + \beta^{(1)} e^{-\alpha_1 I^{1/2}} + \beta^{(2)} e^{-\alpha_2 I^{1/2}}$$

In this equation $\beta^{(0)}$ and $\beta^{(1)}$ represent the effect of short range forces. $\beta^{(2)}$ and α_2 correspond to the anomalous behavior of the 2-2 electrolytes. The parameters α_1 and α_2 are assigned with a series of values by Pitzer et.al. The values of these coefficients are obtained by Pitzer, from experimental data statistically, and are available in literature.

The activity coefficient ' γ ' according to Pitzer's model is given by the following set of equations :

$$\ln \gamma = 4f^\gamma + mB_{MX}^\gamma + m^2 C_{MX}^\gamma$$

And

$$f^\gamma = -A_0 [I^{1/2} / (I + bI^{1/2}) + (2/b) \ln(1 + I + bI^{1/2})]$$

in which

3.1 Ion Pairing Hypothesis of N. Bjerrum

Ions of opposite charge are naturally attracted to each other by the [electrostatic force](#). This is described by Coulomb's law. The most important factor to determine the extent of ion-association is the [dielectric constant](#) of the solvent. The concept has been proposed by [Niels Bjerrum](#), which was studied in detail by *Eigen & Tamm* [41], in their *Nobel prize (for the year 1965) winning work in Chemistry*.

In general *Ion-pairs* are formed when a [cation](#) and an [anion](#) come together, to be shown symbolically as:



At present, three distinct types of ion-pairs on the basis of solvation of the two ions are recognized. In the schematic representation below, the circles are to represent spheres. The sizes are arbitrary and not necessarily similar as illustrated. The mechanism can be broadly viewed as a three step process. The cation is colored red and the anion is colored blue. The green area represents solvent molecules in a primary solvation shell. For the purposes of this presentation secondary solvation is ignored. When both ions have a complete primary solvation sphere the

ion-pair may be termed '*fully solvated*' or *solvent-separated*, when there is about one solvent molecule between cation and anion, the ion-pair may be termed '*solvent-shared*'. Lastly when the ions are in contact with each other the ion-pair is termed a '*contact ion-pair*'. Even in a contact ion-pair, however, the ions retain most of their solvation shell. The nature of this solvation shell is generally not known with any certainty. In aqueous solution and in other donor solvents metal cations are surrounded by between four and nine solvent molecules in the primary [solvation shell](#), [42] but the nature of solvation of anions is mostly unknown.

An alternative name for the solvent-separated & solvent-shared ion-pairs together is an '*outer-sphere complex*' and denotes a complex between a solvated metal cation and an anion. Similarly a contact ion-pair may be termed an '*inner-sphere complex*'. The essential difference between

the three types is the closeness with which the ions approach each other: fully solvated > solvent-shared > contact. With fully solvated and solvent shared ion-pairs the interaction is primarily electrostatic, but in a contact ion-pair there will also be some covalent character in the bond between cation and anion.

An *Ion-triplet* may be formed from one cation and two anions, or from one anion and two cations [43]. Higher aggregates, such as a tetramer, $(AB)_4$ may be formed. Ternary ion-associates involve the association of three species [44]. Another type, named *intrusion ion-pair* has also been characterized [45].

3.2 Probing the Ion-pair Formation Mechanism

To start with the **EIGEN-TAMM mechanism**

INDIVIDUAL ions are shown separately with their dielectric sheaths, represented by the **YELLOW ANNULAR RING** round the ion

Different ions are different in size, that depends on the nature of the element



The blue core represents positive central ion
The brown core represents negative central ion

The **Coulombic electrostatic forces** are responsible to keep the **ionic atmosphere intact**

EFFECT of increase of concentration:
As the **concentration increases** more ions of opposite charge tend to enter the ionic atmosphere, **and increase the internal field** on the **central ion**, there by the effective dielectric constant suffers a reduction

Fig 1(a): state of the electrolyte solution before ion pairing mechanism starts

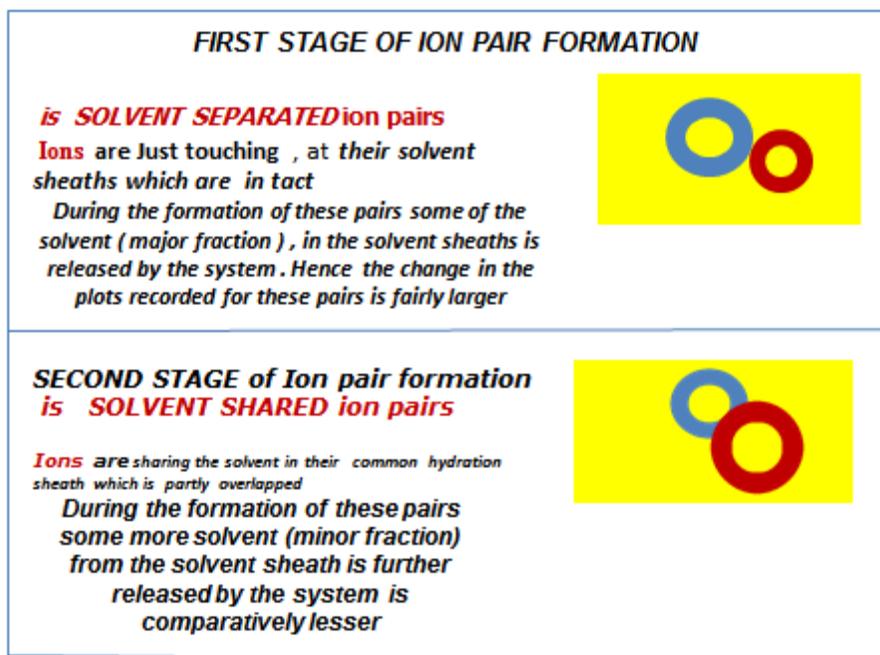


Fig1(b): Formation of the solvent separated and solvent shared pairs getting formed in the solution (both these put together constitute 'outer-sphere complex' and denote a complex between a solvated metal cation and an anion)

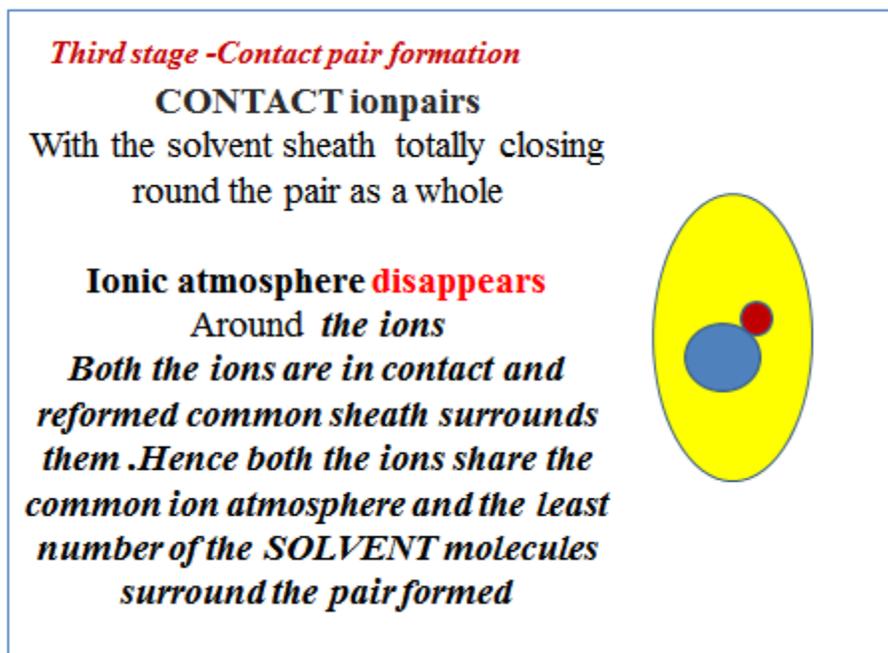


Fig 1 (c): Formation of the contact pairs also called 'inner-sphere complex':

Several details are available in literature about probing the formation, study of the kinetics of Ion-pair formation, and its Technological applications. To mention some of them are the dielectric relaxation studies by Buchner [46] & Hefter [47], phase transfer catalysis studies by Arne Barnstorm [48], Ion Exchange and Solvent Extraction

studies by G. Schill, et. al [49], Apparent, partial & excess molal volume, Cationic mobility & Activity coefficient & compressibility studies by V. Brahmajirao [50], thermodynamic studies of alcoholic electrolyte solutions by T. Gunavardhan Naidu et.al., [51] Ultrasonic studies by V. Brahmajirao [52], Chromatography with Nonpolar

Stationary Phases by Csaba Horvath[53], Ion pair formation from Photo dissociation by Devinder Kaur et.al.,[54], F. Kremer et.al.[55], & R Buchner [56] used Dielectric relaxation spectroscopy (DRS) as a probe, using the fact that for electrolyte solutions, polarization essentially originates from the orientational fluctuations of permanent dipoles (solvent molecules, ion pairs), from intra molecular polarizability and from ion motion. It can be investigated either in the time domain or as a function of the frequency ν of a harmonic field. In the latter case, the response is conveniently expressed in terms of the complex total (relative) permittivity. The attractive interactions between cations and water are dominated by electrostatic forces.

4. DISCUSSION OF RESULTS

We present our findings and the observations of other workers separately, and point out the conclusions at the appropriate points.

4.1 Our Findings

All the plots of the chosen ordinates versus (\sqrt{c}) as abscissa record at least three conspicuous gradient changes per each electrolyte. Each gradient change corresponds to the formation of a type of ion pair. It may be noted that these parameters chosen as ordinates of the plots are expressed in terms of a linear relationship with abscissa. These graphs (1 - 4) record distinct changes in slope, at three concentrations, corresponding to, the formation of solvent separated, solvent shared & contact pairs in tune to the expectations of *Eigen et.al.* and is different from the findings reported earlier in literature. As pointed out by *Margaret Robson Wright [57]* & *Robinson and Stokes [58]* the internal field around the central ion of the ionic atmosphere created by the charged solute ions in the solvent of the electrolytic solution, tend to reduce the value of the dielectric constant of the electrolytic solution. The qualitative explanation of the mechanism of formation of the three types of ion-pairs, was detailed by, the outlines of the same are available at *Brahmajirao et.al.* All our findings with the above cited equations with the Pitzer's model were evaluated using Matlab program given at the end of this paper.

The discrete changes in the slopes of the graphs are prominently observable from our plots cited in our

findings. We notice that the plots of (\sqrt{c}) versus A_ϕ , record sharper changes in the slope than the (\sqrt{c}) versus ($-\ln \gamma$) plots. The reasons for this have been already explained in 2.1 section, i.e., Due to: (1) the omissions in the form of crude assumptions made in the Pitzer's model during its development from earlier models, (2) the

neglect given to the depression in the dielectric constant, of the electrolytic solution when the solute is dissolved in the solvent, and (3) more important is the absence of suitable terms that can explain solute - solvent interactions in the model for the parameters used in the plots taken for analysis.

We also listed the changes in the slope corresponding to the points of formation of the three types of the ion pairs, in table 2, for the electrolytes under our study. It is interesting to note that our findings show very good agreement with those of the findings of Chandrika Akilan. Several details would be presented in our communications to follow in respect of Acoustic, Thermodynamic, Densimetry and other related studies.

4.2 Observations of other Workers in Support of our Findings

Margaret Robson Wright [59], finds that Ultrasonic and spectroscopic methods probably allow a distinction to be made with reasonable certainty [60] between outer and inner-sphere ion pairs, while conductance work and scattering of light experiments allow micelle formation to be picked up very easily. These are quite exceptional achievements in the field of association. Inferences made from thermodynamic and kinetic experiments have often been used, but they rely very heavily on being able to predict a model for the ideal solution, for which a theory is yet to be conceived.

A systematic study of the dielectric relaxation spectra of aqueous solutions of LiCl and Li₂SO₄ was reported by W. Wachter, Š. Fernandez and R. Buchner, G. Hefter [61]. They reported the formation of the presence of double-solvent-separated (2SIP) and solvent-shared (SIP) ion pairs, respectively. Consistent with spectroscopic studies, *no contact ion pairs were detected* over the studied concentration range. The overall ion association constants obtained were in good agreement with literature data for both salts. Detailed analysis of the solvent relaxations indicated that Li⁺ has a significant second solvation sheath although there were differences between the effective hydration numbers obtained from LiCl and Li₂SO₄, which might arise from competition for the solvent from the anions from competition for the solvent from the anion. *Soto et.al.,[62]* developed a model based on the *Pitzer formalism* to correlate the activity coefficient, apparent molar volume and isentropic compressibility of glycine in aqueous solutions of NaCl, based on detailed experimentation with ultrasonic techniques. The results show that the model can accurately correlate the interactions in aqueous solutions of glycine and NaCl. A positive transfer volume of glycine from a NaCl solution to a more concentrated NaCl solution indicates that the size of a glycine molecule is

larger in a solution with higher NaCl concentration. The negative values of apparent isentropic compressibility imply that the water molecules around the glycine molecules are less compressible than the water molecules in the bulk solution. These effects are attributed to the doubly charged behavior of glycine and to the formation of physically bonded ion-pairs between the charged groups of glycine and sodium and chloride ions. The formation of ion-pairs, whose extents of binding reactions depend on the concentrations of both NaCl and glycine, alter the hydration number of glycine. This also explains the reason for the increase in the size of glycine with an increase in the NaCl concentration.

Chandrika Akilan (2008) in the Doctoral thesis made a systematic study of thermodynamic parameters of interaction between the Cu^{2+} and SO_4^{2-} ions in aqueous solutions. A variety of techniques including U.V Visible Spectrophotometry, Cu (II) ion-selective electrode potentiometry, dielectric relaxation spectroscopy, and titration Calorimetry were used in her studies. This work forms a perfect backdrop for the comparison of our results. Incidentally CuSO_4 is one of the sulphate electrolytes we have chosen and our results show excellent agreement with C. Akilan's interesting observations about the Ion pairs, in the case of that electrolyte.

A new excess Gibbs energy function to represent the deviations from ideality of binary electrolyte solutions was derived by *Ali Haghtalab*. The function consists of two contributions, namely: the first due to long-range forces, represented by the Debye-Huckel theory, and the second due to short-range forces represented by the local composition concept. *A. Haghtalab* claims that the model consistently produces better results at higher concentration ranges in which other models deteriorate. One of the possible reasons is the implied ion pair formation mechanism, which is yet to be mathematically incorporated in to several equations, through several missing links one of whom is the dielectric property.

We have tabulated our data calculated with Pitzer model and Bromley model in comparison with that taken from *Robinson & Stokes* and presented the same in table 3. The obvious disagreement is not only due to the missing links between D-H Model and other later developments in it but also due to omissions cited in the Pitzer model, and also due to necessity for the impregnation of the variation of dielectric constant with concentration contemplated by the Glueckauf's model. These are mainly responsible for revealing the traits of the formation of the three types of the ion pairs.

M. A. Petrowsky [63] studied Molar conductivity with square root of molality for the salt lithium triflate. His

studies for different iso-dielectric constant values of dissolved solvent mixtures studied, using methyl acetate, Tetrahydrofuran, Diglyme, 1-decanol, 1-octanol and 1-hexanol as solvents, for solutions of lithium triflate are presented, in his doctoral thesis. Numerous experiments with liquid electrolytes conducted by M.A. Petrowsky lead to the conclusion that the ionic mobility is a function of three variables for salt concentrations less than 0.01 M and fixed temperature: (1) the concentration of "free" ions, (2) the solvent dielectric constant ϵ , and (3) the solvent functional group. This is evidence recorded to confirm the strong solvent solute interactions, and the study of the graphs presented in the thesis reflects this on analysis.

M. K. Khoshkbarchi [64] using a novel method developed for the measurement of the activity coefficients of an amino acid and the mean ionic activity coefficients of an electrolyte in water-electrolyte-amino acid systems, with the aid of an electrochemical cell, with two ion selective electrodes and a reference electrode, The amino acids studied were glycine, DL-alanine, DL-valine and DL-serine and the electrolytes studied were NaCl and KCl. Activity coefficient data, at 298.15 K, for eight water-electrolyte-amino acid systems were obtained. The cell consisted of a cation and an anion ion selective electrode, and the potential of each was measured versus a double junction reference electrode. Data of measurements of chosen amino acids in electrolytic solutions of NaCl and KCl were reported. For the same systems, the solubilities at 298.15 K of the amino acids were measured at various electrolyte concentrations. The results show that the activity coefficients and the solubility of the amino acid in aqueous electrolyte solutions are strongly affected by the concentrations of both the electrolyte and the amino acid, the chemical structure of the amino acid and the nature of the cation of the electrolyte. The activity coefficients of amino acids in aqueous electrolyte solutions were remodelled [65, 66] (*Khoshkbarchi and Vera Model or the K-V Model*) using a two-parameter excess Gibbs free energy model based on the contribution of a long range interaction term represented by the Bromley or the K-V model and a short range interaction term represented by the NRTL or the Wilson model. He also developed a model based on the perturbation of a hard sphere reference system, coupled with a mean spherical approximation model, to correlate the activity coefficient of the amino acid and the mean ionic activity coefficient of the electrolyte in water-electrolyte-amino acid systems. The model can also predict the activity coefficients of amino acids in aqueous electrolyte solutions, without adjusting any

Parameter, at low electrolyte concentrations and slightly deviates from the experimental data at higher electrolyte concentrations. It was shown that upon availability of

independently evaluated. Experimental data for Δh and Δg , the water-amino acid solubility model can accurately predict the solubility of amino acids in aqueous solutions without any adjustable parameter. We completed the evaluation of the activity coefficient, and excess Gibbs

energy data for our systems with the *Bromley's model*, and the evaluation of the same with the *Khoshkbarchi and Vera Model* is in progress. The outcome is being communicated very shortly.

Table: 1. Parameters of Thermodynamic functions for 2-2 electrolytes in water at 25^o C

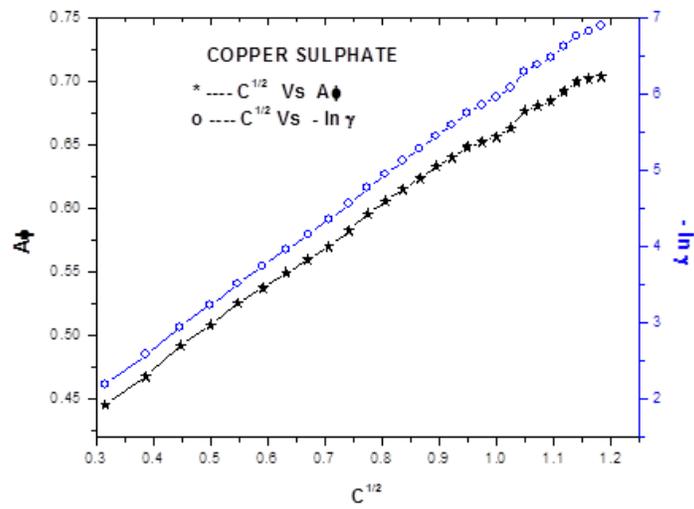
Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^Φ
Copper Sulphate	0.2358	2.4850	-47.3500	-0.0012
Nickel Sulphate	0.1702	2.9070	-40.0600	0.0366
Manganese Sulphate	0.2010	2.9800	-40.0000	0.0182
Cobalt Sulphate	0.2000	2.7000	-30.7000	-

Table 2 : Slopes of $C^{1/2}$ Vs A_ϕ and $C^{1/2}$ Vs $-\ln r$ for sulphates with Pitzer Model using Experimental Dielectric data

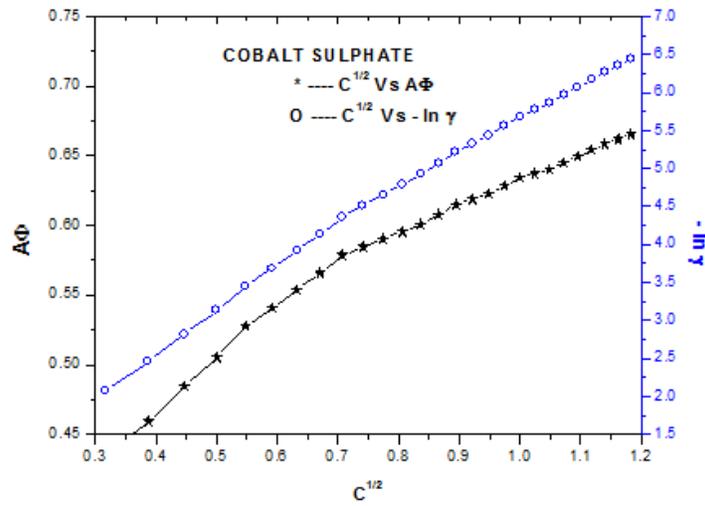
S.No	Electrolyte	Slopes of $C^{1/2}$ Vs A_ϕ			Slopes of $C^{1/2}$ Vs $-\ln r$		
		Solvent Separated Pairs	Solvent Shared Pairs	Solvent Contact Pairs	Solvent Separated Pairs	Solvent Shared Pairs	Solvent Contact Pairs
1	Copper Sulphate	0.3457	0.1673	0.0881	5.6773	4.1303	5.8086
		0.2844	0.1697		5.6229		3.1832
2	Nickel Sulphate	0.3064	0.1129	0.1645	5.3768	2.7073	4.4339
				0.1113			3.1368
3	Manganese Sulphate	0.4725	0.4907	0.0347	6.5292	7.7416	4.5554
			0.4565		5.3702	8.3684	
4	Cobalt Sulphate	0.3956	0.1717	0.1601	5.8383	4.1431	4.9784
		0.318					

Table: 3. Comparison of calculated Activity Coefficient of Sulphates from Pitzer model (γ_P) and Bromley model (γ_B) with the data collected from Robinson and Stokes ($\gamma_{R,S}$) at 25^o C.

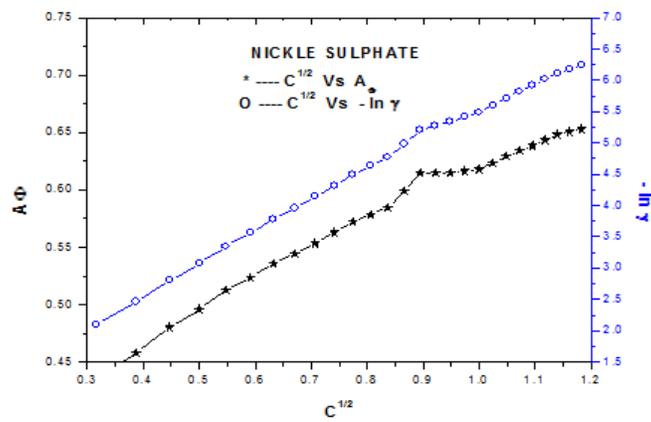
Concentration gr.mol.lit ⁻¹	Copper Sulphate			Nickel sulphate			Manganese Sulphate		
	γ_P	γ_B	$\gamma_{R,S}$	γ_P	γ_B	$\gamma_{R,S}$	γ_P	γ_B	$\gamma_{R,S}$
0.1	0.1116	0.9119	0.1500	0.1229	0.9120	0.1500	0.1394	0.9116	0.1500
0.2	0.0528	0.8788	0.1040	0.0608	0.8788	0.1050	0.0743	0.8781	0.1050
0.3	0.0300	0.8545	0.0829	0.0353	0.8545	0.0841	0.0415	0.8535	0.0848
0.4	0.0191	0.8348	0.0704	0.0229	0.8348	0.0713	0.0225	0.8336	0.0725
0.5	0.0129	0.8188	0.0620	0.0159	0.8181	0.0627	0.0132	0.8165	0.0640
0.6	0.0085	0.8032	0.0559	0.0112	0.8033	0.0562	0.0079	0.8014	0.0578
0.7	0.0060	0.7900	0.0512	0.0085	0.7901	0.0515	0.0047	0.7879	0.0530
0.8	0.0043	0.7779	0.0475	0.0055	0.7781	0.0478	0.0034	0.7757	0.0493
0.9	0.0032	0.7669	0.0446	0.0048	0.7670	0.0448	0.0022	0.7644	0.0463
1.0	0.0026	0.7566	0.0423	0.0041	0.7568	0.0425	0.0016	0.7539	0.0439
1.2	0.0015	0.7381	0.0388	0.0027	0.7383	0.0390	0.0009	0.7349	0.0404
1.4	0.0010	0.7217	0.0365	0.0019	0.7219	0.0368	0.0005	0.7180	0.0380



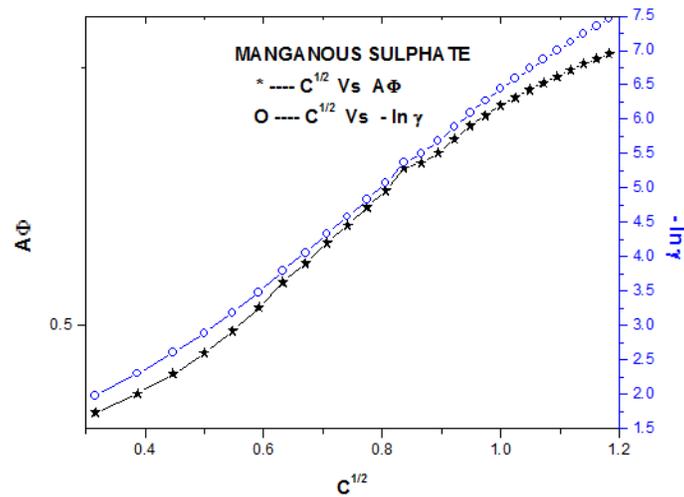
Graph: 1



Graph: 2



Graph 3



Graph 4

MATLAB PROGRAMME USED TO CALCULATE ACTIVITY COEFFICIENT:

```

%%%%%%%%%
clc
clear all
close all
m=[0.1:0.05:1.4];
Api=[0.4453, 0.4675,0.4917,0.5080, 0.5251,0.5370,
0.5493,0.5595,0.5700,0.5825,0.5954,0.6054,0.6149,0.6234,0.6329,0.6400,0.6481,0.6522,
0.6563,...
0.6630, 0.6766, 0.6805, 0.6844, 0.6921, 0.6999, 0.7018, 0.7037];
I=[0.4:0.2:5.6];
beta0=0.2358;
beta1=2.485;
beta2=-47.35;
sigma=0.003;
b=1.2;
alpha1=1.4;
alpha2=12.0;
Cpi=-0.0012;
%%%%%%%%%
for i=1:27
fpi(1,i)=-Api(1,i)*[sqrt(I(1,i))/[1+(b*sqrt(I(1,i)))]];%eq.6
Bpi(1,i)=beta0+(beta1*exp(-alpha1*sqrt(I(1,i))))+(beta2*exp(-
alpha2*sqrt(I(1,i))));%eq.7
end
%%%%%%%%%
for i=1:27
pi(1,i)=1+4*fpi(1,i)+m(1,i)*Bpi(1,i)+(m(1,i).^2)*Cpi;%%%eq.5
end
%%%%%%%%%
Cgamma=(3/2)*Cpi;%%%%%%%%%eq.11
%%%%%%%%%
for i=1:27
a(1,i)=1+b*sqrt(I(1,i));
end
for i=1:27
fgamma(1,i)=-Api(1,i)*((sqrt(I(1,i))/a(1,i))+((2/b)*log(a(1,i))));%eq 9
Bgamma(1,i)=2*beta0+((2*beta1)/((alpha1.^2)*I(1,i)))*(1-(1+(alpha1*sqrt(I(1,i))))...
    
```

```

- (0.5*(alpha1.^2)*I(1,i)))*exp(-
alpha1*sqrt(I(1,i)))+(2*beta2)/((alpha2.^2)*I(1,i))*(1-
(1+(alpha2*sqrt(I(1,i))))...
- (0.5*(alpha2.^2)*I(1,i)))*exp(-alpha2*sqrt(I(1,i)));%eq.10
end
for i=1:27
loggamma(1,i)=4*fgamma(1,i)+m(1,i)*Bgamma(1,i)+m(1,i).^2*Cgamma;%eq.8
end
for i=1:27
gamma(1,i)=exp(loggamma(1,i));
end

```

REFERENCES

- [1] Nic, M., Jirat, J.; Kosata, B., eds. (2006), "Activity Coefficient". *IUPAC Compendium of Chemical Terminology* (OnlineEd.). doi: 10.1351/goldbook.A00116., ISBN0-9678550-98, <http://goldbook.iupac.org/A00116.html>.
- [2] Margules, Max (1895). "Über die Zusammensetzung der gesättigten Dämpfe von Mischungen". *Sitzungsberichte der Kaiserliche Akademie der Wissenschaften Wien Mathematisch-Naturwissenschaftliche Klasse II* **104**: 1243–1278. <http://www.archive.org/details/sitzungsbericht10wiengoog>
- [3] Gokcen, N. A., (1996), "Gibbs-Duhem-Margules Laws". *Journal of Phase Equilibria* **17** (1): 50–51, doi:10.1007/BF02648369.
- [4] C.W. Davies, *Ion Association*, Butterworths, 1962, 37-53
- [5] I. Grenthe and H. Wanner, *Guidelines for the extrapolation to zero ionic strength*, <http://www.nea.fr/html/dbtdb/guidelines/tdb2.pdf>.
- [6] X. Ge, X. Wang, M. Zhang, S. Seetharaman, Correlation and Prediction of Activity and Osmotic Coefficients of Aqueous Electrolytes at 298.15 K by the Modified TCPC Model. *J. Chem. Eng. data.* 52 (2007) 538- 546.
- [7] X. Ge, M. Zhang, M. Guo, X. Wang, Correlation and Prediction of Thermodynamic Properties of Non-aqueous Electrolytes by the Modified TCPC Model. *J. Chem. Eng. Data.* 53 (2008)149-159, <http://pubs.acs.org/doi/abs/10.1021/je700446q>
- [8] X. Ge, M. Zhang, M. Guo, X. Wang. Correlation and Prediction of thermodynamic properties of Some Complex Aqueous Electrolytes by the Modified Three-Characteristic-Parameter Correlation Model. *J. Chem. Eng. Data.* 53(2008)950-958. <http://pubs.acs.org/doi/abs/10.1021/je7006499>
- [9] X. Ge, X. Wang. A Simple Two-Parameter Correlation Model for Aqueous Electrolyte across a wide range of temperature. *J. Chem. Eng. Data.* 54(2009)179-186. <http://pubs.acs.org/doi/abs/10.1021/je800483q>
- [10] "Project: Ionic Strength Corrections for Stability Constants". IUPAC. Archived from the original on 29 October 2008. <http://www.iupac.org/web/ins/2000-003-1-500>. Retrieved 2008-11-15.
- [11] K. Thomsen, P. Rasmussen, R. Gani. *Chem. Eng. Sci.* **51**, 3675 (1996). K. Thomsen and P.Rasmussen. *Chem. Eng. Sci.* **54**, 1787 (1999).
- [12] Renon H., Prausnitz J. M., (1968), "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", *AIChE J.*, 14(1), S.135–144, 1968
- [13] "Historic Papers in Electrochemistry" ,*Physikalische Zeitschrift* (1923), VIERUNDZWANZIGSTER JAHRGANG Mit elf Tafeln, *Electrochemical Science and Technology Information Resource (ESTIR)* P. Debye and E. Hückel (1923). "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und Verwandte Erscheinungen, [The theory of electrolytes. I. Lowering of freezing point and related phenomena](#)" *Physikalische Zeitschrift* **24**: pp185–206. ; *Debye-Hückel equation*, & limiting law *Wikipedia*, http://en.wikipedia.org/wiki/Debye%E2%80%93H%C3%BCckel_equation
- [14] T. Gunavardhan Naidu, N.S.S.V.Raja rao, & V.Brahmajirao (2011), "Acoustic, dielectric and Thermodynamic...of alcoholic electrolyte solutions ...Eigen Mechanism of ON PAIRS", of 'Acoustic waves' (ISBN:978-81-8329-441-6), pp121-131 published by Shree Publishers and Distributors, 22/4735 PrakashDeep Building, Daryaganj, and NewDelhi-110002. Ibid (2011), "Acoustic, Thermodynamic, Electrochemical, and dielectric studies of Eigen Mechanism of ION PAIRS" of 'Acoustic waves' (ISBN: 978-81-8329-441- 6) , pp132-144, published by Shree Publishers and Distributors, 22/4735 Prakash Deep Building, Daryaganj, NewDelhi-110002

- [15] C. C. Chen, H. I. Britt, J. F. Boston, L. B. Evans. *AIChE J.* **24**, 588 (1982) ; C. C. Chen and L. B. Evans. *AIChE J.* **32**, 444 (1986) ; C. C. Chen and Y. Song. *AIChE J.* **50**, 1921. Salzman, William R. (2001-08-21). "Mixtures; Partial Molar Quantities; Ideal Solutions". *Chemical Thermodynamics, University of Arizona, U.S.A.* <http://web.archive.org/web/20070607142802/http://www.chem.arizona.edu/~salzmanr/480a/480ants/mixpmqis/mixpmqis.html>
- [16] McDermott, Fluid Phase Equilibrium 1(1977),p33 ; Flemmer (Coll. Czech. Chem.Comm., 41 (1976), p3347.
- [17] Kaj Thomsen (1997), **Ph.D. Thesis** entitled: 'Aqueous Electrolytes: model parameters and Process simulation', submitted to Department of Chemical Engineering, Technical University of Denmark, DK-2800, Lyngby, Denmark.
- [18] H. Nicolaisen et al., (1993) *Chem. Eng. Sci.* **48**, 3149 (1993)
- [19] K. Thomsen, et al., (1996), *Chem. Eng. Sci.* **51**, 3675 (1996). Symposium on Solubility Phenomena (11th ISSP), Aveiro, Portugal, 25–29 July 20 ; K. Thomsen and P. Rasmussen. (1999), *Chem. Eng. Sci.* **54**, 1787 (1999).; K. Thomsen., (2005), *Pure Appl. Chem.*, Vol. 77, No. 3, pp. 531–542, 2005, (*Paper based on a presentation at the 11th International 2004). **Symposium on Solubility Phenomena (11th ISSP)**, Aveiro, Portugal, 25–29 July 2004.
- [20] E.A. Guggenheim, (193 submitted to 5), *Phil. Mag.*, Vol. 7, No. 19, p. 588 ; E.A. Guggenheim and J.C. Turgeon, (1955), *Trans. Faraday Soc.*, Vol. 51, p. 747; E.A. Guggenheim, (1966), "Applications of, Statistical Mechanics", Clarendon Press, Oxford, pp166-170.
- [21] Lionel Sébastien Belvèze (2004), **Ph.D., Thesis** entitled : 'Modeling & Measurement of Thermodynamic Properties of Ionic liquids', submitted to the University of Notre Dame, Notre Dame, Indiana
- [22] G.Scatchard, (1939) , *Chem.Rev.*, **19**, 309 ; Ibid, (1959) , in "The structure of Electrolytic solutions", WILEY, New York, p9 ; G.Scatchard, *J.Amer.Chem.Soc.* (1961), **83**, p2636. G.Scatchard, R.M.Rush and J.S.Johnson, (1970) , *J.Phys.Chem.* **74**, p 3786
- [23] J.C.Rasalah and H.L.Friedman (1968), *J.Chem.Phys.*, **48**, 7242
- [24] D.N.Card and J.P.Valleau , (1970) , *J.Chem.Phys.*, **52**, p6232 ; J.C.Rasalah, D.N.Card and J.P.Valleau (1972), *J.Chem.Phys.*, **52**, p6232
- [25] A.J. Bard, R. Parsons, and J. Jordan (1985): 'Standard Potentials in Aqueous Solutions', Marcel Dekker, New York, NY, 1985, pp. 567-73
- [26] K.S. Pitzer, "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations" *J. Phys. Chem.*, Vol. 77, No. 2, (1973), pp. 268-277. K.S. Pitzer, "Theory: Ion Interaction Approach," *Activity Coefficients in Electrolyte Solutions*, Pytkowicz, R. ed., Vol.I, (CRC Press Inc., Boca Raton, Florida, U.S.A., (1979). ; K.S. Pitzer, "Fluids, both Ionic and Non-Ionic, over Wide Ranges of Temperature and Composition," *J. Chem. Thermodynamics*, Vol.21, (1989), pp. 1-17. (Seventh Rossini lecture of the commission on Thermodynamics of the IUPAC, Aug. 29, 1988, Prague, ex-Czechoslovakia). ; K.S. Pitzer, *J. Solution Chem.*, Vol. 4, (1975), p 249. ; R.C. Phutela and K.S. Pitzer, "Thermodynamics of Aqueous Calcium Chloride," *J. Solution Chem.*, Vol. 12, No. 3, (1983), pp.201-207
- [27] J. N. Bronsted, (1921), *Kgl .Dan. Vidensk. Selsk. Mat. Fys. Medd.*, **4**(4) ; Ibid (1922), *J. Amer. Chem. Soc.*, **44**, 877; Ibid (1923), *J. Amer. Chem. Soc.*, **45**, 2898
- [28] J. E. Meyer (1959), *J. Chem. Phys.* **18**, p1426; M. H. Leitzke and R. W. Stoughton, (1962) *J. Phys. Chem.*, **66**, p508
- [29] G. Scatchard, *J. Amer. Chem. Soc.* (1961), **83**, p 2636. ; G.Scatchard, R. M. Rush and J. S. Johnson, (19) *J. Phys. Chem.* **74**, p378; J. C. Kirkwood (1936), *Chem. Rev.* **19**, p 275.; Ibid (1954), *J. Phys.Chem.*, **58**, 691
- [30] P. Van Rysselberghe and S. Eisenberg. (1939) *J.Amer. Chem. Soc.* **61**, p3030 ; Ibid (1940), *J. Amer. Chem. Soc.* **62**, p591
- [31] Bagchi S. N., (1950), 'A New Equation for Strong Electrolytes' Parts I and II *J. Ind. Chem. Soc.*, **27**, 199 and 204
- [32] Dutta M. and Bagchi, S. N. (1950) 'On the distribution of Ions in Solutions of Strong Electrolytes', *Ind. J. Phys.*, **24**, 61

- [33] Dutta M. and Sengupta, M. (1954), A Theory of Strong Electrolytes in Solution based on a New Statistics, Proc. Nat. Inst. Sci. India, 20, p1
- [34] Eigen. M. and Wicke, E. (1951) Zur Theorie der Starken Elektrolyte, Naturwiss, 38, p453
- [35] T. L. Hill (1956), 'Statistical mechanics' MCGraw Hill, New York
- [36] K. S. Pitzer (1993), 'Molecular structure and Statistical thermodynamics', Selected Papers of Kenneth .S. Pitzer, Editor K. S. Pitzer, World Scientific, 1993
- [37] Morteza Baghalha (1999), **Ph.D., Thesis** entitled: 'Aqueous $[H_2SO_4-Al_2(SO_4)_3-MgSO_4]$ Solutions Laterites', submitted to The Department of Chemical Engineering and Applied Chemistry, The University of Toronto, Canada, Marcel Dekker, New York, 1985, 567-573
- [38] D.G. Archer and P. Wang: The Dielectric Constant of Water and Debye-Hückel Limiting Law Slopes, *J. Phys. Chem. Ref: Data*. 1990, Vol. 19(2). pp. 37 1-4 1 1.
- [39] K. S. Pitzer, R. N. Roy and L. F. Silvester, 'Thermodynamics of Electrolytes & Sulfuric Acid', *J. Am. Chem. Soc.*, 1977, Vol. 99, 4930-36
- [40] H. F. Holmes and R.E. Mesmer, Isopiestic studies of $H_2SO_4(aq)$ at elevated temperatures & Thermodynamic Properties, *J. Chem. Thermodyn.*, 1992. Vol. 24(3), 17-28.
- [41] F. Kremer, A. Schönhals (Eds.), *Broadband Dielectric Spectroscopy*, Springer, Berlin (2003)
- [42] Burgess, J. (1978) 'Metal Ions in Solution', Ellis Horwood, Chapter 5, "Solvation Numbers"
- [43] Fuoss, R.M., Kraus, C.A. (1935), "Properties of Electrolytic Solutions. XV. Thermodynamic Properties of Very Weak Electrolytes" *J. Amer. Chem. Soc.* 57, 1-4
- [44] Alexandrov, A., Kostova, S. (1984). "Extraction-Spectrophotometric and Radiometric Investigation of the ternary ion-association complex of Niobium(V) with Pyrocatechol and Triphenyl-tetrazolium Chloride" *Journal of Radio Analytical and Nuclear Chemistry* (Springer) 83 (2), 247-255
- [45] Fletcher, R. J., Gans, P., Gill, J.B., Geyer, C. (1997), "Spectro chemistry of Solutions Part 29, Intrusion ion pairing: Identification of a new form of ion pair in transition metal salt solutions in pyridine through their visible spectra". *J. Mol. Liquids*, 73-74, 99-106
- [46] (a) Richard Buchner (2008) A review, "What can belearnt from dielectric relaxation...on solvation and association?", *Pure Appl. Chem.* 80(6), 1239-1252
(b) Akilan, C., Hefter, G., Rohman, N., Buchner, R., 'Ion association and hydration inaqueous solutions of copper(II) sulfate from 5⁰ to 65⁰C by dielectric spectroscopy', *J. Phys. Chem. B.* 2006 Aug 3, 110(30), 14961-14970.
- [47] (a) David A. Turton, Johannes Hunger, Glenn Hefter, Richard Buchner, and Klaas Wynne Glasslike behavior in aqueous electrolyte solutions, (2008) *J. Chem. Phys.* 128, p161102
(b) Richard Buchner and Glenn Hefter (2009), *Phys. Chem Chem. Phys.*, 11, 8984-8999 <http://pubs.rsc.org/en/Content/ArticleLanding/2009/CP/B906555P/Unauth>
(c) Richard Buchner, Stephen, G. Capewell, Glenn Hefter, and Peter M. May, "Ion-Pair and Solvent Relaxation Processes in Aqueous Na₂SO₄ Solutions", <http://pubs.acs.org/doi/abs/10.1021/jp983706c>
- [48] Arne Brändström (1982), 'Ion-Pair Extraction As a toolfor.....Reactions related to phase transfer catalysis', *Pure & Appl.Chm.* 3 Vol.54, No.10, pp.1769 - 1782, 1982
- [49] G. Schill, et.al., (1974) Eds, 'Ion Exchange and Solvent Extraction' 6, 1-57, Dekker, NY(1974)
- [50] V. Brahmajirao, (1977), **Ph.D., thesis** submitted to Andhra University, Visakhapatnam, A.P., INDIA, Entitled: 'Influence of dielectric constant onIon-pair formation', ; V. Brahmajirao, (1979), "Cationic motilities of electrolytic solutions – Ion pairs –Eigen Mechanism", *Transactions of. Saest*, 14(2), p 53, *Ibid*(1976), *Ind. J. Pure. Appl. Phys.* 14, 646 ; *Ibid*(1980), *Ind. J. pure & Appl. Phys.* 12(1980), 1021; *Ibid*(1981), *Ind. J. pure & Appl. Phys.* 19(1981), 254.; *Ibid*(1980), "Influence of variation of dielectric-constant, Gucker's Equations, Proceedings (Conference papers) of International Conference on Ultrasonics, pages 214-219, *ICEU-July 1980*, Held at *NEWDELHI*, (printed by *INSDOC, NEWDELHI*) ; *Ibid*(1980) "Application of Variation of dielectric.....GKG and Dagget equations ", Proceedings of International Conference on Non Aqueous Solutions, *ICNAS-7*, held at *REGENSBURG, West Germany*, (Aug 1981) ; *Ibid* (1979), "Cationic motilities of electrolytic solutions Ion pairs –EIGEN mechanism", *Transactions of Saest*, 14 (2), (1979), 53.

- [51] T. Gunavardhan Naidu, N.S.S.V.Raja rao & V.Brahmajirao (2011), "Acoustic, dielectric and Thermodynamic...of alcoholic electrolyte solutions ...Eigen Mechanism of Ion Pairs", of '**Acoustic waves**' (ISBN:978-81-8329-441-6), pp121-131, Published by Shree Publishers and Distributors, 22/4735 Prakas Deep Building, Daryaganj, and NewDelhi-110002.Ibid (2011), "Acoustic, Thermodynamic, Electrochemical and dielectric studies of Eigen Mechanism of ION PAIRS" of '*Acoustic waves*' (ISBN: 978-81-8329-4416), pp132-144, Published by Shree Publishers and Distributors, 22/4735 Prakash Deep Building, Daryaganj, NewDelhi-110002
- [52] V.Brahmajirao et.al., (2010) , "Glueckauﬀ's model for lowering of dielectric constant of electrolytic Solutions... Ultrasonics -Ion pairs (CHLORIDES)" Journal of Acoustical society of India [ISSN-09733302], 37(1), pp101 to 110, www.nsa2010.gpgcrishikesh.com. V.Brahmajirao et.al., (2010) , "Glueckauﬀ's model for solutions.... Ultrasonics- 'Ion pairs (SULPHATES)" , Journal of Acoustical society of India , [ISSN-0973-3302], .37(1), (2010), pp111 to 121 .Website :www.nsa2010.gpgcrishikesh.com
- [53] Csaba Horvath, (1977) Analytical Chemistry, Vol. 49, No- 14, pp. 2295-2305
- [54] Devinder Kaur et.al.,(1993), 'Ion pair formation from.....', Organic Mass Spectrometry, 28, 327-334
- [55] F. Kremer, A. Schönhals (Eds.). *Broadband Dielectric Spectroscopy*, Springer, Berlin(2003)
- [56] R. Buchner. "Dielectric spectroscopy of solutions", in *Novel Approaches to the Structure and Dynamics of Liquids: Experiments, Theories and Simulations*, J. Samios, V. A. Durov (Eds.), pp.265–288, NATO Science Ser. II: Mathematics, Physics and Chemistry, Vol. 133, Kluwer, Dordrecht (2004)
- [57] Margaret Robson Wright (2007): "An Introduction to Aqueous Electrolyte Solutions" Art.1.12 Formation of Ion pairs from free ions, page 17, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chi Chester, West Sussex PO19 8SQ, England.
- [58] Robinson and stokes (2002) "Electrolytic Solutions ", Second revised edition, Chapter9, page 238: "Theoretical Interpretation of Chemical Potentials & Influence of ion solvent interactions on Ion atmosphere" and Also" Ion Association": Chapter11&14, Pages 392 & 429
- [59] Margaret Robson Wright (2007): "An Introduction to Aqueous Electrolyte Solutions", John Wiley & Sons Ltd, West Sussex PO19 8SQ, U.K., Page 41 &42, chapter 1, ion-ion interactions, ion-solvent interactions, Solvent- solvent- Solute Interactions
- [60] V.Brahmajirao et.al., Proc. NSA-010, Rishikesh, Uttarakhand, India (Nov.11th to 13th 2010) : 'Glueckauﬀ's model for lowering of dielectric constant of electrolytic solutions & Isentropic Compressibility and Ion- association Studies with aqueous electrolytic solutions Using Ultrasonics Ion pairs (CHLORIDES)' Ibid: Proc. NSA 2010, Rishikesh, Uttarakhand, INDIA (Nov. 11th to 13th 2010), 'Glueckauﬀ's model for lowering of dielectric constant of electrolytic solutions & Isentropic Compressibility and Ion- association Studies with aqueous electrolytic solutions using Ultrasonics - Ion pairs (SUPHATES)' .
- [61] W. Wachter, Š. Fernandez, and R. Buchner & G. Heftner(2007), 'Ion Association and Hydration in Aqueous Solutions.... by Dielectric Spectroscopy' J. Phys. Chem. B, 2007, 111 (30), pp9010–9017
- [62] Soto et. al., (1998), *Biophys. Chem.* 74(3): 165-73
- [63] Matt. A. Petrowsky (2008), **Ph.D., Thesis** entitled: 'Ion Transport in Liquid Electrolytes', Submitted to the University of Oklahoma, Graduate college , Norman, Oklahoma
- [64] M. K. Khoshkbarchi, (1996), **Ph.D., Thesis**, Entitled, "Thermodynamics of Amino acids in Aqueous Electrolyte solutions" , Department of Chemical Engineering, McGill University, Montreal, Canada
- [65] Khoshkbarchi, M. K., and Vera, J. H.,(1996) "Measurement and Correlation of Ion Activity Coefficients in Aqueous Single Electrolyte Solutions", *AICHEJ.*, 42, 249, 1996
- [66] Khoshkbarchi, M. K., and Vera J. H. (1996), "Extension to the Mixtures of the Equation of State of Hard Spheres with Correct Limits", *Fluid Phase Equilibria.*, 1996.