

CHAPTER: 1

LITERATURE SURVEY

1. Study of thermodynamic models:

James F. Hinton et.al, [1] suggested that even after the inception of theory of electrolytes by Debye and Huckel until the year 1970, the chemical literature was replete with articles dealing with the measurement, magnitude, and influence on chemical phenomena in solution of the solvation numbers of ions. Several methods were explained for Transference numbers of single and mixed solvents differences in ionic hydration, solvation- numbers and their dependence on current density, conductance and electromotive force measurement, thermodynamics, co-ordination numbers and activity coefficient.

Brahmajirao.V [2] applied the Glueckauff's model for the lowering of the dielectric constant of solvents as the concentration of the electrolyte is increased, and theoretically evaluated the dielectric data for several electrolytic systems in water and alcohol as solvents. This data was verified experimentally, and the experimental data was applied to several parameters like activity coefficients (D-H model), Isentropic-compressibilities, apparent and partial molal volumes, cationic mobilities and related parameters, all of which were experimentally determined using relevant techniques. Analysis of this data established conspicuous evidences of ion- pair formation mechanism.

Barthel and Buchner [3] presented high frequency permittivity of non- aqueous electrolyte solutions and their solvents in the frame work of time domain and frequency domain methods. Evaluation of data was performed on the basis of models presupposing one or more relaxation processes. Depression of the solvent permittivity, relaxation times of the solvent molecules, and dispersion amplitudes and relaxation times of ion pair relaxation are investigated with regard to actual theories underlying these phenomena. Information is obtained on structural and dynamical properties of classes of electrolyte solutions based on protic H-bonding, dipolar aprotic, and low permittivity solvents and mixtures of solvents.

Mark D Cohen [4] reported measurements of water activity as a function of concentration of eleven single electrolyte aqueous solutions and three mixed electrolyte aqueous solutions, using Electro- dynamic balance. The measurements were performed.

Barba et.al, [5] developed a thermodynamic model for aqueous solutions of strong electrolytes in order to evaluate activity and osmotic coefficients of multi-component solutions of strong electrolytes. The excess Gibbs energy was given by three contributions: the Debye- Huckel term, the Born term and the Wilson term, the latter taking into account the effect of short range intermolecular forces. The proposed model needed only binary parameters, which can be obtained by fitting experimental data of binary aqueous electrolyte solutions. It makes valuable when experimental data of multi-component solutions were lacking. The proposed model could be used in calculating boiling point elevation or solubility of strong electrolytes in multi- component aqueous solutions in a wide range of temperature and concentration.

Hitoshi Ohtaki [6] studied structures of solvated metal ions and metal complexes in non-aqueous solvents by means of X- ray diffraction and the results are discussed in connection with thermodynamic quantities and spectroscopic data of these species. Solvation structures of alkali metal ions with special reference to lithium ion in formamide, of copper (II) in N, N- dimethyl formamide (DMF) and in DMF- acetonitrile(AN) mixtures, and of cadmium (II) ion in DMF are discussed. Chloro and bromo complexes of copper (II) ion have been investigated in DMF, AN, DMF- AN mixtures and dimethyl sulfoxide (DMSO) solutions by spectro- photometric and calorimetric measurements, and the structure of the complexes with varying numbers of ligands is estimated.

Rajendran et.al, [7] studied the preferential solvation of copper (II) salts, namely acetate, benzoate and iodate, water- pyridine and water- dimethyl sulphoxide (DMSO) mixtures at 30°C by Gibbs energies of transfer and solvent transport number measurements. While the solubility of copper(II) acetate and copper(II) iodate in water-pyridine mixtures increases up to the pyridine mole fraction $X_{py} = 0.1$, and then decreases, the solubility of copper(II) benzoate increases continuously with the addition of pyridine up to the pure solvent. In the case of water- DMSO mixtures, the solubilities

of copper iodate and copper benzoate increase, whereas that of the acetate decreases continuously with the addition of DMSO. The Gibbs energy of transfer of the Cu^{2+} ion is negative and decreases continuously with the addition of pyridine or DMSO, while that of the acetate, benzoate and iodate anions is positive and increases continuously in both the solvent mixtures. These results, along with the solvent transport number Δ of pyridine or DMSO, have been interpreted in terms of hetero- selective solvation of the salts, with the Cu^{2+} ion being preferentially solvated by pyridine or DMSO and the anions by water in water-pyridine and water- DMSO mixtures respectively.

Barthel, Buchner, et.al, [8] presented details about the microwave dispersion and absorption spectra for various protic and aprotic electrolyte solutions and their solvents over large frequency ranges, in general 0.9-90 GHz. Wider frequency ranges are covered for water (0.9-409 GHz) and for methanol, N- methylformamide and N, N-dimethyl formamide (0.9-293 GHz). The role of insufficient frequency coverage is critically discussed. Permittivity and relaxation times of the underlying relaxation processes are compared for electrolyte solutions of the hydrogen- bonding solvents like water, methanol and higher alcohols, formamide, N- methyl formamide and the dipolar aprotic solvents like aceto- nitrile, propylene carbonate, dimethyl sulfoxide, and N, N- dimethyl formamide. For 1:1-electrolytes ion-pair formation is detectable in all solvents of static permittivity below 50; the concentration dependence of the corresponding relaxation time permits separation into rotational and kinetic modes of ion-pair formation and decomposition.

Ali Haghtalab [9] determined the mean ionic activity coefficients of NaBr in aqueous mixtures of NaBr and $\text{Ca}(\text{NO}_3)_2$ at 25 ⁰ C at a total ionic strength of 3, 4.5 and 6 molal. The measurements were made using an electrochemical cell with the ion-selective electrodes (ISE), Na-ISE against Br-ISE as a reference electrode. The experimental mean activity coefficients of NaBr obey Harned's Rule. The mean activity coefficients of $\text{Ca}(\text{NO}_3)_2$ were calculated using the cross differentiation of the mean activity coefficients. Also focussed on the thermodynamics of aqueous solutions of strong electrolytes for both binary and multi- component systems. A new excess Gibbs energy function to represent the deviations from ideality of binary electrolyte solutions was

derived consisting of two contributions, one due to long-range forces, represented by the Debye- Huckel theory, and the other due to short-range forces represented by the local composition concept, valid for the whole range of electrolyte concentrations. Electrochemical data on constructed electrochemical cell apparatus using Ion-Selective Electrodes is used in the activity coefficient evaluations. A novel mixing rule was proposed for the mean activity coefficients of electrolytes. Predictions are in excellent agreement with Bronsted Specific Ionic theory.

Blandamer et.al, [10] described the basis of a method for analyzing the dependence of rate constants on solvent composition using Kirkwood- Buff integral functions. The background to the treatment was examined with reference to the analysis of thermodynamic properties of binary aqueous mixtures and outlined a procedure for combining this information and kinetic data to yield parameters characterizing interactions between solutes and the components of a binary aqueous solvent mixture. The calculations yield information concerning the affinities of solutes for components of the solvent mixture and hence describing the phenomenon of preferential solvation. Examples were quoted using kinetic data describing reactions involving organic and inorganic substances.

Barthel and Neueder [11] precise osmotic coefficients from absolute vapour pressure measurements on various electrolyte solutions of organic solvents are given as the reference data for use in relative vapour pressure measurement methods. The availability of reliable data is used for a study of the inter dependence of thermodynamic properties and theoretical and experimental McMillan- Mayer level methods, such as chemical model and hypernetted chain calculations and small angle neutron scattering experiments.

Lu and G. Maurer [12] developed their thermodynamic model starting from Gibbs free energy and by combining ionic solvation equilibria and physical interaction forces. It is shown that by using the parameters correlated from single electrolyte aqueous systems, the activity coefficients in mixed electrolyte aqueous solutions can be accurately predicted up to the solubility limit, for example, at very high ionic strength. The Gibbs excess energy, for the mixture of aqueous electrolyte solution consisting of water, un-

solvated and solvated ions, an expression for the Gibbs excess energy is taken from the combination of the D- H model and UNIQUAC model especially to correlate osmotic coefficient and mean activity coefficients of dissolved electrolytes in a mixed electrolyte aqueous solution which are closely inter- related.

Strauch and Cummings [13] reported Gibbs ensemble simulations of vapour liquid equilibrium in water/NaCl , and water/methanol/NaCl mixtures, in which water-water interaction was modelled as simple point charge (SPC) potential of Berendsen et.al., and the Na- Na, Na- Cl and Cl- Cl interactions are given by the Fumi-Tosi potentials .Ion-Water interactions are developed by Chandrasekhar et.al, and Methanol-Methanol potential was by Haughney. Water-methanol interactions are obtained by Lorentz- Bertholet mixing rules. They obtained qualitative agreement in results.

Khoshkbarchi [14] used Ion-selective electrodes to measure the activity coefficients at 298.2 K of individual ions in aqueous solutions of NaCl and NaBr up to of 5 molal and of KCl up to 4 molal. The mean ionic activity coefficients of NaCl, NaBr, and KCl, obtained from the values of the activity coefficients of the individual ions, show good agreement with values reported in the literature. The experimental results show that the activity coefficients are different for the anion and the cation in an aqueous solution of a single electrolyte and that, as expected from the ion-ion and ion-solvent interactions, the activity coefficient of an ion depends on the nature of its counterion. A modified form of the Pitzer's model, which distinguishes between the activity coefficients of the anion and the cation, was used to correlate the experimental results. Anovel method was 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 using electrochemical cell. Using a two- parameter excess Gibbs free energy model, contribution of a long range interaction term represented by the Bromley model, the K- V model, the MSA model and a short range interaction term represented by the NRTL, the Wilson models were estimated and the analysis of the results is presented.

Xiao- hua Lu et.al, [15] further extended the Lu and Maurer model for aqueous electrolyte solutions to predict activity coefficients, enthalpy and solubilities of salts simultaneously, using the Gibbs –Helmholtz Relation. For this it was assumed by them

that dissolving strong electrolytes in water results in a mixture of water molecules, unsolvated and solvated ions. Consequently in this model, when solvation equilibria are used to assess the outcomes through physiochemical determinations and if the formed ion pairs or the Micelle are not accounted in the development of the model, then the results don't reflect the mechanism of formation of ion pairs, or Clusters or Micellar formation.

Kaj Thomsen [16] reported The extended universal quasichemical (UNIQUAC) model which is a thermodynamic model for solutions containing electrolytes and non electrolytes. The model is a Gibbs excess function consisting of a Debye- Huckel term and a standard UNIQUAC term. The model only requires binary ion-specific interaction parameters. A unique choice of standard states makes the model able to reproduce solid-liquid, vapor-liquid, and liquid-liquid phase equilibria as well as thermal properties of electrolyte solutions using one set of parameters.

Jean-Francois and Jacques E. Desnoyers (17), in a publication to the memory of Kenneth S. Pitzer in recognition of his contributions to solution chemistry, attempted a novel method of calculation of the Relaxation effect, a prominent mechanism of the basic D- H Model and also the starting point for 'The Bjerrum association model', by extending their studies to apparent molar heat capacities and compressibilities of these systems. The proposed method of calculation were taken into account to study relaxation effects observed in second derivatives of the excess Gibbs free energy, which can be used to extrapolate to infinite dilution. The experimental data for systems showing a wide range of association constants in aceto- nitrile, propylene carbonate and water. The concentration dependence of the thermodynamic properties can be reproduced quantitatively by the addition of one or two virial coefficients. For dissociated or slightly associated systems ($K_A < 10$), the standard infinite dilution quantities were found to show excellent agreement with literature values. For systems with high K_A , the standard infinite dilution quantities obtained by the model are systematically lower than those reported in the literature. This is not surprising, since the traditional method of extrapolation using the Debye-Huckel limiting law or the Pitzer equation does not take association into account.

Morteza Baghalha [18] reported several interesting results about aqueous sulphate solutions of aluminium and magnesium, in thermodynamic studies. A hybrid ion-association- interaction approach with the Pitzer model is implemented. Measured data of conductance, of the ionic liquid systems using a novel conductivity cell and setup, are analysed.

Robert. A. Marriott [19] reported measurements of heat capacities and densities ; the properties that provide insight into the manner in which chemical equilibria respond to changes in their environment, and also give information to indicate how solutes interact with other solutes and solvent molecules. Partial and apparent molar properties and some electrostatic theories useful in modelling were presented.

Barthel et.al, [20] used the chemical models for the calculation of thermodynamic and transport properties of concentrated electrolyte solutions. Comparison was made with empirical approaches. Molecular ions with delocalized charges abolishing the concept of ionic point charges for the calculation of short range interactions are considered in the framework of chemical models. Novel lithium salts for technical applications are presented and the influence of electron withdrawing substituents at the anions on ion-pair formation, conductivity and anodic stability limit is studied to illustrate the role of molecular ions with delocalized charges.

Anderko et. al., [21] developed a thermodynamic model for calculating phase equilibria and other properties of multi- component electrolyte systems. The model was designed to reproduce the properties of both aqueous and mixed-solvent electrolyte systems ranging from infinite dilution to solid saturation or pure solute limit. The model incorporates formulations for the excess Gibbs energy and standard-state properties coupled with an algorithm for detailed calculations. This excess Gibbs energy model consists of a long-range interaction contribution represented by the Pitzer- Debye-Huckel expression, a second virial coefficient- type term for specific ionic interactions and a short-range interaction term expressed by the UNIQUAC equation. The accuracy of the model was demonstrated for common acids and bases and for multi- component systems containing aluminium species in various environments.

Das et.al, [22] studied the variation of surface tension of a solution with concentration via dimensionless variables and an identity. The behavior at the extremities was analyzed critically via a perturbative route that generated the natural indices of non-ideality. A Padé interpolation leads finally to a general form for the concerned variation. It nicely accounted for the salient features and correlated the change of surface tension with mole fraction in a variety of completely miscible, binary aqueous solutions. The work ability of a few prevalent equations was also scrutinized in the light of the present endeavor.

Hendrik [23], on the applications of the electrolytic systems to industry, discussed in detail several models starting from the D-H to the very recent developed versions of NRTL- MSA model. Details of McMillan- Mayer ensemble and Lewis-Randall systems were applied to Liquid-liquid equilibria and several features like the activity coefficient, and dissociation parameters were analysed with the application of these models.

Tolosa Arroyo et.al, [24] presented Molecular Dynamics Simulations of aqueous solutions of the solutes acetamide , acetic acid and acetaldehyde using Lennard- Jones (12-6-1) potentials to describe the solute- solvent interactions. The Morokuma decomposition scheme and the ESIE solute atomic charges were used to reproduce the exchange, polarization, and electrostatic components of the solute- water interaction energy. A nonlinear perturbation was incorporated into the “slow-growth” technique in order to improve the results for the solvation Gibbs energy that were found to be in agreement with the available experimental and theoretical values.

Nicolas Papaiconomou [25] presented precise vapor pressure data for LiBr solutions in methanol for temperatures ranging from 298.15 to 333.15 K. The molality range is from 0.0411 to 6.8675 mol·kg⁻¹. Osmotic coefficients were calculated by taking into account the second virial coefficient of methanol. The parameters of the Pitzer-Mayorga model, the Archer extension of the Pitzer-Mayorga model, the mole-fraction-based thermodynamic model of Clegg-Pitzer, and the recently developed MSA-NRTL model are evaluated, along with the corresponding standard deviation. These equations were used to calculate activity coefficients of LiBr in methanol solutions. Ornstein-

Zernike (OZ) equation with McMillan Mayer (MM) formalism was used. OZ equation treats statistically the interactions between particles by taking into account all the direct and indirect interactions. MM formalism considers the solvent as a continuum characterised by its permittivity, in which the solute is immersed. Further the chosen thermodynamic models were applied.

Lionel Sébastien Belvèze [26], on Thermodynamic properties of ionic liquids, studied them as “green solvents“. Measurements of Partition coefficients ‘ K_{ow} ’ in the phase behaviour with water for imidazolium based ionic liquids show they do not bio accumulate in systems. The behaviour of ionic liquids in organic solvents is vital for evaluating their many potential uses. Quaternary ammonium salts in water were chosen in this work, to which NRTL model was applied.

Robert H wood [27] reported experimental work on high temperature aqueous solutions, with the development of flow heat- of- mixing calorimeters, flow heat-capacity calorimeters, flow dens meters, and using flow technique electrical conductance setup. Infinite dilution conductance and association constants for a variety of electrolytes were calculated from this work. A compressible continuum model for ions in water was developed, with which the behaviour of volumes, heat capacities, pair correlation functions, conductivities of ions at infinite dilution were explained. Using the ab initio models, hydration Gibbs energies were predicted.

Søren Gregers Christensen [28] studied the distribution of solutes and solvent between an aqueous solution of salt and an ion exchange resin has been measured at ambient temperature. The experiments have been performed for aqueous solutions of KNO_3 , KCl , $Ca(NO_3)_2$ and $CaCl_2$ in the concentration range of 0-3N. The absorption has been measured for 3 gel type and 3 macroreticular resins with a degree of crosslinking varying from 10.5 to 18.5%. The experimental results have been modeled with the Extended UNIQUAC model combined with an elastic term taking the elastic properties of the resin structure into account. The model shows very good predictions with varying degree of crosslinking, and the deviations between model results and experimental data are all within the experimental error. Also studied the thermodynamics involved in describing the properties of aqueous solutions of electrolytes and of mixtures

with ion exchanging materials. The work uses both existing and new approaches for the description of these properties.

Stéphane Krebs [29] attempted to better the earlier Papaiconomou model (which did not account for the solvation of ions) by counting upon the short-range defects and also to implement the calculation of some specific thermo dynamical quantities like the heat capacities and the heats of dilution. Latter calculations required to take into account the effect of the variation of temperature.

Barthel et.al, [30] presented the measurement of electric conductivities of diluted magnesium sulfate solutions in binary mixtures of 1, 4- dioxane with water covering a solvent composition range up to 50 wt.% of 1, 4-dioxane at temperatures from 5 to 35 °C. Evaluation of the limiting molar conductivity Λ^∞ and the association constant K_A was based on the chemical model of electrolyte solutions, including short-range forces. From the temperature dependence of the limiting molar conductivities Eyring's enthalpy of activation of charge transport was estimated. The standard Gibbs energy, enthalpy and entropy of the ion-pairing process were calculated from the temperature dependence of the ion- association constants.

Frank J. Millero et. al., [31] studied the osmotic coefficients of FeCl_3 at 25 °C from 0.15 to 1.7 m to determine the Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$ and $C\phi$) for FeCl_3 . Since the differences in the Pitzer coefficients of rare earths in NaCl and NaClO_4 are small, the values of $\text{Fe}(\text{ClO}_4)_3$ have been estimated using the differences between $\text{La}(\text{ClO}_4)_3$ and LaCl_3 . The Pitzer coefficients for FeCl_3 combined with enthalpy and heat capacity data for the rare earths can be used to estimate the activity coefficients of Fe^{3+} in NaCl over a wide range of temperatures (0 to 50 °C) and ionic strength (0 to 6 m). The activity coefficients of Fe^{3+} in NaCl and NaClO_4 solutions have been used to determine the activity coefficients of $\text{Fe}(\text{OH})^{2+}$ in these solutions from the measured first hydrolysis constants of Fe^{3+} .

Lam Ngoc Phan [32] reported very interesting results, many analytical techniques and applications on switchable polarity solvent which is a liquid where its polarity can change between two forms, having similar characteristics using CO₂ as the switching agent in the form of a trigger .

Angshuman Maitra, et.al, [33] studied solute- solvent and solvent- solvent interactions in fifteen pure solvents and seven binary aqueous mixtures by monitoring the solubility of a dye in the solvents. The standard Gibbs energy of solvation, as given by $\log s$, where s was the solubility had been found to depend on various modes of solute- solvent interaction and also on the Hildebrand solubility parameter representing the cohesive energy density (solvent- solvent interaction) of solvent. In all the binary mixtures the value of $\log s$ had been found to deviate from the average of $\log s$ values in component pure solvents weighted with respect to their mole fractions. A dimensionless quantity had been defined to represent the deviation of the observed $\log s$ values from the mole fraction average. Results had been explained in terms of various modes of solvation interaction.

Rodríguez Vallés [34] used Artificial Neural Network (ANN) techniques and functional group contributions to develop an algorithm to predict chemical activity coefficients. The ANN algorithm was trained using experimental data for more than 900 binary systems obtained from DECHEMA, a phase-equilibrium database. The prediction scheme is based on the fact that the atoms in a chemical compound can be grouped in a functional group with its own physical and chemical properties. Thus, almost any chemical compound can be built by combining the right number of functional groups.

Elaheh K. Goharshadi et. al., [35] studied the excess thermodynamic properties namely, excess molar Gibbs energy, excess molar enthalpy, excess molar entropy, excess molar internal energy and excess molar Helmholtz energy for four polymer mixtures and blends at different temperatures. The activity coefficient for these polymeric mixtures using GMA equation of state was calculated.

Craig J. Peterson [36] applied a Residual Helmholtz Energy model (AP) developed by Anderko and Pitzer for aqueous electrolyte solutions in which the electrolyte is assumed to be fully associated, and found that it is less effective for describing enthalpic properties. The RIV model an improvement over RIII model of Liu et.al, (obtained by adding a term to describe interactions between ions in solution), was applied to solutions in the ranges of 350 °C to 400 °C and 18 MPa to 40 MPa, was also applied and concluded that it is thermodynamically consistent and is capable of describing densities and heats of dilution.

Marija B. Rogac et. al., [37] determined the osmotic coefficient of aqueous solutions of cyclohexylsulfamic acid by freezing point measurements up to the molality 0.65 mol kg⁻¹. The osmotic coefficients were fitted to the Pitzer equation, and ion interaction parameters $\alpha_1, \beta(0)$, and $\beta(1)$ were evaluated. The mean ion activity coefficient of the solute was calculated, and the non Ideal behaviour of the system investigated was characterized by calculation of the excess Gibbs energy of solution, as well as the respective partial molar functions of solute and solvent. The partial molar excess Gibbs energy of the solute is negative, like the excess Gibbs energy of its solution, while the partial molar excess Gibbs energy of the solvent is positive and increases with increasing concentration of the solute. The solvation ability of water was calculated from the difference between the Gibbs energy of solution of water in solution and that of pure water, and found to be positive and small for the solute investigated, throughout the concentration range studied.

Chantal Valeriani et. al., [38] studied the association of ions in electrolyte solutions at very low concentration and low temperature using computer simulations and quasi-chemical ion-pairing theory. The specific case of the restricted primitive model (charged hard spheres) is considered. Specialised simulation techniques are employed that lead to efficient sampling of the arrangements and distributions of clusters and free ions, even at conditions corresponding to Nano molar solutions of simple salts in solvents with dielectric constants in the range 5-10, as used in recent experimental work on charged-colloid suspensions. A direct comparison is affected between theory and simulation using a variety of clustering criteria and theoretical approximations. It is

shown that conventional distance-based cluster criteria can give erroneous results. A reliable set of theoretical and simulation estimators for the degree of association are proposed. The ion-pairing theory is then compared to experimental results for salt solutions in low-polarity solvents. The agreement is excellent, and on this basis some calculations are made for the screening lengths which will figure in the treatment of colloid-colloid interactions in such solutions. The accord with available experimental results is complete.

Brian J. Satola [39], studied UNIFAC method (group-based method), using the experimental data from the Dortmund Data Bank (DDBST Software and Separation Technology GmbH, 2009), applied regression analysis, and compared the results, including calculations of Activity coefficients, with component-based models i.e., Wilson, NRTL, and UNIQUAC equations. He concluded systems defined by only two UNIFAC main groups show good agreement between theory and experiment for the component-based methods.

1.2. Studies on Dielectric constant, Dielectric relaxation and dipolar interactions:

Dielectric Properties were covered in the review by Gilman S. Hooper and Charles A. Kraus [40]. They reported some measurements of the dielectric constants of selected electrolytes in Benzene and found ion pair formation, for which an explanation on the basis of dipolar interactions was attempted.

Hasted et al [41] measured the dielectric constants and loss angles of a series of concentrated aqueous ionic solutions at wave-lengths of 10 cm, 3 cm, and 1.25 cm. From these results the values of the static dielectric constant and relaxation time for these solutions have been calculated on the basis of the Debye formula and the results were discussed in relation to the structure of ionic solutions. The validity of the Debye-Sack saturation theory of the dielectric constant and the effects of the fall of dielectric constant on the electrolytic properties of concentrated solutions were discussed.

Haggis et al., [42] reported data for a wide variety of aqueous solutions of ions and organic molecules. The water relaxation time was shortened by positive ions and lengthened by hydrogen bond-forming molecules. The properties of water were treated

by a statistical method in which the numbers of molecules in four, three, two, one, and zero- bonded states were estimated from dielectric and latent heat data. Kirkwood's dielectric theory and Verwey's calculation of the dipole moment of a four- bonded water molecule were used. The effects of temperature and solutes on the water relaxation time were discussed in terms of a statistical method. The effective number of water molecules "irrotationally bound," is estimated from the depression of the low frequency dielectric constant, using a dielectric theory of mixtures. This number is zero for uncharged solute molecules but is finite for organic or inorganic ions.

Fauss and Kai-Li-Hsia [43] stated that in solvents of low dielectric constant, where the electrostatic potential energy $\{ \epsilon^2/aD \}$ of an anion and a cation at contact is large compared to mean thermal energy kT , one expects and finds association of ions to non-conducting pairs. As the dielectric constant is increased the extent of association should decrease, but in principle it should never become zero. According to them "Association of 1-1 salts in water had been completely disregarded ever since the Debye-Huckel theory, based on the hypothesis of complete dissociation, proved to be so successful in predicting the behaviour of electrolytes in the limit of extreme dilution". Hence they modified the conductance equation with slight occurrence of association. Using this equation the conductance data of electrolytic solutions in binary solvents of dioxane- water mixtures, was analysed and the results were interpreted to locate ion pair formation mechanism.

Marcus et.al, [44], in an interesting International conference plenary lecture pointed out the importance of the entropy of mixing term when applied to the organic phase in a binary solvent system, to understand the thermodynamics of mixtures, since the molar volumes are considerably different. It is the enhanced electrostatic interaction due to the lower dielectric constant, that plays the lead in a interactive electrolytic system.

Thomas Jones and Rexia Ahmed [45] studied ion pair formation of the triphenylene anion radical with alkali metals in four solvents by ESR theoretical techniques. The result of the study suggested that the four distinct species exist and at high temperature and under conditions which favour tight ion pairs, the ion pair no longer possesses a static threefold rotation symmetry.

Kaatze et. al., [46] obtained the complex dielectric spectrum of aqueous solutions of aluminum, indium, and scandium sulphate 10 MHz and 60 GHz using time domain and frequency domain techniques. A difference method especially matched to the study of electrically conducting solutions has been applied in the time domain measurements. Various relaxation spectral functions were fitted to the measured data. The results obtained thereby were discussed with respect to the effects of kinetic depolarization, dielectric saturation and ion complex formation.

Kaatze and Pottel [47], discussed observations about such aqueous systems for which measurements of the complex electric permittivity ($10^3 \text{ Hz} \leq \nu \leq 10^{11} \text{ Hz}$) and of the attenuation coefficient of acoustic waves ($10^5 \text{ Hz} \leq \nu \leq 3 \cdot 10^9 \text{ Hz}$) had been performed over a broad range of frequencies ν . The liquids include aqueous solutions of multivalent electrolytes of, transition metal chlorides, micelles and bilayers, small organic molecules. It was shown that, the two spectroscopic methods can be favorably used to yield complementary aspects of structural properties and of the molecular dynamics of interesting liquid mixtures.

Barthel and R. Buchner [48] from permittivity measurements of liquid electrolyte solutions established that their complex interplay of orientational, intermolecular, kinetic, H- bonding, diffusional and migrational modes facilitate a tool to understand the properties of pure solvents, solvent mixtures and solutions. Protic solvents show three relaxation processes: namely

1. Re- establishment of the perturbed solvent structure,
2. intra- molecular rotation of solvent molecules both as monomers and as H- bonded chains or networks,
3. very short relaxation times of about 1 Pico- second due to H- bond dynamics.

Aprotic solvents display a more or less continuous relaxation time distribution. Solvent mixtures show a particular behaviour related to the properties of their constituents. The addition of salt affects the relaxation times of the solvents, but no new modes are generated by free ions. In contrast, ion pairs and other solute complexes act as dipoles and display specific relaxation processes. Information from high frequency permittivity measurements can explain solution properties required by fundamental and applied research.

Kaatze et.al, [49] summarized results from measurements of the dielectric spectrum of organic solute/water mixtures. A survey of hydrophobic hydration effects as emerging from the experimental data was given. Recent ideas of the mechanism of dielectric relaxation in hydrogen bonded liquids were discussed. Comparison was made with some aspects resulting from computer simulation studies.

Hitoshi Ohtaki and Tamas Radnai [50] point out that determination of hydration number of ions, rates of exchange of coordinated water molecules around ions, and interaction energies between ions and water molecules, can be assessed from the mechanisms on Ionic hydration.

Vladimir I. Gaiduk et.al, [51] suggested a simple model of dielectric response due to the three-dimensional motion of ions inside a spherical ideally reflecting sheath. This model termed as the Sphere- Confined Ionic (SCI) model combined with the so called hybrid model, previously used to describe dipolar orientational relaxation [180]. The wideband (up to 1000 cm^{-1}) complex permittivity $\epsilon(\omega)$ and absorption $\alpha(\omega)$ spectra of NaCl- water and KCl- water diluted solutions were calculated as the sum of the contributions due to cations and anions and to reorientation of polar H₂O molecules.

Anderko [52] developed a general model to calculate static dielectric constant of mixed solvent electrolyte solutions. For systems containing electrolytes, the model takes into account the effects of ions and ion pairs. It is capable of reproducing the dependence of the dielectric constant on electrolyte concentration. The model has also been verified for a number of electrolyte solutions in various solvents over wide composition range temperature ranges.

Anderko et.al, [53], reviewed advances in the modelling of thermodynamic and transport properties of electrolyte solutions, with focus on mixed solvent electrolyte models, equations of state for high temperature and supercritical electrolytic systems and transport property models for multi- component concentrated electrolytic solutions. The models were analysed with respect to their capabilities of computation in wide ranges of conditions and composition. Various frame works for the development of electrolyte models were discussed. A new model for mixed solvent electrolyte system was

developed by them for the simultaneous calculation of speciation and phase equilibria, and the role of speciation with respect to the thermodynamic properties of mixed solvent electrolyte solutions, and diffusion coefficient evaluation of aqueous systems was discussed.

Buchner and Hefter [54] studied dielectric relaxation spectra at frequencies upto 20GHz for CsF in methanol at concentrations upto one mol-L at 25⁰C. The data showed that CsF forms a solvent shared ion pair in MeOH solutions. Solvation numbers of the ions estimated via modified Cavell equation are unrealistically large. This suggests, consistent with the large dielectric decrement and the conductivity data, that the ions significantly break down the chain structure of MeOH.

Andrew J. Tromans [55] dealt with certain aspects of the solution chemistry of the simple dicarboxylate anions: oxalate, malonate and succinate up to high concentration. Formation constants of weak ion pairs ($\text{Log}\beta$) formed between Sodium (Na^+) and Oxalate (Ox^{2-}) ions was determined, as a function of ionic strength. Vibrating Tube Densimetry (VTD) and Flow Micro- calorimetry Studies (FCS) on the above ionic liquids were performed to determine the apparent molal volume and heat capacities at constant pressure. This data was fitted to Pitzer model.

Etienne Baucke et.al, [56] reported about ultrasonic absorption spectra at frequencies between 300 kHz and 3 GHz for aqueous solutions of MgCl_2 , CaCl_2 , SrCl_2 , NiCl_2 , and CuCl_2 . All spectra reveal a Debye- type relaxation term with small amplitude. The relaxation time values derived from the spectra display a small range only ($0.2 \text{ ns} \leq \tau \leq 0.6 \text{ ns}$), corresponding with the τ values for solutions of $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ in water. The relaxation term is suggested to be due to the second step in the Eigen-Tamm scheme of stepwise association and dissociation of ions, namely the equilibrium between the complex of encounter and the outer sphere complex. The relaxation amplitudes reflect special properties of the ions.

Abolghasem Jouyban et.al., [57] proposed a simple computational method for calculating dielectric constants of solvent mixtures based on Redlich- Kister extension

and correlative and predictive analyses of dielectric constants of non-aqueous ternary solvent mixtures was done with good accuracy between theory and hypothesis.

Chen [58] presented a detailed investigation of aqueous solutions of MgSO_4 by dielectric relaxation spectroscopy over a wide range of frequencies ($0.2 \leq \nu/\text{GHz} \leq 89$) and concentrations ($0.017 \leq c/M \leq 2.24$). Detailed analysis of the spectra shows conclusively, as has long been inferred from ultrasonic absorption studies, the simultaneous presence of double solvent separated (2SIP), solvent-shared (SIP), and contact (CIP) ion pairs. The constants derived for the stepwise formation of each ion pair type and for the overall association are in excellent agreement with literature estimates based on other kinds of measurements.

Kasthury [59], studied Dielectric aspects of Some Nitriles, Phenols and their mixtures, (Amino benzonitrile +Nitro phenol) mixture in benzene and made calculation of dipolar increment, dielectric relaxation times , related thermodynamic parameters. Higasi's Parameters for benzonitrile and o- nitro phenol mixture in benzene, benzonitrile and o- chlorophenol mixture in benzene were reported.

Watanabe and Hamaguchi [60] presented a new perspective on the interaction between the sulphate ion and its counter cation in aqueous solutions. The dynamic exchange model of ion association proposed by them instead of the conventional static equilibrium model, was used to interpret the concentration dependence of the Raman band shape of the totally symmetric stretch mode of the sulphate ion that was investigated systematically for four sulphate ions, MgSO_4 , $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , and Li_2SO_4 .

Chen, Hefter and Buchner [61] investigated aqueous solutions of nickel and cobalt sulphates at 25^0 C by dielectric relaxation spectroscopy over a wide range of frequencies and salt concentrations. The stepwise formation constants for each ion pair and the overall association constant obtained from the data are in good agreement with ultrasonic relaxation and other estimates.

Marcus and Hefter [62] presented an overview about Ion-pairing in good detail ,and cites evidences of useful methods from conductometry, Potentiometry,salt or solvent

activity measurements, solubility measurements, relaxation techniques (Dielectric and ultrasonic). Also NMR, and Spectroscopic methods, Electron diffraction, XRD, are used in the study of structure of hydrated ions and clusters for their detection and study. Very recent additions to this list are Molecular Dynamics Simulations (MDS), Neutron Diffraction Techniques (NDT), and Electromagnetic Interaction Studies with Visible, Infrared, and Ultraviolet radiation.

Amirjahed .et.al [63] derived an equation which relates the dielectric constant of mixtures of a binary solvent system to the mole fraction of the polar and non-polar components of the system. The coefficients of the formula are readily calculated from the dielectric constant and the molar volume of the pure components of the binary solvent system. These calculated values are employed in graphical representations of the theoretical relationship of the dielectric constant of the binary solvent system and the mole fraction of the polar component of the solvent system. Experimental measurements are employed to demonstrate deviations from ideality.

Chandrika Akhilan [64] reported very important thermodynamic and related studies about properties of aqueous copper sulphate solutions, under the guidance of Hefter, May and Buchner. The results in this thesis are direct verifications of several conclusions about the ion pair formation mechanism and other different physio-chemical aspects which were presented in the work of Akhilan. She worked on Entropy, Enthalpy, UV-Visible Spectrophotometry, Potentiometry, Dielectric Relaxation Spectroscopy, Titration Calorimetry, Isopiestic studies. Experimental studies in this thesis on copper sulphate solution in Water-Ethylene Glycol mixed solvent systems using Antonpaar (Austrian made) equipment, provide data of a different set of Physio-chemical parameters and arrive at striking comparison to Akhilan's results.

Buchner [65] in the presentation "Dielectric Relaxation Spectroscopy of Ion Association in Aqueous and Non-Aqueous Electrolytes" at Yokohama, detailed as to how to probe polarization as the response of the sample to a time-dependent electric field. Ion Association and Eigen model were detailed. This mechanism depends on the relative strength of ion-ion and ion-solvent interactions. The common problems come across while investigating ion association are 1. Thermodynamic methods only

determine overall association 2. Spectroscopic methods (NMR, IR, Raman) sensitive to contact ion pairs and higher aggregates.

In the Review by Richard Buchner [66], ion solvation and ion association the key features of ion- solvent interactions were discussed at length. Their balance largely determines structure, thermodynamics, and dynamics of electrolyte solutions. Despite being studied for many years with various techniques, these effects are still intriguing because results obtained with different methods, each having its individual merits and limitations, cannot be connected properly due to lacking information. It was pointed out that the dielectric relaxation spectroscopy (DRS) is a precious tool for solution studies. The principles of DRS and the required instrumentation were briefly presented. The versatility of this technique to interpret ion solvation and association and how information revealed by these studies compare with results obtained from other techniques was analysed.

Buchner et.al, [67] commented on the “dynamic exchange” model of ion association proposed by Watanabe and Hamaguchi, for aqueous solutions of MgSO_4 is shown to be inconsistent with the extensive information available from Raman, relaxation, and thermodynamic studies, all of which can be explained by the Eigen equilibrium model. Watanabe et. al., suggested that the Raman spectra of aqueous solutions of MgSO_4 at ambient temperatures can only be explained in terms of their dynamic exchange model rather than the other conventional static equilibrium model. They claim the latter to be actually Eigen’s dynamic three- step ion- pairing model of ion association, designated as static model.

Petrowsky [68] studied ion transport in liquid electrolytes and mixed solvent systems, ionic mobility and its dependence on dielectric constant of solvent and its temperature dependence, conductivity and its variations in Protic and Aprotic solvents and their solvent functional groups.

Holovko [69] developed mean spherical approximation- mass action law approach to describe the influence of ion association on solvent and solution dielectric constants in electrolyte solutions. The dependences of the dielectric constants on

electrolyte concentration, ionic sizes, and the degree of ion association were analysed. The results were compared with recent experimental data for aqueous solutions of nitrate and format salts and a fair agreement was obtained. He also used Analytical solution of the associative mean spherical approximation (AMSA) and the modified version of the mean spherical approximation- mass action law (MSA-MAL) approach for ion and ion-dipole models ,to revise the concept of ion association in the theory of electrolyte solutions.

Christoffer J Fennell et. al.,[70] studied ion- ion interactions in water using classical molecular dynamics simulations. From observations on the relative depths of the free energies of the contact ion pair and the solvent- shared ion pair, along with related solvent structure analysis, they find a good correlation with this position : small-small and large- large should associate in water, and small- large should be more dissociated.

Richard P. Matthews et.al,[71] attempted the calculation of association constants from computer simulations which was historically known to be complicated because of difficulties in validating metal ion force fields for solution simulations. They developed a method that produces a force field for divalent metal ions in metal sulphate.

Johannes Hunger et.al, [72] conducted a detailed investigation using broadband Dielectric Relaxation Spectroscopy on the aqueous solutions of aqueous guanidinium chloride and carbonate, GdmCl and Gdm₂ CO₃ at 25 °C. The spectra indicated that Gdm⁺ ions, C(NH₂)₃⁺, neither bind strongly to water nor they hydrophobically hydrated; rather they appear to have a most unusual ability to dissolve in water without altering its dynamics. Although DRS is particularly sensitive to the presence of ion pairs, only weak ion pairing was detected in Gdm₂CO₃(aq) solutions and none at all in GdmCl (aq). Surprisingly, no evidence was found for the existence of the higher order homo- and heteroionic nanoscale aggregates that have been identified in recent years by Mason and co-workers using molecular dynamics simulations and neutron diffraction. Possible reasons for this discrepancy are discussed. The present dielectric relaxation spectra and other solution properties of GdmCl (aq) and Gdm₂CO₃ (aq), such as apparent molar

volumes and electrical conductivities, are shown to have strong similarities to those of the corresponding Na⁺ salts.

Davis Morgan Warren [73] studied Eigen mechanism, and molecular dynamics study of the association reactions for aqueous BaSO₄ and SrSO₄ pairs through potential of mean force calculations.

Kumar. S. et.al, [74] presented the dielectric relaxation and dipole moment of different concentration binary mixtures of Ethylene glycol, Propylene glycol and Butylene glycol with dilute solutions of 1,4- Dioxane at 33°C. The dielectric relaxation of binary mixtures of polar liquids in non- polar solvents at microwave frequencies was attempted such studies provide meaningful information regarding intermolecular and intra- molecular association between the solutes and solvent molecules. The static dielectric constants of glycols like ethylene glycol, propylene glycol and butylene glycol in dilute solutions of 1,4- Dioxane were determined at 303K. The measuring frequency of the dipole meter was 2MHz. X-band and J-band microwave benches operating at 9.52GHz and 7.72GHz were used for determination dielectric permittivity and dielectric loss factor. The values of molecular relaxation time and dipole moment for the different composition of binary mixtures are determined. The comparative values of relaxation time are presented for the two bands (X-Band) and (J- Band) for various binary mixture

Veerati Radhika [75] measured molar conductivities of dilute solutions of Nicotinium dichromate in binary aqueous mixtures containing up to 100 % co-solvent N,N- dimethylformamide at 293 K ± 0.1 and benzimidazolium dichromate in aqueous-acetone and in aqueous DMSO. Data were treated by the Shedlovsky equation, and its parameters, the limiting equivalent conductivity Λ_0 and the association constants K_A were evaluated. Variations in Walden products and K_A were interpreted in terms of ionic properties as well as solvent structure and dielectric constant. The distances of closest approach which were determined were compared with those found using the Kraus-Bray equation. The effective ionic Radii (r_i) of the electrolytic ions have been determined from Λ_0 values using Gill's modification of the Stokes law. The influence of the mixed solvent composition on the solvation of ions has been discussed with the help of 'R'- factor. Thermodynamic parameters are evaluated and reported. The results

of the study have been interpreted in terms of ion- solvent interactions and solvent properties.

Dan Ben Yaakov et. al., [76] suggested a source of ion specificity originating from the local variations of the dielectric constant due to the presence of ions in the solution and presented a mean field model to account for the heterogeneity of dielectric constant caused by the ions.

Hiroshi Takeuchi [77], The structures of the simplest aromatic benzene clusters $(C_6H_6)_n$, were not well elucidated. He investigated, the clusters of benzene $(C_6H_6)_n$ ($n \leq 30$) with the all- atom optimized parameters for liquid simulation potential. The global minima and low- lying minima of the benzene clusters were searched with the heuristic method combined with geometrical perturbations.

Gamielien et.al, [78] in their study of the thermodynamics of benzene association in water, showed that although the potential energy and enthalpy play an important role in the association of benzene dimers, they do not determine the relative orientation of these molecules on close contact in solution. They observed a large variation in the configurations that contribute to the vacuum (i.e., solvent-free) minimum free energy wells of the benzene contact pair.

Ishwara Bhat et.al [79] reported on the solvation of Sodium citrate in water, aqueous CH_3CN and aqueous DMSO, under varying dielectric constant at different temperature. The specific conductance data obtained was analyzed by Kraus- Bray and Shedlovsky conductivity models. Limiting molar conductance, dissociation constant/ association constant were evaluated for all the solvent compositions. The limiting molar conductance decreases with the increase in amount of co-solvent in water, due to increased solvent- solvent interaction and decrease in dielectric constant. The limiting molar conductance, due to high viscosity and molecular size of DMSO in water, lower conductance was observed in water + DMSO media. The K_a values increases with the increase in amount co-solvent in water at all the temperatures studied.

1.4. Studies on Ultrasonic, Densimetric Refractive Index and related parameters:

Blandamer et.al, [80] in a series of publications reported the ultrasonic properties of binary aqueous mixtures. Several interesting aspects about hydrogen bonding in solutions of alcohols like isomeric octyl alcohols in non- polar solvents. Application of Kirkwood- Buff integral functions characterising preferential solvation, for the analysis of the data for reactions in binary aqueous mixtures was presented at length. The properties of aqueous solutions were considered from the standpoint of solute- water and solute-solute interactions. In both cases, the important role played by water- water interactions in aqueous solutions was stressed. Solute-solute interactions in dilute aqueous solutions are described using pair wise interaction parameters. Procedures which express these parameters in terms of group interaction parameters were discussed. With an increase in the amount of solute, strong evidence was obtained for clustering of aqueous and non- aqueous components. Aqueous mixtures also provided convenient reaction media with quite diverse properties which, in some cases, accelerate and, in other cases, inhibit the rates of chemical reactions. The authors indicated how these trends could be understood in terms of preferential solvation of initial and transition states using Kirkwood-Buff integral functions.

Desnoyers et.al, [81], in his studies on apparent molal volumes of electrolytic solutions of alkali halides in aqueous binary solvent systems with butanol, interpreted in their findings solute- solute pair and triplet formations. At low butanol concentrations, electrolyte- non- electrolyte pair interactions were attributed to be the reason for this. At intermediate butanol concentrations association of the butanol was suspected. In another communication by the same authors about volumetric and compressibility and heat capacity studies on alkali halides (NaCl) in Urea- Water binary mixtures. Decrease in the structure breaking effect was observed at a fixed aqua molality, recorded by the decrement in the parameter.

Atkins et.al, [82] studied Apparent molar volumes of seven electrolytes determined by vibrating tube Densimetry in non- aqueous solvent mixtures of propylene carbonate with acetonitrile, dimethoxymethane and Tetra hydrofuran. Ionic apparent molar volumes of transfer tV (ion) were obtained via the tetraphenyl arsonium

tetraphenyl borate assumption. tV (ion) from PC to the mixed solvents are generally strongly negative for both cations and anions consistent with the greater compressibilities and lower dielectric constants of the cosolvents.

Tejramj et. al., [83] studied densities and viscosities of ten binary and four ternary mixtures containing bromoform, bromobenzene, chlorobenzene, toluene, mesitylene, and dimethylformamide at 25°C have been measured over the whole range of mixture compositions. Excess molar volumes, apparent values of excess molar viscosities, and Gibbs energy of activation of flow have been calculated for these mixtures. The calculated results have been fitted to a linear regression equation to estimate the parameters and the standard deviation between the calculated and the experimental data.

Shigeo Kato et.al., [84] from the ultrasonic absorption measurements of aqueous solutions of sodium perfluorooctanoate (SPFO) and of Cesium perfluorooctanoate (CsPFO) in the frequency range 0.2–90 MHz at 25°C. Observed single ultrasonic relaxation process in all solutions investigated, that should be ascribed to a fast relaxation process due to an exchange of surfactant monomer between micelle and bulk solution. The mean dissociation rate constant and the magnitude of the volume difference due to the exchange process were determined by applying the relations derived by Aniansson, Wall and Teubner respectively. Density measurements were also carried out to support information obtained from the ultrasonic relaxation study. Magnitudes of the volume difference estimated from the two independent studies above are in approximate agreement with each other. However, the volume difference determined from the density measurements is slightly larger than that determined by ultrasonic study and almost independent of the species of the counterion.

Ravichandran. G [85] studied Excess molar volumes, excess viscosities and excess Gibbs energy changes for viscous flow GE and interaction parameters d for binary mixtures of nitrobenzene with aniline, N-methylaniline and m-chloroaniline at selected compositions from the measured values of densities and viscosities of pure components and their mixtures at 30°C. UV-visible spectra for all the binary mixtures were recorded and showed a characteristic absorption maximum. The results are analyzed in terms of

interactions arising due to electron-donor-acceptor (EDA) or charge transfer (CT) complexation.

Ragouramane [86] studied the nature of inter- and intra-molecular interactions in liquid systems of electrolytes in aqueous ethylene glycol leading to structural modifications of ethylene glycol, and structural studies of amino acids in aqueous alcohol solutions, carboxylic acids in aprotic solvents and in binary mixtures of ortho-chlorophenol and some carbonyl systems, (using the studies about ultrasonic velocity, absorption, density and viscosity). Promotion of the structure making effect was observed due to molecular interactions in amino acid systems. Similarly structure making and structure breaking effects were observed in the electrolytic systems. The nonlinear behaviour observed in the electrolytic solutions with aprotic solvents like DMF, Dioxane, and Tetrahydrofuran is attributed to the complex formation, due to hydrogen bonding between -OH and -COOH groups of solute and free oxygen of the aprotic solvents.

Srinivasulu et al., [87] measured ultrasonic velocity (U), density (ρ) and viscosity (η) for polyethylene glycols (PEG 4000 & 6000) in two solvents namely water and chloroform at 303, 313 and 323 K. Using the experimental values, the adiabatic compressibility (β), free length (L_f), acoustic impedance (Z), free volume (V_f), internal pressure (π_i) and cohesive energy were calculated. The variations of these parameters have been discussed in the light of intermolecular interactions.

Osakai et al. [88, 90] measured the amount of water molecules extracted together with hydrophilic ions (Na^+ , Li^+ , Ca^{2+}) in a nitrobenzene (NB)-rich phase with a small water composition (0:168M). In NB-water binary mixture at room temperatures, the number of co-extracted water molecules in a NB-rich phase was estimated to be 4 for Na^+ , 6 for Li^+ , and 15 for Ca^{2+} . Furthermore, using proton NMR spectroscopy, Osakai et al. studied successive formation of complex structures of anions (such as Cl^- and Br^-) and water molecules by gradually increasing the water composition in NB.

Roshan Abraham [89] studied a theoretical estimation of ultrasonic velocity using Flory-Patterson theory (FPT), Jacobson's free length theory, Schaaffs' collision factor theory, Nomoto's relation, and Van Dael's ideal mixture relation (IMR) the three-

component (ternary) mixtures of methyl ethyl ketone and toluene with *n*-alkanols. The theoretically predicted ultrasonic velocities are compared with the experimentally determined velocities in the ternary mixtures at 30°C. It is found that the velocities evaluated using all the theories except FPT and IMR are in fairly good agreement with the experimental velocity values. Acoustic nonlinearity parameter (B/A) and a few thermodynamic parameters have been evaluated theoretically for the ternary mixtures using the Tong and Dong equation combined with Flory's statistical theory and its extended version to ternary mixtures.

Hefter et.al [91] reported studies about enthalpies and entropies of transfer of electrolytes and ions from water to mixed aqueous organic solvents. Spectroscopic techniques such as UV visible, NMR and Raman which are powerful tools for the investigation of chemical speciation in solution were used in his studies and concluded that such techniques do not always provide reliable information about ion association equilibria.

Buchner et.al, [92] studied dielectric spectra for aqueous sodium oxalate solutions up to the saturation concentration at 25°C over the approximate frequency range 0.2 - 20MHz. The spectra exhibited a process at about 1 GHz associated with the presence of ion pairs, in addition to the dominant solvent relaxation process at about 18 GHz.

Talat Zamir [93] in his thesis, densities, viscosities and relative viscosities of solutions of several chosen univalent electrolytes were measured over the entire range of concentration and temperature, in pure DMSO, pure water and DMSO- Water binary mixtures. Data was analysed by Jones-Dole equation to determine ion- ion interactions and ion- solvent interactions.

Sethu Raman [94] made some Interpretations for ultrasonic studies Ultrasonic velocity and density measurements of tetra hydrated manganous chloride in aqueous media at 303.15, 308.15, 313.15 and 318.15K to investigate ion-solvent interactions. The gradual increase of ultrasonic velocity (U), density (ρ) and acoustic impedance (Z) and gradual decrease of adiabatic compressibility (β), intermolecular free length (L_f) suggested the presence of strong ion-solvent interactions. Mn^{+2} ions possess structure

making tendency for the cluster of water molecules. The solvation number (S_n) shows non linear variation with temperature and gradual decrease with concentration also confirms strong interactions between Mn^{+2} ions and dipolar water molecules.

Etienne Baucke et.al, [95] reported ultrasonic absorption spectra at frequencies between 300 kHz and 3 GHz for aqueous solutions of $MgCl_2$, $CaCl_2$, $SrCl_2$, $NiCl_2$, and $CuCl_2$. All spectra revealed a Debye- type relaxation term with small amplitude. The relaxation time values derived from the spectra display a small range only ($0.2 \text{ ns} \leq \tau \leq 0.6 \text{ ns}$), corresponding with the τ values for solutions of $Mg(NO_3)_2$ and $Ca(NO_3)_2$ in water. The relaxation term is suggested to be due to the second step in the Eigen- Tamm scheme of stepwise association and dissociation of ions, namely the equilibrium between the complex of encounter and the outer sphere complex. The relaxation amplitudes reflect special properties of the ions.

Bijan das [96], studied the apparent molar volumes of six symmetrical tetra alkyl ammonium bromides, have been determined in (methanol + acetonitrile) binary mixtures (containing 0.20, 0.40, 0.60 and 0.80 mole fractions of acetonitrile) over the concentration range $0.005 - 0.065 \text{ mol. kg}^{-1}$ at 298.15 K from precise density measurements. He used the non-thermodynamic, so-called extrapolation method to split the limiting apparent molar volumes into ionic contributions. The results were interpreted in terms of ion-ion and ion-solvent interactions. Further they applied Pitzer ion interaction approach to describe thermodynamic properties of electrolytic solutions. They generated a comprehensive equation for the thermodynamic properties of hydrochloric acid in dioxane water mixtures in a wide temperature range. This model claims to reproduce the cell E.M.F. values obtained experimentally. The results and implications about the Pitzer's parameters were discussed by them in the light of interionic forces.

Venkata Ramana. G et. al., [97] determined ultrasonic velocity in dilute solutions of water in n- alcohols and 2- alkoxyethanols at 298.15K using single crystal variable path interferometer working at 3GHz. The excess ultrasonic velocities have been evaluated using the formula which is thermodynamically valid.

Rajarajan [98] studied Ultrasonic Relaxation in aqueous Amino acids and in water- glycerine mixtures, Carboxylic acids in non- aqueous solutions and arrived at interesting results about Micellar formation with the ultrasonic relaxation mechanism. The ultrasonic velocity and absorption studies are carried out in water- glycerine mixtures of Manganese sulphate, Vanadyl sulphate, Copper sulphate, Copper nitrate, and Chromium sulphate and chromium nitrate. In all the systems, the ultrasonic velocity increases non-linearly with increase in concentration of paramagnetic ion, which may be due to formation of hydrogen bonds.

Minerva González-Melcher et.al, [99] reported molecular dynamics computer simulations of the surface tension and interfacial thickness of ionic liquid-vapor interfaces modeled with a soft core primitive model potential. We found that the surface tension showed an anomalous oscillatory behavior with interfacial area, explained in terms of finite size effects introduced by the periodic boundary conditions employed in computer simulations. They showed that the thickness of the liquid-vapour interface increased with surface area as predicted by the capillary wave theory. Data on the surface tension of size-asymmetric ionic liquids were reported and compared with experimental data of molten salts. Their data suggested that the surface tensions of size-asymmetric ionic liquids do not follow a corresponding states law.

Mehdi Hasan et. al., [100] measured densities, viscosities, and ultrasonic velocities of binary mixtures of chloroform with octan-1-ol and decan-1-ol over the entire range of composition at (303.15 and 313.15) K and at atmospheric pressure. From the experimental values of density, viscosity, and ultrasonic velocity, the excess molar volumes V^E , deviations in viscosity $\Delta\eta$, and excess isentropic compressibility have been calculated. The excess molar volumes and excess isentropic compressibility are positive for both the binaries studied over the whole composition, while deviations in viscosities are negative for both the binary mixtures. The excess molar volumes, deviations in viscosity, and deviations in isentropic compressibility have been fitted to the Redlich–Kister polynomial equation. The very recently proposed Jouyban–Acree model is used to correlate the experimental values of density, viscosity, and ultrasonic velocity at different temperatures.

Kannappan et.al,[101]obtained Ultrasonic velocities and densities of sulphate solutions of manganese, cobalt, nickel, ferrous, copper, zinc and some nitrates, in aqueous DMSO solvent, in a wide range of concentrations at a temperature of 303⁰K. On analysis of computed acoustical parameters like adiabatic compressibility, free length, and solvation number they concluded that the ion solvent interactions in these solutions reveal, and the nature of the metal ion. The transition and inner transition metal ions show structure breaking effect of the associated clusters of water molecules, especially in dilute solutions, which is evident from the variation of solvation number with molarity. Even the strength of ion- dipole interaction in the aqueous solution of the metal ion depends on concentration.

Bjørndal [102] investigated, methods for measuring liquid density by acoustic means, and to investigate one or more promising methods experimentally. The acoustic plane- wave theory used in this work, along with a description of the most important non-ideal characteristics that may need to be corrected for, if accurate measurements are to be performed is presented.

Badriah Ali Mahammed [103] in his work on transition ionic liquids, studied the conductance of some chosen alkaline earth and transition earth metal cations in the ionic liquid form to obtain association parameters, in different solvents. Several parameters like densities, refractive indices, molar solvated volumes, Vander wall' s volumes, electrostriction volumes, activity coefficients and solvated radii of chosen nitrates and sulphates in pure Me OH ,and DMF and also MeOH-DMF mixtures were also studied.

Pereiro et.al [104] reported densities, speeds of sound, and refractive indices of the binary mixtures of 1-butyl-3-methyl imidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium hexafluorophosphate, 1-methyl-3-octylimidazolium hexafluorophosphate and 1,3-dimethylimidazolium methyl sulphate with 2-butanone, ethyl acetate, and 2-propanol from 293.15 to 303.15 K. Excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility were calculated for the above systems. The liquid-liquid equilibrium data of the binary

mixtures ionic liquid + 2-propanol were carried out, and they were compared with the correlated values obtained by means of the NRTL and UNIQUAC equations.

Pottel, et.al, [105] studied the Broadband ultrasonic absorption spectra and complex dielectric spectra for aqueous solutions of electrolytes and discussed their results in terms of cation- anion association schemes. They developed techniques adopted by Eigen, Tamm and Kurtz and demonstrated the relaxation characteristics in the frequency dependent sonic absorption coefficient of 2:2 valent electrolyte solutions.

Khoan Chandra [106], studied about Critical Micelle Concentration (CMC) of surfactant solution using the conductivity data and found that the Critical Micelle Concentration of the aqueous surfactant solution decreases with increasing addition of $C_{12}OH$. This was explained due to electrical repulsion forces.

Iglesias [107] measured density and ultrasonic velocity of the mixtures of the new ionic liquid 2-hydroxy ethyl ammonium formate and short hydroxylic solvents like water, methanol, and ethanol, at the range of temperature 288.15 to 323.15 K and atmospheric pressure. The corresponding apparent molar volume and the apparent molar isentropic compressibility values were evaluated from the experimental data and fitted to a temperature dependent Redlich–Mayer equation.

Anna Płaczek et.al [108] measured Densities and heat capacities of various 1:1 and higher-charged electrolytes in *N,N*- dimethyl formamide (DMF) at 25 °C using a series-connected flow densimeter and Picker calorimeter. Standard molar volumes V_o and isobaric heat capacities C_{po} derived from these data were split into their ionic contributions using the tetraphenyl phosphonium tetraphenyl borate reference electrolyte assumption. The values so obtained have enabled a meaningful separation of the effects of cationic size and charge for the first time in a non aqueous solvent.

Israfilov, et.al [109] reported new modernized high pressure- high temperature vibrating tube densimeter DMA HPM (Anton paar, Austria), at seven molalities, the (p, ρ, T) properties and apparent molar volumes in the temperature range (298.15 to 398.15) K and pressures up to ($p = 40$ MPa) of $LiNO_3$ in ethanol. The measurements with a vibrating tube are based on the dependence between the period of oscillation of a

unilaterally fixed U-tube Hastelloy C-276 and its mass. This mass consists of the U-tube material and the mass of the fluid filled into the U-tube.

Daniel Colegate [110] using small- angle neutron scattering (SANS) and pulsed field gradient spin echo NMR, investigated into the kinetic processes that occur in micellar surfactant solutions subjected to both bulk perturbations and close to expanding surfaces. Bulk exchange kinetics between micelles and monomers in solution has been investigated. He has hypothesised an alternative monomer- micelle exchange mechanism, which has been tested using numerical modelling and comparison of theoretical predictions with the results of Stopped- Flow Velocity (SFV) studies using Laser Doppler Velocimetry (LDV) perturbation experiments. Also a detailed experimental investigation of adsorption kinetics from micellar systems on the millisecond timescale was conducted. An alternative adsorption path way that should be included in future theories of adsorption from micellar surfactant solutions was detailed by him.

Radina Hadgiivanova [111] in his work addressed current issues in the theory of micellar aggregation and aimed to give a unified theoretical description of some of the universal features of micellar solutions. Throughout his work a simple free- energy formalism was used which views micellization as restricted nucleation. The micelles are treated as nuclei of an aggregated phase, with the difference between micellization and macroscopic phase transition being the finite size of the micelles. Despite its simplicity this model enables the study of a host of new issues related to amphiphilic aggregation in and out of equilibrium. Sensitive spectroscopic techniques like FCS as well as NMR measurements, show in some cases the appearance of micelles at concentrations as low as 3- 4 times below the literature known value of the CMC measured by macroscopic techniques such as conductivity and surface tension. This is attributed to the presence of a third component in the system.

Kasper Kristensen [112] used ultrasonic velocimetry technique , for interpreting ultrasonic velocities recorded in aqueous solutions in the limit of infinite solute dilution, for three different classes of aqueous solutions containing low-weight molecules, surfactants and proteins, respectively.

Palani [113] measured ultrasonic velocity (U), density (ρ) and viscosity (η) for polyethylene glycols (PEG 4000 & 6000) in two solvents namely water and chloroform at 303, 313 and 323 K. Using the experimental values, the adiabatic compressibility (β), free length (L_f), acoustic impedance (Z), free volume(V_f), internal pressure (π_i) and cohesive energy were calculated. The variations of these parameters have been discussed in the light of intermolecular interactions.

Ravichandran. S. [114] measured ultrasonic velocities and densities for the aqueous solution of manganese sulphate, nickel sulphate and copper sulphate in polyvinyl alcohol solution, in different concentration at 303K. Adiabatic compressibility, intermolecular free length, acoustic impedance, surface tension and other acoustical parameters have been calculated to assess the polymer-ion interaction. It is seen that the ultrasonic velocity increases initially with the increase in the concentration of manganese sulphate, nickel sulphate and copper sulphate salts in polyvinyl alcohol solution. The increase in velocity with concentrations suggests the increase in cohesive forces due to polymer-solvent interactions. The ion-solvent interaction is relatively weak in the case of polyvinyl alcohol solution containing Mn^{+2} and copper ions. Further study may give more details about complex ion formation.

Kanhekar et. al., [115] measured ultrasonic velocity, density viscosity, adiabatic compressibility, acoustic impedance, intermolecular free length, and relative association for NaCl and $MgCl_2$ in aqueous glycine at different temperatures with a view to investigate nature of the molecular interactions. These parameters further used to interpret the hydrophilic part of the solute and molecular interactions in the mixtures.

.Shinde et.al,[116] studied Ion-solvent interactions in aqueous manganous chloride solution by ultrasonic velocity measurement at different temperatures and reported ultrasonic velocity and density measurements of tetra hydrated manganous chloride in aqueous media have been made at 303.15, 308.15, 313.15 and 318.15K to investigate ion-solvent interactions. The gradual increase of ultrasonic velocity, density and acoustic impedance and gradual decrease of adiabatic compressibility, intermolecular free length suggested the presence of strong ion-solvent interactions. Mn^{+2} ions are found to possess structure making tendency for the cluster of water molecules. The solvation

number showed non linear variation with temperature and gradual decrease with concentration also confirmed strong interactions between Mn^{+2} ions and dipolar water molecules.

Thirumaran et.al, [117] studied the structure- making and structure- breaking behaviour of some divalent metal Sulphates in aqueous ethylene glycol at 308.15, 313.15 and 318.15K. and attempted to explore the possible molecular interactions between the metal sulphate and ethylene glycol which is known to have much dissociation of metal sulphates in the solvent mixture. Experimental values of density, viscosity and ultrasonic velocities were obtained on the liquid ternary mixtures of water+ethylene glycol + metal sulphates at 308.15,313.15 and318.15K. The related and relevant parameters correlated to our present study such as adiabatic compressibility, apparent molal compressibility, apparent molal volume were meticulously evaluated. The molecular associations such as ion-ion, ion-solvent, solute-solvent, solute- solute etc are identified and critically discussed in terms of the structure-making and structure-breaking behaviour of metal sulphates in the solvent mixture. It was attributed by them that in solvent, the attraction between the solute and solvent was essentially was of ion-dipole interaction type which depends mainly on ion size and polarity of the solvent.

Wang, Anderko and Young [118] developed a comprehensive model for calculating the surface tension of aqueous, non- aqueous, and mixed-solvent electrolyte systems ranging from dilute solutions to fused salts, which consists of a correlation for computing the surface tension of solvent mixtures and an expression for the dependence of Surface tension on the electrolyte concentration, derived from the Gibbs equation combined with a modified Langmuir adsorption isotherm to model the surface excess of species. The effects of binary interactions between solute species (ions or molecules) on the surface were also introduced, especially important for high electrolyte concentrations and in strongly speciated systems. The surface tension of mixed solvents was calculated by utilizing the surface tensions of the constituent pure components together with an effective surface concentration, which was defined for each component and took into account interactions between solvent molecules. This procedure was shown to reproduce experimental data for a variety of mixtures. In particular, it accurately predicted the

surface tension of ternary solvent mixtures using parameters determined from only binary data. The surface tension model has been coupled with a previously developed thermodynamic equilibrium model to provide speciation and activity coefficients, which were necessary for electrolyte systems. This made it possible to reproduce the effects of complexation or other reactions in solution. In all cases for which experimental data were available and were tested, the new model had been shown to be accurate in reproducing surface tension over wide ranges of temperature and concentration.

Griffith's et.al, [119], using Becker- Doring system of equations, deduced expressions for the reaction constants fit to molecular dynamics simulations. It develops Becker Doring model, reaction kinetics in micellar surfactant solutions.

Sachin Zade [120] studied the molecular interaction between solute-solute and solute-solvent with the help of acoustic properties determined by ultrasonic interferometer at 303.15 K in polar acetone and non polar dioxane solvents. The effect of introduction of metal ions viz Cu(II), Fe(III) in the same solution was found out. Also the effect of position of same group at ortho or para position on the molecular interaction was simultaneously examined.

Bidare et. al., [121] measured the ultrasonic velocity, density and viscosity at 308 K in the binary systems of 1,4-dioxane and ethanol with methanol. From the experimental data, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (Lf), free volume (Vf), internal pressure (Ji), were calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Marcus [122] in his partial molal volume studies of 12 univalent ions (alkali metal, ammonium, halide, nitrate, and perchlorate) and five divalent ions (alkaline earth and sulphate) in water at different temperatures and at and at 2 MPa pressure(using the data of Ellis), deduced theoretically the (negative) electrostrictive volumes, of these ions at infinite dilution, from the shell- by- shell calculation of the electrostriction. According to Marcus and Hefter who took into account the mutual dependence of the relative permittivity of the water around the ion and the electrical field strength at it. The

expanded volumes of the ions are derived and compared with their intrinsic volumes, (calculated according to Glueckauf's model, used by the author in the dielectric studies). The calculation yields also the spatial extension of the dielectrically saturated region around the ions. The numbers of water molecules, the molar volume of which is affected by the ions at infinite dilution, were estimated, by Marcus and Hefter.

Thirumaran et. al.,[123] determined experimental parameters such as density (ρ), viscosity (η) and ultrasonic velocity (U) of ternary liquid mixtures of primary alkanols such as 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with *N-N* dimethylformamide (DMF) in acetophenone at 303.15 K. The observed experimental data have been utilized to evaluate some of the thermo acoustical parameters and also their excess values such as adiabatic compressibility (β_E), intermolecular free length (Lf_E), free volume (Vf_E), internal pressure ($\pi_i E$), Gibb's energy (ΔG_E) and viscosity (η_E) and observed that present investigation observed that the interaction between DMF (Proton acceptor) and 1-alkanols is due to hydrogen bonding.

Muratov et.al [124] found that the stability of micelles self- assembled from block co-polymers could be altered by the degradation of the blocks. Slow degradation shifted the equilibrium size distribution of block co- polymer micelles and changed their properties. The quasi- equilibrium scaling theory showed that the degradation of hydrophobic blocks in the core of micelles destabilizes the micelles, reducing their size, while the degradation of hydrophilic blocks forming coronas of micelles favours larger micelles and may induce the formation of micelles from individual chains.

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