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A Review On Solvation Studies Of Copper (I) Sulphates In Non Aqueous Solvent Mixtures

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Abstract- *Aqueous solutions of electrolytes have received far more attention than the corresponding non-aqueous solutions, even though it has been realised for a long time that water cannot be regarded as the prototype of electrolytic solvents. Nevertheless during recent years there has been an increasing interest in the behavior of electrolytes in non-aqueous solvents with a view to investigate ion-ion and ion-solvent or solute-solvent interactions under varied conditions.*

The salvation of copper(I) sulfate in binary mixtures of water and N,N-dimethyl formamide (DMF) is studied by a combined approach using electrochemical studies in solution and a mass spectrometric assay of the solvated ions formed from these solutions upon electro spray ionization (ESI). This paper is consolidated form of the previous research done in the same fields

Keywords:- *Limiting molar conductance, Ion-pair association Constants, Binary Mixed solvents, Walden product, Association constant.*

1. INTRODUCTION

Thermodynamic properties are very useful study of the intermolecular interactions and geometrical effects in the systems and thermo-physical and bulk properties of solutions. Also, they are necessary in theoretical and applied areas of research and used in many other fields of industry [1-3]. Studying the information of the transport properties (conductance, viscosity, ionic mobility) of electrolytes in aqueous and partially aqueous media tell us all about ion-ion and ion-solvent interactions in these solutions .

The Fuoss-Shedlov sky which is one of the mathematic equations of conductivity theories has been successfully used to investigate many electrolytes in solutions . The physical properties of the binary mixed solvents like the viscosity and the relative permittivity can be varied making them more favor to solvent system for the study of ion association and ion mobility. Recently, a study of the properties of copper sulfate has become essential in many fields such as biochemistry and other different industry.

Copper sulfate used as a coloring ingredient in artworks, especially glasses and potteries and also used in fireworkmanufacture as a blue coloring agent, but it is not safe to mix copper sulfate with chlorates when mixing firework powders.

Accurate data about the interactions of electrolytes in mixed solvents find applications in many industrial processes, as they provide a wide choice of solutions with engineer ableproperties. Interactions involving symmetrical 1:1 electrolytes in mixedsolvents have received quite a bit of attention, whereas fewer reports on 2:2 electrolytes in mixed-solvent systems appeared. The investigation of ionic interactions usually is performed via the determination of thermodynamic properties of the bulk, suchas the partial molar volume, the salvation enthalpy, the isentropic compressibility, the free energy of transfer, and transport properties, such as conductivity, viscosity, and transference numbers.

It is important to realize, however, that these methods probe macroscopic quantities of the bulk solution. Informationabout the microscopic interactions existing in solution can be obtained with several spectroscopic methods,2-7but the achiev-able molecular insight still remains limited. In part, this is dueto the fluxional behavior in solution (e.g., ref 3), but it is also a result of the indirect nature of most measured quantities, which require extensive modeling and assumptions in the deduction of the underlying molecular circumstances.

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Hence, complementary information about the microsolvation of ions in thetas phase light add helpful information for a molecular understanding of salvation phenomena.9-11In general, the behavior of ions in an electrolyte solutiondepends on the physicochemical properties of the solvent.

Specifically, the extent of ion association and ion salvation is related not only to the size and charge of the involved ions, but also to properties of the solvent such as the dipoleoment of the separate solvent molecules or the dielectric constant and the viscosity, where the latter two reflect the sum of the dipoles in the bulk. Some of the advantages which motivate the use of mixed solvents derive from the possibility to gradually change physicochemical properties of a bulk solvent by a change in composition.

2 STRUCTUREOF SOLVATED METAL IONS IN NON-AQUEOUS SOLVENTS

Alkali metal ions Solvation numbers of alkali metal ions in various non-aqueous solvents have mostly been determined by measuringthe transference number of the ions in solvents. A few results have been obtained from conductivity measurements of alkali halides in organic solvents. Only one experiment, as far as I know, has been carried out by the X-ray dif-fraction method for the determination of the solvation number of lithium ion in form amide.

The fractional solvation number of lithium ion in form amide obtained by the X-ray diffraction method indicates that it is an averaged number of various solvation numbers of lithium ions but the distribution of the solvation numbers remains unchanged with time, according to the view from studies of molecular dynamics simulations in aqueous solutions of lithium salts . It may be surprising to see that the averaged solvation number of lithium ion inform amide determined by the X-ray diffraction method accidentally coincides with the value from the measurementof the transference number of the ion in the same solvent.

2.1 Copper(I) ion

Solvation of multi-charged ions, except for ions in group 2A, in non-aqueous solvents has scercely been investigated, because most of these ions associate with counter anions in such solvents with relatively low dielectric con-stints, and thus reliable information for solvation of naked multi-charged ions is difficult to obtain in non-aqueous systems. Salvation equilibrium of the copper (I) ion are calorimetrically and spectrometric allystadied in pure DMF and in DMF-AN mixtures in which perch orate ions are contained as the counter anions.

It is known that copper(l) ion has a distorted octahedral structure with an elongated axis in water, and the C_u— OH_2distances are 194 pm within the plane and 243 pm along the axis . According to calorimetric studies on sol-vation of copper(l) ion with DMF in DMF-AN mixtures, solvated complexes $[Cu(dmf),]^1$ (n =1—4,6) forms the formation of $Cu(dmf)5]^1$ has not being confirmed.

2.2 Solutions

Binary mixed solvent of ethanol–water with the alcohol mass fractions of 0%, 20%, and 40% were selected to be the solvent media for this study and were prepared by mixing required volume of ethanol and water (with error ± 0.01%) by applying the following equation:

$$\text{Alcohol percentage} = (V_1d_1)100/(V_1d_1+V_2d_2) \quad (1)$$

Where d1 and d2 are the density of alcohol and water respectively, V1 is the volume of alcohol which will be added to the volume V2 of water to get the mixture of the required percentage.

The unknown values of the (ηo) and (ε) were evaluated by applying the empirical relations of these properties at the temperatures taken from the referred references. Seventeen solutions of CuSO4 were prepared by mass (Mettler AE 200 balance with a sensitivity of ± 0.0002 g) with a concentration range (1 x 10-3 – 7.1 x 10-4 mol.dm-3) in the previously prepared mixed solvents taken a certain volume of the salt standard solution and diluted to the required volume.

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3 REVIEW OF LITERATURE

Heftier et.al [1] 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 equilibrium.

Buchner et.al, [2] studied dielectric spectra for aqueous sodium oxalate solutions up to the saturation concentration at 25oC 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 [3] 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 analyse by Jones-Dole equation to determine ion- ion interactions and ion- solvent interactions.

Sethu Raman [4] made omen Interpretations for ultrasonic studies Ultrasonic velocity and density measurements of tetra hydrated manga nous 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 (Lf) suggested the presence of strong ion-solvent interactions. Mn+2 ions possess structure 28 making tendency for the cluster of water molecules. The solvation number (Sn) shows nonlinear variation with temperature and gradual decrease with concentration also confirms strong interactions between Mn+2 ions and dipolar water molecules.

Etienne Backed et.al, [5] reported ultrasonic absorption spectra at frequencies between 300 kHz and 3 GHz for aqueous solutions of MgCl2, CaCl2, SrCl2, NiCl2, and CuCl2. 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 ns τ 0.6 ns), corresponding with the τ values for solutions of Mg(NO3)2 and Ca(NO3)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 [6], 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 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 dioxin 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 Ramona. G et. al., [7] 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 [8] studied Ultrasonic Relaxation in aqueous Amino acids and in water- glycerin mixtures, Carboxylic acids in non- aqueous solutions and arrived at interesting results about MI cellar formation with the ultrasonic relaxation mechanism. The ultrasonic velocity and absorption studies are carried out in water- glycerin mixtures of Manganese sulphate, Vandal sulphate, Copper sulphate, Copper nitrate, and Chromium sulphate and chromium nitrate. In all the systems, the ultrasonic

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velocity increases non-linearly with increase in concentration of paramagnetic ion, which may due to formation of hydrogen bonds.

Minerva González-Melcher et.al, [9] 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-vapor 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 Hassan et. al., [10] 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 VE, 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,[11]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 [12] 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 noni deal characteristics that may need to be corrected for, if accurate measurements are to be performed is presented.

Badriah Ali Mahammed [13] in his work on transition ionic liquids, studied the conductance of some chosen alkalaine earth and transition earth metal cautions 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.

Pereira et.al [14] reported densities, speeds of sound, and refractive indices of the binary mixtures of 1-butyl-3-methyl iimidazolium 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 is entropic compressibility were calculated for the above systems. The liquid-liquid equilibrium data of the binary 31 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, [15] studied the Broadband ultrasonic absorption spectra and complex dielectric spectra for aqueous solutions of electrolytes and discussed their results in terms of caution- anion association schemes. They developed techniques adopted by Eigen, Tamm and Kurtz and

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demonstrated the relaxation characteristics in the frequency dependent sonic absorption coefficient of 2:2 valiant electrolyte solutions.

Khoan Chandra [16], 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 C12OH. This was explained due to electrical repulsion forces.

Iglesias [17] measured density and ultrasonic velocity of the mixtures of the new ionic liquid 2-hydroxy ethyl ammonium format and short hydroxyl 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 Płaczeket,al [18] measured Densities and heat capacities of various 1:1 and higher-charged electrolytes in N,N- dimethyl form amide (DMF) at 25 °C using a series-connected flow dens meter and Picker calorimeter. Standard molar volumes Vo and isobaric heat capacities Cpo derived from these data were split into their ionic contributions using the tetra phenyl phosphoniumtetraphenyl 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 [19] reported new modernized high pressure- high temperature vibrating tube dens meter DMA HPM (Anton par, Austria), at seven modalities, 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 LiNO3 in ethanol. The measurements with a vibrating tube are based on the dependence between the period of oscillation of a 32 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 Colgate [20] 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 hypothesized an alternative monomer- micelle exchange mechanism, which has been tested using numerical modeling 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 [21] 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 [22] 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 [23] 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 (Lf), acoustic impedance

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(Z), free volume(Vf), internal pressure (πi) and cohesive energy were calculated. The variations of these parameters have been discussed in the light of intermolecular interactions.

Ravichandran. S. [24] measured ultrasonic velocities and densities for the aqueous solution of manganese sulphate, nickelsulphate 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., [25] measured ultrasonic velocity, density viscosity, adiabatic compressibility, acoustic impedance, intermolecular free length, and relative association for NaCl and MgCl2 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,[26] studied Ion-solvent interactions in aqueous manga nous chloride solution by ultrasonic velocity measurement at different temperatures and reported ultrasonic velocity and density measurements of tetra hydrated manga nous 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 34 number showed nonlinear variation with temperature and gradual decrease with concentration also confirmed strong interactions between Mn+2 ions and dipolar water molecules.

Thirumaran et.al, [27] studied the structure- making and structure- breaking behavior 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 and 318.15K. 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- solutes are identified and critically discussed in terms of the structure-making and structure-breaking behavior of metalsulphates 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, Anadarko and Young [28] developed a comprehensive model for calculating the surface tension of aqueous, on- 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 spectated 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 35 surface tension of ternary solvent mixtures using parameters determined from only binary data. The surface tension model has been

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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 complication 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, [29], using Becker- During system of equations, deduced expressions for the reaction constants fit to molecular dynamics simulations. It develops Becker During model, reaction kinetics in micellar surfactant solutions.

Sachin Zade [30] 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 vizCu(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.

Bidareet. al., [31] 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 (βa), 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 [32] in his partial molar 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 MP apressure(using the data of Ellis), deduced theoretically the (negative) electro strictive volumes, of these ions at infinite dilution, from the shell-by- shell calculation of the electrostriction. According to Marcus and Heftier 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 36 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 Heftier.

Thirumaran et. al.,[33) 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 dimethylfomamide (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 (βE), intermolecular free length (LfE), free volume (VfE), internal pressure (πiE), Gibb's energy (ΔGE) and viscosity (ηE) and observed that present investigation observed that the interaction between DMF (Proton acceptor) and 1-alkanols is due to hydrogen bonding.

Muratov et.al [34] 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 favors larger micelles and may induce the formation of micelles from individual chains.

Esam A. Gomaaet. al. [35] Presented The volumetric properties of copper sulphateinEtOH–H2O solvents were described. The standard partial molar volumes of transfer for copper sulphate were determined. The different solvation volumes were determined. The difference of the volumetric properties reflects the significant influence of solvent and temperature on the salt behavior. The nature of the ion–solvent interaction that takes place in solution controls the extentof ion-pairing in the salt solutions under study. In addition, he ion-pairing depends on the dielectric constant and different properties of the medium. The association decreases as the temperature increases and increases as the proportion of organic solvent increases.

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R.C.Thakur et. al. [36] Proposed Partial molar volumes of copper sulphate and zinc sulphate have been determined in water and binary aqueous mixtures of propylene glycol (2,4,6 and 8% by weight of propylene glycol) at303.15 K with the help of density measurements. Effect of temperature on the partial molar volumes was also analyzed for these salts in water and binary aqueous mixtures of propylene glycol.

Results obtained have been analyzed by Masson's equation and the experimental values of slopes and partial molar volumes of these transition metals sulphates have been interpreted interms of ion-ion or ion –solvent interactions. Limiting molar expansibilities (▪ 0E) have also been determined which are interpreted in terms of structure making or breaking capacities of transition metal sulphates. The transition metal sulphates have been found as structure promoter in water and binary aqueous mixture of propylene glycol.

A. Zuber et. al. [37] Received In this study, the Q-electro lattice equation of state was applied to model electrolyte solutions whose solvent is methanol or ethanol. Thermodynamic properties of sixteen methanol and ten ethanol single salt solutions were obtained using two adjustable parameters per ion, namely the ionic diameter and the solvent-ion interaction energy.

Particularly for the captions, the parameters exhibit some reasonable trends related to the solvation phenomenon. Vapor pressure and density are correlated satisfactorily bussing the Q-electro lattice equation of state. Correlated mean ionic activity coefficients and predicted osmotic coefficients have larger deviations compared to the other thermodynamic properties. Predictions of liquid density at temperatures different than298.15 K are in good agreement with experimental data.

Esam A. Gomaa et. al. [38] Indicated We can conclude that, the extent of ion-pairing in salt solution sunder study depends upon the nature of the ion-solvent interaction taking place in the solution. Moreover it depends on the dielectric constant and the properties of the medium. The association increases as the temperature in creases and as the proportion of organic solvent increases.

Mohamed A. Tahoon et. al. [39] Presented Copper sulfate volumetric properties in EtOH-H2O solvents have been described. The standard partial molar volumes of transfer for copper sulfate are determined. The different salvation volumes are determined. The difference of volumetric properties reflects the significant influence of solvent and temperature on thesalt behavior. The nature of the ion-solvent interaction taking placein the solution is controlling the extent of ion-pairing in saltsolutions under study. Additionally, it hangs on the dielectricconstant and the different properties of the medium. The association decreases as the temperature increases and increases in theproportion of organic solvent increases.

Ahmed S. Abou- Elyazedet. al. [40] Proposed We concluded from this work that the complex association parameters are greater for 1:2 (M/L) stoichiometry complexes than that of 1:1 (M/L) stoichiometry complexes for both bulk copper sulfate and Nano copper sulfate in all used mixed solvents at 298.15 K indicating that more possibility to occur and observed from given data that the maximum complication between bulk and Nano- copper ions and spiramycin adipose antibiotic were by using 60% MeOH in the mixtures. Whereas the least completing ability at 40% by volume of MeOH.

A. K. Sharmaet. al. [41] Received Ultrasonic velocities and densities have been measured in ternary mixtures containing coppersoapffiurea complexes derived from groundnut and sesame oils in a 20% and a 40% methanol benzene mixture. From these values, the specific acoustic impedance Z, adiabatic compressibility, intermolecular free length Lf , apparent molar compressibility k, molar sound velocity R, primary solvation number Sn have been calculated. The results have been analyzed in terms of Masson's equation.

The results have been explained on the basis of intermolecular interactions and the effect of the polarity of the solvent molecules and the concentration of solute molecules were accessed on various acoustic parameters. Our results also suggest that the behavior of soap complex in benzene dominated environment and methanol dominated environment is quite different as they occupy different positions in palisade layers of soap complexes agglomerations.

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Disha Mungalpara et. al. [42] Indicated Complementing the family of anion receptors by compound 3 improved our understanding of the effects that govern preferred conformations and binding properties ofthese compounds.

Esam A. Goma et. al. [43] Presented conductivity measurements for copper sulfate in a binary mixed solvent with alcohol mass fraction of 0%, 20%, and 40% (EtOH-H2O)at different temperatures from 298.15to 313.15oK (with a step of 5oK)have been reported. The conductivity data have been analyzed using Fuoss – Shedlovsky equation. The extent of ion-pairing in copper sulfate solutions under study depends on the nature of the (ion-solvent) and (solvent-solvent) interaction taking place in the solution.

3 STRUCTUREOF COMPLEXES IN NON-AQUEOUS SOLVENTS

Anumber of investigations have been carried out for determining structures of metal complexes in various solvents and for studies of the solvent effect on the formation of various complexes. Thermodynamic measurements and spectroscopic investigations have most widely been employed for the studies. However, a very limited number of investigations have been reported in which the X.ray and neutron diffraction methods have been applied. NMR measurements have sometimes provided very useful information for the structure of complexes in non-aqueous sol. vents, and the method is extremely useful for kinetic studies of complex formation reactions in solutions. It has often been pointed out that most complexes existing in non-aqueous solvents have similar structures to those in water, except for coordinated solvent molecules, but there are exceptions in which the structure of complexes innon.aqueous solvents differs remarkably from that in aqueous solutions. Interesting work has been carried out by a group of Swedish solution chemists in the structural investigation of com-plexes in non.aqueous solutions. They also reported valuable data of thermodynamic quantities for complex formations reactions in various systems. In this review we focus our attention on the structure of thiocyanato complexes ofsome divalent metal ions in DMF and DMSO and then we try to elucidate the role of solvents in the formation reactions of the thiocyanato complexes of cadmium(l) ion in the solvents. Structures of some halogens complexes ofcopper(l) ion in methanol, DMF, AN, DMF-AN mixtures and in DMSO have been reviewed in this paper, most of these investigations were carried out by Japanese solution chemists.

3.1Thermodynamics of association

The standard Gibbs free energy of association (ΔG°A) was calculated using Eq. for all salts under study in all solvent mixtures at all temperatures. The values were tabulated in Table.

$$\Delta G^{\circ}_{A} = -RT \ln K_{A} \quad (2)$$

Here, R is the gas constant and equal (8.314 J.mol-1.K-1).The values of the standard enthalpy (ΔH°A) and the standard entropy (ΔS°A) of association process were obtained from van't Hoff equation($\ln K dT$) = ($\Delta HA^{\circ} RT2$) by plotting (log KA) versus (1/T), where the slope is equal to the value of (−ΔHA/2.303R), the entropies of association (ΔS°A) were calculated by the use of Gibbs–Helmohltz equation Eq. (15).

$$\Delta G^{\circ}_{A} = \Delta H^{\circ}_{A} - T\Delta S^{\circ}_{A} \quad (3)$$

The thermodynamic parameters of association values showed the effect of temperature when increased in the negative values of the associating free energy (ΔG°A) as the temperature rise from 298.15 to 313.15 K. It was found that the association processes in all studied systems are spontaneous processes and the associating free energy becomes more negative with the increase in temperatures. This indicates that an ion-pair association is favored with lowering the dielectric constant of the medium. The association processes are endothermic in nature due to the positive value of (ΔH°A).

A positive entropy values (ΔS°A) can be explained on the assumption that iceberg structure around the action is broken when association takes place leading to an increase in the degree of

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disorderliness and the positive (ΔH°A) and (ΔS°A) values are in a good agreement with several theories in many solvents. Positive values of (ΔH°A) and (ΔS°A) for association can be attributed to counter balance of the enthalpy term by a favorable entropy change resulting from the short- and long-range desolation of both ions. Positive (ΔS°A) values attributed to desolation of both ions are also supported by the positive enthalpy values indicating a lack of covalent bonds.

4. CONCLUSIONS

In this paper, we reviewed number of research article in the respective field for my proposed research area. The study of ion-solvent interactions in mixed solvents has attracted the attention of a large number of workers 27-33 only during the last few years .

The solvation of $CuSO_4$in binary water/DMF mixtures has-been investigated in a combined approach based on electro-chemical measurements of bulk solutions on the one hand admass spectrometric studies employing electrospray ionization(ESI) on the other. Both the solution studies and the gas-phase experiments clearly demonstrate that, as expected, DMF mol-ecules progressively replace water molecules bound to copper.

A detailed survey of the literature reveals that physicochemical investigations of electrolytes have been carried out in v/ater + organic solvent mixtures. In such solvent mixtures major solvent structural changes usually occur by the presence of electrolytes and it is very difficult to obtain actual information about ion-solvent interaction. The transport properties and thermodynamic properties by conductance, viscosity^emf and ultrasonic measurement methods provide useful and important information about ion-solvent interaction in such mixed solvents.

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