CHAPTER 1
INTRODUCTION

1.1 General Introduction

Studies of the transport properties of electrolytes in different solvent media are of great importance for obtaining information on ion-association and solvation behaviour of ions in solution. Though transport studies of electrolytes in pure solvents have been extensively carried out, yet such studies are still lacking in mixed solvents. The ever increasing interest in the behaviour of electrolytic solutions is due to the fact that there is a need for better understanding of the nature of ion–ion and ion–solvent interactions in different solvents. Sometimes one of the solvent components solvates a particular ion more strongly than the other. Also some ions have a special tendency to get preferentially solvated by one of the solvent components. The term, “preferential solvation” is applied when the composition of the solvent components in the neighbourhood of the ions is different from the composition of bulk solution. When both the ions of electrolyte prefer the same solvent, the preferential solvation is called “homoselective” and when one ion prefers one solvent and other is strongly solvated by the second solvent, it is known as the “heteroselective” preferential solvation. Preferential solvation of ions in mixed solvents has been proved to be of great significance in reaction kinetics. Solubility and in many hydrometallurgical problems. To have a better insight into the ion–solvent interactions, the properties of the individual ions are important than those of the electrolyte as such. Consequently, a number of experimental methods and theoretical approximations based on the results of measurements in aqueous solutions, it would not be surprising if such theories do not fit in well with the present measurements in non aqueous mixed solvents. This may be due to different sequences of solubilities, differences in solvating powers and possibilities of certain chemical and electrochemical reactions in mixed solvents unknown in aqueous chemistry. Consequently, various theories have been proposed and many techniques have been developed to extend the range of
properties from which the nature is electrolytic solutions may be inferred. The solvation behaviour of ions in mixed solvents can be interpreted with the help of transport properties such as conductance, viscosity and other properties like ultrasonic velocity and NMR. An escalating data and valuable information has been reported in a variety of non aqueous solvents and mixed solvents highlighting the scope of such studies. So there is a need to comprehend the solvation behaviour of electrolytes in non aqueous mixed solvents. A brief survey of literature is presented below.

1.2 Literature Survey on Conductance Studies

Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolyte solutions. Because of its relative simplicity and versatility, the measurement of the conductivity of electrolyte solutions, which can be carried out to a very high precision, remains an important tool to obtain information about electrolytes in different solvents. Conductance is a characteristic property of electrolytic solutions, which determines the nature of ion – ion, ion – solvent and also in a way, the solvent – solvent interactions in mixed solvents. These studies provide kinetic information in the form of ionic conductances and thermodynamic information in the form of association constants.

Since conductance studies are of vital importance in solution chemistry, a brief survey of literature of conductance studies is reported below.

Perron and coworkers\(^1\) had measured the conductivity, viscosity and density of LiAsF\(_6\), LiBr and LiClO\(_4\) in aprotic solvent mixtures. The conductivity of lithium bis (trifluoromethylsulfone)imide (LiTFSI) was also obtained in a large number of mixed aprotic solvents. The solvents were chosen to verify the effect of various parameters such as viscosity, permittivity, volume, acceptor number and donor on the conductivity. These results were used to develop a simple model for excess conductivities based on the viscosity and volume of the solvents. Without adjustable parameters, this model predicted the correct sign of the excess conductivities in ~ 90 % of the cases and the magnitude of the conductivity of the ternary mixtures within an average of 15 %.
Desnoyers et al.\textsuperscript{12} measured, conductance and apparent molar volume and heat capacity of LiTFSI over a wide range of condensation in glymes, tetraethylsulfamide (TESA), acetonitrile (AN), $\gamma$-butyrolactone and propylene carbonate (PC) at 298 K and were compared with those of LiClO$_4$ in the same solvents. At low concentrations, LiTFSI in ethylene glycol dimethyl ethers (EGDME) exists in the solutions state. At high concentrations, the thermodynamic properties of the two lithium salts approach those of the molten salts. They reported that these salts have a reasonably high specific conductivity in most of the solvents.

Nandi et al.\textsuperscript{13} reported the electrical conductance data for R$_4$NBr ($R = \text{Bu to heptyl}$), (LiBF$_4$) and LiAsF$_6$ in Tetrahydrofuran (THF) at 298 K. Analysis of data by the Fuss-Kraus theory of conductance revealed the presence of both ion-pairs and triple ions. The ion-pair (KP) and triple-ion (KT) formation constant of these salts in THF have been compared with the values obtained in 1,2-dimethoxyethane (1,2-DME). The comparison shows that the lower homologues of the studied R$_4$NBr salts were more associated in THF than in 1,2-DME whereas the KT values in majority cases were much higher in 1,2-DME than THF with the exception of LiAsF$_6$.

Muhuri and Hazra\textsuperscript{14} reported the electrical conductance and viscosity measurements for the solutions of Ph$_4$PCI, Bu$_4$NBPh$_4$ in PC at 298, 308 and 318 K. Viscosity data were analyzed by using the Jones-Dole equation and B-coefficients were calculated. The conductance data were analyzed by using the 1978 Fuoss conductance equation which contained terms for equivalent conductance ($\Lambda_0$), association constant ($K_a$) and association distance (R). The limiting ionic values were determined by using reference electrolytes Bu$_4$NBPh$_4$ and Bu$_4$NClO$_4$. Calculated Stokes radii indicated that Na$^+$ and Cl$^-$ were substantially solvated and remained as free ions in the medium. In another study Hazra and coworkers\textsuperscript{15} measured electrical conductance of Hex$_4$NBr, HEP$_4$NBr and Bu$_4$NBPh$_4$ in methanol (MeOH), AN, and MeOH (1) + AN (2) binary mixtures at 298.15 K. The conductance data have been analyzed by the Fuoss equation in terms of the limiting molar conductance ($\Lambda_0$), the association constant
(Kₐ), and the distance of closest approach of ions (R). Single-ion conductivities have been determined on the basis of Bu₄NBPh₄ as the reference electrolyte. The results have been interpreted in terms of ion-ion and ion-solvent interactions. In a recent study Hazra and coworkers have carried out precise measurements of electrical conductances of the solutions of LiCl, LiBr, LiI, LiClO₄, LiBF₄, NaBr, NaBPh₄, KBr, RbBr, CsBr and Bu₄NBr in N,N-dimethylacetamide (DMA) + water (H₂O) (50 v/v) mixtures in the concentration range 0.02 – 0.05 mol dm⁻³. The conductance data had been analyzed by the 1978 Fuoss equation in terms of the limiting molar conductance (Λ₀), the association constant (Kₐ) and the association constant (R). The limiting ionic conductance (λ⁺₀) had been estimated from the appropriate division of the limiting molar conductivity value of the reference electrolyte Bu₄NBPh₄. The electrolytes investigated were found to be significantly dissociated in this solvent medium and all ions remained unsolved in DMA + H₂O (50 v/v) mixed solvent system with exception of the lithium ion where significant solvation has been noticed.

Sadeghi and Valavi studied the complex formation of ammonium and four n-alkylammonium perchlorate salts with dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7) and dibenzo-24-crown-8 (DB24C8) was studied by conductometry in AN, nitrobenzene (NB) and nitromethane (NM) solvents at different temperatures and their binary mixtures at 298 K. The stability constants of the resulting 1 : 1 complexes were determined and found to decrease in the order: DB21C7 > DB18C8 > DB24C8. In all cases, the stability constants of the resulting complexes in solvents used varied in the order: NB > NM > AN.

Shamsipur and Khayatin have carried out conductance study of the interaction between Tl⁺ ion and 18-crown-6 (18C6), dichlorohexano-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6), diaza-18-crown-6 (DA18C6), dibenzyldiaza-18-crown-6 (DbzDA18C6) and hexaaza-18-crown-6 (HA18C6) in N,N-dimethylformamide (DMF) – An mixture at various temperatures. The formation constants of the resulting 1 : 1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order HA18C6 > DA18C6 > DbzDA18C6 > 18C6 > DC18C6 > B18C6. The enthalpy and entropy
of complexation reactions were determined from the temperature dependence of the formation constants.

In another study Ghasemi and Shamsipur\textsuperscript{19} reported conductance study of the interaction between cobalt, nickel, copper, zinc, cadmium and lead ions with 1,10-diaza-18-crown-6 in different AN-dimethylsulfoxide (DMSO) mixtures at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order Zn\(^{2+}\) < Co\(^{2+}\) < Ni\(^{2+}\) < Cu\(^{2+}\) < Cd\(^{2+}\), Pb\(^{2+}\). The enthalpy and entropy of complexation reactions were determined from the temperature dependence of the formation constants. A linear relationship was observed between the log K\(_f\) of different complexes and mole fraction of AN in the solvent mixtures.

Marji and Taha\textsuperscript{20} have studied the complexation reactions between Ag\(^+\) and Tl\(^+\) ions 15-crown-5 (15C5) and phenylaza-15-crown-5 (PhA15C5) conductometrically in 90\% An – H\(_2\)O and 50\% An – H\(_2\)O mixed solvents at temperatures 293, 298, 303 and 308 K. The stability constants of the resulting 1 : 1 complexes were determined, indicating that the Tl\(^+\) complexes are more stable than the Ag\(^+\) complexes. The enthalpy and entropy of crown complexation reactions were determined from the temperature dependence of the complexation constants.

Rienvatana\textsuperscript{21} reported evidence for the existence of 2 chemically distinct species of Tl (I) in solution of TlOAc in AN, isopropyl alcohol and p-dioxane (p-DO). These species were the solvated free Tl (I) ion and ion – pairs of Tl (I) ion with acetate and formate ions. UV absorption spectra of the Tl (I) salts show that the position of an absorption maximum due to ion-pair formation occurs at longer wavelengths than that due to the free solvated ion. The ion-pair band is sensitive to changes in the nature of solvent and concentration of added Me\(_4\)NOAc, while that of the solvated free ion is not strongly solvent dependent. Electrical conductivities of TlOAc in water and of binary mixtures with AN, isopropyl alcohol (I-PrOH), and (p-DO), were also determined at 298 K. The results showed that TlOAc behaved as a weak electrolyte existing largely as ion-pairs.
Susha and Bhat\textsuperscript{22} carried out conductance measurements of N-bromo-N-sodio-p-toluenesulfonamide (Bromamine-T, BAT) in H\textsubscript{2}O, AN and DMF, and in various mixtures of these solvents at 283, 293, 303 and 313 K. Conductance data were analyzed by different conductance models. Limiting molar conductance, dissociation/association constants, product of limiting conductance and viscosity of the solvent (Walden product), thermodynamically parameters and limiting ionic conductance were systematically computed. Limiting molar conductance values were higher in AN or H\textsubscript{2}O + AN mixtures as compared to H\textsubscript{2}O, DMF or H\textsubscript{2}O + DMF mixtures. Preferential solvation of cation by non aqueous solvent was identified. The association process involved in the system is exothermic.

Bhat and Shivkumar\textsuperscript{23} reported the investigations made on the ion-solvation behaviour of tartaric acid in different compositions (v/v) of H\textsubscript{2}O + MeOH/ethano(EtOH)/DMSO/DMF/p-DO mixtures between 288 – 313 K. The electrical conductance data were analyzed by Kraus-Bnary and Shedlovsky model of conductance. The limiting molar conductance, \( \lambda_0^a \) sharply decreased for the increased amount of cosolvent and solvent-solvent interactions. Association constant \( K_A \) was compared in all the cases. In H\textsubscript{2}O + MeoH / EtOH mixtures the \( K_A \) increased with increase in temperature suggesting endothermic behaviour of the system. Walden product, Stoke’s molecular radii and thermodynamical parameters related to association and solvation were determined using Born model in all the cases of solvent mixtures. The energy of activation was also calculated and was found to be the highest in the case of H\textsubscript{2}O + EtOH. In another study Bhat and Sreelatha\textsuperscript{24} have carried out investigations to study the effect of added ethanol on the conductance behaviour of bismuth triiodide in AN, MeOH and DMF at 288, 298, 308 and 318 K. From the experimental molar conductance value, the limiting molar conductance was determined for all the cases using the Shedlovsky model of conductance. The limiting molar conductance was found continuously with the increase in the amount of ethanol either to AN, MeOH or DMF. In pure solvents, conductance varied in the order of AN > MeOH > EtOH. Association constant was determined in the three solvent systems. Results predicted the endothermic behaviour of the process in most of the cases. Energy of activation of
the conducting rate process and thermodynamic parameters of association were calculated and reported. Wladen product and corrected Stokes molecular radii were also computed. The solvation number of the species was calculated in the case of pure solvents and the value indicated the existence of solvent shared or separated ion-pair in the system.

Kundu and coworkers\textsuperscript{25} measured the equivalent conductances ($\Lambda$) of some potential electrolytes, e.g., KI, KBPh\textsubscript{4}, Ph\textsubscript{4}AsI and n-Bu\textsubscript{4}NI in AN, DMF and their iso-dielectric binary mixtures at 298.15 K. The equivalent conductance at infinite dilution ($\Lambda_0$) and ion-association constant ($K_a$) for each of the solvent-electrolyte pairs have been evaluated from the data by computation using extended Fuoss-Hsia equation for the associated electrolytes, using a least squares program. $\Lambda_0$ values were then dissected into ionic contributions $\lambda_0^i$ by using two propositions : (1) reference electrolyte assumption : $\lambda_0^i$ (Ph\textsubscript{4}As$^+$) = $\lambda_0^i$ (Ph\textsubscript{4}B$^-$) = $\frac{1}{2}$ $\Lambda_0$ (Ph\textsubscript{4}AsBPh\textsubscript{4}) and (2) Krumgalz’s assumption : $\lambda_0^i$ (n-Bu\textsubscript{4}N$^+$) $\eta_0 = 0.213$ for all the solvents.

Chauhan et al.\textsuperscript{26} measured the molar conductances of Bu\textsubscript{4}NBPh\textsubscript{4}, Bu\textsubscript{4}NCIO\textsubscript{4}, Bu\textsubscript{4}NI, NaClO\textsubscript{4}, LiClO\textsubscript{4} and AgClO\textsubscript{4} in the concentration range (5-62) x 10\textsuperscript{-4} mol dm\textsuperscript{-1} in AN rich region of PC mixtures containing 5, 10, 15, 20 and 25 mol % PC by weight at 298 and 318 K. The entire conductance data had been analyzed using a least squares computer program to fit to Shedlovsky conductance equation to obtain limiting molar conductance equation ($\Lambda_0$) and ion-association constant ($K_A$). $\Lambda_0$ values had been split into limiting ionic conductances ($\lambda_0^i$) values and from these the effective ionic radii ($r_i$) in these solvent mixtures were calculated. The results were discussed in terms of ion-solvent interaction both specific and non-specific. The effect of temperature had also been discussed.

In another study Chauhan et al.\textsuperscript{27} reported the solvation behaviour of Li$^+$, Na$^+$, K$^+$, Ag$^+$ and NO\textsubscript{3}$^-$ ions from the conductance measurements of solutions of LiNO\textsubscript{3}, NaNO\textsubscript{3}, KNO\textsubscript{3}, AgNO\textsubscript{3} and Bu\textsubscript{4}NNO\textsubscript{3} in DMSO-MeOH mixtures. The data had been analyzed in terms of the limiting molar conductance ($\Lambda_0$) and non-association constant ($K_A$) using a least squares computer program of the
Shedlovsky conductance model. The limiting molar ionic conductance \( (\lambda c^0) \) has been calculated on the basis of \( \text{Ph}_4\text{PBPtq} \) assumption; \( \lambda^0 (\text{Ph}_4\text{P}) = \lambda^0 (\text{Ph}_4\text{B}) \) and effective ionic radii \( (r_i) \) calculated using empirical modification of the Stoke’s model. The \( r_i \) values were compatible with \( K_A \) values. An obviously typical difference in selective solvation for various cations, \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Ag}^+ \) was observed. Weak preferential solvation of \( \text{NO}_3^- \) by MeOH was reflected over the entire solvent composition range, which is in contrast to the solvation of \( \text{ClO}_4^- \) in DMSO-MeOH mixtures. In a subsequent study Chauhan and coworkers\(^{28} \) reported molar conductance and viscosity of \( \text{Bu}_4\text{NBPI}_{14}, \text{NaBPI}_{14}, \text{Bu}_4\text{NBr}, \text{BuNI}, \text{LiClO}_4 \) and \( \text{NcClO}_4 \) in AN rich regions of benzene and EtOH at 298 K. The conductance data were analyzed in terms of limiting molar conductance equation. The viscosity data were analyzed in terms of viscosity A- and B-coefficients of the Jones-Dole viscosity equation. Both \( \Lambda_0 \) and B-coefficients had been resolved into ionic conductance \( (\lambda_{c^0}) \) and \( B_4 \) values for various ions on the basis of \( \text{Bu}_4\text{NBPI}_{14} \) assumption. The effective ionic radii \( (r_i) \) of \( \text{Bu}_4\text{N}^+, \text{Ph}_4\text{B}^-, \text{Li}^+, \text{Na}^+, \text{Br}^-, \text{I}^- \) and \( \text{ClO}_4^- \) have been determined from \( \lambda_{c^0} \) values using Gill’s modification of the Stoke’s law. The ionic \( B_4 \) values for these ions have also been discussed in terms of Einstein equation. The analysis of data showed that \( \text{Bu}_4\text{N}^+ \) and \( \text{Ph}_4\text{B}^- \) lost their spherical shape, while \( \text{Li}^+, \text{Na}^+, \text{Br}^-, \text{I}^-, \) and \( \text{ClO}_4^- \) behave as spherical entities during viscous flow process.

Lebed et al.\(^{29} \) reported conductance data for \( \text{LiCl}, \text{NaCl}, \text{KCl}, \text{RbCl}, \text{CsCl}, \text{Me}_4\text{NCl}, \text{Et}_4\text{NCl}, \text{Bu}_4\text{NCl}, \text{NaF} \) and \( \text{NaBPh}_4 \) in ethylene glycol (EG) with molarity \( 1 \times 10^{-4} - 1 \times 10^{-2} \text{ mol dm}^{-3} \) over the temperature range 278-448 K. From conductance limiting ionic conductance of \( \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}, \text{Cs}, \text{Me}_4\text{M}^+, \text{Et}_4\text{N}^+, \text{Bu}_4\text{N}^+, \text{F}^-, \text{Cl}^- \) and \( \text{Ph}_4\text{B}^+ \) ions and the structural dynamical parameters of ion-ion of the model proposed by the authors have been calculated. The thickness of the ion solvation shell (Gurney co-sphere) had also been obtained. It was shown that single charged ions with the smallest radii \( (\text{Li}^+, \text{Na}^+, \text{F}^-) \), moderate radii \( (\text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Cl}^-, \text{Br}^-) \) and large complex ions \( (\text{Me}_4\text{N}^+, \text{Et}_4\text{N}^+, \text{Bu}_4\text{N}^+, \text{Ph}_4\text{B}^+) \), had different mechanisms of influence on the solvent structure and dynamics. It was concluded
that temperature dependence of near solvation parameters was caused by a significant change in the solvent hydrogen bond network.

Jauhar and Sandhu reported molar conductances and viscosities of some 1 : 1 alkali metal and tetraalkylammonium salts in DMF-MeOH mixture containing 100, 89.3, 69.1, 49.6, 29.9 and 10.7 mol % DMF and pure MeOH at 298 K. The conductance data had been analyzed by Shedlovsky method setting ion – size parameter equal to Bjerrum critical distance suggested by Justice to calculate $\Lambda_0$ and $K_A$. Calculation of limiting ionic conductances and solvated radii showed preferential solvation of ion in these mixtures. The viscosity data had been analyzed using the Jones – Dole equation. The ion – solvent interaction parameter, viscosity B – coefficient had been found to be positive for all the electrolytes in all systems. The ionic $B_+$ coefficients had been evaluated by taking Bu$_4$NBP liable as reference electrolyte. Conductances and viscosities of the salts NaBr, NaBP$_4$ and Bu$_4$NBr, had been measured at 303 and 313 K in different solvent mixtures. The limiting ionic conductances and ionic viscosity $B$-coefficients for the ions showed decreased solvation with increase in temperature.

Goldfarb et al. measured the electrical conductance of tetrabutylammonium hexafluorophosphate in acetone (AC) and of decamethylferricinium hexafluorophosphate in AC, AN, 1,2-dichloroethane (DCE) and dichloromethane (DCM) at 298 K. The Walden product of the Bu$_4$N$^+$ cation and the PF$_6^-$ anion in acetone and other solvents was discussed in relation to the dielectric friction. The electrical conductance at infinite dilution and the association constant of dimethylferrocinium hexafluorophosphate were determined in the four solvents investigated. The association constant of this electrolyte increased with reduced temperature.

Gill and coworkers reported a good account of preferential solvation behaviour of ions in terms effective ionic radii, $r_i$ values from conductance data of various mixed nonaqueous solvent systems. Similarly conductance study of a number of electrolytes had been carried out to various binary solvent systems of mixtures of DMSO with An, MeOH, AC and p-DO in order to derive
information about the preferential solvation of ions in these solvent systems on the basis of the $\eta$ values of ions. In another study Gill and Bakshi$^{32}$ reported heteroselective solvation of Ag$^+$ and NO$_3^-$ ions from $\lambda_\infty\eta_0$ data in water – organic solvent mixtures. In a recent study Gill and coworkers$^{33}$ have measured the molar conductances of Bu$_4$NBPh$_4$, Bu$_4$NCIO$_4$, AhClO$_4$ and TlClO$_4$ in the concentration range (0.25 – 75) x 10$^{-4}$ mol dm$^{-3}$ in AN – triethylphosphite (TEP), benzonitrile (BN) – TEP and pyridine (PY) – TEP mixtures over the entire composition range at 298.15 K. The conductance data had been analyzed by the Shedlovsky equation to obtain $\lambda_\infty$ and $K_A$ values of electrolytes. The $K_A$ values showed that all these electrolytes were highly associated in the TEP rich region of these solvent systems. Limiting ion conductances $\lambda_\infty^0$ and solvated radii ($r_i$) for Bu$_4$N$^+$, Ph$_4$B$^-$, Cu$^+$, Ag$^+$, Tl$^+$ and ClO$_4^-$ had been calculated. The $r_i$ values showed that Cu$^+$ was highly solvated in An – TEP, BN – TEP and PY – TEP mixtures and the extent of solvation increased with increase in TEP composition in all the cases. Ag$^+$ and Tl$^+$ were relatively less solvated than Cu$^+$ in all the three solvent systems. The extent of solvation of these two ions decreased with increase in TEP composition. ClO$_4^-$ was poorly solvated in AN – TEP, BN – TEP and PY – TEP mixtures. The extent of solvation of ions increased in the third case with increase in TEP composition. Bu$_4$NB$^+$ had no solvation but Ph$_4$B$^-$ showed some solvophobic interaction in the BN and PY.

Roses et al.$^{44}$ reported molar conductances and dissociation constants of perchloric, hydrochloric, picric and benzoic acids as well as their tetrabutylammonium salts in 2-PrOH / H$_2$O mixtures in the whole composition range at 298 K. The variation of Walden Product (conductance times viscosity) with solvent composition showed a maximum for all the acids studied at the mole fraction of 2-PrOH of about 0.1, whereas the Walden product of the salts showed a constant value irrespective of the solvent composition.

Izonfou et al.$^{45}$ measured the limiting ionic conductivities of lithium, sodium, potassium and cesium iodides in DMF and AN and in their mixtures at 298 K. The plots of the limiting ionic conductivities as a function of the mole
fraction of DMF in the solvent mixtures were similar for all the ions studies and showed a valley at 0.20 mol fraction of DMF. The conductance and solvent viscosity data had been utilized in the modified Stokes equation to estimate the solvation numbers of the ions in various solvent systems. For Li\(^+\), the solvation numbers ranged between 2.38 and 3.85; for Na\(^+\), K\(^+\) and Cs\(^+\), the solvation numbers ranged between 2.25-4.14; 1.97-3.10 and 1.12-2.23 respectively in the various solvent systems. The results of the study had been interpreted in terms of ion-solvent interactions and solvent properties.

Electrolyte conductance and thermal properties of LiClO\(_4\) salt in mixtures of ethylene carbonate (EC)/PC solvents, having fixed molar ratio EC 46.5/PC 19.0, had been measured by Croce et al.\(^{46}\) over salt concentrations ranging from 0.22 to 1.01, expressed as moles of salt divided by moles of solvent. The higher value represented the saturation limit for this system. Both the measurements seem to confirm the findings of the previous study in which a critical concentration value was detected near the ratio of approx. 0.5.

Conductances of diamine bis-1-amido-O-methylurea cobalt (III) monochloride had been measured by Bag and coworkers\(^{47}\) in various H\(_2\)O + AN mixtures at 283.15, 288.15, 193.15, 198.15 and 303.15 K. The conductance data in all the cases had been analyzed by Shedlovsky equation to obtain \(\lambda_0\) and \(K_A\) value for the electrolyte. The influence of the mixed solvent composition on the solvation of ions had been discussed based on the composition dependence of the Walden product. Based on the \(K_A\) values and temperature dependence of \(\lambda_0\), the thermodynamic parameters and Arrhenius activation energy (\(E_a\)) of transport processes had been determined. The results had been discussed in terms of ion – ion, ion – solvent and solvent – solvent interactions.

Rounagi and Sanavi\(^{48}\) studied the complexation reactions between Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) metal cations with 15-crown-5(15C5) in AN - MeOH binary mixtures at different temperatures using a conductometric method. 15C5 formed 1:1 complexes with Mg\(^{2+}\), Ca\(^{2+}\) and Sr\(^{2+}\) cations in solutions. The Ba\(^{2+}\) cation formed a 2:1 complex (ratio of ligand to cation) in solutions. A linear relation was observed for variation of log \(K_f\) of 15C5 - Ca\(^{2+}\) and 15C5 - Sr\(^{2+}\) complexes versus
the composition of AN - MeOH binary systems, but a non-linear behaviour was observed in the case of 15C5 - Mg$^{2+}$ complex in these binary mixtures. Selectivity of 15C5 for Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ cations is sensitive to solvent composition. In some cases and in certain compositions of the mixed solvent systems, the selectivity order was changed. The values of thermodynamic parameters ($\Delta H^0, \Delta S^0$) for formation of 15C5 - Mg$^{2+}$, 15C5 - Ca$^{2+}$ and 15C5 - Sr$^{2+}$ complexes were obtained from temperature dependence of stability constants and the results show that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents.

Singh and coworkers$^{49}$ reported the conductance measurements at temperatures between 288 to 303 K in MeOH - H$_2$O mixtures of the $\alpha$-alanine bis – biguanide cobalt (III) bromide complex. The ion association constants ($K_a$) of the complex ion with the anion and the limiting molar conductances ($\lambda_0$) were calculated using Shedlovsky technique. The Walden products ($\lambda_0 \eta_0$) were determined. The thermodynamical properties viz. change in free energy ($\Delta G_0$), enthalpy ($\Delta H_0$) and entropy ($\Delta S_0$) for the ion-pair formation had been calculated from the values of association constants at different temperatures. Sizes of the ion-pair had also been calculated from the Walden product values.

D’Aprano and coworkers$^{50}$ reported electrical conductance measurements of lithium picrate and lithium perchlorate in isodielectric solvents (i.e AN, MeOH and DMF) in the concentration range $10^{-4} \leq c/\text{mol dm}^{-3} \leq 10^{-2}$. In spite of the similarity of the macroscopic dielectric constants of the solvents, the ion pair association constants of both electrolyte strongly depended on the molecular details of ions and solvent molecules. The complexation of lithium ion by the 15-crown-5 (15C5) macrocyclic ligand in the above solvents had also been investigated. The presence of 15C5 increased the ionization of the electrolytes in relation to the solvation efficiency of the solvents.

1.3 Literature Survey on Ultrasonic Studies

Some compressibility data are available on binary solvent mixtures but compressibility data for electrolytic solutions is scanty. A brief review of the
ultrasonic velocity measurements in nonaqueous and mixed solvents is reported below.

Ai et al. \(^{51}\) measured the densities and ultrasonic speeds, \(u\), is binary mixtures of THF with n-heptane, n-octane and n-decane at 308.15 K. From these experimental data, the values of isentropic compressibility \((K_s)\), intermolecular free length \((L_f)\), relative association \((R_a)\), acoustic impedance \((Z)\), isothermal compressibility \((\beta_i)\), thermal expansion coefficient \((\alpha)\), deviations in ultrasonic speed \((\Delta u)\), excess free length \((L^E_f)\), excess volume \((V^E)\), excess acoustic impedance \((Z^E)\), apparent molar isentropic compressibility \((K^s)\), and partial molar volume \(V^0\) of n-alkane in THF at infinite dilution were calculated. The variations in these parameters with composition of the mixtures were found to be significant, dependent on the nature of interaction between the unlike molecules in these mixtures. Moreover, the effect of the size of alkyl group of alkanes on intermolecular interaction in binary had been examined.

The ultrasonic velocities \((u)\) and densities \((p)\) of pure benzene, n-BuOH, I-BuOH, sec-BuOH and tert-BuOH and their binary mixtures with benzene as a common component were also measured by Ali et al. \(^{52}\) at 303 K over the whole composition range. The dependence of ultrasonic speed on composition of the mixture was checked by using an empirical relation. From the experimental data, the values of isentropic compressibility \((K_S)\), intermolecular free length \((L_f)\), relative association \((R_a)\), acoustic impedance \((Z)\), molar sound speed \((R_m)\), deviations in isentropic compressibility \((\Delta K_s)\), excess intermolecular free length \((L^E_f)\), deviations in ultrasonic speed \((\Delta u)\), excess acoustic impedance \((Z^E)\), apparent molar compressibility \((K^c_1)\) and \((K^c_2)\), and partial molar compressibilities \((K^c_0)\) and \((K^c_0)\) of benzene, respectively, at infinite dilution decrease of weak interactions between the component molecules and this interaction decrease in the order: n-BuOH > I-BuOH > sec-BuOH > tert-BuOH. Further, the ultrasonic speeds in these mixtures were theoretically calculated with the help of several theories and empirical relations by using data on pure components. In a recent study Ali and coworkers \(^{53}\) had measured densities \((p)\), ultrasonic speeds \((u)\),
viscosities (\( \eta \)) and refractive indexes (\( n \)) of pure benzene, benzyl alcohol (BA), BN, benzoyl chloride (BC), chlorobenzene (CB) and their thirty six binary mixtures, with benzene as common component, at 303.15 K over the entire mole fraction range. From these experimental data the values of deviations in ultrasonic speed (\( \Delta u \)), isentropic compressibility (\( \Delta K_s \)), excess acoustic impedance (\( Z^E \)), deviation in viscosity (\( \Delta \eta \)), and excess Gibbs free energy of activation of viscous flow, \( G^E \), and partial molar isentropic compressibility (\( K_s^E \)) of BA, BN, BC and CB in benzene were computed. The variation of these derived functions with composition of the mixtures suggested the increased cohesion (molecular order) in the solution and that interaction (A-B) > (A-A) or (B-B). Comparison of theoretical results with the experimental values was made in order to assess the suitability of these relations in reproducing the experimental values of \( u \), \( \eta \) and \( n \). The average molecular radii of binary mixtures were found to be additive with respect to mole fraction of the pure component.

Pal and coworkers\(^5\) measured speeds of sound, \( u \), at the temperature 298.15 K and atmosphere pressure as a function of composition for the three binary liquid mixtures. EtAc + ethylene glycol di - Me ether (EGDME) + diethylene glycol di - Me ether (Di-EG-DME) and + triethylene glycol di – Me ether (Tri-EGDME) using a NUSONIC velocimeter based on the sing – around technique. Their values have been combined with those of the excess molar volumes converted to densities to give estimates of the product \( K_{s,m} \) of the molar volumes and isentropic compressibility \( K_s \) and the excess quantity \( K_{a,m}^E \). The \( K_{a,m}^E \) values were negative for all mixtures. Measurements had been carried out in order to assess the effects of inserting oxyethylene groups with a common alkyl group in polyether. The deviations \( \Delta u \) of the speeds of sound from their values in an ideal mixture were also evaluated for all measured values of \( x \). These values were compared with the mixing function \( \delta u \). The behaviour of \( \Delta u \), \( \delta u \) and \( K_{a,m}^E \) with composition and the number of \(-OC_2H_4\) units of the ether molecule was discussed. Also, the theoretical values of speeds of sound had been calculated.
using Prigogine-Flory-Patterson theory (PFP) and the results obtained from PFP theory were compared with experimental results.

In another study Pal and Bhardwaj reported the excess molar volume and ultrasonic speed in dipropylene glycol monoethyl ether + butylamine, dibutylamine, and tributylamine across the entire composition range, at the temperature 298.15 K and atmosphere pressure. The ultrasonic speed values had been combined with those of the excess molar volumes converted to densities to give estimates of the products $K_{s,m}$ of the molar volumes were negative over the entire range of composition for all mixtures with the exception of the speeds of sound $\Delta u$ from their ideal values $u_{jd}$ in an ideal mixture were also calculated for all measured mole fractions.

Nath had carried out measurements of speeds of sound ($u$), in binary mixtures of $C_6H_5OCH_3$ with $CH_2Cl_2$, $CH_2ClCH_2Cl$, $CCl_2-CCl_2$ and $C_6H_{12}$ at 303.15 K. The densities of present mixtures had been calculated at 303.15 K using available data on excess molar volumes, whereas the densities of the pure component liquids had been measured at 303.15K with a pycometer. The values of $u$ had been used to calculate the apparent excess speeds of sound $\Delta u$ and the isentropic compressibilities $K_s$ for these mixtures. The excess isentropic compressibilities $K_{sE}$ had been found to be slightly positive for $\{x \ C_6H_5OCH_3 + (1+x) \ CH_2ClCH_2Cl\}$ and $\{x \ C_6H_5OCH_3 + (1+x) \ CCl_2-CCl_2\}$. For $\{x \ C_6H_5OCH_3 + (1+x) \ CH_2Cl_2\}$, $K_{sE}$ is very slightly positive at low mole fractions of $C_6H_5OCH_3$. Values of $K_{sE}$ for the various mixtures were discussed in the light of intermolecular interactions between the components. In recent study Nath had measured speeds of sound $u$ in binary liquid mixtures of $n-C_7H_{15}OH$ and $n-C_8H_{14}$ or $n-C_6H_{14}$ or $n-C_7H_{16}$ or $n-C_8H_{18}$ at $T = 303.15$ K and in binary liquid mixtures of $n-C_7H_{12}OH$ and $2,2,4-(CH_3)3-C_5H_9$ at $T = 293.15$ and 303.15 K. The values of $u$ had been used to calculate the apparent excess speeds of sound ($\Delta u$) and the isentropic compressibilities $K_s$ for these mixtures. The excess isentropic compressibilities $K_{sE}$ had also been calculated from the values of $K_s$. The $K_{sE}$ property was negative throughout the entire composition range for $\{x \ n-C_2H_{13}OH + (1+x)n-C_3H_{12}\}$, $\{x \ n-C_7H_{15}OH + (1-x)n-C_6H_{14}\}$, $\{x \ n-C_3H_{13}OH + (1-x)n-C_5H_{16}\}$
and \{xn-C_{15}H_{15}OH + (1-x) 2,2,4-(CH_3)_3C_8H_9\}. For \{x n-C_7H_{15}OH + (1-x)n-C_9H_{18}\}, the \(K_s\) was positive at very low mole fractions of n-C_7H_{15}OH, and negative at other mole fractions.

Resa et al.\textsuperscript{58} reported ultrasonic velocities and isentropic compressibilities of mixtures enclosing BuOAc and aromatic hydrocarbons (toluene, ethylbenzene, p-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, or t-butylbenzene) that had been measured at several temperatures and atmospheric conditions. The values of these properties were calculated over the whole range of composition, different acoustic magnitudes being theoretical due to their importance in the study of specific molecular interactions and theoretical calculations. The application of different models to predict the mixing trend in terms of isentropic compressibility showed adequate agreement between experimental and computed sets of data both in magnitude or sign.

The ultrasonic velocity and density at different concentrations of N-bromosuccinimide (NBS) in H_2O and in various compositions (vol./vol.) of H_2O + p-DO and N-chlorosuccinimide (NCS) in H_2O and in various compositions (vol./vol.) of H_2O + MeOH / p-DO were studied by Bhat and Varaprasad\textsuperscript{59} at 303 K. The data obtained were used to evaluate adiabatic compressibility, apparent molar compressibility, intermolecular free length, specific acoustic impedance, and relative association. These results were used to get the limiting molar compressibility. Gucker’s relation was verified for NBS in dioxane and NCS in methanol. Formation of complex at 20% dioxane for NBS and at 20% MeOH and 40% dioxane for NCS were identified. Further, these data were utilized in the qualitative study of ion – ion and ion – solvent interactions involved in the system.

Excess molar volumes \(V^E\) and speed of sound \(u\) of the binary liquid mixtures of EtOAc and BuOAc with 2-alkoxyethanols at 308.15 K had been measured by Chandrashekhara et al.\textsuperscript{60} over the entire range of composition. The 2-alkoxyethanols are 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. The \(V^E\) values are positive in mixtures of EtOAc and BuOAc with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. The speed of sound data were used to compute isentropic compressibilities \(K_s\) and excess isentropic
compressibilities ($K_s^E$). The $K_s^E$ values were negative over the entire range of composition for all the systems at 308.15 K.

Densities and sound speeds of ten ternary mixtures of Me acrylate (1) + 1-PrOH (2) or 1-BuOH (2) + n-hexane (3), n-heptane (3), cyclohexane (3), benzene (3) and toluene (3) had been measured at 308.15 K by Bahadur and Sastry. The excess volumes ($V^E$), and excess isentropic compressibilities ($K_s^E$) had been estimated. These two experimental derived excess functions were also compared with those predicted by empirical equations of Redlich-Kister, Kohler and Tsao - Smith. A qualitative analysis of $V^E$ and $K_s^E$, data of ternary mixtures revealed that in MA (1) + 1-alcohols (2) + n-hexane (3), n-heptane (3), and cyclohexane (3), structure disruptions are more predominant, while in MA (1) + 1-alcohols (2) + benzene (3) or toluene (3) mixtures, the weak but specific structure making interactions dominated. A perusal of deviation between the experimental and calculated $V^E$ and $K_s^E$ results showed that the predictive expressions gave only a rough estimation of the functions for the ten studied mixtures.

Mehta and Chauhan have reported the ultrasonic velocities for binary mixtures of PY + n-alkanol (C_1–C_{10}) over the whole composition range at 298 K. The excess isentropic compressibilities ($K_s^E$) and apparent molar isentropic compressibilities ($K_{s,a}$) were estimated from these measurements. The $K_s^E$ values were negative for all the systems over the complete mole – fraction range except PY – decanol for which small positive values were obtained. The standard partial molar isentropic compressibilities ($K_{s,\phi}$) of the alkanols were positive and increased linearly with the chain length of the alkanol molecules. It indicates that a methylene functional group made a positive contribution to the expansion coefficient of a solute in these mixtures.

Miyanaga and coworkers had measured excess molar volumes, $V_m^E$ and excess isentropic compressibilities ($K_s^E$) of binary mixtures of DMF with AN and benzene. The excess isothermal compressibilities, $K_{\phi}^E$ and excess isochoric heat capacities ($C_{p,m}$). The $V_m^E$ of [x AN + (1-x)C_6H_6] changed sign from negative to positive with increase of $X_E$; $V_m^E$ of [x C_6H_6 + (1-x)HCON(CH_3)_2] and $V_m^E$ of [x AN + (1-x)HCON(CH_3)_2] are negative over the whole composition range, $K_s^E$.
and $K_T^E$ of the mixture were in similar trend to the corresponding $V_m^E$. The $C_{v,m}^E$ of \( \{x \text{ An} + (1-x)\text{C}_6\text{H}_6\} \) changes sign from positive to negative with increase of $x$, and $C_{v,m}^E$ of \( \{x \text{ C}_6\text{H}_6 + (1-x)\text{HCON(CH}_3\text{)}_2\} \) was negative with a small positive region at $x > 0.95$.

Palaniappan\textsuperscript{64} reported the ultrasonic velocity, density and viscosity at 303, 308 and 313 K in the ternary system of 2-BuOH in cyclohexane with toluene. The acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure at the said temperatures were calculated. The results were interpreted in terms of molecular interaction between the component of the mixtures. The existence of weak interactions were confirmed by the observed excess values.

Soto et al.\textsuperscript{65} performed experiments at 298.15 K to measure the density, sound velocity and refractive index of glycine in aqueous solutions of NaCl over a wide range of both glycine and NaCl concentrations. The values of apparent molar volume and isentropic compressibility of glycine were calculated from the measured data. The results show a positive transfer volume of glycine from an NaCl solutions to a more concentrated NaCl solution. This indicates that the size of a glycine molecule was larger in a solution with higher NaCl concentration. The negative values of apparent molecules were less compressible than the water molecules in the bulk solution. These effects were attributed to the doubly charged behaviour of glycine and to the formation of physically bonded ion – pair between the charged groups of glycine, sodium and chloride ions.

Hazra and coworkers\textsuperscript{66,67} measured the ultrasonic velocities of Pr$_4$NBr, Bu$_4$NBr, Pen$_4$NBr, Hex$_4$NBr, Hep$_4$NBr, and Oct$_4$NBr in DMA 298.15 K. They had also reported the ultrasonic velocities of LiBF$_4$, NaBF$_4$, Ph$_4$PCl, Ph$_4$PBr, and Ph$_4$AsCl in ME at 288, 298 and 308 K. Apparent molar isentropic compressibilities ($K_\phi^0$) of these electrolytes were derived from these data supplemented with their densities. The limiting apparent molar isentropic compressibilities ($K_\phi^0$) were obtained by extrapolation from the plot of $K_\phi$ versus the square root of the molarity. The ($K_\phi^0$) values of the electrolytes were split into
approximate limiting ionic compressibilities ($K^0$) on the basis of the assumption 
that $K^0$ (Br') = 0. In case of tetrafluoroborate salts the $K^0$ values of the 
electrolytes were split into approximate limiting ionic compressibilities ($K^0$) on 
the basis of the assumption that $K^0$ (BF$_4^-$) = 0.

Gill et al. measured the ultrasonic velocities (u) and densities ($\rho$) of 
copper (I) salts, sodium and tetraalkylammonium salts in BN, PY and AN at 298, 
308 and 318 K. The isentropic compressibilities ($K_s$) and apparent molar 
compressibilities ($K_4$) of various electrolytes had been evaluated. The limiting 
apparent molar isentropic compressibilities ($K^0$) for all electrolytes had been 
obtained by extrapolation of the plots of $K_s$ versus square root of molarity ($m^{1/2}$) 
and split into ionic compressibilities ($K^\pm$). Cu$^+$ was highly solvated in all three 
solvents with solvation decreasing in the order PY > AN > BN. Na$^+$ in all solvents 
was relatively less solvated and the solvation decreases in the order AN > BN > 
PY. ($K^0$) was positive in BN except for Et$_4$N$^+$ and was negative in An except for 
BuN$^+$, Ph$_4$B$^-$ and Pr$_4$N$^+$. The results indicated stronger solvation of ions in An than 
in BN. In another study Gill and coworkers had reported the ultrasonic 
velocities (u) and densities ($\rho$) of CuClO$_4$·4BN, Bu$_4$NBPh$_4$, Bu$_4$NClO$_4$ at different 
salt concentrations in the concentration range 0.002-0.28 mol kg$^{-1}$ in binary 
mixtures of TEP with AN, BN and PY containing 0, 20, 40, 60 and 80 mol % 
TEP. They had also measured ultrasonic velocity and densities of Bu$_4$NBP$^-$, 
Bu$_4$NC$lO_4$. CuClO$_4$·4AN, NaClO$_4$ and NaBPh$_4$ in binary mixtures of AN with 
DMF containing 0, 10, 20, 40, 60, 75, 80, 90 and 100 mol % DMF. The isentropic 
compressibilities ($K_s$) and apparent molar compressibilities ($K_4$) of various 
electrolytes had been evaluated. The limiting apparent molar compressibilities 
($K^0$) for all electrolytes had been obtained by extrapolation of the plots of $K_s$ 
versus square root of molarity ($m^{1/2}$) and split into ionic compressibilities ($K^\pm$) 
values with solvent composition showed that Cu$^+$ indicated strong solvation in AN + TEP, BN + TEP and PY + TEP mixtures over the entire solvent composition 
range and the solvation with TEP was relatively stronger than that with AN, BN 
and PY. ClO$_4^-$ was better solvated in AN + TEP mixture by having some

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interaction with AN but was poorly solvated in BN + TEP and PY + TEP mixtures. Both Bu$_4$N$^+$ and Ph$_4$B$^+$ showed some interaction with TEP in the TEP–rich region of all the solvent systems. Na$^+$ had very large negative stronger than that with AN. Cu$^+$ also showed strong but relatively less solvation as compared to Na$^+$ in AN + DMF mixtures over the entire solvent composition range. ClO$_4^-$ showed much weaker solvation in AN + DMF mixtures by having some interaction with AN in the AN rich region of the mixtures.

Ultrasonic velocities and densities of some electrolytes namely Bu$_4$NI, Pr$_4$NI, Et$_4$NI, KI, NaI and LiNO$_3$ had been measured in CB + MeOH mixtures at 2 MHz at 298 K by Syal and coworkers. Various derived parameters such as acoustical impedance ($Z$), adiabatic compressibility ($\beta$), apparent molar compressibilities ($K_\lambda$), relative association ($R_\lambda$), intermolecular free length ($L_\lambda$) and solvation number ($S_\lambda$) had been calculated. The results had been discussed in terms of nature of electrolyte and solvent mixtures.

Murthy and coworkers calculated compressibilities from ultrasonic velocity and density measurements in solutions of DMF. Apparent molar compressibilities were calculated and $K_\lambda^0$ values were obtained by fitting $K_\lambda$ against the electrolyte concentration $C_A$ by the method of least squares. Acoustic impedance, molar sound velocity, molar adiabatic compressibility and solvation numbers were calculated. The results were discussed in terms of ion–solvent interactions.

Babu and coworkers measured the ultrasonic velocities and densities for H$_2$O + i-PrOH at 303.15 K. From these data, experimental compressibilities had been calculated. Ideal compressibilities and excess compressibilities had been estimated by three recently developed expressions. The results had been analyzed on the basis of the variations of ultrasonic velocities, compressibilities and excess compressibilities. H$_2$O – i-PrOH clathrate like structures were observed at lower concentrations of alcohol in water. Water pyridine complexes had been observed at lower concentrations of pyridine in water. The presence of weakly bonded alcohol-pyridine structures were noticed in the binary mixture PY + i-PrOH.
Ramana and coworkers\textsuperscript{75} investigated ion - solvent interactions in aqueous solutions of mixed electrolytes, namely (NaCl + NaBr), (NaCl + NaI) and (NaBr + NaI), by studying their effect on the temperature of the sound velocity maxima (TSVM) of water (T\textsubscript{w}). The ultrasonic velocity as a function of temperature over a range of 278 K either side of the TSVM was determined using a single-crystal variable-path interferometer working at 3 MHz with an accuracy $\pm 0.003 \%$. The structural contribution to the shift in T\textsubscript{w} of pure water due to the addition of mixed electrolytes, $\Delta T_{\text{str}}$, had been found to be negative and increasing with concentration of the mixed electrolytes. At any given concentration, the $\Delta T_{\text{str}}$ of (NaCl + NaBr) > (NaCl + NaI) > (NaBr + NaI). This indicated that the structure promoting nature of Na\textsuperscript{+} was balanced and subdued by the presence of halide ions in disrupting the hydrogen bonded structure of water, which is in the order I\textsuperscript{-} > Br\textsuperscript{-} > Cl\textsuperscript{-}. The results were also explained as due to the reduction in the structure breaking efficiency of Cl\textsuperscript{-}, Br\textsuperscript{-} and I\textsuperscript{-} in the presence of Na\textsuperscript{+} in aqueous mixed electrolyte solutions.

Singh and coworkers\textsuperscript{76} measured partial molar volumes $V_\phi$ of NaCl, CH\textsubscript{3}COONa (NaAc), HCOONa, HCl, CH\textsubscript{3}COOH (AcH) and HCOOH, dilatometrically in some quasi-isodielectric [H\textsubscript{2}O + cosolvent (aprotic (p-DO), dipolar aprotic (DMF) and protic (formamide, FD))] media at 308.15 K and the same had been analyzed to evaluate their limiting $V_\phi^0$ values. These values had been coupled with the corresponding limiting values in W to compute $\Delta V_\phi^0$ data which suggested that for a particular HA or NaA, the $\Delta V_\phi^0$ values generally varies as FD < DMF < p-DO as required by the Gutmann’s donor and the electron pair acceptance indexes of FD, DMF and p-DO cosolvents in the present mixed solvent media. The variation of $\Delta V_\phi^0$ (AcH or NaA) within the same mixed solvent media suggested that while the chemical effects of protons of acids on the cosolvent have a dominant influence (based on Ben-Naïms approach) on their $\Delta V_\phi^0$ data, the electrostriction effects of CH\textsubscript{3}COO\textsuperscript{-}, HCOO\textsuperscript{-} and Cl\textsuperscript{-} on H\textsubscript{2}O played an important role in determining the values of $\Delta V_\phi^0$ of their sodium salts.
Marcus\textsuperscript{77} reported standard partial molar volumes of 1 : 1 salts in aqueous mixtures of EtOH, DMSO and AN at 298.15 K. In such mixtures there was evidence that preferential solvation occurred in the solvent shell around the ion where electrostriction takes place. Specifically, the anions are better solvated by water whereas the cations were generally solvated by both the water and the non aqueous component of the mixtures of the salts by calculation of the electrostriction around the ions. Only taking into the account of the solvation shell yielded calculated results of the standard partial molar volumes of the salts in agreement with the experimental data.

Blanco and Vargas\textsuperscript{78} reported the apparent molar volumes, \( V_0 \), of Me\textsubscript{4}NBr, Et\textsubscript{4}NBr, Bu\textsubscript{4}NBr, BuEt\textsubscript{3}NBr, Bu\textsubscript{2}Et\textsubscript{2}NBr and Bu\textsubscript{3}EtNBr at 298.15 K in the concentration range from 0.01 to 0.04 mol kg\(^{-1}\). The concentration dependence of \( V_0 \) was given using the Redlich and Meyer constant (\( B_v \)), had been calculated. The CH\textsubscript{2} group contribution had been obtained by the additivity rule. The results were interpreted in terms of solute – solvent interactions.

Arce et al.\textsuperscript{79} have measured densities, refractive indices, speeds of sound and dynamic viscosities of [Omim][BF\textsubscript{4}], the room temperature ionic liquid (IL) in binary mixtures with methanol, ethanol, 1-propanol and 2-propanol were measured at 298.15 K and atmospheric pressure. The excess molar volumes and molar refraction, isentropic compressibilities and dynamic viscosity changes of mixing had been calculated and were satisfactorily correlated by the Redlich – Kister polynomial.

1.4 Literature Survey on Viscosity Studies

Viscosity of electrolytic solutions is another variable parameter which is helpful in providing information about the nature of electrolytes in solution. The concentration dependence of viscosity of electrolyte solutions provides a viscosity B-coefficient of Jones Dole equation which is of immense value in qualitative explication of the effects of ions on solvent structure. The solvation behaviour obtained from these studies is co-related with the results obtained from the
conductance data. Owing to the importance of viscosity in solution chemistry extensive survey of literature was carried out and is reported below.

Roy and coworkers\textsuperscript{80} reported the apparent molar volumes and viscosities of three alkali metal chlorides, namely LiCl, NaCl and KCl in a 40 mass % THF + H\textsubscript{2}O mixtures at 303, 308, 313 and 318 K. The limiting molar volumes (V\textsubscript{\phi}^0) and slopes (S\textsubscript{\phi}^v) had been interpreted in terms of ion – solvent and ion – ion interactions, respectively. Structure making / structure breaking capacities of various electrolytes had been inferred from the sign of (d\textsuperscript{2}V\textsubscript{\phi}^0 /dT\textsuperscript{2}), dB/dT and the B-coefficient for all electrolytes studied. The viscosity data had been analyzed using the Jones – Dole equation. The results showed that the three electrolytes act as structure promoters in this solvent mixture.

Parmar and Chauhan\textsuperscript{81} measured the partial molar volumes and viscosities of some common tetraalkyl and multivalent electrolytes viz., ammonium sulfate, Bu\textsubscript{4}NBr, aluminium ammonium sulfate and aluminium potassium sulfate in PG + H\textsubscript{2}O (4, 8, 12 and 16 wt %) mixtures. The density data had been analyzed by means of Masson’s equation. The particular molar volumes (V\textsubscript{\phi}^\text{p}) and slopes (S\textsubscript{\phi}^v) had been interpreted in terms of ion – solvent and ion – ion interactions, respective structure making /breaking capacities of the various electrolytes had been inferred from the sign of (\delta\textsuperscript{2}V\textsubscript{\phi}^0 /\delta T\textsuperscript{2}). Both the multivalent electrolytes behaved like the symmetrical tetrabutylammonium salt but not like common electrolyte in PG + H\textsubscript{2}O mixtures. The multivalent electrolytes and tetraalkyl salt acts as structure makers/promoters while the common electrolyte acts as structure breaker. The experimental results of velocity had been analyzed using the Jones – Dole equation. The activation parameters of viscous flow had also been obtained to throw light on the mechanism of viscous flow.

Queimada et al.\textsuperscript{82} had made viscosity and density measurements at atmosphere pressure, in pure and mixed n-decane, n-eicosane, n-docosane and n-tetracosane from 293.15 K (or above the melting point) upto 343.15 K. The viscosity was determined with a rolling ball viscometer and liquid densities with a vibrating U-tube densimeter. Pure component results agreed, on average, with

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literature values within 0.2% for liquid density and 3% for viscosity. The measured data were used to evaluate the performance of two models for their predictions: the friction theory coupled with the Peng-Robinson equation of state and a corresponding states model recently proposed for surface tension, viscosity, vapor pressure, and liquid densities of the series of n-alkanes.

Jouyban et al. investigated the applicability of the Jouyban-Acree model for calculating absolute viscosity of binary liquid mixtures with respect to temperature and mixture composition. The correlation ability of the model was evaluated by employing viscosity data of 143 various aqueous and non-aqueous liquid mixtures at various temperatures collected from the literature. The results show that the model was able to correlate the data with an overall percentage deviation (PD) of 1.9 ± 2.5%.

Ultrasound speed (u), density (ρ) and viscosity (η) had been measured by Rita Mehra for pure liquids and their binary mixtures formed from hexadecane with 1-pentanol, 1-hexanol, and 1-heptanol at 298, 398, and 318 K covering the entire mole fraction range of hexadecane. From the experimental data, adiabatic compressibility (Kₐ), intermolecular free length (Lᵢ), molar sound speed (Rₘ), acoustic impedance (Z), excess adiabatic compressibility (Kₑₑ), excess free volume (Vₑₑ), excess viscosity (ηₑₑ), Gibbs energy of activation of viscous flow (Gₑₑ) and interaction parameter (α) had been computed. These parameters were used to discuss the nature and extent of intermolecular interactions between the component molecules. All the excess functions studied were lifted to Redlich-Kister relation to estimate the adjustable parameters along with their standard deviations.

The alkyl chain length of ([Rmim][CF₃SO₂]N), (R = methyl (m), ethyl (e), butyl (b), hexyl (C₆), and octyl (C₈)) was varied by Tokuda and coworkers to prepare a series of room temperature ionic liquids (RTILs) and the thermal behavior, density, viscosity, self-diffusion coefficients of the cation and anion, and ionic conductivity were measured over a wide temperature range. The self-diffusion coefficient, viscosity, ionic conductivity, and molar conductivity...
changed with temperature following the Vogel-Fulcher-Tamman equation and the
density shows a linear decrease. The pulsed-field-gradient spin-echo NMR
method revealed a higher self diffusion coefficient for the cation compared to that
for the anion over a wide temperature range, even if the cationic radius was
larger than that of the anion. The summation of the cationic and anionic diffusion
coefficients for the RTILs followed the order [emim][CF_{3}SO_{2}N] >
[mmim][CF_{3}SO_{2}N] > [C_{6}mim][CF_{3}SO_{2}N] > [C_{8}mim][CF_{3}SO_{2}N], which
greatly contrasted to the viscosity data. The ratio of molar conductivity obtained
from impedance measurements to that calculated by the ionic diffusivity using the
Nernst-Einstein equation quantified the active ions contributing to ionic
conduction in the diffusion components, in other words, ionicity of the ionic
liquids. The ratio decreased with increasing number of carbon atoms in the alkyl
chain. Finally, a balance between the electrostatic and induction forces had been
discussed in terms of the main contribution factor in determining the
physiochemical properties.

Artigas et al.\textsuperscript{86} reported the densities and viscosities for the binary
mixtures of CB, chlorocyclohexane, bromobenzene and bromocyclohexane with
2-methyl-1-propanol over the entire concentration range at the temperatures
298.15 K and 313.15 K. These values had been used in the determination of the
excess volumes, (V\textsuperscript{E}) and the viscosity deviations (\Delta\eta). All mixtures presented
negative values of V\textsuperscript{E} in a wide region corresponding to the high concentration in
alkanol, although this zone became smaller at 313.15 K. For \Delta\eta, the mixtures
showed negative values over the whole composition range at both temperatures.

Sulzner and Luft\textsuperscript{87} reported the viscosities and densities of several alcohol-
ethene and vinyl acetate – ethane mixtures with a rolling ball viscometer. The
viscosity measurements were performed at temperatures from 298 K to 413 K and
pressures upto 195 Mpa with an estimated uncertainty of ± 2 %. The appearance
of hydrogen bonds forming alcohols association had a notable effect on the
viscosity of alcohol-ethane mixtures above an alcohol mole fraction from the
Arrhenius law which occurred when alcohol associations were formed. An effect
of pressure on the association of alcohol molecules through hydrogen bonding was not observable from the viscosity data.

Ratkovics and coworkers\textsuperscript{88} measured the density, viscosity, relative permittivity, conductance and refractive index values at 293.15 K – 313.15 K. The results indicated the formation of association complexes of Bu\textsubscript{3}N and the enol form of the MeCOEt. The electrolytic dissociation of the Bu\textsubscript{3}N – enol association complexes also contributed to the conductance of the mixture. In addition to the concentration the relative permittivity exerted a considerable influence on the conductance, as a considerable number of ion pairs were formed according to the Bjerrum theory.

Wankhede and coworkers\textsuperscript{89} measured densities and viscosities of the binary mixtures of PC with MeOH, EtOH, PrOH, BuOH and HexOH, along with those of the pure liquids over the entire mole fraction range at 298 K. Using the experimental values of densities (\( \rho \)) and viscosities (\( \eta \)), the excess molar volumes (\( V^E \)), viscosity deviation (\( \Delta \eta \)), excess Gibbs energies of activation of viscous flow (\( \Delta G^E \)), and Grunberg-Nissan interaction parameter \( d_{12} \) were calculated from the linear dependence of these parameters on the composition of the mixtures.

Jyotsana and Satyanarayana\textsuperscript{90} measured the densities and viscosities for the binary mixtures of An + aromatic ketones (Aph, PPh, Me-Aph and Cl-Aph) at 308.15 K over the entire range of composition. The densities and viscosities were used to calculate the excess molar volumes and deviations in viscosity. The excess molar volumes and deviations in viscosity were fitted to a Redlich-Kister type of equation. The negative \( \Delta \eta \) values at equimolar concentrations of AN and ketone followed the order Cl-Aph > PPh > Me-Aph > Aph. The trend was same in overall order, p-chloroacetophenone being the highest and acetophenone lowest, when \( V^E \) and \( \Delta \eta \) values were compared.

The excess molar volume \( V^E \), shear viscosity deviation \( \Delta \eta \) and excess Gibbd energy of activation \( \Delta G^E \) of viscous flow had been investigated by Querfelli and Bouanz\textsuperscript{91} using density (\( \rho \)) and shear viscosity (\( \eta \)) measurements for isobutyric acid (IBA) + H\textsubscript{2}O (IBA + H\textsubscript{2}O) mixtures over the entire range of mole
fractions at five different temperatures, both near and close to the critical
temperature (2.055 K ≤ (T - T_c) ≤ 13.055 K). The results were also fitted with the
Redlich-Kister equation. This system exhibited very large negative values of V^E
and very large positive values of Δη due to increased hydrogen bonding
interactions and correlation length between unlike molecules in the critical region
and to very large differences between parameters Δη_0 and ΔS_0 were also
calculated which showed that the critical region had an important effect on the
volumetric properties.

Liau et al. measured densities and viscosities of binary liquid mixtures of
Bu acrylate + 1-butanol and Et Laurate +1-BuOH mixtures over the concentration
range. The densities were measured using a vibrating tube digital densitimeter and
the viscosities were measured by a capillary viscometer. Excess molar volumes
and viscosity deviations were then calculated at various temperatures. All excess
molar volumes are positive indicating the effect of disruption of the hydrogen
bonding between 1-butanol molecules. Excess molar volumes and viscosity
deviations were correlated by the Redlich-Kister type equation.

Burghate and coworkers measured the viscosities and densities of 2-
hydroxyl-5-methyl-4-dimethylaminochalcone, 2'-hydroxyl-5'-methyl-4-methoxy-
chalcone and 2'-hydroxyl-5'-chloro-4-methoxychalcone in 70 % p-DO – H_2O
mixture at different concentrations at 299 K. The value of B-coefficients, relative
viscosity (η_r) had been deduced from viscosity and density data. At different
temperatures, thermodynamic parameter enthalpy change (ΔH), entropy change
(ΔS) and free energy change (ΔG) had been evaluated. The structure making and
structure breaking properties of systems were considered as a measure of solute –
solvent interaction.

Chauhan and coworkers measured the viscosity of Ph_4PBPPh_4, Bu_4NBPh_4,
Bu_4NNO_3, LiNO_3, NaNO_3, KNO_3 and AgNO_3 in DMSO, DMF, MeOH, DMSO –
DMF and DMSO – MeOH solvent systems at 298 K and the data were analyzed
to arrive at Jones-Dole A and B-coefficients. The B-coefficients had been
separated to ionic contributions using the data of symmetrical reference electrolyte

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Das et al.\textsuperscript{95} reported the relative viscosities of solutions of tetraalkylammonium bromides and iodides in DMSO at 298, 308 and 318 K. The experimental results were analyzed by using the Jones-Dole equation. The ionic viscosity B-coefficients for the tetraalkylammonium salts were analyzed on the basis of the Einstein equation and structural contributions. Comparison of the ionic B-coefficients based on the Krumgalz method was also made and transition state parameters for viscous flow were also determined. In a subsequent study Hazra and coworkers\textsuperscript{96} reported the relative viscosities of solutions of R\textsubscript{4}NBr (R = C\textsubscript{2}H\textsubscript{5} to C\textsubscript{7}H\textsubscript{15}) in ME at 298 K. The data were analyzed in the form of associated electrolytes and the B-coefficients were evaluated. The ionic B-values were determined using reference electrolyte viz. Bu\textsubscript{4}NBPh\textsubscript{4}. The results were discussed on the basis of the Einstein equation and in terms of a transition state treatment.

Nandi and Hazra\textsuperscript{97} reported viscosity coefficients of alkali metal bromides (MBr) [where M = Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+} and cs\textsuperscript{+}], Bu\textsubscript{4}NBr and NaBPht in aqueous mixtures of ME. The analysis of the data were carried out in terms of extended form of Jones-Dole equation for associated electrolytes. The ionic B\textsubscript{t} values and other single ion parameters were determined using Bu\textsubscript{4}NBPh\textsubscript{4} reference electrolyte assumption. These results indicated structural consequences of intermolecular interactions.

Das et al.\textsuperscript{98} also reported the viscosities of solutions of Et\textsubscript{4}NClO\textsubscript{4}, Pr\textsubscript{4}NClO\textsubscript{4} and Bu\textsubscript{4}NClO\textsubscript{4} in ME (1) + H\textsubscript{2}O (2) mixtures at 298.15, 308.15 and 318.15 K. The data had been analyzed by the Jones-Dole equation for the associated as well as unassociated electrolytes to evaluate viscosity B-coefficients of the electrolytes. The resulting viscosity B-coefficient and its dependence on temperature provided useful information with regard to changes in the solvent structure.

Yang and coworkers\textsuperscript{99} determined viscosity B-coefficients for the Et\textsubscript{4}NBr, Pr\textsubscript{4}NBr, Bu\textsubscript{4}NBr and Hex\textsubscript{4}NBr at 298.15 K in solvent mixtures of PC with DMF.
Ionic B-coefficients and corresponding activation free energies for Et₄N⁺, Pr₄N⁺, Bu₄N⁺, Hex₄N⁺ and associated anions were derived from an extrapolating method. It was shown that B-coefficients for all ions were quite independent of the nature of the solvent and the composition of the solvent mixtures. The constancy in B-coefficients for tetraalkylammonium cations in the organic solvents. Solvation numbers for the ions had also been derived for discussing the interaction of ions with solvents.

Gill and Sharma¹⁰⁰ measured the viscosities of Bu₄NBPh₄, Bu₄NNO₃, Bu₄NI, NaBPh₄, KI and AgNO₃ in AC + DMF mixtures over the whole composition range of the solvent mixtures at 298.15 K. They calculated A and B-coefficients were split into ionic B+ and B- coefficients using a new model they proposed. The results indicated that Na⁺ and Ag⁺ were preferentially solvated in these solvent mixtures. In subsequent studies Gill and Cheema¹⁰¹ and Gill and Chauhan¹⁰² reported viscosities of a large number of 1 : 1 electrolytes including copper (I) and silver (I) salts in DMF + AN and MeOH + AN mixtures. The variation of ionic B+ and B- and B-coefficients with the solvent composition showed a strong preferential solvation of ions by a specific solvent in these mixtures.

Gill et al.¹⁰³ measured the viscosities and the molar conductances of Bu₄NBPh₄, Bu₄NCIO₄, CuClO₄, AgClO₄ and TIClO₄ in the concentration ranges (30 – 425) x 10⁻⁴ and (1 – 35) x 10⁻⁴ mol dm⁻³ in AN + PY mixtures containing 0 – 100 mol % AN at 288 – 308 K. The viscosity data were analyzed by using the Jones-Dole equation. The A-coefficients of the Jones-Dole equation were positive and in reasonably good agreement with the limiting theoretical values (A∞) calculated at all the 3 temperatures using Falkenhausen-Vernon equation. The B-coefficients of the electrolytes were also positive and large in all cases and they showed a significant decrease with increase in temperature. The ionic B+ and B- and B-coefficients were evaluated from the B-coefficients of the electrolytes using method reported by Gill and Sharma.¹⁰⁰ The derived viscosity results showed preferential solvation of Cu⁺, Ag⁺ and Tl⁺ by PY in AN – PY mixtures at all the temperatures studied.
In another study Gill and coworkers measured the viscosities of copper (I) perchloride tetraacetonitrile and bis(2,9-dimethyl-1,10-phenanthroline) copper (I) perchlorate in AN + H$_2$O, AN + AC, AN + DMF and AN + MeOH mixtures over the whole composition range of the solvent mixtures at 298.15 K. The results have been interpreted to explain the solvation behaviour of Cu$^+$ and [Cu(NEC)$_2$]$^+$ cations in these solvent mixtures.

Madhurambal reported the relative viscosities of the uni-univalent, uni-bivalent, bi-univalent and bi-bivalent electrolytes KCl, Na$_2$SO$_4$, MgCl$_2$, ZnSO$_4$ in different solvent mixtures (20, 40 and 60 % benzene – water) with varying concentrations of the salts at temperatures 303 and 308 K. The data were analyzed using Jones-Dole equation and Bresler Miler equation. The B-coefficient values were found to be positive and so the salts could be considered as structure makers in the solvent mixture. Solvation and effective flow volume for all the electrolyte were analyzed by the application of Bresler Miller equation.

Jauha et al. measured the relative viscosities of some alkali metal acetates and tetraalkylammonium salts in the concentrations range 5 – 700 x $10^{-4}$ mol dm$^{-3}$ in acetic acid + H$_2$O mixtures containing 20, 40, 60, 80, 90, 95 and 100 wt % acetic acid at 298 K. The viscosity data were analyzed using Jones-Dole equation. The viscosity B-coefficient, an ion – solventinteraction parameter were found to be positive for the electrolytes in all systems. The ionic viscosity B$_i$ coefficients were calculated by taking Bu$_4$NBPh$_4$ as reference electrolyte. The viscosity B-coefficient for all the alkali metal ions and tetraalkylammonium ions were found to increase upto 90 wt % acetic acid and 80 wt % acetic acid respectively indicating increase in extent of solvation and enhancement in structure. Li$^+$ ion showed anomalous behaviour while Br$^-$ ion showed structure breaking effect in the water rich region of the solvent mixture.

Rohman and coworkers reported viscosities, electrical conductances, the shear relaxation times and Raman spectra of aqueous and methanolic sodium thiocyanate solutions as functions of concentration (0.0237 ≤ m (mol kg$^{-1}$) ≤ 19.685) and temperature (273.15 ≤ T(K) 323.15). The non-Arrhenius temperature dependence of viscosity, electrical conductance and shear relaxation time was
analyzed by using the Vogel-Tammam-Fulcher (VTF) equation. Variation of the B parameter of the VTF equation with concentration evoked some kind of structural transition over a narrow concentration range. The concentration dependence of the viscosity and conductance data were analyzed by using the reported equations. In an aqueous sodium thiocyanate solutions, the existence of the hydrated ions due to the ion – solvent interactions in the concentration range from dilute to 3.0 mol kg\(^{-1}\), the solvent – separated and / or the solvent shared ion pairs due to the competition between the ion – solvent and the ion – ion interactions beyond 6.2 mol kg\(^{-1}\) governed the transport processes. In methanolic sodium thiocyanate solution from dilute to ~ 3.9 mol kg\(^{-1}\), free and H-bonded SCN\(^{-}\) and beyond ~3.9 mol kg\(^{-1}\), solvent – shared ion – pairs dominated in the solutions and governed the transport processes. The Raman spectra recorded for the v\(_{\text{C-N}}\) and v\(_{\text{C-S}}\) stretching frequencies shifted to higher frequency regions and revealed the existence of the complex adduct of SCN\(^{-}\) with the solvent molecules.

Sacco and coworkers\(^{108,109}\) determined the B-coefficients of NaCl, NaBr, NaI and NaClO\(_4\) at different temperatures in aqueous rich regions of HMPTA and tetramethylene sulphone (TMS). Existence of strong structural consequences of intermolecular interactions on viscous flow pattern of the electrolyte was reported. A similar conclusion was drawn from viscosity studies of NaCl, NaBr, NaI and KI in H\(_2\)O – rich regions of DMSO at 298 and 308 K.

Viscosity data for chlorides and bromides of calcium, strontium and barium in aqueous mixtures of DMF was reported by Sinha and coworkers\(^{110}\) to study ion – solvent interactions. In order to explain the structure making and breaking abilities of electrolytes, NaCl and KCl in hydrazine (N\(_2\)H\(_4\)), Huque and Akhter\(^{111}\) determined the viscosity B-coefficients, intrinsic viscosity (\(\eta\)) and changes in thermodynamic quantities, such as \(\Delta G\), \(\Delta H\) and difference in chemical potential (\(\Delta \mu_2 – \Delta \mu_1\)). The results indicated that at low percentage of N\(_2\)H\(_4\), NaCl acted as structure maker, while KCl behaved as solvent structure breaker. At high percentage of N\(_2\)H\(_4\), on the other hand, KCl behaved as structure maker.
1.5 Literature Survey on Spectroscopic Studies

The field of ion–solvent interactions has observed a great advancement with the introduction of various spectroscopic techniques. The link between spectroscopic and thermodynamic and transport properties on the other side, is not yet completely established. Nuclear magnetic resonance (NMR) spectroscopy has rapidly become a major physical technique of chemistry because of the wealth of information obtainable using it. Besides yielding information of purely spectroscopic and theoretical interest, the technique is applied to a wide range of kinetic problems, solution equilibria, solvation phenomenon and intermolecular and interionic interactions, and in certain cases, the electron distribution in molecules. The actual recording of NMR spectra is not significantly different from one solvent to another except in the case of liquid crystal solvents, and in fact the bulk of NMR studies to date have been in organic solvents.

Chemical shifts are the principle source of experimental information obtainable in an NMR experiment, and to date they have been the most used. In addition to this line width and relaxation times which are obtained from NMR measurements are used to obtain quantitative information about the solvation behaviour of electrolytes in solution.

Apperley and coworkers\textsuperscript{112} reported mononuclear cryptates of Pb$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ with the small host 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacos-4,6,13,15,21,23-hexane showed satellite peaks in $^1$H NMR solution spectra throughout the accessible (233 to +343 K) fluid range of solvents used, indicating kinetic inertness towards decomplexation. They also studied solid-state MAS NMR of these cryptates and of dinuclear Ag (I) and Cu (I) analogs, in the latter case establishing coupling of $^{63}$Cu, $^{65}$Cu, to $^{15}$N. The X-ray crystal structure of the Hg$^{2+}$ cryptate showed a symmetrical 6-coordinate site for Hg$^{2+}$ with all imino N atoms coordinated, consistent with the observation, for the isomorphous Cd (II) complex, of a 13 – line\textsuperscript{113}Cd resonance in the CP MAS NMR spectrum.

Shamsipur and coworkers\textsuperscript{113} used proton NMR to study the complexation between silver ion and hexathia-18-crown-6-in a number of binary mixed solvents of DMSO with AN and MeOH. Formation constants for the resulting 1 : 1
complexes in different solvent mixtures were determined by computer fitting of the chemical shift-mole ratio data. The influence of solvent composition on the stability of the resulting complex was discussed. The exchange kinetics of Ag⁺-hexathia-18-crown-6 in 70 – 30 wt % SMDO – AN and 75 – 25 wt % DMSO – MeOH were studied by proton NMR line-shape analysis. In both solvent mixtures the exchange of thiacrown ether between the free and complexed sites was found to proceed via a dissociative pathway.

Hasan and Shamispur used Li NMR spectrometry to study the complexation reaction between lithium ions and several 12, 15 and 18 membered crown ethers in a number of binary AN – NB mixtures. Formation constants of the resulting 1 : 1 complexes in different solvent mixtures were determined by computer fitting of the chemical shift-mole ratio data. There was an inverse relationship between the complex stability and the amount of AN in the mixed solvent. Among different sized crown ethers used, 15-crowns were found to form the most stable Li⁺ complexes in the series. The influence of substitution on the macrocyclic rings on the stability of the resulting complexes is discussed.

Bich et al. measured H NMR chemical shifts δOH of the proton in the hydroxyl group of n-BuOH and tert-BuOH as a function of mixture composition in the binary mixtures n-BuOH + CH, tert-BuOH + CH, and n-BuOH + PY at 303, 313 and 323 K. In addition the molar excess enthalpy H of n-BuOH + PY had been determined as a function of the mixture composition at 298 K using a flow calorimeter. The ERAS (extended real associated solution) model has been applied for describing simultaneously the data of δOH and H for n-BuOH + CH accounting for self association of n-BuOH via hydrogen bonding. The mixtue of n-BuOH + PY was treated similarly using the ERAS model considering self association of n-BuOH as well as cross association of n-butanol with pyridine. The results obtained indicated that self association in n-BuOH and tert-BuOH as well as cross association between n-BuOH and pyridine played an important role in these mixtures. The ERAS model is able to describe the dependence of δOH and H on mixture composition and temperature for all mixtures with a minimum...
of adjustable parameters providing a realistic insight into the liquid structure of these systems.

Gill and coworkers\textsuperscript{116} studies copper (I) solvation in mixed solvent systems containing AN and cosolvents H\textsubscript{2}O, MeOH, DMF, TMPA, TMP and PY by using \textsuperscript{63}C, \textsuperscript{65}C and \textsuperscript{31}P NMR. Evidence for the preferential solvation by AN was given for the first four systems whereas the latter two were characterized by strong preferential solvation of the Cu\textsuperscript{+} ion by the co-solvent. From the line widths of the \textsuperscript{63}Cu and \textsuperscript{65}Cu signals the rotational correlation times $\tau_R$ of the solvates Cu(AN)$_4$\textsuperscript{+} and Cu(PY)$_4$\textsuperscript{+} had been determined.

Gill et al.\textsuperscript{117} made the \textsuperscript{63}Cu and \textsuperscript{109}Ag studies of copper (I) and silver salts in mixed solvent systems containing AN or BN and the co-solvents PN, VN and TEP. They studied the variation of the chemical shift with solvents composition. In another study Gill and coworkers\textsuperscript{118} carried out the \textsuperscript{63}Cu NMR and viscosity studies of 0.064 M CuClO\textsubscript{4} solutions at 298 K in binary mixtures of AN with DMSO, HMPA, DMA, NM, PC and 3-HPN at several compositions of the mixtures using a 500 MHz NMR spectrometer and ubbelohde viscometer, respectively. The chemical shift, line width, and line intensity of the \textsuperscript{63}Cu NMR signal in these mixed solvents were measured relative to the \textsuperscript{63}Cu NMR signal in 0.064 M CuClO\textsubscript{4} solution in pure AN. The quadrupolar relaxation rates, reorientational correlation times, and quadrupolar coupling constants of the Cu (I) solvates were also determined from the data. The QCC values showed a big variation in all the solvent systems with the change of solvent composition; indicating the formation of mixed complexes. The variation of all NMR parameters with solvent composition showed strong effect of DMSO, HMPA and DMA on the solvation behaviour of Cu\textsuperscript{+} in the first 3 mixtures; and relatively much weaker effects of PC, NM and 3-HPN in the other 3 mixtures. In a recent study Gill and coworkers\textsuperscript{119} made \textsuperscript{63}Cu NMR, density and viscosity studies of copper (I) perchlorate solutions at 298 K in binary mixtures of AN with D\textsubscript{2}O, 4-picoline, 3-MPN and EB at several compositions of the mixtures. The chemical shift ($\delta$), linewidth ($\Delta$) and relative intensity (I) of the \textsuperscript{63}C NMR signal were measured relative to 0.064 M CuClO\textsubscript{4} solution in pure anhydrous AN. The
quadrupole relaxation rate, reorientational correlation time and quadrupole coupling constant had been evaluated in all cases. The variation of quadrupole coupling constant with solvent composition showed that 4-picoline and D$_2$O had a strong effect on the solvation behaviour of Cu$^+$. Cu$^+$ displays preferential solvation by 4-picoline in AN + 4-picoline mixtures while it showed preferential solvation by AN in all other cases.

Kitigawa and Munakta$^{120}$ synthesized four coordinated Cu (I) complexes [CuL$_4$]ClO$_4$ (L = alkylnitrile, pyridines, alkyl, aryl isocyanide and cyanide) under a large excess of ligands. $^{63}$Cu NMR spectra determined at 298 K and 52.92 MHz exhibited a single resonance line corresponding to that of [CuL$_4$]ClO$_4$. The $^{63}$Cu chemical shift was remarkably affected by the $\pi$-acceptor capability. The downfield shift occurred in the following order, RCN < PY < RNC < ArNC. This order agreed fairly well with that of the $\pi$-acceptor capability obtained from IR studies. This trend also hold for the homologous series of the ligand. The $^{63}$Cu chemical shift of isocyanide complexes of Cu (I) provided a large shift range (~ 100 ppm). For the commonly used ligands containing C or N as donor atom, the good $\pi$-acceptor capability of the ligand caused the $^{63}$Cu resonance line to shift downfield.

Kroneck et al.$^{121}$ investigated the behaviour of the $^{63}$Cu NMR signals in the tetrahedrally coordinated Cu (I) complexes as function of temperature, solvent and anion. From the strong dependence of the linewidth and the chemical shift on these parameters, exchange processes with complexes of lower symmetry were concluded.

Berus and coworkers$^{122}$ examined the complexes of acetylacetonate with pyridine as well as similar complexes of pyridine with Cu benzylacetylacetonate and copper diethylthiocarbamate by PMR. The process of complex formation between these components could be followed by high resolution NMR and in the products the degree of covalence in the planar sigma bond had almost no effect on the spin that was transferred to the base molecule. Combination of NMR and EPR methods showed that this transfer occurs at axial coordination of the ligand.
spectroscopic constants of 3 complexes were tabulated. The diathiocarbamic complex with pyridine failed to show the paramagnetic shifts of the \( \alpha \)-protons under conditions of partially decomposed complex but at \(-25^\circ C\) the equilibrium was shifted sufficiently to the side of this complex to show the paramagnetic shifts in the NMR spectrum especially with large amounts of added pyridine; the lower limits of the paramagnetic shifts for the 2 kinds of protons were 5 and 1.5 ppm; for the pyridine complex of the benzyl derivative only the lower boundary for equilibrium constant could be established since large deviation existed in relation between the NMR shift and the reactant concentration ratio, making line widening too great for accurate estimation of the shifts.

Oschsenbein and Schlaefer\textsuperscript{123} have reported \( ^{63}\text{Cu} \) NMR spectra of Cu(AN)\(_4\)X (X = ClO\(_4^\text{−}\), BF\(_4^\text{−}\), PF\(_6^\text{−}\)) in solution at different temperatures and concentrations. The influence of temperature on linewidth and chemical shift indicated an equilibrium of Cu(AN)\(_4^\text{−}\) and Cu(PY)\(_4^+\) with another complex of lower symmetry. The solvation of Cu (I) by pyridine in a mixture of AN and PY is clearly shown.

Kronenbitter and coworkers\textsuperscript{124} from NMR study of AgNO\(_3\), AgCl and AgBr in H\(_2\)O + EA mixtures reported preferential solvation of Ag\(^+\) by EA.

Schneider and coworkers\textsuperscript{125} from NMR measurements of AgNO\(_3\) in aqueous mixtures of DMSO, reported that Ag\(^+\) was preferentially hydrated at \( X_{\text{DMSO}} < 0.2 \) and was preferentially solvated by DMSO at \( X_{\text{DMSO}} > 0.2 \).

Parker and coworkers,\textsuperscript{126} using NMR technique estimated the composition of inner coordination sphere of Na\(^+\), Cu\(^+\), Cu\(^{2+}\) and Ag\(^+\) in several mixed solvents.

Briggs and Hinton\textsuperscript{127} studied the solvation of Tl\(^+\) in H\(_2\)O + formamide, H\(_2\)O + NMF, H\(_2\)O + NEF, formamide + NEF and formamide + NMF mixtures with Tl\(^+\) NMR spectroscopy. An attempt was made to separate solvation effects arising from electron donating ability of the solvents from those arising from the solvent structural effects in the solvation sphere of the ion. The structural effects arising from the electron donating ability of the solvents from that arising from the solvent structural effects in the solvation sphere of the ion. The structural effects
were found to be greatest in H₂O + NMF system and the least in formamide + NMF system. In a similar study these authors studied the solvation of Tl⁺ in 0.005 M solutions of TINO₃ and TiClO₄ in H₂O + PY, H₂O + DMSP and DMSO + PY mixtures. They reported that Tl⁺ was preferentially solvated by DMSO despite the greater electron donation ability of PY. Ion – pairing was evident in the DMSO + PY and H₂O + PY solvent systems.

An exhaustive review article on Tl and Tl NMR of inorganic and organometallic Tl compounds in solid state as well as solution had been given by Hinton et al. This review article compiled the work from 318 references on Tl NMR.

Rahimi and Popov studied the Ag NMR of AgNO₃ in An + H₂O mixture as a function of changing concentration of AN. From the variations of chemical shift δ as function of mole fraction of AN showed heteroselective preferential solvation of AgNO₃ with Ag⁺ preferentially solvated by AN and NO₃⁻ solvated by water.

Oliver and Janz studied the behaviour of AgNO₃ in H₂O + AN by Raman spectra using He-He (6328 Å) and Ar⁺ (4880 Å) lasers as excitation sources. The variations in relative intensities of the bands with concentration were interpreted relative to ion – pair formation and selective solvation of ions in this mixed solvent system. The studies indicated that Ag⁺ was preferentially solvated by AN and NO₃⁻ by H₂O.

Istvan and Julius investigated kinetics of ligands exchange in the Tl (III) Br system in aqueous 3 M HClO₄ solutions by measuring ⁰⁻Tl NMR in the widths at 298.15 K. The result were discussed and compared to the corresponding data for the Tl (III) chloride system.

Blixt et al. found that in contrast to what was usually assumed, Tl (III) formed very strong CN – complexes in aqueous solution. This system was studied by using ⁰⁻Tl, ¹⁵C and ¹⁴N NMR and potentiometer. The existence of Tl (III) complexes Tl(CN)₃⁻.(n = 1-4) was established. The chemical shift and spin – spin coupling constants were also measured.
Marcus investigated the preferential solvation of Ag⁺, Cu⁺ and Cu²⁺ ions in the mixed solvent H₂O + AN on the basis of spectroscopic and other relevant data from the literature and calculated according to the quasi lattice chemical method. This study confirmed that the monovalent ions were strongly preferentially solvated by the AN component of the mixture whereas the divalent ion was strongly preferentially solvated by the H₂O component.

Lutz et al. measured chemical shift and spin – spin coupling constant with phosphorous using ⁶³Cu and ¹³C NMR measurements. The nuclear magnetic shielding constant derived from the chemical shifts were given in atomic reference scale. No isotope effect for the spin – spin coupling constant was found.

An exhaustive review article on the ability of vibrational spectroscopy (IR and Raman) to probe the different interactions which take place in a solution had been given by Alia.

Gill et al. measured the proton magnetic relaxation time in the systems KI + D₂O + CD₃OD + CD₂OH, Rbl + D₂O + CD₃OD + CD₂OH, KI + D₂O + CD₃OD + CD₂HOD, Rbl + D₂O + CD₃OD + CD₂HOD. The resulting relaxation rates are extrapolated to zero proton concentration. The extrapolation values contain the ion – nucleus proton intermolecular relaxation rates. Apart from magnetic dipole – dipole interaction there seems to be an electronic interaction causing the relaxation mechanism. The experimental results are evaluated so as to yield information regarding preferential solvation. We find no preferential solvation for I⁻ but preferential hydration for Rb⁺. The requirements of experimental precision render our results as yet preliminary.

Capparelli et al. derived the formulae which describe the increase in the total proton magnetic relaxation rate relative to the intramolecular relaxation rate in a solvent mixture when solvent molecules of one kind are enriched in the solution sphere of a dissolved ion. Experimental nuclear magnetic relaxation results regarding the application of these formulae for solutions of Mg(ClO₄)₂, KI and Rbl in water + methanol mixtures are reported. It is shown that preferential solvation effects are present in these systems, they are ascribed to preferential hydration of the cations.
Capparelli et al.\textsuperscript{139} found that in the mixture of ROH/H\textsubscript{2}O (R = C\textsubscript{n}D\textsubscript{2n+1}) an intramolecular proton relaxation contribution due to magnetic dipole interaction only occurs in the water molecule. If the water molecules are preferentially bound to a hydrated cation undergoing relatively slow molecular motions, then only this intramolecular part reflects the slow motion. This principle was used to study preferential solvation of ions in MeOH + H\textsubscript{2}O mixtures. From the experimental results reported, it is deduced that Mg\textsuperscript{+} is preferentially hydrated whereas, in agreement with the theory, for K\textsuperscript{+} and Rb\textsuperscript{+} the dynamical effect of preferential solvation is so small that it cannot be detected with the present method.

Gill et al.\textsuperscript{140} measured the proton NMR relaxation rates of CD\textsubscript{3}OH and proton and oxygen-17 NMR relaxation rates of CD\textsubscript{3}\textsuperscript{17}OH with 6.11, 7 and 26.8\% \textsuperscript{17}O enrichment in binary mixtures with deuteriated Tetrahydrofuran ([\textsuperscript{2}H]THF) containing 10, 20, 30, 50, 60, 75, 85 and 95 mol \% methanol at 288, 298 and 308 K. Deuteron NMR relaxation rates of CH\textsubscript{3}OD have also been measured in Tetrahydrofuran (THF) at the same compositions and temperatures. From the measured proton relaxation rates, the \textsuperscript{17}O-induced intramolecular proton relaxation rates have been extracted. Using these values, the rotational correlation time ($\tau_2^{\text{OH}}$) of the OH bond of methanol has been determined at various compositions. The variation of $\tau_2^{\text{OH}}$ with composition indicates that the hydrogen bonding (self-association) of methanol begins to break up after the addition of ca. 25 mol \% [\textsuperscript{2}H]THF and at > 40 mol \% [\textsuperscript{2}H]THF the structure breaking of methanol becomes much more pronounced. Negative values of the excess isentropic compressibility ($K_v^E$), excess permittivity ($\epsilon^E$), excess viscosity ($\eta^E$) and excess volume ($V^E$) of CH\textsubscript{3}OH – THF mixtures over the whole composition range also indicate strong structure breaking, especially in the range 30-60 mol\% THF, where all these excess parameters pass through a minimum. Proton NMR measurements also confirm that structure breaking of CH\textsubscript{3}OH by THF is strong at > 40 mol\% THF. The deuteron and \textsuperscript{17}O quadrupole coupling constants of methanol in various CH\textsubscript{3}OD-THF and CD\textsubscript{3} \textsuperscript{17}OH-[\textsuperscript{2}H]THF mixture have been evaluated and a strong variation of the deuteron quadrupole coupling constant with composition and temperature as compared to that of \textsuperscript{17}O is observed.
Gill et al.\textsuperscript{141} measured the viscosities and molar conductances of \( \text{Bu}_4\text{NBPI14}, \text{Bu}_4\text{NCIO4} \) and \( \text{CuClO}_4 \) in the salt concentration range \((4 - 1100) \times 10^4 \text{ mol dm}^{-1}\) in propionitrile (PN), 3-hydroxypropionitrile (3-HPN), propionitrile-acetonitrile (PN – AN) and 3-hydroxypropionitrile-acetonitrile (3HPN - AN) mixtures at 298.15 K. \textsuperscript{63}Cu NMR parameters like chemical shift (\(\delta\)), linewidth (\(\Delta\)) and relative intensity (I) of \( \text{CuClO}_4 \) have also been measured in 3HPN – AN mixtures at several compositions and at different concentrations of \( \text{CuClO}_4 \) (between 0.034 to 0.468 M) in 3HPN – AN mixture containing 43.66 mol\% 3HPN. The viscosity data have been analyzed by the Jones-Dole equation \( \eta/\eta_0 = 1 + AC/\eta + BC \) to evaluate A and B coefficients of the electrolytes and the ionic viscosity B and B-coefficients have been evaluated using the method reported by Gill and Sharma. The conductance data have been analyzed by the Shedlovsky equation to evaluate \(\Lambda_a\) and \(K_a\) values of the electrolytes and the NMR data to obtain quadrupolar coupling constants \((e^2Q_q/h)\) of the solvated \(\text{Cu}^+\) ion. The viscosity results show that \(\text{Cu}^+\) is better solvated by AN and \(\text{ClO}_4^-\) by PN and 3HPN in PN – AN and 3HPN – AN mixtures respectively. The \((e^2Q_q/h)\) results in 3HPN – AN mixtures show that 3HPN slowly replaces the AN molecules from the solution sphere of \(\text{Cu}^+\) as the composition of 3HPN increases in the mixture but no change in the solvation sphere of \(\text{Cu}^+\) occurs at constant composition of 3HPN with change of \(\text{CuClO}_4\) concentration.

Irangu and Jordan\textsuperscript{142} studied the \textsuperscript{63}Cu NMR line widths in Cu(I)-acetonitrile (AN) solutions. The variations with the concentrations of Cu(I) salts (trifluoromethanesulfonate and perchlorate), added salts, water, chloride ion, and temperature have been studied. A quantitative analysis shows that the anomalous temperature dependence of the line widths is not due to ion pairing or anion complexation but results primarily from formation of a species with a different coordination number or less symmetrical arrangement of AN ligands than in the normal tetrahedral Cu(AN)\textsuperscript{4+} ion. Solvent viscosity and ion pairing (with triflate) also are identified as factors having the expected effects on the widths. The results of earlier studies also are discussed and analyzed by the current model where possible.
1.6 Aim and Scope of Present Work

The stability of Cu (I) relative to Cu (II) has long been established in acetonitrile because of solvation. In acetonitrile, Cu (I) is known to form tetrahedral ion \([\text{Cu(AN)}_4]^+\) which can be isolated in salts with large anions such as \(\text{ClO}_4^-, \text{BF}_4^-\) and \(\text{PF}_6^-\). The Cu (I) compounds are diamagnetic and are colourless except those where colour results from charge transfer bands. The stability of Cu (I) in organic nitriles has proved to be of practical applications and has provided an alternative for electrowinning and electrorefining of copper. Though there are a large number of investigations of several electrolytes in pure and mixed solvents, the studies of complexes of Cu (I) salts are scarce. Therefore, in the present dissertation, it is planned to make the electrochemical, ultrasonic velocity and NMR studies of some new Cu (I) complexes with different variety of ligands, which are expected to highlight the solvation behaviour of these complexes and their stability in different solvent systems. These studies will also be of significant theoretical interest because these will provide interesting solvation behaviour of these complex ions in which the charge seems to be screened by bulky groups causing great differences from the normal ions.

Acetonitrile (AN) and dimethylsulfoxide (DMSO) belong to very different categories of solvents. Dimethylsulfoxide has larger dipole moment than acetonitrile \((\mu_{\text{AN}} = 3.37 \text{ D} \text{ and } \mu_{\text{DMSO}} = 3.90 \text{ D})\). Both of these solvents have good dielectric constants \((\varepsilon_{\text{AN}} = 36.0 \text{ and } \varepsilon_{\text{DMSO}} = 46.7)\) and dissolve a large number of salts. Dimethylsulfoxide has a very strong tendency to solvate the alkali metal cations but its capacity to solvate copper (I) ions is not well investigated. Acetonitrile on the other hand solvates copper (I) ions strongly due to specific \(d\pi – p\pi\) interactions. The binary mixtures of acetonitrile with dimethylsulfoxide are, therefore, expected to be very interesting solvent systems for the study of copper (I) perchlorate complexes.
1.7 References