1.1 General Introduction

The study of solvation behaviour of electrolytes in mixed solvents has been an important subject of solution chemistry during the last few years\textsuperscript{1-8}. Since in mixed solvents the dielectric constant and viscosity of the medium can be varied to a desired value, therefore, the solvation behaviour can be better understood in mixed solvents than in pure solvents. The behaviour of electrolytes in mixed solvents gives an intricate picture of solvation. The solvation studies are generally based upon three types of approaches, which help us to estimate the extent of solvation. The first one is the solvational approach which includes conductance, viscosity measurements etc. of electrolytes and derivation of various factors associated with ionic solvation. The second approach involves the thermodynamic properties like Gibbs free energy, enthalpy and entropy of transfer of electrolytes to elucidate the extent of solvation\textsuperscript{9}. The third method involves the use of spectroscopic measurements\textsuperscript{10,11} of the electrolytes, where the spectral solvent shifts and line width of the NMR signal determine the qualitative and quantitative nature of solvation.

In addition to the ion-solvent and ion-ion interactions, solvent-solvent interactions and resulting structural changes may play an important role in the mixed solvents. In mixed solvents sometimes one of the solvent component 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 neighborhood 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. With the advancements in technology and increasing applications of solution chemistry in research and industry like hydrometallurgical purification of metals and especially of copper, silver and gold this field has been gaining importance decade by decade. Besides this, these studies are playing important roles in reaction kinetics, electrode potentials, high energy primary and secondary non-aqueous batteries, wet double layer capacitors, electro deposition, electroplating and many other electrochemical processes\textsuperscript{12-15}. Some other areas where the non-aqueous electrolytes are extensively
used include electro chromic displays, smart window, etching and electro synthesis etc. Due to wide technical applications, these studies getting more attention from both theoretical and practical points of view. 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 certain assumptions have been suggested from time to time. Since most of these explanations have been advanced keeping in view the physical picture of water and the results of measurements in aqueous solutions, but these theories do not fit 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 of electrolytic solutions may be inferred. The solvation behaviour of ions in mixed solvents can be interpreted with the help of different techniques such as conductance, transport number, solubility, vapour pressure, EMF, NMR, ESR and Raman spectroscopic methods. 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 large number of studies on this subject have already made in literature in which alkali metal and tetraalkylammonium salts were frequently employed as 1:1 electrolytes, which are usually solvated by purely electrostatic ion-dipole interactions on the other hand studies on highly ionic copper (I) and silver (I) salts are very rare. Such copper and silver ions are found to be solvated by special type of interactions with some solvents such as nitriles.

The specific type of stability for copper (I) cations in nitrile solvents has been established to be due to \( \text{d}t\text{-p}\pi \) type of interactions of \( \text{Cu}^+ \) with \(-\text{C}=\text{N}\) group of nitrile solvents. Though some solvation studies of Cu (I) salts were attempted in the recent years. Yet these are limited only to acetonitrile, benzonitrile, and their binary mixtures with some other organic solvents like acetone, methanol, benzene, pyridine etc. No attempt, however, has been made to study solvation behaviour of copper (I)
and Silver (I) salts in mixtures of acetonitrile (AN) and N,N-Dimethylacetamide (DMA) in which both the solvents have tendency to interact with both ions. Both AN and DMA are dipolar, aprotic solvents with almost similar dielectric constant [AN (ε=36.0) and DMA (ε=37.8)] but different Gutman numbers [AN (14.1) and DMA (27.8)]. Binary mixtures of AN and DMA are therefore expected to provide interesting results for the ion-association and solvation behaviour of Cu (I), Ag (I) and tetrabutyl ammonium salts.

1.2 Literature survey on conductance studies
Electrolytic conductivity is a very useful classical experimental technique to determine solvation and ion-association 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 solvent-solvent interactions in mixed solvents. These studies provide kinetic information in the form of ionic conductance 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.
Bhat and Sreelatha⁶ studied the effect of addition of DMF on the conductance and solvation behaviour of BiCl₃ in MeOH and AN at four different temperatures. In both the solvents, the conductance was found to decrease and the solvation was found to increase on addition of DMF at all temperatures. Kraus-Bray and Shedlovsky conductance models were used to evaluate the limiting molar conductance, dissociation and association constants. Ion pair formation constant and triple ion constant have also been computed. Walden product and thermodynamic parameters were also reported. Solvation number of the species of BiCl₃ has been calculated in pure solvents by the mobility method.
Hood and Williamson¹⁷ made conductance, viscosity and near IR (NIR) spectroscopic studies on a series of solution of lithium salts (LiF, LiCl, LiBr, LiI, LiNO₃ and LiClO₄) in propylene carbonate (PC) and binary mixtures of PC and tetrahydrofuran.
(THF), dimethoxyethane (DME), dimethylcarbonate (DMC) and diethylcarbonate (DEC). Lithium salt concentrations were ranged from 0.01 M to 2.0 M for the conductance measurements. Viscosity measurements were made in temperature range from 5°C to 80°C for lithium salts in solutions and pure solvents. Near IR and UV-visible spectra were recorded between 180 and 220 nm at room temperature. The conductance for most salt solutions increased linearly between 0.01 M and 1.0 M. LiBr, LiCl, LiNO₃ and LiF all showed evidence of aggregate formation between 1.0 M and 2.0 M. UV spectra of the lithium salt solutions all exhibited a peak around 270 nm. Although this peak varies with concentration, the relationship is not linear. The Near IR spectra of the perchlorate solutions show a strong absorbance around 190 nm. Padhi and Dash have measured the conductivities of tungstate, selenate, selenite of sodium and chromate, sulfate, tellurite of potassium in 11.52, 20.31 and 29.64 %w/w urea + water mixtures at 25, 30 and 35 °C and analyzed by using Shedlovsky and Fuoss-Kraus extrapolation techniques for calculating the association parameters (λₒ and Kₐ). A comparison of these parameters showed that the Shedlovsky method was superior to other methods and predicted better association constants for the sodium and potassium salts in aqueous urea solvents. The thermodynamic functions for the association process has been calculated and discussed. Chauhan and coworkers have reported limiting molar conductances (λₒ) of Ph₄PB₉₄, Bu₄NB₉₄, Bu₄NNO₃, Bu₄NClO₄, Bu₄NB₉₄, Bu₄NI, Ph₄PB₉₄, NaBP₉₄, AgClO₄, AgNO₃, LiNO₃, NaNO₃, KNO₃ and NaBr in DMF-DMSO mixtures at 25, 35 and 45°C using Shedlovsky conductance equation. Limiting molar ionic conductances have been calculated from reference Ph₄PB₉₄. Discussion of effective ionic radii (r) calculated from λₒ values was based on ion-solvent interactions. The results indicate the existence of electrostatic ion-solvent interactions in the case of alkali metal cations via O atom of both the solvents and specific interactions between Ag⁺ ion and DMSO via S atom of S=O group of DMSO molecule. The latter was found to be in agreement with the concept of soft acid-base type of interactions. Association constants (Kₐ), however, yield no significant contribution. Jha and coworkers have reported conductance data for tetraethylammonium bromide (Et₄NBr), tetrapropylammonium bromide (Pr₄NBr) and lithium bromide (LiBr) in
THF + water mixtures containing 0, 20, 40, 60, 80 and 100 %w/w of THF at 303, 313 and 323 K. The conductance data have been analyzed by the Fuoss conductance-concentration equation in terms of limiting molar conductance \( (\Lambda_0) \), association constant \( (K_A) \) and the distance of closest approach of ions \( (R) \). The results have been interpreted in terms of ion-ion and ion-solvent interactions.

Jauhar and coworkers\(^{21}\) have measured the molar conductances of some 1:1 alkali metal and tetraalkylammonium salts and silver nitrate in acetic acid + water mixtures containing 0, 20, 40, 60, 80 and 90 %w/w acetic acid at 298 K. The conductance data have been analyzed by using Shedlovsky method setting ion-size parameter equal to Bjerrum critical distance suggested by Justice to calculate \( \Lambda_0 \) and \( K_A \). Transference numbers of \( \text{NO}_3^- \) ion in \( \text{AgNO}_3 \) have also been measured in water and acetic acid + water mixtures containing 20, 40, 60, 80 and 90 %w/w acetic acid by modified Hittorf’s method and e.m.f method. The limiting transference numbers were combined with \( \Lambda_0 \) values of \( \text{AgNO}_3 \) to obtain limiting ionic conductances \( (\chi_\text{L}) \) for \( \text{Ag}^+ \) and \( \text{NO}_3^- \) ion and these values have been further used to calculate limiting ionic molar conductances of all other ions using Kohlrausch law. These studies suggest the solvation pattern in acetic acid + water mixtures as: \( \text{Li}^+ > \text{Na}^+ > \text{Ag}^+ > \text{K}^+ > \text{NH}_4^+ \) and \( \text{BPh}_4^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- \).

Bhat and Susha\(^{22}\) have reported the effect of solvation of the species \( \text{N-chlorosuccinimide} \) (NCS) on its conductance behaviour. The study was carried out in water and various compositions (%v/v) of water + MeOH between 283 to 323 K. Conductance data were analyzed initially by DHO and then by Shedlovsky model to get the limiting ionic conductance \( (\chi_\text{L}) \). The \( \chi_\text{L} \) decreases with the increase in MeOH indicating the increased ion-solvent interaction and solvent-solvent interactions and also the preferential solvation. The association constant was very high in the case of water and decreased sharply in presence of MeOH. Thermodynamic parameters of solvation was detected and presented here.

Preferential solvation of the cation by MeOH was identified.

Bhat and Shivakumar\(^{23}\) have investigate the ion-solvation behaviour of tartaric acid in different compositions (%v/v) of \( \text{H}_2\text{O} + \text{MeOH} / \text{EtOH} / \text{DMSO} / \text{DMF} / p-\text{DO} \) mixtures from 288 K to 313 K. The electrical conductance data were analyzed by Kraus -
Binary and Shedlovsky model of conductance. The $\Lambda_0$ sharply decreased for the increased amount of co-solvent due to solvent-solvent interactions. Association constant ($K_A$) was compared in all the cases. In $\text{H}_2\text{O} + \text{MeOH} / \text{EtOH}$ mixtures the $K_A$ increased with increase in temperature suggesting endothermic behaviour of the system. Walden product, Stoke’s molecular radius 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 $\text{H}_2\text{O} + \text{EtOH}$.

Bakr$^{24}$ have measured the conductance of some transition metal perchlorates, $\text{M(ClO}_4)_2$ (M$^{2+} = \text{Mn, Co, Ni, Cu and Zn}$) in urea-water mixtures at 288-318 K. The limiting molar conductivities and the ion-association constants of these electrolytes were calculated by the Shedlovsky extrapolation method. The ion-association constant decreased in the order $\text{Co} > \text{Ni} > \text{Zn}$ with increasing atomic number, whereas $\text{Cu} > \text{Mn}$ in the ionic association constants as a result of the maximum temperature dependencies of $\text{Cu}^{2+}$. The thermodynamic functions, $\Delta H^\circ$ and $\Delta S^\circ$, for the formation of the ion pairs had also been obtained. Both $\Delta H^\circ$ and $\Delta S^\circ$ for all the salts under study are positive values. On the other hand, the Walden products of the salts increase with an increase in temperature at 288-318 K, which indicated that these electrolytes behave as structure-makers or promoters.

Mukhopadhyay and Pal$^{25}$ have measured the conductance of 1-ethyl-4-cyanopyridinium iodide in the concentration range $(7.8-19.1) \times 10^{-4}$ mol dm$^{-3}$ in binary solvent mixtures of water and aprotic co-solvents (acetone and 1,4-dioxane) at different temperatures (293-308 K). The conductance data in all cases have been analyzed by the Shedlovsky equation to obtain $\Lambda_0$ and $K_A$. The association constant ($K_A$) are used to get information about the influence of solvent components on the various equilibrium present in the solution. The association enthalpy ($\Delta H^\circ$) has also been detected as a function of solvent composition.

Bhat and coworkers$^{26}$ have reported the results of the conductance of perchloric acid, sodium perchlorate and potassium perchlorate in water and DMF in the temperature range 283 to 313 K. Conductance data were analyzed by using Fuoss-Onsager and Shedlovsky conductance models. The limiting conductance of these electrolytes and
association constants were computed. The Walden product and energy of activation of the rate process were also computed and reported. The sodium ion was more solvated in water than in DMF as compared to the potassium ion. The potassium ion was found to be a good structure breaker in water as compared to the sodium ion and hydrogen ion.

Kovalevskii and Shishalov\textsuperscript{27} studied the temperature dependences of the specific and molar conductance of CeCl\textsubscript{3}-MCl and LnCl\textsubscript{3}-KCl (M = Li, Na, K, and Cs; Ln = Er and Yb) in molten binary mixtures of various compounds. The size of the cations of alkali and rare-earth metals was demonstrated to affect the intensity of the interactions of the components of the systems. Deviations of the molar conductance isotherms from additivity and dependence of the isotherms on the ratio between the mixture components were explained by the formation of complexes in the melts.

Safonova and coworkers\textsuperscript{28} have reported the conductance data for NaNC\textsubscript{3}, KI, Pr\textsubscript{4}NBr and Bu\textsubscript{4}NI in DMF at -40, -35, -25, -15, -5, 5, 15, 25, 35 and 45°C. The data have been analyzed by using the Lee-Wheaton conductance equation in terms of the limiting molar conductance ($\Lambda_0$) and association constant ($K_a$). Evaluation of single ionic conductances have been carried out on these data and on preceding exploitation conductance data for MBr (M = Na\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Et\textsubscript{4}N\textsuperscript{+}, Pr\textsubscript{4}N\textsuperscript{+}, Ph\textsubscript{4}P\textsuperscript{+}), KClO\textsubscript{4}, NaBPh\textsubscript{4}, Ph\textsubscript{3}Cl and Bu\textsubscript{4}NBPh\textsubscript{4} using the Walden product of Bu\textsubscript{4}N\textsuperscript{+}. The temperature dependences of $\Lambda_0$ and $K_a$ were discussed. The values of $K_a$ indicate that all these salts were weakly associated in DMF.

Das and Hazra\textsuperscript{29} performed precise conductance measurements for lithium perchlorate, lithium tetrafluoroborate, lithium hexafluoroarsenate, sodium perchlorate, and sodium tetraphenylborate in 2-methoxyethanol-water mixtures at four different mole fractions, i.e., 0.056, 0.136, 0.262, and 0.486 of 2-methoxyethanol (69.73 $\geq$ D $\geq$ 26.55) at 298 K in the concentration range 0.0004-0.0642 mol/dm\textsuperscript{3}. The limiting molar conductance ($\Lambda_0$), association constant ($K_a$) and the association distance (R) for the solvent mixtures have been evaluated from the conductance data using the 1978 Fuoss conductance equation. The single-ion conductance have been calculated using the "reference electrolyte" Bu\textsubscript{4}NBPh\textsubscript{4}. The analysis of the data indicates that for most salts ion-association was appreciable in the solvent mixtures with a mole fraction of
the co-solvent of 0.262 or higher. The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvent media.

Gritsan et al.\textsuperscript{30} have investigated the solvation properties of LiCl, LiNO\textsubscript{3}, LiClO\textsubscript{4} and NaClO\textsubscript{4} in binary mixtures of THF with ethylene glycol and THF with water at 298 K. In the region with low dielectric constant essential change in solvation properties was observed, namely, inversion of the strength of electrolytes with various anions and increased in the effective ionic radii in both systems.

Bhat and Sreelatha\textsuperscript{31} have carried out investigations to study the effect of added EtOH on the conductance behaviour of BiI\textsubscript{3} 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 to decrease 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 > DMF > EtOH. Association constant was determined in the three solvent systems. Results predicted the endothermic behavior 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. Walden product and corrected Stokes molecular radius 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.

Muhuri and Hazra\textsuperscript{32} reported the electrical conductance and viscosity measurements for the solutions of Ph\textsubscript{4}PCl, Bu\textsubscript{4}NBPh\textsubscript{4} and NaBPh\textsubscript{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 Fuoss conductance equation which contained terms for equivalent conductance (A\textsubscript{0}), association constant (K\textsubscript{A}) and association distance (R). The limiting ionic values were determined by using reference electrolytes Bu\textsubscript{4}NBPh\textsubscript{4} and Bu\textsubscript{4}NCIO\textsubscript{4}. Calculated Stokes radii indicated that Na\textsuperscript{+} and Cl\textsuperscript{-} were substantially solvated and remained as free ions in the medium.

In another study Hazra and coworkers\textsuperscript{33} measured electrical conductance’s of Hex\textsubscript{4}NBr, Hep\textsubscript{4}NBr and Bu\textsubscript{4}NBPh\textsubscript{4} in MeOH, AN, and MeOH + AN 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 \((K_a)\) and the distance of closest approach of ions \((R)\). Single-ion conductivities have been determined on the basis of Bu4NBPPh4 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\(^{34}\) have carried out precise measurements of electrical conductance’s of the solutions of LiCl, LiBr, LiI, LiClO4, LiBF4, NaBr, NaBPPh4, KBr, RbBr, CsBr and Bu4NBr in DMA + H2O (50 %v/v) mixtures in the concentration range 0.02-0.05 mol dm\(^{-3}\). The conductance data have been analyzed by the Fuoss equation in terms of the limiting molar conductance \((\Lambda_0)\), the association constant \((K_a)\) and the association diameter \((R)\). The limiting ionic conductances \((\lambda^*_n)\) have been estimated from the appropriate division of the limiting molar conductivity value of the reference electrolyte Bu4NBPPh4. The electrolytes investigated were found to be significantly dissociated in this solvent medium and all ions remained unsolvated in DMA + H2O (50 %v/v) mixed solvent system with exception of the lithium ion where significant solvation has been noticed.

Sadeghi and Valavi\(^{35}\) 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) 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 > DB18C6 > DB24C8. In all cases, the stability constants of the resulting complexes in solvents used varied in the order: NB > NM > AN.

Gill and coworkers\(^{36-39}\) reported a good account of preferential solvation of ions in terms of their effective ionic radii, \(r_i\) values from conductance data of various mixed non-aqueous solvent systems. Similarly conductance study of a number of electrolytes have been carried out in various binary solvent systems of mixtures of DMSO with AN\(^{40}\), MeOH\(^{41}\), AC\(^{42}\) and p-DO\(^{43}\) in order to derive information about preferential solvation of ions in these solvent systems on the basis of the \(r_i\) values of ions.

Gill and coworkers\(^{44}\) have measured the molar conductance’s of Bu4NBPPh4, Bu4NClO4, CuClO4, AgClO4 and TiClO4 in the concentration range \((0.25 - 75) \times 10^4\)
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 have been analyzed by the Shedlovsky equation to obtain $\Lambda_0$ 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 conductance $\Lambda_\infty$ and solvated radii ($r_i$) for Bu$_4$N$^+$, Ph$_4$B$^+$, Cu$^+$, Ag$^+$, Ti$^+$ and ClO$_4^-$ have 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 Ti$^+$ 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$_4$N$^+$ show no solvation but Ph$_4$B$^+$ showed some solvophobic interaction in the BN and PY.

Jauhar and Sandhu$^{45}$ have measured 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 have 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 ions in these mixtures. The viscosity data have been analyzed using the Jones-Dole equation. The ion-solvent interaction parameter, viscosity B-coefficients has been found to be positive for all the electrolytes in all systems. The ionic B$_e$ coefficients have been evaluated by taking Bu$_4$NBPh$_4$ as reference electrolyte. Conductance and viscosity of the salts NaBr, NaBPh$_4$ and Bu$_4$NBr have 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.$^{46}$ have measured the conductances of tetrabutylammonium hexafluorophosphate in AC and of decamethylferricinium hexafluorophosphate in AC, AN, 1,2 - dichloroethane (DCE) and dichloromethane (DCM) at 298 K. The
Walden product of the Bu4N+ cation and the PF6- 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 decamethylferrocenium hexafluorophosphate were determined in the four solvents investigated. The association constant of this electrolyte increased with reduced temperature.

Rounagi and Sanavi studied the complexation reactions between Mg2+, Ca2+, Sr2+ and Ba2+ metal cations with 15-crown-5 (15C5) in AN-MeOH mixtures at different temperatures using a conductometric method. 15C5 formed 1:1 complexes with Mg2+, Ca2+ and Sr2+ cations in solutions. The Ba2+ cation formed a 2:1 complex (ratio of ligand to cation) in solutions. A linear relation was observed for variation of log Kf of 15C5 - Ca2+ and 15C5 - Sr2+ complexes versus the composition of AN-MeOH mixtures, but a non-linear behaviour was observed in the case of 15C5-Mg2+ complex in these binary mixtures. Selectivity of 15C5 for Mg2+, Ca2+ and Sr2+ 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 (ΔH°, ΔS°) for formation of 15C5-Mg2+, 15C5-Ca2+ and 15C5-Sr2+ complexes were obtained from temperature dependence of stability constants and the result shows that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents.

Shamsipur and Khayatin have carried out conductance study of the interaction between Tl+ ion and 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), benzo-18-crown-6 (B18C6), diaza-18-crown-6 (DA18C6), dibenzyl diaza-18-crown-6 (DBzDA18C6) and hexaaza-18-crown-6 (HA18C6) in DMF-AN 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 HA18C6 > DA18C6 > DBzDA18C6 > 18C6 > DC18C6 > B18C6. The enthalpy and entropy of the complexation reactions were determined from the temperature dependence of the formation constants.

Susha and Bhat have carried out conductance measurements of N-bromo-N-sodium-p-toluenesulphonamide (Bromamine-T, BAT) in H2O, 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, association constant, product of limiting conductance and viscosity of the solvent (Walden product), thermodynamical parameters and limiting ionic conductance were systematically computed. Limiting molar conductance values were higher in AN and H₂O + AN mixtures as compared to H₂O, DMF or H₂O + DMF mixtures. Preferential solvation of cation by non aqueous solvent was identified. The association process involved in the system is exothermic.

Chauhan et al. have measured the molar conductance of Bu₄NBPh₄, Bu₄NClO₄, Bu₄NI, NaClO₄, LiClO₄ and AgClO₄ in the concentration range (5 - 62) x 10⁻⁴ mol dm⁻³ 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 have been analyzed using a least squares computer program to fit to Shedlovsky conductance equation to obtain limiting molar conductance equation (Λ₀) and ion-association constant (Kₐ). Λ₀ values were split into limiting ionic conductances (Λₒᵢ) values and from these the effective ionic radii (rᵢ) in these solvent mixtures were calculated. The results were discussed in terms of ion-solvent interaction both specific and non-specific.

In another study Chauhan et al. reported the solvation behaviour of Li⁺, Na⁺, K⁺, Ag⁺ and NO₃⁻ ions from the conductance measurements of solutions of LiNO₃, NaNO₃, KNO₃, AgNO₃ and Bu₄NNO₃ in DMSO-MeOH mixtures. The conductance data were analyzed in terms of the limiting molar conductance (Λₒ) and ion-association constant (Kₐ) using a least squares computer program of the Shedlovsky conductance model. The limiting molar ionic conductance (Λₒᵢ) have been calculated on the basis of Ph₄PB₄ assumption; Λₒᵢ(Ph₄P⁺) = Λₒᵢ(Ph₄B⁻) and effective ionic radii (rᵢ) calculated using empirical modification of the stoke’s model. The rᵢ values were compatible with Kₐ values. An obviously typical difference in selective solvation for various cations, Li⁺, Na⁺, K⁺ and Ag⁺ was observed. Weak preferential solvation of NO₃⁻ by MeOH was reflected over the entire solvent composition range, which is in contrast to the solvation of ClO₄⁻ in DMSO - MeOH mixtures.

In a subsequent study Chauhan et al. reported molar conductance and viscosity of Bu₄NBPh₄, NaBPh₄, Bu₄NBr, Bu₄NI, LiClO₄ and NaClO₄ 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 $A_0$ and $B$-coefficients have been resolved into ionic conductance ($\lambda^+$) and $B^-$ values for various ions on the basis of $Bu_4NB{PPh}_4$ assumption. The effective ionic radii ($\tau_0$) of $Bu_4N^+$, $Ph_4B^-$, $Li^+$, $Na^+$, $Br^-$, $I^-$ and $ClO_4^-$ have been determined from $\lambda^+$ values using Gill’s modification of the Stoke’s law. The ionic $B^-$ values for these ions have also discussed in terms of Einstein equation. The analysis of data showed that $Bu_4N^+$ and $Ph_4B^-$ lost their spherical shape, while $Li^+$, $Na^+$, $Br^-$, $I^-$ and $ClO_4^-$ behave as spherical entities during viscous flow process.

Izonfou et al. have measured the limiting ionic conductivities of lithium, sodium, potassium and cesium iodides in DMF, AN and 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 studied and showed a valley at 0.20 mol fraction of DMF. The conductance and viscosity data have been utilized in the modified S:okes equation to estimate the solvation numbers of the ions in various solvent systems. For $Li^+$, the solvation numbers ranged between 2.38-3.85 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 have been interpreted in terms of ion-solvent interactions and solvent properties.

Electrolytic conductance and thermal properties of LiClO$_4$ salt in mixtures of ethylene carbonate (EC)/propylene carbonate (PC) solvents, having fixed molar ratio 46.5/19.0, have been measured by Croce et al. over salt concentrations ranging from 0.22 to 1.0, 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 approximately 0.5.

Singh and et al. reported the conductance measurements at temperatures from 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 conductance ($A_0$) were calculated using Shedlovsky technique. The Walden products ($A_0\eta_0$) were determined. The thermodynamical properties viz.
change in free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) for the ion-pair formation have been calculated from the values of association constants at different temperatures. Sizes of the ion-pair have also been calculated from the Walden product values.

Perron and coworkers\textsuperscript{56} have 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 number on the conductivity. These results were used to develop a simple model for excess conductivities based on the viscosity and volume of the pure solvents. Without adjustable parameters, this model predicted the correct sign of the excess conductivities in $\approx$ 90 % of the cases and the magnitude of the conductivity of the ternary mixtures within an average of 15 %.

Desnoyers and coworkers\textsuperscript{57} have measured conductance and apparent molar volume and heat capacity of LiTFSI over a wide range of concentration in glymes, tetraethylsulfamidne (TESA), $\gamma$-butyrolactone, AN and PC at 298 K and were compared with those of LiClO$_4$ in the same solvents. At low concentrations, LiTFSI is strongly associated in the glymes and moderately associated in TESA. At intermediate concentrations, the thermodynamic data suggested that a stable solvate of LiTFSI in ethylene glycol dimethyl ethers (EGDME) exists in the solution state. At high concentrations, the thermodynamic properties of the two lithium salts approach those of the molten salts. They have reported that these salts have a reasonably high specific conductivity in most of the solvents.

Lebed et al.\textsuperscript{58} reported conductance data for LiCl, NaCl, KCl, RbCl, CsCl, Me$_4$NCl, Et$_4$NCl, Bu$_4$NCl, NaF, NaBr and NaBPht in EG with $10^{-4}-10^{-2}$ mol dm$^{-3}$ over the temperature range 278-448 K. From conductance limiting ionic conductances of Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Me$_4$N$^+$, Et$_4$N$^+$, Bu$_4$N$^+$, F$^-$, Cl$^-$ and Ph$_4$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) has also been obtained. It was shown that single charged ions with the smallest radii (Li$^+$, Na$^+$, F$^-$), moderate radii (K$^+$, Rb$^+$, Cs$^+$, Cl$^-$, Br$^-$) and large complex ions (Me$_4$N$^+$, Et$_4$N$^+$, Bu$_4$N$^+$, ...
PlqB), have 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.

Ghasemi and Shamsipur reported conductance study of the interaction between Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Cd\textsuperscript{2+} and Pb\textsuperscript{2+} with 1,10-diaza-18-crown-6 in different AN-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\textsuperscript{2+} < Co\textsuperscript{2+} < Ni\textsuperscript{2+} < Cu\textsuperscript{2+} < Cd\textsuperscript{2+}, Pb\textsuperscript{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\textsubscript{f} of different complexes and mole fraction of AN in the solvent mixtures.

Kundu and coworkers have measured the equivalent conductances (\(\Lambda\textsubscript{eq}\)) of KI, KBPh\textsubscript{4}, Ph\textsubscript{4}AsI and n-Bu\textsubscript{4}NI in AN, DMF and AN+DMF mixtures at 298.15 K. The equivalent conductance at infinite dilution (\(\Lambda\infty\)) and ion-association constant (K\textsubscript{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. \(\Lambda\infty\) values were then split into their ionic contributions \(\lambda\textsubscript{i}\) by using two propositions: (1) reference electrolyte assumption: \(\lambda\textsuperscript{"} (\text{Ph}_4\text{As}^+) = \lambda\textsuperscript{"} (\text{Ph}_4\text{B}) = 1/2 \Lambda\infty (\text{Ph}_4\text{AsBPh}_4)\) and (2) Krumgalz's assumption: \(\lambda\textsuperscript{"} (\text{n - Bu}_4\text{N})\eta\infty = 0.213\) for all the solvents.

Roses et al. reported molar conductances and dissociation constants of perchloric acid, hydrochloric acid, picric acid, benzoic acid and their tetrabutylammonium salts in 2-PrOH/H\textsubscript{2}O mixtures in the whole composition range at 298 K. The variation of Walden product 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.

1.3 Literature survey on viscosity studies

Viscosity of electrolytic solutions is another valuable parameter which is helpful in providing information about the nature of electrolytes in solution. The concentration dependence of viscosity of electrolytic 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.

Haidar and Das\textsuperscript{62} reported viscosities of the solutions of tetraethylammonium bromide (Et\textsubscript{4}NBr), tetrapropylammonium bromide (Pr\textsubscript{4}NBr), tetrabutylammonium bromide (Bu\textsubscript{4}NBr), tetrapentylammonium bromide (Pe\textsubscript{4}NBr), and tetraheptylammonium bromide (He\textsubscript{4}NBr) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The viscosity data have been analyzed by using Jones-Dole equation for the associated electrolytes to evaluate the viscosity B-coefficients of the electrolytes. These data have also been analyzed by the transition-state treatment to obtain the contribution of the solutes to the free energy of activation for viscous flow of the solution. The viscosity of the solvent was found to be greatly modified by the presence of all of the tetraalkylammonium ions investigated. Moreover, the tetraalkylammonium ions were found to be unsolvated in 2-ethoxyethanol solutions, they behave neither as structure-breaker nor as structure-maker and the formation of the transition state is made less favorable in their presence.

Das and Hazra\textsuperscript{63} have measured viscosities and molar conductances in the concentration range 0.022-0.044 mol dm\textsuperscript{-3} for tetraalkylammonium bromides, R\textsubscript{4}NBr (R = Et to hexyl), NaBr, and NaBPh\textsubscript{4} in binary mixtures of DMA+water at 0.5 mol fraction of DMA at 298.15 K. Viscosities of these salts except Hex\textsubscript{4}NBr were also measured in the concentration range 0.008-0.10 mol dm\textsuperscript{-3} in this aqueous binary mixture at the same temperature. The conductance data were analyzed by the 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance ($\Lambda_0$), association constant ($K_A$) and association distance (R). Viscosity data were analyzed by using Jones-Dole equation and B-coefficients were evaluated. The limiting ionic conductances and the ionic contributions to the viscosity B-coefficients were determined by using the reference electrolyte method. The results were interpreted considering the selective solvation, size and structure forming effect of ions and also the movement of ions in a strongly hydrogen bonded solvent system formed between water and the peptido dipole in DMA.

Abdulagatov et al.\textsuperscript{64} have measured the viscosity of seven compositions (0.062, 0.166,
0.456, 0.552, 1.754, 3.062, and 4.700) mol kg\(^{-1}\) of binary aqueous NaI solutions with a capillary-flow technique. Measurements were performed at pressures up to 30 MPa. The range of temperature was from 298 to 575 K. The total uncertainty of viscosity, pressure, temperature and composition measurements was less than 1.6 %, 0.05 %, 15 mK, and 0.015 %, respectively. The effect of temperature, pressure and concentration on viscosity of binary aqueous NaI solution was studied. The measured values of the viscosity of NaI (aqueous) were compared with data, predictions, and correlations reported in the literature. The viscosity data have been analyzed and interpreted in terms of the extended Jones-Dole equation for the relative viscosity \((\eta/\eta_0)\) of strong electrolytes. The derived values of the viscosity A and B-coefficients were compared with the values calculated from the Falkenhagen-Dole theory and ionic B-coefficients data, respectively. The physical parameters \(V\) and \(E\) in the Eyring's absorbance rate theory of viscosity was explained, the hydrodynamic molar volume \(V_h\) (effective rigid molar volume of salt) in the extended Einstein relation for the relative viscosity, and the Arrhenius-Andrade parameters \(A\) and \(b=Ea/R\) (where \(Ea\) is the flow activation energy) were calculated using the viscosity data. The effective pressures due to the salt (NaI) in water were calculated from the present viscosity measurements by using the TTG model. The predictive capability of the various models for viscosity for electrolyte solutions has been tested.

In another study Abdulagatov and Azizov\(^{65}\) have measured the viscosity of 10 compositions (0.049, 0.205, 0.464, 0.564, 0.820, 1.105, 1.496, 2.007, 2.382, and 2.961 mol kg\(^{-1}\)) of aqueous NaBr solutions with a capillary-flow technique. Measurements were made at pressures up to 40 MPa. The range of temperature was 288-595 K. The total uncertainty of viscosity, pressure, temperature and composition measurements was less than 1.6 %, 0.05 %, 15 mK, and 0.02 %, respectively. The effect of temperature, pressure and concentration on viscosity of binary aqueous NaBr solution were studied. The measured values of the viscosity of NaBr (aqueous) were compared with data, predictions and correlations reported in the literature. The temperature and pressure coefficient of viscosity of NaBr (aqueous) were studied as a function of concentration and temperature. The viscosity data have been interpreted in terms of the extended Jones-Dole equation for the relative viscosity \((\eta/\eta_0)\). The derived values of the viscosity A and B-coefficients were compared with the results...
predicted by the Falkenhagen-Dole theory of electrolyte solution and calculated with the ionic B-coefficient data.

Tsierkezos and Molinou\textsuperscript{66} have measured viscosities of sodium, potassium, ammonium thiocyanates and manganese, cobalt, nickel, cadmium sulfates in water+DMF mixtures at 293 K. The data have been analyzed using Jones-Dole equation and the B-coefficients have been calculated. The results have been discussed in terms of ion-solvent and solvent-solvent interactions.

Roy et al.\textsuperscript{67} have measured densities, viscosities, and ultrasonic speeds of resorcinol in 1,4-dioxane + water mixtures and in pure 1,4-dioxane at 303.15, 313.15, and 323.15 K. Apparent molar volumes and viscosity B-coefficients were obtained from these data supplemented with densities and viscosities, respectively. The limiting apparent molar volumes and exploded slopes derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data have been analyzed by using Jones-Dole equation, and the derived parameters B and A had also been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The structure making/breaking capacities of resorcinol in the studied solvent systems were discussed.

In another study Roy et al.\textsuperscript{68} reported the apparent molar volumes and viscosities of three alkali metal chlorides, LiCl, NaCl and KCl in 40 %w/w THF + water mixtures at 303, 308, 313 and 318 K. The limiting molar volumes \((V^\infty_\phi)\) and slopes \((S^*\phi)\) have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. Structure making/breaking capacities of various electrolytes have been inferred from the sign of \((d^2V^\infty_\phi/dT^2)\), dB/dT and the B-coefficient for all electrolytes studied. The viscosity data were analyzed by using Jones–Dole equation. The results showed that these electrolytes act as structure promoters in this solvent mixture.

Nikam et al.\textsuperscript{69} have measured the viscosities of cesium halides (Cl-, Br- and I-), \((C_4H_{10})_4\)NBr, NaBr and NaBPh\textsubscript{4} in 0, 20, 40, 80 %w/w aqueous acetone at 298.15 K. The viscosity B-coefficients have been calculated by using Jones-Dole equation. The ionic B-coefficients have been detected using the reference electrolytes NaBPh\textsubscript{4}, NaBr and \((C_4H_{10})_4\)NBr.

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Parmar and Chauhan\textsuperscript{70} have 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 + water (4.8, 12 and 16 \%w/w) mixtures. The density data were analyzed by means of Masson's equation. The partial molar volumes ($V''_i$) and slopes ($S_{v*}$) have been interpreted in terms of ion-solvent and ion-ion interactions, respective structure making/breaking capacities of the various electrolytes were inferred from the sign of ($\frac{\partial^2 V''_i}{\partial T^2}$). Both the multivalent electrolytes behaved like the symmetrical tetrabutylammonium salt but not like common electrolyte in PG + water mixtures. The multivalent electrolytes and tetraalkyl salt acted as structure makers/promoters while the common electrolyte acted as structure breaker. The experimental results of viscosity were analyzed using the Jones-Dole equation. The activation parameters of viscous flow have also obtained to throw light on the mechanism of viscous flow.

In another study Parmar and Guleria\textsuperscript{71} have reported relative viscosities for the solutions of oxalic acid and its salts, viz. ammonium oxalate, sodium oxalate and potassium oxalate, at different concentrations in water and in binary aqueous mixtures of THF [5, 10, 15 and 20 \%w/w of THF] at 298.15 K and in water at five different temperatures. The data were evaluated using the Jones-Dole equation and the obtained parameters were interpreted in terms of solute-solute and solute-solvent interactions. The activation parameters of viscous flow were obtained which depicts the mechanism of viscous flow. The oxalic acid and its salts behave as structure breakers in water and in binary aqueous mixtures of THF.

In another study Parmar and Thakur\textsuperscript{72} have measured relative viscosities for the solutions of some divalent transition metal sulfates, viz. MnSO\textsubscript{4}, CoSO\textsubscript{4}, NiSO\textsubscript{4}, CuSO\textsubscript{4}, ZnSO\textsubscript{4}, and MgSO\textsubscript{4} at different concentrations in water and in water + EG binary mixtures at 303.15 K. The data were analyzed using the Jones-Dole equation and the obtained parameters were interpreted in terms of ion-ion and ion-solvent interactions. The activation parameters of viscous flow were obtained which depicts the mechanism of viscous flow. The transition metal sulfates and MgSO\textsubscript{4} act as structure makers/promoters in water and in EG + water binary mixtures.

Huque et al.\textsuperscript{73} have measured viscosity and densities of MgCl\textsubscript{2}, NH\textsubscript{4}Cl, CuCl\textsubscript{2}, and
AlCl₃ in MeOH and water solvents at 303.15, 308.15, and 313.15 K and 1 atm.
pressure. B-coefficients were calculated by using Jones-Dole equation. From the
results, structure making/breaking properties of MgCl₂ and NH₄Cl were observed.
Results also show that both CuCl₂ and AlCl₃ act as structure makers in (MeOH+
water) solvent mixtures.

Zamir and Khan⁷⁴ have measured the relative viscosities of LiBr and reference salt
Bu₄NBPh₄, KCl in binary mixture of DMSO and water at 298 K. B-coefficients were
obtained by using Jones-Dole equation. The B-coefficients of these electrolytes in
DMSO were positive which behave as structure makers while in H₂O and
DMSO+H₂O mixtures, the B-coefficients values were less positive showing weak
structure-making effects. The values of ionic B-coefficients suggests that the Li⁺ ion
is structure-maker while Br⁻ is structure-breaking in H₂O and binary mixture
containing 20% DMSO + 80% water.

The alkyl chain length of ([Rmim][CF₃SO₂]₂N], (R = methyl (m), ethyl (e), butyl (b),
hexyl (C₆), and octyl (C₈)) was varied by Tokuda and coworkers⁷⁵ 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][CF₃SO₂]₂N > [mmim][CF₃SO₂]₂N > [bmim][CF₃SO₂]₂N >
[C₆mim][CF₃SO₂]₂N > [C₈mim][CF₃SO₂]₂N, 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 physicochemical properties. Queimada and coworkers\textsuperscript{76} have measured viscosity and density at atmospheric pressure, in pure and mixed $n$-decane, $n$-eicosane, $n$-docosane, and $n$-tetraicosane from $293.15 \text{ K}$ (or above the melting point) up to $343.15 \text{ K}$. 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 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 \textit{n}-alkanes.

Wankhede and coworkers\textsuperscript{77} have 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 were calculated from the linear dependence of these parameters on the composition of the mixtures.

Jouyban et al.\textsuperscript{78} 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 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 of 1.9 $\pm$ 2.5 \( \% \).

Viscosity ($\eta$), ultrasound speed ($u$) and density ($\rho$) have been measured by Mehra\textsuperscript{79} for pure liquids and their binary mixtures formed from hexadecane with 1-pentanol, 1-hexanol, and 1-heptanol at 298, 308 and 318 K covering the entire mole fraction range of hexadecane. From the experimental data, adiabatic compressibility ($K_a$), intermolecular free length ($L_i$), molar sound speed ($R_m$), acoustic impedance ($Z$), excess adiabatic compressibility ($K'^e$), excess free volume ($V_j^e$), excess viscosity
The excess molar volume \( V^E \), shear viscosity deviation \( \Delta \eta \) and excess Gibbs energy of activation \( \Delta G^E \) have been investigated by Querfelli and Bouanz\(^2\) using density \( \rho \) and shear viscosity \( \eta \) measurements for isobutyric acid +H\(_2\)O mixtures over the entire range of mole fractions at five different temperatures, both near and close to the critical temperature \( 2.055 \text{ K} \leq (T - T_c) \leq 13.055 \text{ K} \). 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 \( \Delta \eta \) due to increased hydrogen bonding interactions and correlation length between unlike molecules in the critical region and to very large differences between the molar volumes of the pure components at low temperatures. The activation parameters \( \Delta H^0 \) and \( \Delta S^0 \) were also

Artigas and coworkers\(^8\) reported the densities and viscosities for the binary mixtures of chlorobenzene, chlorocyclohexane, bromobenzene and bromocyclohexane with 2-methyl-1-propanol over the entire concentration range at 298.15 K and 313.15 K. These values have been used in the determination of the excess volumes \( V^E \) and the viscosity deviations \( \Delta \eta \). All mixtures presented negative values of \( V^E \) 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.

Madhurambal\(^9\) 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 analysed using Jones-Dole equation and Bresler Miller 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 electrolytes were analysed by the application of Bresler Miller equation.

The excess molar volume \( V^E \), shear viscosity deviation \( \Delta \eta \) and excess Gibbs energy of activation \( \Delta G^E \) of viscous flow have 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 fitted to Redlich–Kister relation to estimate the adjustable parameters along with their standard deviations.
calculated which showed that the critical region have an important effect on the volumetric properties.

Jyotsana and Satyanarayana\textsuperscript{83} have 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.

Yang et al.\textsuperscript{84} determined viscosity B-coefficients for the Et$_4$NBr, Pr$_4$NBr, Bu$_4$NBr and Hex$_4$NBr at 298.15 K in solvent mixtures of PC with DMF. Ionic B-coefficients and corresponding activation free energies for Et$_4$N$^+$, Pr$_4$N$^+$, Bu$_4$N$^+$, Hex$_4$N$^+$ 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 ion provided an indirect evidence for the unsolvation of large tetraalkylammonium cations in the organic solvents. Solvation numbers for the ions had also been derived for discussing the interaction of ion with solvents.

Burghate et al.\textsuperscript{85} have measured viscosities and densities of 2-hydroxyl-5-methyl-4-dimethylaminochalcone, 2'-hydroxyl-5'-methyl-4-methoxychalcone and 2'-hydroxyl-5'-chloro-4-methoxy chalcone in 70% p-DO + water mixture at different concentrations at 299 K. The value of B-coefficients, relative viscosity ($\eta_r$) were deduced from viscosity and density data. At different temperatures, thermodynamic parameter enthalpy change ($\Delta H$), entropy change ($\Delta S$) and free energy change ($\Delta G$) have been evaluated. The structure making and structure breaking properties of systems were considered as a measure of solute-solvent interaction.

Sulzner and Lat\textsuperscript{86} reported the viscosities and densities of several alcohol-ethane and vinyl acetate-ethene mixtures with a rolling ball viscometer. The viscosity measurements were performed at temperatures from 298 to 413 K and pressures upto
195 Mpa with an estimated uncertainty of ± 2 %. The appearances of hydrogen bonds forming alcohol association have a notable affect on the viscosity of alcohol-ethane mixtures above an alcohol mole fraction from the Arrhenius law which occured 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. Liau and coworkers\(^8\) have measured densities and viscosities of binary liquid mixtures of butyl acrylate + 1-BuOH and ethyl laurate + 1-BuOH mixtures over the entire concentration range. The densities were measured using a vibrating tube digital densimeter 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-BuOH molecules. Excess molar volumes and viscosity deviations were correlated by the Redlich- Kister type equations.

Nandi and Hazra\(^8\) reported viscosity coefficients of alkali metal bromides (MBr) [where M= Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\) and Cs\(^+\)], Bu\(_4\)NBr and NaBPB\(_4\) in aqueous mixtures of ME. The data were analyzed in terms of extended form of Jones-Dole equation for associated electrolytes. The ionic B\(_v\) values and other single ion parameters were determined using Bu\(_4\)NBPh\(_4\) reference electrolyte assumption. These results indicated structural consequences of intermolecular interactions.

Das and coworkers\(^9\) also reported the viscosities of solutions of Et\(_4\)NCIO\(_4\), Pr\(_4\)NCIO\(_4\) and Bu\(_4\)NCIO\(_4\) in ME + H\(_2\)O mixtures at 298.15, 308.15 and 318.15 K. The data were analyzed by using 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.

Chauhan et al.\(^10\) measured the viscosity of Ph\(_4\)PBPh\(_4\), Bu\(_4\)NBPh\(_4\), Bu\(_4\)NNO\(_3\), 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 obtain Jones-Dole A and B-coefficients. The B-coefficients have been separated to ionic contributions using the data of symmetrical reference electrolyte Ph\(_4\)PBPh\(_4\). The results were interpreted in terms of different behaviour of ions in two solvent mixtures.
In subsequent studies Gill and Cheema\textsuperscript{91} and Gill and Chauhan\textsuperscript{92} 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. coefficients with the solvent composition showed a strong preferential solvation of ions by a specific solvent in these mixtures.

Gill and Singh\textsuperscript{93} have measured the viscosities and molar conductances of \( \text{Bu}_4\text{NBPh}_4 \), \( \text{Bu}_4\text{NClO}_4 \), \( \text{CuClO}_4 \), \( \text{AgClO}_4 \) and \( \text{TiClO}_4 \) in the concentration ranges (30- 425) \( \times 10^{-4} \) and (1-35) \( \times 10^{-4} \) 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 (\( A_n \)) calculated at all the three temperatures using Falkenhagen-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. coefficients were evaluated from the B-coefficients of the electrolytes. 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\textsuperscript{94} measured the viscosities of copper (I) perchlorate tetraacetonitrile and bis (2,9-dimethyl-1,10-phenanthroline) copper (I) perchlorate in AN + water, 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 \([\text{Cu (NEC)}_2]^+\) cations in these solvent mixtures.

Rohman et al.\textsuperscript{95} reported viscosities, electrical conductances, the shear relaxation times and Raman spectra of aqueous and methanolic sodium thiocyanate solutions as functions of concentration (0.0237 \( \leq m \) (mol kg\(^{-1}\)) \( \leq 19.685 \)) and temperature \( (273.15 \leq T(K) \leq 323.15) \). The non-Arrhenius temperature dependence of viscosity, electrical conductance and shear relaxation time was analyzed by using the Vogel-Tammann-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 was
analyzed by using the reported equations. The Raman spectra recorded for the $\nu_{C\cdot N}$ and $\nu_{C\cdot S}$ stretching frequencies shifted to higher frequency regions and revealed the existence of the complex adduct of SCN$^-$ with the solvent molecules. Jauhar and coworkers$^{96}$ measured the relative viscosities of some alkali metal acetates and tetraalkylammonium salts in the concentration range 5-700 x $10^{-4}$ mol dm$^{-3}$ in acetic acid + water mixtures containing 20, 40, 60, 80, 90, 95 and 100 %w/w acetic acid at 298 K. The viscosity data were analyzed by using Jones-Dole equation. The viscosity B-coefficient, an ion-solvent interaction parameter was found to be positive for the electrolytes in all systems. The ionic viscosity B$_+\text{e}$ 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 up to 90 %w/w acetic acid and 80 %w/w 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.

Viscosity data for chlorides and bromides of calcium, strontium and barium in aqueous mixtures of DMF was reported by Sinha and coworkers$^{97}$ 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 Akister$^{98}$ determined the viscosity B-coefficients, intrinsic viscosity ($\eta$) and changes in thermodynamic quantities, such as $\Delta G$, $\Delta H$ and difference in chemical potential ($\Delta \mu_1 - \Delta \mu_2$). 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.

### 1.4 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 non-aqueous and mixed solvents is reported below.
Apelblat have measured sound velocities in aqueous 0.1, 0.5 and 1.0 mol kg\(^{-1}\) LiCl solutions at 1 K temperature intervals from 278.15 to 323.15 K. These velocities served to evaluate the isentropic compressibilities \(K_s\), the isothermal compressibilities \(K_T\) and apparent molar compressibilities.

Sinha and Roy studied densities and viscosities of ammonium acetate, potassium acetate, sodium acetate, and lithium acetate in 10, 20 and 30 %w/w of THF + MeOH binary solvent mixtures at 303.15, 313.15 and 323.15 K. Apparent molar volumes \(V_a\), viscosity B-coefficients and free energy of activation for viscous flow were obtained from these data. The limiting apparent molar volumes \(V_a^0\) and extra plotted slopes derived from the Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. The viscosity data were analyzed by using Jones-Dole equation, and the derived parameters B and A have also been interpreted in terms of ion-solvent and ion-ion interactions. The sound speeds measured at 303.15 K have been used to study the apparent molal isentropic compressibility, intermolecular free length \(L_f\), relative association \(R_a\), relaxation strength \(r'\) and specific acoustic impedance \(Z\) of the solutions.

Gurung and Roy studied densities \((\rho)\), viscosities \((\eta)\) and ultrasonic speeds \((u)\) of different strengths of lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate in varying proportions of ethylene glycol + water mixed solvents at the temperatures 298.13, 308.15, and 318.15 K. The extra plotted values of densities were used to calculate the values of the apparent molar volume. The limiting apparent molar volume and the extra plotted slope have been interpreted in terms of ion-solvent and ion-ion interactions and various acoustic parameters at 298.15 K. The behavior of these parameters suggests strong ion-solvent interactions in these systems. The structure making/breaking capacities of the salts investigated have also been discussed.

Singh and coworkers studied the densities, viscosities and ultrasonic speeds and hence calculate apparent molar volumes, viscosity B-coefficients and adiabatic compressibility’s of ammonium acetate, lithium acetate, sodium acetate and potassium acetate in aqueous mixtures of THF at temperatures 303.15, 313.15 and 323.15 K. The limiting apparent molar volumes \(V_a^0\) and extra plotted slopes obtained from the Masson equation have been interpreted in terms of solute-solvent
and solute-solute interactions respectively. The viscosity data were analyzed by using Jones-Dole equation and the derived parameters B and A have also been interpreted in terms of solute-solvent and solute-solute interactions respectively. The structure making or structure breaking nature of the acetates in the solvent mixtures were studied and discussed on the basis of the B-values and the sign of the second derivative of limiting apparent molar volumes with respect to temperature at constant pressure. The compressibility’s obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent mixtures around the ammonium and metal ions.

Dagade and coworkers\textsuperscript{103} studied sound velocities of 18-crown-6 (18C6) in dilute aqueous as well as in dilute CCl\textsubscript{4} solutions at 298.15 K and these data were combined with density and specific heat data to yield isentropic and isothermal compressibility properties in solutions. The compressibility data were further used to obtain apparent molar compressibility values of 18C6 in solutions as well as the parameter energy volume coefficient (\(\delta U/\delta V\))\textsubscript{T} in both solvent media. The calculation of hydration number in aqueous solution was made by following the method developed by Shiio and co-workers. The hydration number for 18C6 was found to be approximately 2. These observations have been explained on the basis of occupation of crown cavity by four water molecules, two of them (bridged) were firmly held while the other two are exchangeable. The corresponding studies in CCl\textsubscript{4} solution provide further information about transfer compressibility of 18C6 molecules and the effect due to conformational status of 18C6 as well as the solvent effect. It was noted that the geometrical relaxational properties of Ci and Cs conformations contributes largely towards the isothermal compressibility behavior exhibited in CCl\textsubscript{4} solutions.

Kannappan and Vinayagam\textsuperscript{104} studied ultrasonic velocities (u) and densities (\(\rho\)) of aqueous and DMSO solutions of manganous (II) sulfate, cobalt (II) chloride, nickel (II) sulfate, ferrous (II) sulfate, copper (II) sulfate, zinc (II) sulfate, lanthanum (III) nitrate, cerium (IV) nitrate, uranyl (IV) nitrate and thorium (IV) nitrate in a wide range of concentrations at 303 K. Acoustical parameters, such as, adiabatic compressibility (\(\beta\)), free length (\(L_f\)) and solvation number (\(S_n\)) were computed to assess the ion-solvent interaction in these solutions. It was found that the ion-solvent interactions depend on concentration, ionic size and nature of metal ion. The
transition and inner transition metal ions behave as structure breaker for the associated clusters of water molecules, especially in dilute solution, as evidenced from the trend in the solvation number with molarity. It was also found that the strength of ion-dipole interaction in aqueous solution of the metal ion was also dependent on concentration.

Choudhury and Roy\textsuperscript{105} studied the densities, viscosities and ultrasonic speeds of some tetraalkyl and monovalent electrolytes, such as tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, lithium bromide, sodium bromide and ammonium bromide in MeOH at 303, 308, 313, 318 and 323 K. The limiting apparent molar volumes ($V_\Phi$) and slopes ($S_v$), supplemented with density data have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed by using Jones-Dole equation, and the derived parameters B and A have also been interpreted in terms of ion-solvent and ion-ion interactions. The results show that these electrolytes have structure-making capacities in this solvent. The compressibility data supplemented with the ultrasonic speeds explain the electrostriction of the solvent molecules around the positive ions.

Sarkar et al.\textsuperscript{106} studied the densities, viscosities and ultrasonic velocities of some minerals salts, viz. ammonium nitrate ($\text{NH}_4\text{NO}_3$), potassium nitrate ($\text{KNO}_3$), calcium nitrate ($\text{Ca(NO}_3)_2$) and magnesium nitrate ($\text{Mg(NO}_3)_2$) in 10 \%w/w THF + water mixture at 303, 308, 313, 318 and 323 K. Apparent molar volumes ($V_\Phi$), viscosity B-coefficient and adiabatic compressibility ($\beta$) of these electrolytes were obtained from these data supplemented with their densities, viscosities and ultrasonic velocities respectively. The limiting apparent molar volumes ($V_\Phi$) and experimental slopes ($S_v$) derived from Masson equation and the obtained parameters have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The viscosity data were evaluated by using Jones-Dole equation. The results show that all the electrolytes have structure-making capacities in this solvent mixture. The compressibility data also indicate the electrostriction of the solvent molecules around the metal ions.

Kushare et al.\textsuperscript{107} have measured the speed of sound and density in binary solutions of MeOH, EtOH, n-PrOH, n-BuOH, AN, DMF, THF and 1,4-dioxane as solvents and...
water as the solute in the concentration range of 0.02 mol kg$^{-1}$ - 1 mol kg$^{-1}$ at 298.15 K. The data were used to obtain the isentropic compressibility of solution. The apparent molar volume and compressibility of water at different concentrations were evaluated. The data of limiting volume and compressibility and their concentration variation were examined to study the effect due to water-solvent and water-water interactions. It was observed that there is loss of volume and compressibility of liquid water molecules in transferring them from the pure liquid state to a non-aqueous solvent. An attempt was made to explain the large negative value of limiting compressibility in alcohols due to hydrogen bonding characteristics of water and alcohol and the effect of the presence of non-polar groups. The possibilities of the presence of water-centered complexes or participation of water in a chain like structure along with pressure effects are examined on the basis of concentration variation of the derived properties.

Ali et al.\textsuperscript{108} measured the densities and ultrasonic speeds in binary mixtures of THF with n-heptane, n-octane and n-decane at 308.15K. From these experimental data, the values of isentropic compressibility ($K_s$), intermolecular free length ($L_d$), relative association ($R_A$), acoustic impedance ($Z$), isothermal compressibility ($\beta_T$), thermal expansion coefficient ($\alpha$), deviations in ultrasonic speed ($\Delta u$), excess free length ($L'_f$), excess volume ($V'_E$), excess acoustic impedance ($Z'_E$), apparent molar isentropic compressibility ($K_{s1}$), and partial molar volume $V'_{m(3)}$ 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 mixtures has been examined.

The ultrasonic velocities ($u$) and densities ($\rho$) of pure benzene, n-BuOH, iso-BuOH, sec-BuOH and tert-BuOH and their binary mixtures with benzene as a common component were also measured by Ali et al.\textsuperscript{109} 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 ($L_d$), relative association ($R_A$), acoustic impedance ($Z$), molar sound speed ($R_m$), deviations in isentropic
compressibility ($\Delta K_s$), excess intermolecular free length ($L^E$), deviations in ultrasonic speed ($\Delta u$), excess acoustic impedance ($Z^E$), apparent molar compressibilities ($K_{\phi,1}$) and ($K_{\phi,2}$), and partial molar compressibilities ($K'_{\phi,1}$) and ($K'_{\phi,2}$) of benzene in alcohols and alcohols in benzene, respectively, at infinite dilution were calculated. The variation of these parameters with composition indicated the presence of weak interactions between the component molecules and this interaction decrease in the order: n-BuOH > iso-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 et al. have measured densities ($\rho$), ultrasonic speeds ($u$), viscosities ($\eta$) and refractive indexes ($n$) of pure benzene, benzyl alcohol, BN, benzoyl chloride, chlorobenzene 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 ($K_{\phi,2}$) 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.

Nath has carried out measurements of speeds of sound ($u$) in binary mixtures of $C_6H_5OCH_3$ with $CH_2Cl_2$, $CH_2ClCH_2Cl$, $CHCl_2CHCl_2$ and $C_6H_12$ at 303.15 K. The densities of present mixtures were calculated at 303.15 K using available data on excess molar volumes, whereas the densities of the pure component liquids have measured at 303.15 K with a pycnometer. The values of $u$ were used to calculate the apparent excess speeds of sound ($\Delta u$) and the isentropic compressibilities ($K_s$) for these mixtures. The excess isentropic compressibilities ($K_s^E$) were calculated from the
values of $K_s$. The $K^{e}_s$ have found to be slightly positive for \( \{ x C_6H_5OCH_3 + (1-x) CH_2ClCH_2Cl \} \) and \( \{ x C_6H_5OCH_3 + (1-x) CHCl_2CHCl_2 \} \). For \( \{ x C_6H_5OCH_3 + (1-x) CH_2Cl_2 \} \), $K^{e}_s$ is very slightly positive at low mole fractions of $C_6H_5OCH_3$. Values of $K^{e}_s$ for the various mixtures were discussed in the light of intermolecular interactions between the components.

In recent study Nath\(^{112}\) have measured speeds of sound ($u$) in binary liquid mixtures of $n-C_7H_5OH$ and $n-C_8H_{12}$ or $n-C_6H_{14}$ or $n-C_7H_{16}$ or $n-C_8H_{18}$ at 303.15 K and in binary liquid mixtures of $n-C_7H_{15}OH$ and 2,2,4-(CH\(_3\))\(_3\)C\(_5\)H\(_9\) at 293.15 and 303.15 K. The values of $u$ were used to calculate the apparent excess speeds of sound ($\Delta u$) and the isentropic compressibilities $K_s$ for these mixtures. The excess isentropic compressibilities ($K^{e}_s$) were calculated from the values of $K_s$. The $K^{e}_s$ value was negative throughout the entire composition range for \( \{ x n-C_7H_{15}OH + (1-x) n-C_8H_{12} \} \), \( \{ x n-C_7H_{15}OH + (1-x) n-C_8H_{14} \} \), \( \{ x n-C_7H_{15}OH + (1-x) n-C_7H_{16} \} \), and \( \{ x n-C_7H_{15}OH + (1-x) 2,2,4-(CH\(_3\))\(_3\)C\(_5\)H\(_9\) \}. For \( \{ x n-C_7H_{15}OH + (1-x) n-C_8H_{18} \} \), the $K^{e}_s$ was positive at very low mole fractions of $n-C_7H_{15}OH$, and negative at other mole fractions.

Pal and coworkers\(^{113}\) have measured speeds of sound ($u$) at 298.15 K and atmospheric pressure as a function of composition for the three binary liquid mixtures ethyl acetate + ethylene glycol di-methyl ether (EGDME), ethyl acetate + diethylene glycol di-methyl ether (Di-EG-DME) and ethyl acetate + triethylene glycol di-methyl ether (Tri-EGDME) using a NUSONIC velocimeter based on the ring-around technique. Their values have been combined with those of the excess molar volumes converted to densities to give estimates of the product $K^{e}_{s,m}$ of the molar volumes and isentropic compressibility ($K_s$), and the excess quantity $K^{e}_{s,m}$. The $K^{e}_{s,m}$ values were negative for all mixtures. Measurements have been carried out in order to assess the effects of inserting oxyethylene groups with a common alkyl group in polyether. The deviations of the speeds of sound ($\Delta u$) 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 behavior of $\Delta u$, $\delta u$, and $K^{e}_{s,m}$ with composition and the number of -OC\(_2\)H\(_5\) units of the ether molecule was discussed. Also, the theoretical values of speeds of sound were 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\textsuperscript{14} reported the excess molar volume and ultrasonic speed in dipropylene glycol monomethyl ether + butylamine, dibutylamine and tributylamine across the entire composition range at 298.15 K and atmospheric pressure. The ultrasonic speed values were 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 $K_{s,m}^\circ$. The excess volumes were negative over the entire range of composition for all mixtures with the exception of tributylamine. The $K_{s,m}^\circ$ values were negative for all mixtures. The deviation of speed of sound ($\Delta u$) from their ideal value ($u_{id}$) in ideal mixture was also calculated for all measured mole fractions.

Hazra and coworkers\textsuperscript{15,16} have measured the ultrasonic velocities of Pr$_4$NBr, Bu$_4$NBr, Pent$_4$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 ($K_v^\alpha$) of these electrolytes were derived from these data supplemented with their densities. The limiting apparent molar isentropic compressibilities ($K_v^\gamma$) were obtained by extrapolation from the plot of $K_4$ versus the square root of the molality. The ($K_v^\gamma$) values of the electrolytes were split into approximate limiting ionic compressibilities ($K_1^\gamma$) on the basis of the assumption that $K_v^\gamma$ (Br$^-$) = 0. In case of tetrafluoroborate salts the $K_v^\gamma$ values of the electrolytes were split into approximate limiting ionic compressibilities ($K_1^\gamma$) on the basis of the assumption that $K_1^\gamma$ (BF$_4^-$) = 0.

Resa and coworkers\textsuperscript{117} 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 have 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 computed 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.

Ultrasonic velocity and density at different concentrations of N-bromosuccinimide (NBS) in water and in various compositions (%v/v) of water + p-DO and N-chlorosuccinimide (NCS) in water and in various compositions (%v/v) of water + MeOH/ p-DO were studied by Bhat and Varaprasad\textsuperscript{118} 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 for 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.

Blanco and Vargas\textsuperscript{119} reported the apparent molar volumes ($V_\text{app}$) of Me$_4$NBr, Et$_4$NBr, Bu$_4$NBr, BuEt$_3$NBr, Bu$_2$Et$_2$NBr, and Bu$_3$EtNBr at 298.15 K in the concentration range from 0.01 to 0.04 mol kg$^{-1}$. The concentration dependence of $V_\text{app}$ was given using the Redlich and Meyer relation. The apparent molar volume at infinite dilution ($V_{\text{app}}^\infty$) and the empirical constant ($B_\text{app}$) were calculated. The contribution of CH$_2$ group has been obtained by the additivity rule. The results were interpreted in terms of solute-solvent interactions.

Arce and coworkers\textsuperscript{120} have measured densities, refractive indices, speeds of sound and dynamic viscosities of [Omim][BF$_4$], the room temperature ionic liquid 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 compressibility and dynamic viscosity changes of mixing were calculated and were satisfactorily correlated by the Redlich-Kister polynomial.

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 have measured by Chandrashekhar and coworkers\textsuperscript{121} 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 ($K_x^E$). The
$K_x^E$ 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 Methyl acrylate (MA) (1) + 1-
PrOH (2) or 1- BuOH (2) + n - hexane (3), n - heptane (3), cyclohexane (3), benzene
(3) and toluene (3) have measured at 308.15 K by Bahadur and Sastry. The excess
volumes ($V^E$) and excess isentropic compressibilities ($K_x^E$) were 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 $K_x^E$ data of ternary mixtures revealed that in MA (1) + 1-alcohals (2) + n-
hexane (3), n-heptane (3), and cyclohexane (3), structure disruptions are more
predominant; while in MA (1) + 1-alcohals (2) + benzene (3) or toluene (3) mixtures,
the weak but specific structure making interactions dominated. A perusal of
deviations between the experimental and calculated $V^E$ and $K_x^E$ results showed that
the predictive expressions gave only a rough estimation of the functions for the ten
studied mixtures.

Mehta and Chauhan 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 ($K_x^E$) and apparent molar isentropic compressibilities ($K_s^A$) were
estimated from these measurements. The $K_x^E$ values were negative for all the systems
over the complete mole-fraction range except Pyridine-decanol for which small
positive values were obtained. The standard partial molar isentropic compressibilities
($K_s^\alpha$) 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 reported excess molar volumes ($V_w^E$) and excess
isentropic compressibilities ($K_x^E$) of binary mixtures of N,N-dimethyl formamide

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(DMF) with AN and benzene. The excess isothermal compressibilities \( K_{tj}^{E} \) and excess isochoric molar heat capacities \( C_{IV}^{E} \) of \( [x \text{ AN} + (1-x) \text{ C}_6\text{H}_6] \) changed sign from negative to positive with increase of \( x \); \( V_{m}^{E} \) of \( [x \text{ C}_6\text{H}_6 + (1-x) \text{ HCON(CH}_3\text{)}_2] \) and \( V_{m}^{E} \) of \( [x \text{ AN} + (1-x) \text{ HCON(CH}_3\text{)}_2] \) are negative over the whole composition range. \( K_{tj}^{E} \) and \( K_{tj}^{E} \) of the mixtures were in similar trend to the corresponding \( V_{m}^{E} \). The \( C_{IV}^{E} \) of \( [x \text{ AN} + (1-x) \text{ C}_6\text{H}_6] \) changes sign from positive to negative with increase of \( x \), and \( C_{IV}^{E} \) 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\(^{125}\) reported the ultrasonic velocity, density and viscosity at 303, 308 and 313 K in 2-BuOH + cyclohexane + toluene mixture. 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 components of the mixtures. The existence of weak interactions was confirmed by the observed excess values.

Soto et al.\(^{126}\) 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 solution 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 isentropic compressibility imply that the water molecules around the glycine molecules were less compressible than the water molecules in the bulk solution. These effects were attributed to the doubly charged behavior of glycine and to the formation of physically bonded ion-pairs between the charged groups of glycine, sodium and chloride ions.

Ramana et al.\(^{127}\) 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 \( (T_{SM}) \). 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 ± 0.003 %. The structural contribution to the shift in $T_w$ of pure water due to the addition of mixed electrolytes, $\Delta T_{str}$ was found to be negative and increasing with concentration of the mixed electrolytes. At any given concentration $\Delta T_{str}$ of $(\text{NaCl} + \text{NaBr}) > (\text{NaCl} + \text{NaI}) > (\text{NaBr} + \text{NaI})$. This indicated that the structure promoting nature of Na$^+$ was balanced and subdued by the presence of halide ions in the order $(\text{Br}^- + \text{I}^-) > (\text{Cl}^- + \text{I}^-) > (\text{Cl}^- + \text{Br}^-)$, consistent with the behavior of halide ions in disrupting the hydrogen bonded structure of water, which is in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. The results were also explained as due to the reduction in the structure breaking efficiency of $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ in the presence of Na$^+$ in aqueous mixed electrolyte solutions.

Gill and coworkers 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 molal compressibilities ($K_a^\gamma$) of various electrolytes were evaluated. The limiting apparent molal compressibilities ($K_a^\gamma$) for all electrolytes were obtained by extrapolation of the plots of $K_a^\gamma$ versus square root of molality ($m^{1/2}$) and split into ionic compressibilities ($K_a^\gamma$). 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. ($K_a^\gamma$)$_{\text{Na}^+}$ was positive in BN except for Et$_4$N$^+$ and was negative in AN except for Bu$_4$N$^+$, 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 reported the ultrasonic velocities ($u$) and densities ($\rho$) of CuClO$_4$.4BN, Bu$_4$NBPh$_4$, Bu$_4$NCIO$_4$ 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 have also measured ultrasonic velocity ($u$) and densities ($\rho$) of Bu$_4$NBPh$_4$, Bu$_4$NCIO$_4$, 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 molal compressibilities ($K_a^\gamma$) of various electrolytes have been evaluated. The limiting
apparent molal compressibilities \( (K^\phi) \) for all electrolytes were obtained by extrapolation of the plots of apparent molal compressibilities \( (K^\phi) \) versus square root of molality \( (m^{1/2}) \) and split into ionic compressibilities \( (K''^\phi) \). The variation of \( (K^\phi) \) 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 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 \( (K''^\phi) \) values which showed strong solvation of Na\(^+\) in AN + DMF mixtures over the entire solvent composition range and the solvation of Na\(^+\) by DMF was relatively 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.

Babu et al.\(^{132}\) measured the ultrasonic velocities and densities for water + i-PrOH at 303.15 K. From these data, experimental compressibilities were calculated. Ideal compressibilities and excess compressibilities were estimated by three recently developed expressions. The results have been analyzed on the basis of the variations in ultrasonic velocities, compressibilities and excess compressibilities. Water - i-PrOH clathrate like structures were observed at lower concentrations of alcohol in water. Water pyridine complexes have been observed at lower concentration of pyridine in water. The presence of weakly bonded alcohol-pyridine structures were noticed in the binary mixture PY + i-PrOH.

Ultrasonic velocities and densities of some electrolytes namely Bu\(_4\)NI, Pr\(_4\)NI, Et\(_4\)NI, KI, NaI and LiNO\(_3\) have measured in cyclobenzene + MeOH mixtures at 2 MHz at 298 K by Syal and coworkers\(^{133}\). Various derived parameters such as acoustical impedance \( (Z) \), adiabatic compressibility \( (\beta) \), apparent molal compressibility \( (K^\phi) \), relative association \( (R_A) \), intermolecular free length \( (L_0) \) and solvation number \( (S_n) \) were calculated. The results were discussed in terms of nature of electrolyte and solvent mixtures.
Marcus\textsuperscript{134} 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 to various extents. Various solvation models were used to estimate the volumes of the salts by calculation of the electrostriction around the ions. Only the taking into account of the solvation shell yielded calculated results of the standard partial molar volumes of the salts in agreement with the experimental data.

Singh and Vibha\textsuperscript{135} have 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_2O + co-solvent (aprotic (p - DO), dipolar aprotic (DMF) and protic (formamide, FD))] media at 308.15 K and the same have been analyzed to evaluate their limiting $V_\phi^{\infty}$ values. These values were coupled with the corresponding limiting values in W to compute $\Delta V_\phi^{\infty}$ data which suggested that for a particular AcH or NaAc, the $\Delta V_\phi^{\infty}$ values generally varied as $FD < DMF < p$-DO as required by the Gutmann's conor and the electron pair acceptance indexes of FD, DMF and p - DO co-solvents in the present mixed solvent media. The variation of $\Delta V_\phi^{\infty}$ (AcH or NaAc) within the same mixed solvent media suggested that while the chemical effects of protons of acids on the co-solvent have a dominant influence on their $\Delta V_\phi^{\infty}$ data, the electrostriction effects of CH\textsubscript{3}COO', HCOO' and CF on H\textsubscript{2}O played an important role in determining the values of $\Delta V_\phi^{\infty}$ of their sodium salts.

Murthy and coworkers\textsuperscript{136} calculated adiabatic compressibilities from ultrasonic velocity and density measurements in solutions of DMF. Apparent molar compressibilities were calculated and $K_\phi^{\infty}$ values were obtained by fitting $K_\phi$ against the electrolyte concentration $C^{1/2}$ by the method of least squares. Acoustic Impedence, molar sound velocity, molar adiabatic compressibility and solvation numbers were calculated. The results were discussed in terms of ion-solvent interactions.
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 and intermolecular and inter ionic 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.

Irangu and Jordan\textsuperscript{137} studied the Cu\textsuperscript{63} NMR line widths in Cu (I)-AN solutions. The variations with concentration of Cu (I) salts (trifluoromethanesulfonate and perchlorate), added salts, water, Cl\textsuperscript{-} ion and temperature have been studied. A quantitative analysis showed 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 co-ordination number or less symmetrical arrangement of AN ligands than in the normal tetrahedral [Cu(AN)]\textsuperscript{+} ion. Solvent viscosity and ion pairing with triflate also are identified as factors having the expected effects on line widths.

Shamsipur and coworkers\textsuperscript{138} 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 %w/w DMSO-AN and 75-25 %w/w 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.

Bich and coworkers measured ¹H 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 + Cyclohexane, tert-BuOH + cyclohexane, and n-BuOH + PY at 303, 313 and 323 K. In addition the molar excess enthalpy HE of n-BuOH + PY was 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 HE for n-BuOH + Cyclohexane accounting for self association of n-BuOH via hydrogen bonding. The mixture 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 HE 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 made the ⁶³Cu and ¹⁰⁹Ag 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 solvent composition. In another study Gill and coworkers carried out the ⁶³Cu NMR and viscosity studies of 0.064 M CuClO₄ 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 ⁶³Cu NMR signal in these mixed solvents were measured relative to the ⁶³Cu NMR signal in 0.064 M CuClO₄ 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$^+$ 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 made $^{63}$Cu NMR, density and viscosity studies of copper (I) perchlorate solutions at 298 K in binary mixtures of AN with D$_2$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 $^{63}$Cu NMR signal were measured relative to 0.064 M CuClO$_4$ 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 and 3-methoxypropionitrile and ethylbenzene have relatively weak 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. Hasan and Shamsipur 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. Apperley and coworkers reported that 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]hexacosa-4,6,13,15,21,23 - hexaene showed satellite peaks in $^1$H NMR solution spectra throughout the accessible (233 to 343 K) fluid range of solvents used, indicating kinetic inertness toward 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 $^{65}$Cu, $^{64}$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 $^{113}$Cd resonance in the CP MAS NMR spectrum.

Blixt and coworkers$^{145}$ 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 $^{205}$Tl, $^{12}$C and $^{14}$N NMR and potentiometer. The existence of Tl (III) complexes Tl(CN)$_{3-n}$ ($n = 1$-4) was established. The chemical shift and spin-spin coupling constants were also measured.

Marcus$^{146}$ investigated the preferential solvation of Ag$^+$, Cu$^+$ and Cu$^{2+}$ ions in the mixed solvent water + 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 water component.

An exhaustive review article on the ability of vibrational spectroscopy (IR and Raman) to probe the different interactions which take place in a solution was given by Alia$^{147}$.

Istvan and Julius$^{148}$ investigated kinetics of ligands exchange in the Tl (III) Br system in aqueous 2M HClO$_4$ solutions by measuring $^{205}$Tl NMR line widths at 298.15 K. The result were discussed and compared to the corresponding data for the Tl (III) chloride system.

Gill et al.$^{49}$ studied copper (I) solvation in mixed solvent systems containing AN and co-solvents water, MeOH, DMF, TMPA, TMP and PY by using $^{63}$Cu, $^{65}$Cu and $^{31}$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$^+$ ion by the co-solvent. From the linewidths of the $^{63}$Cu and $^{65}$Cu signals the rotational correlation times $\tau_R$ of the solvates Cu(AN)$_4$$^+$ and Cu(PY)$_4$$^+$ have determined.

An exhaustive review article on $^{203}$Tl and $^{205}$Tl NMR of inorganic and organometallic Tl compounds in solid state as well as in solution has given by Hinton and co-workers$^{150}$. This review article compiled the work from 318 references on Tl NMR.

Kitigawa and Munakta$^{151}$ synthesized four coordinated Cu (I) complexes [CuL$_4$]ClO$_4$ (L = alkyl nitriles, 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 $[\text{CuL}_4]\text{ClO}_4$. The $^{63}$Cu chemical shift was remarkably affected by the $\pi$-acceptor capability. The downfield shift occurred in the following order, $\text{RCN} < \text{Py} < \text{RNC} < \text{ArNC}$. This order agreed fairly well with that of the $\pi$-acceptor capability obtained from IR studies. This trend also holds 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 and co-workers$^{152}$ 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.

Oschsenbein and Schlaefer$^{153}$ have reported $^{63}$Cu NMR spectra of Cu(AN)$_4$X ($X = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$) in solution at different temperatures and concentrations. The influence of temperature on linewidth and chemical shift indicated an equilibrium of Cu(AN)$_4^+$ 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$^{154}$ from NMR study of AgNC$_3^+$, AgCl and AgBr in water + EA mixtures reported preferential solvation of Ag$^+$ by EA.

1.6 Aim and scope of present work

The survey of literature reveals that a large number of studies$^{1-8}$ on ion-association and solvation behaviour have been already made in literature in which alkali metal and tetraalkylammonium salts have been frequently employed as 1:1 electrolytes, which are usually solvated by purely electrostatic ion-dipole interactions on the other hand studies on highly ionic copper (I) and silver (I) salts are very rare.

Such copper and silver ions are found to be solvated by special type of $d\pi$-$p\pi$ type interactions$^{2-5}$ of Cu$^+$ with -C≡N group of nitrile solvents. Though some solvation studies of Cu (I) salts have been attempted in the recent years. Yet these are limited only to acetonitrile, benzonitrile, and their binary mixtures with some other organic solvents like acetone, methanol, benzene, pyridine etc. No attempt, however,
has been made to study solvation of copper (I) salts in mixtures of acetonitrile (AN) and N,N-Dimethylacetamide (DMA) in which both the solvents have tendency to interact with the copper (I) ion. Both AN and DMA are dipolar, aprotic solvents with almost similar dielectric constant [AN (\(\epsilon=36.0\)) and DMA (\(\epsilon=37.8\))] but different Gutman numbers [AN (14.1) and DMA (27.8)]. Gutman number is \(-ve\) enthalpy value (i.e. the energy released when particular solvent gets neutralized by common Lewis acid SbCl₅). Binary mixtures of AN and DMA are therefore expected to provide interesting results for the ion-association and solvation behaviour of Cu (I) and Ag (I) salts.

In the present work attempt has been made to study the solvation behaviour of some tetrabutylammonium, copper (I) and silver (I) salts in AN + DMA mixtures. Tetrabutylammonium ions are symmetrical with large ionic radii and hence small surface charge densities. Their solvation mechanism in organic solvents is different from the solvation mechanism of inorganic ions. This is because such complex ions cannot form donor acceptor bonds with solvent molecules and one expects only extremely weak electrostatic interactions in their electrolytic solutions. Tetrabutylammonium ions have shown some hydrophobic interactions in AN. With this intention, in the present work, we have carried out conductance, viscosity, ultrasonic velocity, density and NMR measurements of some tetrabutylammonium, copper (I) and silver (I) salts in AN + DMA mixtures at 298 K.

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1.7 References
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