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THE STUDY OF IONIC LIQUID BEHAVIOUR AT SOLID INTERFACES

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INTRODUCTION

A typical salt in solid form with symmetric cation and anion is known as an ionic solid. Chemical combinations of metallic and non-metallic elements make up the majority of ionic solids. "Salt" is a wide chemical term that refers to ionic compounds (ionic solids) formed when an acid and a base combine. Because of the strong interactions between the particles, ionic solids and salts are rigid, brittle crystals with a high melting point. Ionic solids do not conduct electricity in their solid form because there are no free moving particles. Ionic solids conduct electricity only in a molten state or in a solution with free moving particles. Ionic salts are hard yet brittle, and their melting and boiling temperatures are high. The peculiar characteristics of ionic solids indicate strong interactions between the particles, and moving them all relative to one

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other requires a lot of energy. The three-dimensional lattice of an ionic solid is kept together by electrostatic forces of attraction between positive and negative ions. Ionic bonding is the name for this electrostatic force. Salt is now a major monetary corollary, with thousands of applications ranging from accumulating to senescing and preserving food. Sodium chloride (NaCl) is found in large subversive deposits on every continent as the mineral halide, often called as rock salt. Salts may be used for a variety of purposes, including Salt became an important part of business transactions and was often used as a kind of payment or exchange.

Ionic solids are utilised as phase transfer catalysts, surface-active agents, and other similar applications. Ionic solids are used as an active component in conditioners, antistatic agents, detergent sanitizers, textile and paper softeners, and other industrial applications. But 4NI has recently emerged as a potential alternative as a catalyst for functionalization of C–H bonds [2] due to its cheap cost and low toxicity [1]. It is used as antimicrobials, algaecide, slimicidal agents, disinfection agents, and sanitizers in the medical sector.

Ionic Liquids (ILs), a novel class of materials that exist as a salt in a liquid form, have sparked a lot of interest in scientific and engineering research. ILs are a type of materials that are completely made up of ions and are liquid at temperatures below 100°C. Salts having a low melting point, usually below 373K, are often referred to as low melting point salts. [3] The simple combinatory study indicates that 1018 ILs may possibly be produced. These collections provide a wide range of events in the couture of ILs that are ideal for practical equipment. The performance of ILs and their characteristics must be considered for any practical significance.

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e call ionic liquids that become liquid at ambient temperature "room temperature ionic liquids" (RTILs). The characteristics of RTILs must be known in order to choose a suitable liquid for each of their commercial applications. The term'solution' is most often used when a small amount of solid, liquid, or gaseous substances disperse to a definite limit in a liquid or solid material (which may be pure or a mixture itself), solvent. An ionic solid is a solid-state conformist salt with symmetric cation and anion. An ionic liquid (IL) on the other hand is a salt in the liquid state or phase with symmetric anion and asymmetric cation. Ionic Liquids (ILs) is a general term for a group of resources that are entirely made up of ions and turn liquid at temperatures below 100°C. (See Figure 1). Ils are a revolutionary chemical innovation with a significant potential to contribute to the greenness of chemical processes and the development of new appliances in industries such as pharmaceuticals. Green chemistry plays a critical role in long-term improvement by decreasing and avoiding effluent at its source, as well as lowering vulnerability and maximising the efficacy of chemical processes.

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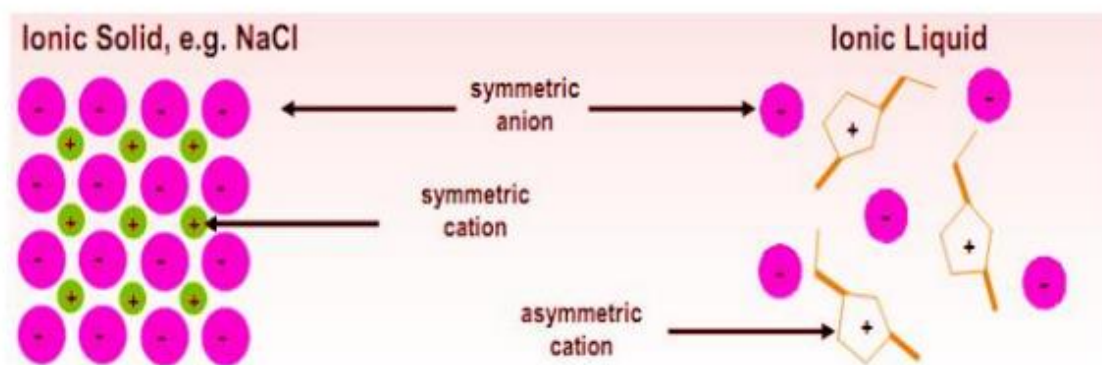
Figure 1: Basic structural differences between ionic solid and ionic liquid

HOST−GUEST INCLUSION CHEMISTRY

The most significant advancement in supramolecular chemistry came when Lehn, Cram, and Pedersen were awarded the Nobel Prize in chemistry in 1987 for their work on hostguest systems. Complexes made up of two or more molecules that are kept together in unique structural relationships by non-covalent interactions are known as host-guest chemistry. Yet, as a result of its novelty, the concept of supramolecular chemistry has piqued the interest of chemists, biologists, and material scientists, who use noncovalent interactions such as hydrogen-bonding communication, stacking interface, electrostatic interface, van der Waals force, and hydrophobic/hydrophilic attraction [6–10]. Efforts to develop many supramolecular structures and examine their applications in catalysis, electrical devices, functional materials, nanomedicine, sensors, and other fields have been remunerated for decades [710]. Because of the reversibility and adaptability of hostguest communication, supramolecular systems (Figure 2) have been evolved into a variety of morphologies for a variety of functions in biological applications.

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Figure 2: Schematic Representation of Host-Guest Inclusion Complex

Formation

In an emblematic host−guest inclusion complex, a host molecule affords a cavity to encapsulate a guest molecule through noncovalent communications. Due to having a variety of noncovalent interfaces in host-guest complexation, host−guest interaction based on macrocyclic molecules is an extremely imperative incident that has been widely explored. Two or more chemical moieties can be incorporated together during such host−guest inclusion, in a facile and reversible manner which provides immense potential for the edifice of new-fangled supramolecular structures.

Major uses of host-guest chemistry are as follows

Pharmaceutical industry: Treatment of inflammation or throat infection (with iodine), coronary dilatation (with nitro-glycerine), anti-ulcerate (with benexate), vectors for vitamins or hormones, decrease of side-effects and amplify in efficiency of anticancer drugs.

Cosmetics & Hygiene: Long-lasting perfume release deodoriser (with peppermint oil, i.e.), to remove dryness wrinkles (with seaweed compounds, vitamin A & E), ant cellulitis compound, shampoo industry, teeth cleaning, anti-plaque compound, antibacterial in refrigerators.

Food industry: Emulsion stabiliser, taste-masking, long-lasting flavouring, removal of cholesterol from milk, butter, eggs etc.

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Paint industry: Increase in compatibility of paint ingredients, enhance in stability of the paint, increase in the range of colours and in the quality of dyes. Environmental protection: Reduction in oxidiser requirements in paper production, environmentally friendly oil-spill clean-up, treatment of tree-wounds (with auxin), mobilisation of toxins without leaving toxic residues behind (innovative technique), removal or detoxification of dissipate stuff, especially aromatic toxins, employ in agriculture for increasing the steadiness and the competence of herbicides, insecticides, repellents.

Chemical and biochemical appliances: Reaction catalyst in glue, apply in chromatography (separation of stereoisomers), enhance in speed of diagnostic test reaction. In my present research study ionic solids and ionic liquids are taken as guest molecules and the major host molecules such as CDs and CBs are taken owing to their extensive appliances in the biomedical field.

Objective The significance and exploits of chemical electrolytes (ionic solids and ionic liquids) in non-aqueous pure and mixed solvents have been abridged by very legendary scientists [11-23]. In recent times solute-solute/ion-ion and solute-solvent/ion-solvent communications have been focus of extensive attention.

The main aim of my present research work is to discuss and explain various interactions of some electrolytes especially ionic solids and ionic liquids in different industrially important solvent media through various physicochemical techniques. Elementary exploration on non-aqueous electrolyte solutions has catalysed their broad procedural appliance in a lot of grounds. Due to their elevated suppleness based on the variety of various solvents, additives and electrolytes with extensively varying properties, non-aqueous electrolyte solutions are essentially challenging with other ionic

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conductors. Prevalent achievement of non-aqueous electrolytic solutions are high energy primary and secondary batteries, photoelectrochemical cells, electro machining, etching, polishing, electrosynthesis, wet double layer capacitors, electro-deposition and electroplating.

IONIC LIQUIDS

Ionic liquids (ILs) are a salt in the liquid state/phase. In some contexts, the term has been classified to Liquids (ILs) are liquid salts that consist of combinations of organic-ionic species existing in liquid state, whose melting point is below some capricious temperature, for instance 100°C (212°F). Generally, Ionic organic-organic or organic-inorganic. cation or anions (Figure 2).
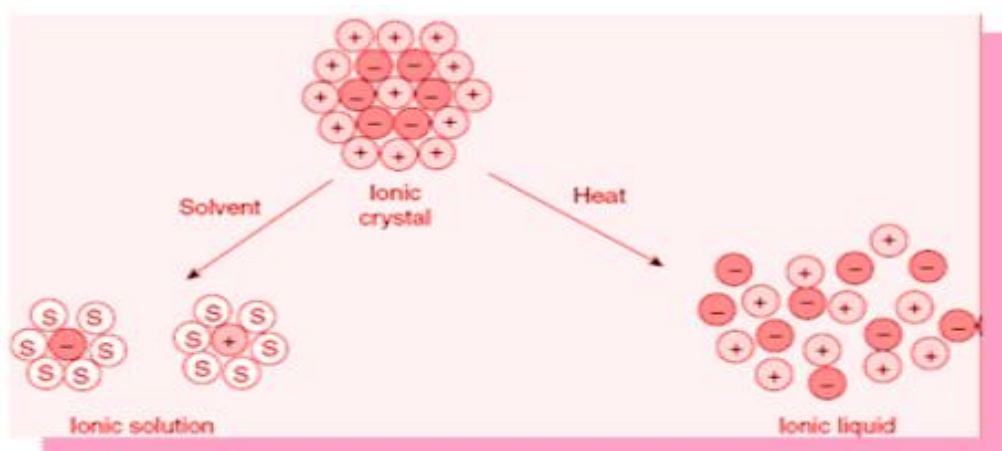
Figure 2.1:Difference between an ionic solution and an ionic liquid

It is widely known that decreasing the melting temperature may be accomplished by increasing the size of the ions and making them asymmetric [1]. This is easily explained by the fact that the ions in ionic liquids have a natural tendency to attract one another owing to electrostatic forces. The ions will be near to each other and interact strongly if the ions are tiny and

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symmetric, as in the case of an ionic solid like sodium chloride (NaCl). Crystals also have a favourable development owing to their symmetry. The distance between the ions increases as the size of the ions increases, and the electrostatic attractive force decreases as a consequence. The melting point of the ionic liquid may be protected in this way. Furthermore, if the ions are asymmetric, the melting point may be further reduced or even inhibited. The versatility of ionic liquids lies in the fact that thousands of them may be synthesised by just changing a functional group, and that change will define the ionic liquid's ultimate macroscopic properties. Ionic liquids have found a variety of uses in recent years, such as electroplating solvents, catalyzers, and electrolytes [2]. In the case of electrolytes, interest in ionic liquid has grown considerably, and some of the potential applications have been discovered in lithium-ion batteries, [3,4], fuel cells, [5,] and solar cells [6,7]. Despite the previously mentioned advantages of ionic liquids as electrolytes, there are certain disadvantages, such as toxicity, compatibility with the real materials used, manufacturing expense, and all the other issues that come with the introduction of a new technology. Ionic liquids have recently received a lot of interest because of their potential as environmentally benign "green" solvents [8,9]. Both homogeneous and heterogeneous catalysts may be found in ionic liquids. Because preferred ionic liquids are immiscible with reactants and products yet dissolve catalysts, this is the case. Enzymes are also stable in ionic liquids, allowing them to be utilised in biological processes such as pharmaceutical production [10,11]. Ionic liquids are unaffected by ionising radiation, thus they may be utilised to remediate high-level nuclear waste. Ionic liquids can dissolve and remove gases selectively, and may be used to purify the air aboard submarines and spacecraft. Ionic liquid is now being utilised in solvent extraction, liquid–liquid extraction, electrochemical research, and dye-sensitized solar cells [12-15]. Furthermore, ILs have been used to substitute organic solvents in organic synthesis because

of their excellent thermal stability, variable viscosity, lack of effective vapour pressure, recyclability, and conformist nature [16-18]. Ionic liquids are a novel class of chemicals that has piqued the interest of numerous research organisations across the globe in recent decades (IL). Over the past 10 years, the number of publications on the subject of "ionic liquids" has gradually increased. But, what exactly are ionic liquids, and why are they so fascinating? The next section provides a quick summary of this vast subject. The new book "Ionic

LIQUIDS (RTILs):

ILs which are liquid at room temperature are called room temperature ionic liquid (RTIL). In the older (and some current) literature, ionic liquids are occasionally called liquid organic salts, fused salts, molten salts, ionic melts, NAILs (non-aqueous ionic liquids), room-temperature molten salts, OILs (organic ionic liquids) and ionic fluids . Heating normal salts, such as sodium chloride (NaCl, mp 801oC), to high temperature produces also a liquid, that consists entirely of ions, but this is a molten salt and not defined as an ionic liquid. In existing times Ionic liquids (IL) have appeared as room temperature ionic liquids (RTILs) and atmosphere responsive solvents for the development for the manufacturing accumulate of chemicals. Ionic liquids have been progressively more used for various commercial and potential applications such as organic synthesis, catalysis, electrochemical devices and solvent extraction of a assortment of compounds. Most of the cases of ILs the cations may be organic or inorganic while the anions are inorganic.

Usually ILs consist of a large hulking and asymmetric organic cations based on 1- alkyl-3-methylimidazolium (abbreviated $[C_nmim]^+$, where n = number of carbon atoms in a linear alkyl chain), N-alkyl pyridinium (accordingly abbreviated $[C_npy]^+$), tetraalkylammonium (Bu_4N^+) or tetra alkyl

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phosphonium (Bu_4P^+) cations, and many others; and inorganic anions such as hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, alkylsulfates $[RSO_4]^-$, alkyl sulfonates $[RSO_3]^-$, halides such as chloride $[Cl]^-$, bromide $[Br]^-$ or iodide $[I]^-$, nitrate $[NO_3]^-$, sulfate $[SO_4]^-$, aluminum chloride $[AlCl_4]^-$, triflate ($[CF_3SO_3]^- = [TfO]^-$), bis(trifluoro methyl sulfonyl)imide ($[(CF_3SO_2)_2N]^- = [Tf_2N]^-$), etc. Recently very long alkyl, aryl or both are act as cationic part of the ionic liquids and that ionic liquids are called surface active ionic liquids (SAIL) [39]. Some commonly used ionic liquid systems are presented in Figure 2.2.
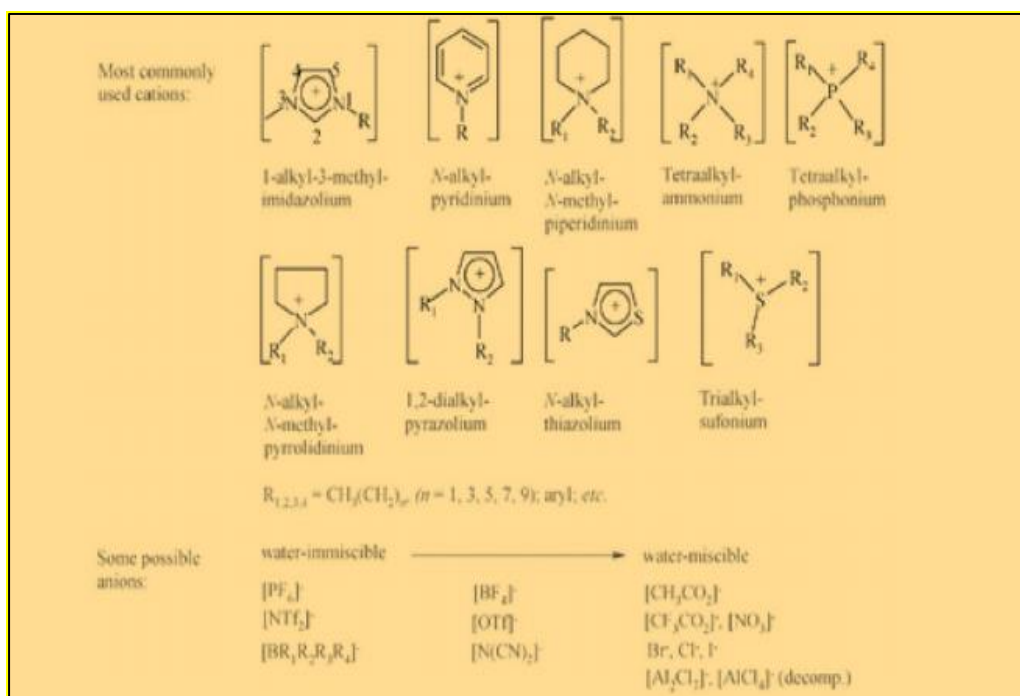
Figure 2.2: Some commonly used ionic liquid systems. The abbreviation $[C_npyr]^+$ represents the 1-alkyl-1-methylpyrrolidinium cation, where the index n stands for the number of carbon atoms in the linear alkyl chain. $[P_{wxyz}]^+$, $[N_{wxyz}]^+$ and $[S_{xyz}]^+$ are normally used to represent tetraalkylphosphonium, trialkylsulfonium and tetraalkylammonium cations, respectively, where the indices w, x, y and z indicate the length of the corresponding linear alkyl chains

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PROPERTIES OF IONIC LIQUIDS:

Asymmetry of the cation is believed to be responsible for the little melting points of ionic liquids, while the nature of the anion is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity . They are frequently referred to as "Green Solvents" due to their immeasurably low vapour pressure. A key feature of ionic liquids is that their physical properties such as melting point, viscosity, density, and hydrophobicity can be tailored to design different ionic liquids with a particular end use in mind by selection of different cation, anion, and substituents. Therefore ionic liquids are also described as "Designer Solvent" . Ionic liquids have a number of advantages as solvents over molecular solvents such as negligible vapor pressure, high thermal stability, non-flammability, wide temperature range, Lewis acidity, hydrophobicity, gas solubility and hydrogen-bonding capability, therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for "green processing". Replacement of conventional solvents with ionic liquids would prevent the emission of VOCs, a major source of environmental pollution [42].

PHYICOCHEMICAL APPROACH

Behaviour of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity. A number of conductometric [1] and related studies of different electrolytes in non-aqueous solvents, have been done in relation to the use of the electrolyte in high-energy batteries [2] and for understanding organic reaction mechanisms [3]. The

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formation of triple-ion in media having low permittivity ($\varepsilon < 10$) [4] have been investigated from the conductivity studies of $Hept_4NI$ [5,6]. The minima observed in conductometric curves (Λ versus $\sqrt{c}$) in this type of solvents were interpreted by the formation of M_2X^+ and MX_2^- triple-ion species [7].

Volumetric and viscometric studies also render an insight into the molecular interactions prevailing in solution and helps in the better understanding of the behaviour of electrolytic solutions. Studies on the apparent and limiting apparent molar volumes of the electrolyte and the dependence of viscosity on the concentration of salt have been employed as a function of studying ion-ion and ion-solvent interactions [8].

EXPERIMENTAL

Materials

$Hept_4NI$ of puriss grade was procured from Sigma Aldrich, Switzerland. It was used as purchased as the purity assay of the salt was $\geq 99\%$. o-Toluidine procured from Merck, India; o-Xylene procured from Sisco Research Laboratory Pvt. Ltd. Bombay, India and 2- Nitrotoluene procured from Sisco Chem. Industries, India. The solvents were purified using standard methods [9].

Apparatus and Procedure

A stock solution for the electrolyte was prepared by mass (Mettler Toledo AG285 with uncertainty 0.0003 g), and the working solutions were obtained by mass dilution at 298.15 K. The uncertainty of molarity of different solutions was evaluated to $\pm$ 0.0001 mol dm-3. The density (ρ) was measured by means of vibrating-tube Anton Paar density meter (DMA 4500M) with a

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precision   of ± 0.00005 g·cm-3. It was calibrated by double distilled water and dry air [10]. The temperature was automatically kept constant within ± 0.01 K.

The solvent properties are given in Table 3.1. The concentrations and molar conductances (Λ) of o-Toluidine, o-Xylene, and 2-Nitrotoluidine are given in Table 3.2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation

$$\Lambda = (1000 \, \kappa) / c \qquad\qquad (1)$$

Linear conductance curve (Λ versus √c) was obtained for the electrolyte in 2- Nitrotoluene, extrapolation of √c = 0 evaluated the starting limiting molar conductance for the electrolyte. But for the electrolyte in o-Xylene and o-Toluidine, a deviation in the conductance curve was obtained and shows a decrease in conductance values up to a certain concentration reaches a minimum and then increases indicating triple-ion formation.

The conductance data for the electrolyte in o-Xylene and o-Toluidine have been analysed using the classical Fuoss-Kraus equation [12] for triple-ion formation.

$$\Lambda \, g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \qquad (2)$$

$$g(c) = \frac{\exp\{-2.303 \, \beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \qquad (3)$$

$$\beta' = 1.8247 \times 10^6/(\varepsilon T)^{1.5} \qquad (4)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \qquad (5)$$

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In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; $\Lambda_0 T$ is the sum of the conductances of the two triple ions $[(Hept)_4N]_2{}^+I$ and $(Hept)_4N(I)_2{}^-$. $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make equation (2) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted [13] and Λ_0 values for the studied electrolytes have been calculated [14]. $\Lambda_0 T$ is calculated by setting the triple ion conductance equal to $2/3\ \Lambda_0$ [15].

The ratio $\Lambda_0 T/\ \Lambda_0$ was thus set equal to 0.667 during linear regression analysis of equation (2). A perusal of Table 3.3, Figure 3.1 and 3.2 show that the limiting molar conductance (Λ_0) of $Hept_4NI$ is higher in o-Toluidine than o-Xylene. Limiting molar conductance of triple-ions ($\Lambda_0 T$), slope and intercept of Eq. (2) for $Hept_4NI$ in o-Toluidine and o-Xylene are given in Table 3.3.

At very low permittivity of the solvent ($\varepsilon < 10$) electrostatic ionic interactions are very large. So the ion-pairs attract the free +ve and -ve ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. These results in the formation of triple-ions, which acquire the charge of the respective ions in the solution [17] i.e.

$$M^+ + A^- \leftrightarrow M^+ \cdots\cdots A^- \leftrightarrow MA \qquad \text{(ion-pair)} \qquad (6)$$

$$MA + M^+ \quad \leftrightarrow MA\ M^+ \qquad \text{(triple-ion)} \qquad (7)$$

$$MA + A^- \leftrightarrow MAA^- \qquad \text{(triple-ion)} \qquad (8)$$

Where M^+ and A^- are $Hept_4N^+$ and I^- respectively. The effect of ternary association [18] thus removes some non-conducting species, MA, from solution, and replaces them with triple ions which increase the conductance manifested

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by non-linearity observed in conductance curves for the electrolyte in o-Toluidine and o-Xylene.

Furthermore, the ion-pair and triple-ion concentrations, c_P and c_T respectively of the electrolyte have also been calculated at the minimum conductance concentration $Hept_4NI$ in o-Toluidine and o-Xylene using the following relations [19].

$$\alpha = 1 / (K_P^{1/2} \cdot c^{1/2}) \qquad (9)$$

$$\alpha T = (K_T / K_P^{1/2}) \, c^{1/2} \qquad (10)$$

$$C_P = c \, (1 - \alpha - 3\alpha_T) \qquad (11)$$

$$C_T = (K_T / K_P^{1/2}) \, c^{3/2} \qquad (12)$$

Here α and α_T are the fractions of ion-pairs and triple-ions present in the salt solutions respectively and are given in Table 3.5. Thus, the values of C_P and C_T also given in Table 3.5 indicate that the ions are mainly present as ion-pairs even at high concentration and a small fraction existing as triple-ions. The ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) have also been calculated over the whole concentration range of [$Hept_4NI$] in o-Toluidine and o-Xylene and the data are provided in Table 3.5.

The ion-pair formation in case of conductometric study of $Hept_4NI$ in 2-Nitrotoluene was analysed using the Fuoss conductance equation [20]. With a given set of conductivity values (c_j, Λ_j; j = 1……. n), three adjustable parameters, i.e., Λ_0, K_A and R have been derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant

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and R is the association distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs.

There is no precise method [21] for determining the R value but in order to treat the data in our system, R value is assumed to be, R = a + d, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule.

The distance, d is given by:

$$d = 1.183 \, M / \rho^{1/3} \qquad (13)$$

where, M is the molar mass and ρ is the density of the solvent.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \qquad (14)$$
$$P = 1-\alpha(1-\gamma) \qquad (15)$$
$$\gamma = 1-K_A c\gamma^2 f^2 \qquad (16)$$
$$-\ln f = \beta\kappa / 2(1+\kappa R) \qquad (17)$$
$$\beta = e^2 / \left(\varepsilon_r k_B T\right) \qquad (18)$$
$$K_A = K_R / (1-\alpha) = K_R / (1+K_S) \qquad (19)$$

where, Λ_0 is the limiting molar conductance, K_A is the observed association constant, R is the association distance, R_X is the relaxation field effect, E_L is the electrophoretic counter current, k is the radius of the ion atmosphere, ε is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute

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temperature and β is twice the Bjerrum distance. The computations were performed using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [22]. Input for the program is the no. of data, n, followed by ε, η (viscosity of the solvent mixture), initial Λ_0 value, T, ρ (density of the solvent mixture), mole fraction of the first component, molar masses, M_1 and M_2 along with c_j, Λ_j values where j = 1, 2……. n and an instruction to cover preselected range of R values.

In practice, calculations are performed by finding the values of Λ_0 and α which minimize the standard deviation, δ, whereby

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n-m) \qquad (20)$$

for a sequence of R values and then plotting δ against R, the best- fit R corresponds to the minimum of the δ–R versus R curve. So, an approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minima is found in the δ - R curves, thus R values is assumed to be R = a + d, with terms having usual significance.

The Gibb's energy change of solvation, ΔGo, for $Hept_4NI$ in 2-Nitrotoluene is given by the following equation [23]

$$\Delta G^0 = - RT \ln K_A \qquad (21)$$

It is observed from the Table III.7 that the value of the Gibb's free energy is entirely negative for 2-Nitrotoluene and it can be explained by considering the participation of specific covalent interaction in the ion-association process.

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Table III.8 shows the value of ionic conductance ($\lambda_0^{\pm}$) and ionic Walden product ($\lambda_0^{\pm} \eta$) (product of ionic conductance and viscosity of the solvent) along with Stokes' radii (r_s) and Crystallographic Radii (r_c) of $Hept_4NI$ in 2-Nitrotoluene .It is seen from this table that I- has higher ionic conductance and Walden product than $Hept_4N+$ and in case of Stokes' radii and Crystallographic Radii reverse order of value is observed for I- and $Hept_4N^+$ of $Hept_4NI$.

The measured values of densities of $Hept_4NI$ in o-Toluidine, o-Xylene and 2- Nitro toluidine at 298.15 K are listed in Table III.9. The densities and viscosities of the electrolytes in different solvents increase linearly with the concentration at the experimental temperature. For this purpose, the apparent molar volumes ϕ_V given in Table 3.9 were determined from the solution densities using the following equation [24]

$$\phi_V = M / \rho_o - 1000(\rho - \rho_o)/c\, \rho_o \qquad (22)$$

where M is the molar mass of the solute, c is the molarity of the solution, ρ and ρ_0 are the densities of the solution and solvent, respectively. The limiting apparent molar volumes ϕ^0_V were calculated using a least-squares treatment to the plots of ϕ_V versus $c^{1/2}$ using the following Masson equation [25]

$$\phi_{V =} \phi^0_V + Sv^*.\, \sqrt{c} \qquad (23)$$

where ϕ^0_V is the limiting apparent molar volume at infinite dilution and Sv* is the experimental slope.

RESULT AND DISSCUSSION

TABLES

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Table 3.1. Density (ρ), viscosity (η) and relative permittivity (ε) of the different solvents o-Toluidine, o-Xylene and 2-Nitrotoluene.

Solvents	$\rho \cdot 10^{-3}/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	ε
o-Toluidine	0.998	0.339	6.14
o-Xylene	0.87557	0.759	2.6
2-Nitrotoluene	1.163	2.218	26.1

Table 3.2. Concentration (c) and molar conductance (Λ) of o-Toluidine, o-Xylene and 2-Nitrotoluene at 298.15 K.

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$c \cdot 10^4/$ mol·dm^{-3}	$\Lambda \cdot 10^4/$ S·m^2·mol^{-1}	$c \cdot 10^4/$ mol·dm^{-3}	$\Lambda \cdot 10^4/$ S·m^2·mol^{-1}	$c \cdot 10^4/$ mol·dm^{-3}	$\Lambda \cdot 10^4/$ S·m^2·mol^{-1}
			Hept$_4$NI		
o-Toluidine		o-Xylene		2-Nitrotoluene	
3.5044	14.82	3.3672	44.54	3.9720	56.31
4.4521	14.77	3.9641	44.50	4.7394	54.21
5.1938	14.72	4.7350	44.46	5.5180	52.31
5.8081	14.69	5.7600	44.41	6.2078	51.50
6.2001	14.68	6.6203	44.37	6.8164	50.20
6.9169	14.64	7.3984	44.33	7.2146	49.90
7.7841	14.60	8.2254	44.29	7.8414	48.50
8.7557	14.55	9.0721	44.27	8.2770	48.00
9.6534	14.51	10.1188	44.25	9.0000	46.40
10.6406	14.48	11.1422	44.25	9.7032	45.50
11.8542	14.44	11.9578	44.25	10.2400	44.70
13.3810	14.40	13.2642	44.27	11.0224	43.11

Table 3.3. Calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductances of triple ion Λ_0^T, experimental slope and intercept obtained from Fuoss-Kraus Equation for Hept$_4$NI in o-Toluidine and o-Xylene at 298.15 K.

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Solvents	$\Lambda_0 \cdot 10^4$ /S·m²·mol⁻¹	$\Lambda_o^T \times 10^4$ /S·m²·mol⁻¹	Slope×10⁻²	Intercept ×10⁻²
		Hept₄NI		
o-Toluidine	69.12	46.10	0.20	0.15
o-Xylene	60.34	40.25	0.11	0.45

Table 3.4. Salt concentration at the minimum conductivity (C_{min}) along with the ion-pair formation constant (K_P), triple ion formation constant (K_T) for Hept₄NI in o-Toluidine and o-Xylene at 298.15 K.

Solvents	$c_{min} \cdot 10^4$/ mol·dm⁻³	log c_{min}	$K_P \cdot 10^{-5}$/ (mol·dm⁻³)⁻¹	K_T/ (mol·dm⁻³)⁻¹	K_T / K_P ·10⁵	log K_T / K_P
			Hept₄NI			
o-Toluidine	9.92	-3.0034	0.36	48.96	136.4	-2.86
o-Xylene	9.24	-3.0343	0.32	75.33	235.4	-2.62

Table 3.5. Salt concentration at the minimum conductivity (C_{min}), the ion pair fraction (α), triple ion fraction ($α_T$), ion pair concentration (c_P) and triple-ion concentration(c_T) for Hept₄NI in   o-Toluidine and o-Xylene at 298.15 K.

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Solvents	$c_{min} \cdot 10^4$/ mol·dm^{-3}	$\alpha \cdot 10^5$	$\alpha_T \cdot 10^3$	$c_P \cdot 10^4$/ mol·dm^{-3}	$c_T \cdot 10^6$/ mol ·dm^{-3}
			Hept$_4$NI		
O-Toluidine	9.92	16.6	8.13	9.68	8.1
O-Xylene	9.24	6.91	12.88	9.10	8.9

Table 3.6. Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for Hept$_4$NI in 2-Nitrotoluene at 298.15 K.
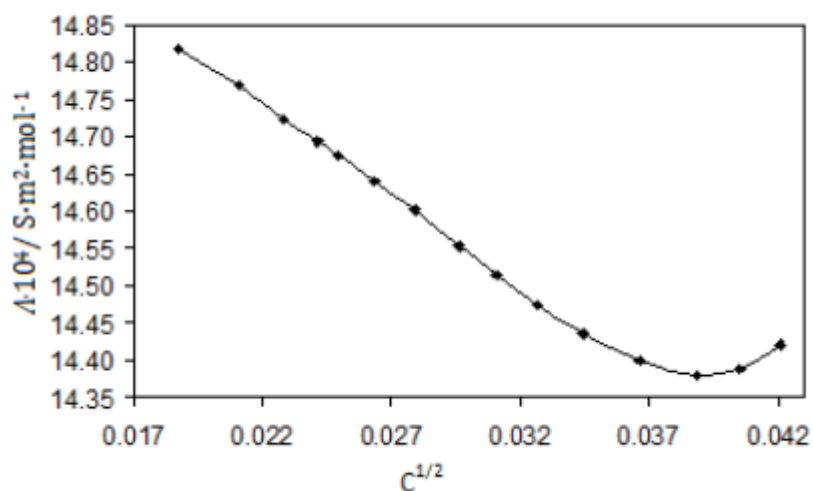
FIGURES

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Figure 3.1. Plot of molar conductance (Λ) versus $C^{1/2}$ for Hept$_4$NI in o-Toluidine at 298.15 K
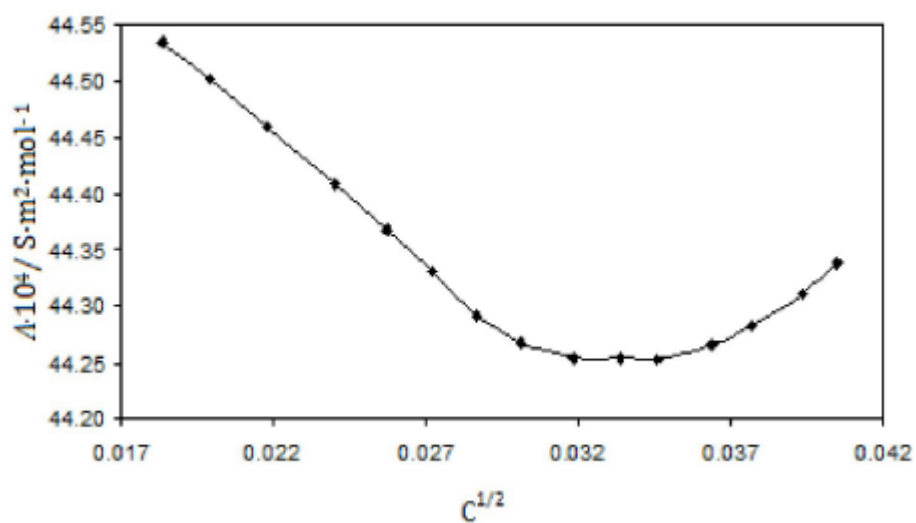
Figure 3.2. Plot of molar conductance (Λ) versus $C^{1/2}$ for Hept$_4$NI in o-Xylene at 298.15 K.

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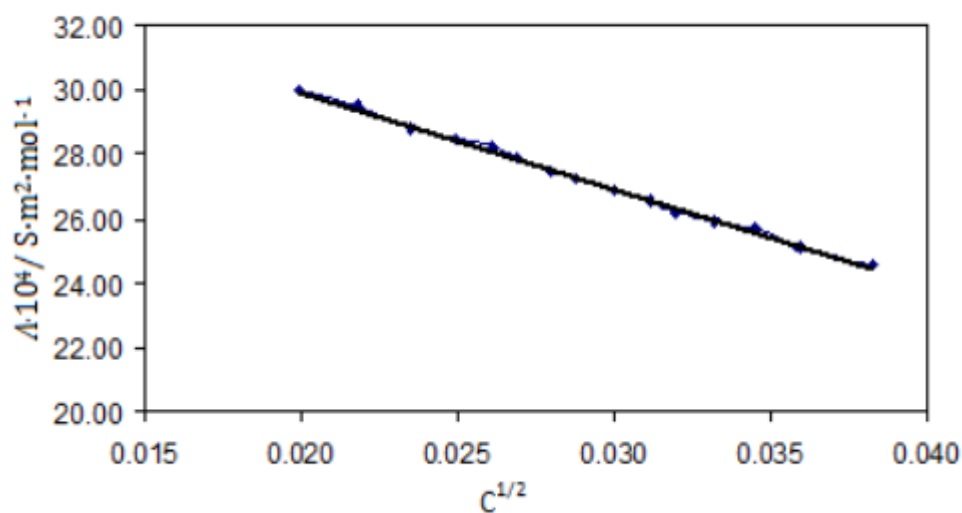**Figure 3.3. Plot of molar conductance (Λ) versus $C^{1/2}$ for Hept$_4$NI in 2-Nitrotoluene at 298.15 K.**
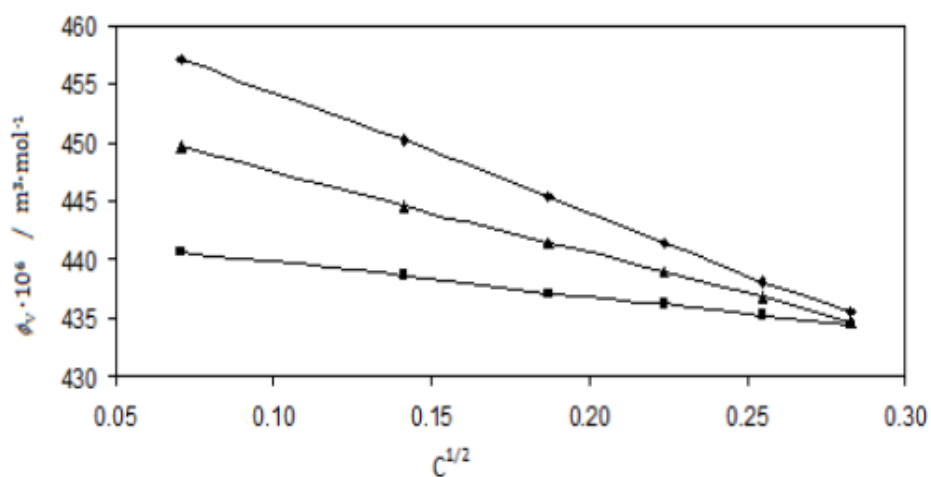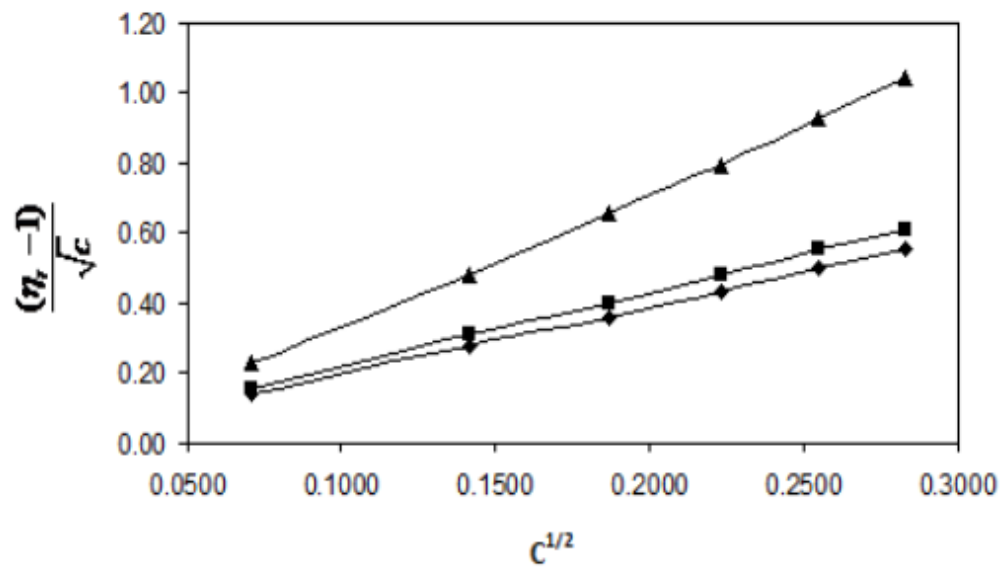

Figure 3.4. Plot of $C^{1/2}$ versus Limiting apparent molar volume (ϕ^o V) for Hept $_4$NI in o-Toluidine(—■—),o-Xylene(—▲ —) and 2-Nitrotoluene(—♦—) at 298.15 K.

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CONCLUSION

The research reported in this dissertation explains the procedures and results as well as the studies of the molecular interactions that have been carried out on ionic liquids and amino acids. The overall goal of initiating an understanding of the structure property relationship of ionic liquids has been reached. This was done through work on several ionic liquids differing mainly in their cationic and anionic parts. By looking at thermophysical, thermodynamic and transport properties of these materials, a more complete knowledge of phosphonium, ammonium, imidazolium, pyridinium and pyrrolidinium -based ionic liquids and ionic solids was achieved. The volumetric, viscometric, interferometric, conductometric refractive index studies helped us to evaluate the extent of molecular interaction in a particular solution quantitatively whereas the FTIR measurements gave an insight into the type of molecular interaction occurring in any solution systems. Various types of interactions exist between the ions in solutions, and of these, ion-ion and ion-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent. Mixed solvents enabled the variation of properties such as dielectric constant or viscosity, and therefore the ion-ion and ion-solvent interactions occurring in the solutions systems could be better understood. Moreover, different quantities strongly influenced by solvent properties could be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric and related studies of different electrolytes in nonaqueous solvents, especially mixed organic solvents, have been made for their optimal

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use in high-energy batteries and for understanding organic reaction mechanisms. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Thus, extensive studies on electrical conductance in mixed organic solvents have been performed to examine the nature and magnitude of ion-ion and ion-solvent interactions.

The extensive study of $Hept_4NI$ in o-Toluidine, o-Xylene and 2-Nitrotoluene leads to the conclusion that, the salt more associated in 2-Nitrotoluene than the other two studied solvents. It can also be seen that in the conductometric studies in o-Toluidine and o-Xylene the $Hept_4NI$ remains as triple-ions and ion-pairs and the extent of triple-ion formation is higher in o-Xylene than o-Toluidine. But in 2-Nitrotoluene the $Hept_4NI$ remains as only ion-pairs. The experimental values obtained from the volumetric and viscometric studies suggest that in solution there is more ion-solvent interaction than the ion-ion interaction and the extent of ion-solvent interaction of $Hept_4NI$ is highest in 2-Nitrotoluene.

we have focused on the characteristic interfaces of some model biological systems [D(-)fructose and D(+)galactose], with an IL. The studied physicochemical properties provide us complete explanation for the interfaces of IL with carbohydrates. From the analysis of thermodynamic data, it is revealed that the association process for [bmp]Cl is higher in case of D(-)fructose than in D(+)galactose solution. This process is endothermic and entropy controlled at all the studied temperatures. Density and viscosity studies

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interpret limiting apparent molar volume, $\phi_0 V$ and viscosity B-coefficient which describes that ion-solvent interaction is increased with increasing the conc. of D(-)fructose and D(+)galactose and decreased with increasing temperature. NMR study analysis reveals that no specific and stronger interactions occur between IL and carbohydrates. However the study confirms that interaction of IL with carbohydrates is higher in D(-)fructose than that of D(+)galactose. The study provides a profound insight into the potential toxicity of ILs in mixed systems of IL and biomolecules.

More extensive studies of the different thermophysical, thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes. The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics and industrial products etc. is essential for confirming that their viscosity is appropriate for the contemplated used of the products. The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry. However, it is necessary to remember that molecular interactions are very complex in nature. There are strong forces existing in the molecule and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid conclusions can be drawn in many cases relating to degree of structure and order of the system. The broad studies of the different physicochemical, thermodynamic, transport and spectral properties of the ionic solids and ionic liquids in different solvents will be of sufficient in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes. Here in this research work I have also tried to explore the formation of host-guest inclusion

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complexes of ionic solids and ionic liquids with several host molecules such as α and β cyclodextrins. This host-guest complexation has been confirmed by conductance, surface tension, FTIR and NMR spectroscopy.

The extensive conductometric study of [BMP][Br] in FA, DMA, and DMF leads the conclusion that the electrolyte more associated in FA than in the other two solvents. The reliable value of volumetric, viscometric and interferometric studies also intends to map the physicochemical behaviour in solution and suggests that in solution there is more ion–solvent interaction than ion–ion interaction. The molar refraction values also support the above fact that the highest ion-solvent interaction is seen in case of FA solvent. In all the solvents the electrolyte forms ion-dipole interactions as evident from the FT- IR studies.

These studies are very much important in pharmaceutical industries, food industries, paint industries, cosmetic and hygiene industries and in also enhance the speed of diagnostic test reaction. So, it may be concluded that our research work has adequate significance in the different branches of sciences and demands a far reaching effect for the augmentation of the advance research. In the near future we endeavour to widen our research work with ionic solids and ionic liquids which I hope will certainly complement our present findings. In recent years, with the advent of new synthetic technologies such as catalytic symmetric/asymmetric synthesis, phase transfer catalysis, and catalysis, the diversity of molecular interactions that can be studied, has increased to the highest degree.

REFERRENCES

[1] X. Li, X. Xu and C. Zhou, Chem. Commun. 48 (2012) 12240.

Research Paper

[2] Z. J. Liu, J. Zhang, S. L. Chen, E. Shi, Y. Xu and X. B. Wan, Angew. Chem. Int. Ed. 51 (2012) 3231.

[3] A. Triolo, O. Russina, H. J. Bleif and E. Di Cola, J. Phys. Chem. B 111 (2007) 4641.

[4] P. Vanysek, CRC Handbook of Chemistry and Physics, 82nd Edition, CRC Press, Boca Raton (2001-2002).

[5] G. Charlot and B. Tremillon, Chemica Reactions in Solvents and Melts, Pergamon, Oxford (1969).

[6] H. A. Laitinen, Chemical Analysis, McGraw Hill, New York (1960).

[7] T. O'Donnell, Superacids and Acidic Melts, VCH, Weinheim (1993).

[8] The Structure and Properties of Ionic Melts, Discuss. Faraday Soc., 32, University Press, Aberdeen (1962).

[9] J. O'M Bockris and A. K. N. Reddy, Modern Electrochemistry, Plenum, New York (1970).

[10] Xing Ma and Yanli Zhao, Chem. Rev. 115 (2015) 7794.

[11] D. K. Meck, The Chemistry of Non- Aqueous solvents, Academic Press, New York (1996).

[12] O. Popovych and R. O. Bates, Crit. Rev. Anal. Chem. 1 (1970) 73-117.

[13] F. Franks, Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann Educational Books Ltd., London (1967).

[14] R. G. Bates, Determination of pH Theory and Practice, John Wiley and sons: New York (1973).

[15] (a) R. G. Bates, Solute –solvent Interactions, Marcel Dekker, New York (1969). (b) R. G. Bates and A. J. Parker, Chemical Physics of Ionic solutions, John Wiley and Sons. Inc, New York (1966). 320 Bibliography

[16] A. J. Parker and J. H. Sharp, Proceeding of the Royal Australian Chemical Institute (1972).

Research Paper

[17] A. J. Parker, Electrochim. Acta. 21 (1976) 671.

[18] C. M. Criss and M. Salomon, J. Chem. Educ. 53 (1976) 763.

[19] Y. Mercus, Ion-solvation, Wiley, Chinchester (1986).

[20] E. J. King, Acid-Base Equilibria, Pergamon Press, London (1965).