Ionic liquids: New materials with wide applications

Nageshwar D Khupse* & Anil Kumar
Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India
Email: nd.khupse@ncl.res.in (NDK)/ a.kumar@ncl.res.in (AK)

Received 7 April 2010; accepted 21 April 2010

Ionic liquids have emerged as possible substitutes for volatile organic solvents and have found many applications in a variety of research areas. In this review, an effort has been made to discuss the special properties of ionic liquids that render these unique solvent media useful in chemical transformations, electrochemical applications, extractions, etc.

Keywords: Ionic liquids, Physicochemical properties, Solvent properties, Viscosity, Chemical processes, Electrochemical devices

Ionic liquids have recently emerged as “green” and environment friendly solvents for their use in the industrial manufacture of chemicals. In the past decade, ionic liquids have been increasingly used for diverse applications such as organic synthesis, catalysis, electrochemical devices and solvent extraction of a variety of compounds.\(^1\) Ionic liquids are composed of cations and anions having low melting point (<100 °C). While the cations may be organic or inorganic, the anions are inorganic. From the historical point of view, it is interesting to mention here that the ethyl ammonium nitrate \([\text{C}_2\text{H}_5\text{NH}_3]^{+}\) \([\text{NO}_3^-]\) with m. pt. \(~\sim12\) °C was the first ionic liquid synthesized about 90 years ago. However, this ionic liquid did not find further application-based research due to its explosive nature.

There are several reasons that ionic liquids are considered as “green solvents”. The interest in ionic liquids was initiated because of their advantageous physicochemical properties such as negligible vapor pressure, high thermal and electrochemical stability, high solvating power, etc.\(^4,5\) The choice of the cation and the anion constituting an ionic liquid has a profound effect on the physical properties such as viscosity, density, conductivity and polarity.\(^6\) Ionic liquids offer a great flexibility in their properties since the possible combinations of cations and anions are quite high. However, the wide variety of cations and anions available makes a systematic study very difficult. The selection of an appropriate ionic liquid for a particular application would require a comprehensive database of the fundamental properties like stability, density, miscibility, viscosity and polarity of ionic liquids over a wide range of temperature and pressure, which unfortunately are not available at present for all the classes of ionic liquids. Ionic liquids can be recycled to offer comparable performance in chemical transformations. We recently demonstrated that a bimolecular organic cycloaddition reaction was inhibited in ionic liquids possessing high viscosities.\(^7\) Similarly, the high viscosity of ionic liquid is a constraint in obtaining the optimum performance in many electrochemical devices employing these compounds as electrolytes.

There exists two possibilities of handling high viscosity of ionic liquids: (1) to synthesize ionic liquids with low viscosity; but this approach may not be suitable for a wide range of applications as one needs to replace either cation or anion by another species imparting low viscosity, while compromising on the efficiency, and, (2) to use viscous ionic liquids in conjunction with molecular solvents to provide a clear liquid phase that will offer low viscosity but still be useful for a variety of applications. The forces operating between cation and anion of an ionic liquid are overwhelmingly columbic in nature.

In Scheme 1 are displayed some typical cations and anions that are commonly employed in synthesizing ionic liquids. The first generation ionic liquids include a mixture of organic species with \(\text{AlCl}_3\) in which one can vary the nature of medium by changing the
amount of AlCl₃. These ionic liquids are known as chloroaluminates. Though one can have a more efficient control over the nature of these ionic liquids, their extremely hygroscopic nature restrict their use in organic processes and one needs to take strict precautions for using them under a dry atmosphere. In spite of their hygroscopic nature these ionic liquids have however been used as electrolytes in batteries. Ionic liquids with [BF₄]⁻, [PF₆]⁻ anions, etc., are air stable and neutral. The ionic liquids can react exothermically with Lewis acids and water. Ionic liquids containing [CF₃SO₃]⁻ or [Tf₂N]⁻ anions possess low melting points and are stable in water and the medium containing Lewis acids. Some ionic liquids under this category are noted to act as moderately coordinating solvents.

Synthesis of Ionic Liquids
Ionic liquids can be synthesized according to the previously reported literature procedure and excellent reviews are available on their synthesis and handling techniques. The synthesis of ionic liquids has been carried out in two steps: (1) formation of cation by quaternization reaction, and, (2) anion exchange reaction. The characterization and their purities have been determined by NMR. The water content of the pure and dried ionic liquids has been measured by Karl Fischer coulometer analysis. The preparation of ionic liquids, even in large quantities, presents no significant difficulties. Provided they are of sufficient purity, most ionic liquids can be stored without decomposition for extended periods although some are relatively hygroscopic. Besides brief discussion on the types of ionic liquids, one should note that it is possible to synthesize numerous ionic liquids with varying properties.

Physicochemical Properties
Melting point and thermal stability
This is the most significant characteristic property of ionic liquids that can be correlated with the structure and composition of ionic liquids. Selection of both the cation and anion determines the melting point of an ionic liquid. An ionic liquid with a cation with low symmetry possesses lower melting points than the one with high symmetry. Weak intermolecular interactions and a good distribution of charge in the cation favor low melting point of ionic liquid.

Most of the ionic liquids are stable at and above 400 °C. The thermal decomposition depends on the nature of anions rather than of cations. Further, thermal decomposition also decreases with an increase in hydrophilicity of anions.

Viscosity
Viscosity of pure ionic liquids
Before we elaborate on the viscosity of mixtures of ionic liquids, we summarize herein the viscosity profiles of pure ionic liquids. Chloroaluminate ionic liquids have been widely used in electrochemical devices and also in carrying out chemical processes. Hussey and his school contributed significantly to determine several physico-chemical properties of this early class of ionic liquids. A compilation on the viscosities of a number of air-and moisture-stable ionic liquids is available in the literature. The major problem in handling this class of ionic liquids is with regard to their sensitivity to water and chloride impurities, and hence, measurement should make with utmost care. The presence of small amounts of chloride impurities could lead to a dramatic increase in the viscosity of ionic liquids. The variation of viscosity of pure ionic liquids changes with a variation in the structure of ionic liquids. The effect of cation is smaller as compared to anion effect. The [NTf₂]⁻ anion offers low viscosity compared to several other anions, while [PF₆]⁻ anion contributes significantly to the viscosity increase of ionic liquids. The [EtSO₃]⁻ anion shows increase in viscosity compared to the [BF₄]⁻ anion.

The fact that the viscosity of ionic liquids is sensitive to the presence of small amounts of impurities is responsible for the disagreement in the values. However, the same fact can be employed to our advantage, since the addition of small amounts of cosolvents can reduce the viscosity to suit our needs, without compromising on the promising capabilities of ionic liquid media. For example, the viscosity of [BMIM][BF₄] increased by 25 % in the presence of 0.5 mol kg⁻¹ of chloride content. The presence of water had a stronger but inverse effect, i.e., the viscosity decreased greatly in the presence of small amounts of water for not only hydrophilic but also hydrophobic ionic liquids. In view of the potential applications of such systems, a critical analysis of the published data related to binary mixtures is important while applying it for further studies. Drastic discrepancies in the literature values of ionic liquids [BMIM][BF₄] and [BMIM][NTf₂] are observed. The observed viscosity values for [BMIM][BF₄] is given in literature as 92 (ref. 15), 115 (ref. 16), 180 (ref. 17),
The physico-chemical properties of ionic liquids vary with structure of cations and anions. The effect of anions on viscosity of imidazolium based ionic liquids can be broadly depicted as $[\text{BMIM}]^+ [\text{NTf}_2^-] < [\text{BMIM}]^+ [\text{CF}_3\text{SO}_2\text{N}]^- < [\text{BMIM}]^+ [\text{BF}_4^-] < [\text{BMIM}]^+ [(\text{C}_2\text{F}_5\text{SO}_2)\text{N}]^- < [\text{BMIM}]^+ [\text{PF}_6^-]$. The alkyl ammonium-based ionic liquids exhibit a higher viscosity than the imidazolium-based ionic liquids with the same anion. The viscosity of ionic liquids increases with the length of the alkyl chain on the imidazolium ring. For example, $[\text{EMIM}]^+ [\text{NTf}_2^-] < [\text{MMIM}]^+ [\text{NTf}_2^-] < [\text{BMIM}]^+ [\text{NTf}_2^-] < [\text{HMIM}]^+ [\text{NTf}_2^-] < [\text{OMIM}]^+ [\text{NTf}_2^-]$. One would expect that the overall contribution of the strong electrostatic terms to the interactions diminishes with an increase in the side-chain length. However, the contribution of weaker, non-associating, dispersion forces also enhances the viscosity. This results into higher viscosity, as the size of the non-polar part of the cations becomes larger. The justification put forward by Bonhote et al. is that the increase in the van der Waal’s interactions due to the presence of a long alkyl chain leads to higher viscosities. Methylation at C(2) position in the imidazolium cation, leads to a greater increase in viscosity as compared to that at C(4) position. This was contrary to the expectation that H-bonding suppression is likely to reduce the viscosity. This was explained on the basis of a decrease in the entropy of the system due to the constraints in ionic interactions.

Highly viscous ionic liquids can be employed for various applications in conjunction with molecular solvents. The viscosity of pure ionic liquids is affected on addition of cosolvent, i.e., significant decrease in viscosity of ionic liquids is observed on addition of the cosolvent. The decrease in viscosity depends on the solvent added and the extent of resulting dissociation of ionic liquids into ions. Furthermore, the magnitude of changes in viscosity was noted to be the greatest for polar solvents like water and the least for benzene. This suggests that the organic cosolvents "solvate" the constituent ions of the molten salt, resulting in a decrease in the aggregation of these ions. Since imidazolium ionic liquids are widely used in different fields, it is important to know the physical properties of their binary mixtures. Addition of other solvents like ethanenitrile, trimethylethenenitrile, 2-propenenitrile, 1-methylimidazole, toluene, 1,4-dimethylbenzene, 1,2-dimethoxyethane, etc., also result in a similar decrease in viscosity values. The viscosity, in the case of water saturated ionic liquids, decreases strongly due to the presence of water. For the ionic liquid $[\text{BMIM}]^+ [\text{PF}_6^-]$, the viscosity at 293 K is four times lower in the saturated sample as compared to the viscosity of pure one.

It has also been reported that the temperature affects the viscosity of both pure ionic liquids as well as ionic liquids saturated with water. It is found that effect of water on the viscosity of pure ionic liquid is less prominent at higher temperatures. The viscosities of dried imidazolium based ionic liquids are in the range of 40-376 mPa s at 293 K and for water saturated ionic liquids in the range of 22-85 mPa s at 298 K. Water may therefore be termed as a viscosity-reducer for ionic liquids. Thus, the hydrophobic ionic liquids which are immiscible in water, are also affected by the presence of small amounts of water.

Wang et al. have studied the viscosity behavior of pure and binary mixtures of $[\text{BMIM}]^+ [\text{BF}_4^-]$ ionic liquids with acetonitrile, dichloromethane, 2-butanone and $N, N$-dimethylformamide at 298.15 K. An exponential function based on concentration parameter has been fitted to the data. The viscosity for the binary mixtures of $[\text{BMIM}]^+ [\text{PF}_6^-]$ with tetrahydrofuran, methanol, dimethyl sulfoxide and acetonitrile is shown in Fig. 1. The negative values of viscosity deviation of the system suggested that viscosities of associates formed between unlike

![Fig. 1 — The $\eta-x_2$ plots for mixtures of $[\text{BMIM}]^+ [\text{PF}_6^-]$ with tetrahydrofuran (○), dimethyl sulfoxide (△), methanol (◇), acetonitrile (◇) at 298.15 K. [Data plotted from ref. 27.](image)]
molecules are relatively less than those of pure components. The relationship describing the viscosity deviation, $\Delta \eta$ as a function of the energy and the extent of H-bonds in liquid mixtures has been reported.\(^{27,28}\)

It was shown that $\Delta \eta$ decreases as the number and strength of H-bonds are decreased. This indicates that H-bonding in the ionic liquids is more dominant in determining the viscosities than in typical polar protic molecular solvents.\(^{29}\) The negative $\Delta \eta$ values obtained for this system suggest that there may be a reduction in the number and strength of H-bonds upon mixing (Fig. 2). It should be noted that the negative viscosity deviation may also occur where dispersion forces are dominated for the systems having different molecular sizes.\(^{30}\) The results are discussed in term of ion dipole interaction between the cation of the ionic liquids and organic solvents. This led to the prediction of viscosity of the mixture as a function of concentration of dissolved solvents and in terms of polarity of the solvents. Mention should be made of the attempts made for determining the critical viscosity near liquid-liquid phase transition in [HMIM][BF$_4$] + 1-pentanol.\(^{31}\) It is observed that the critical viscosity follows the Arrhenius behavior. Data also exist on the viscosity of [EMIM][BF$_4$] in H$_2$O at various temperatures.\(^{32}\) It was also reported that viscosity is more sensitive to temperature than density. The viscosity of [EMIM][BF$_4$] is 1 or 2 order greater than the organic solvents in comparison with typical oils.

The pyridinium\(^{33}\) based ionic liquids show almost similar behavior as the other ionic liquids. In order to demonstrate the effect of mixture compositions on the viscosities, these results are depicted in the form of the $\ln \eta$ - $V_{f,2}$ plots in Fig. 3. As seen in Fig. 3, the viscosity of [BP][BF$_4$] falls very sharply upon addition of water. For example, the viscosity of [BP][BF$_4$] decreases by about 48 % upon addition of water ($V_{f,2} = 0.98$). On the other hand, an addition of methanol results in a drop in viscosity by 30 % for [BP][BF$_4$] ionic liquid. However, the viscosities of ionic liquids did not decrease sharply upon addition of dichloromethane. This decrease in the viscosity value was about 15 % from the viscosity data. Pure ionic liquids are characterized by the presence of aggregates, caused by short range interaction forces. Molecular organization of ionic liquids as revealed by diffraction data\(^{34}\) can be considered in terms of enhanced local structure in contrast to that noted in homogeneous liquids.

The presence of aggregates in pure ionic liquids has been supported by computer simulations\(^{35}\) suggesting the aggregation of alkyl tails through van der Waal attraction. On the other hand, the ionic head groups and the anions are distributed more homogeneously forming a continuous network of ionic channels. Upon addition of solvents like water in pure ionic liquids, these aggregates begin to dissociate into free cations and anions. Cations and anions are more free in the water-rich mixtures than in the water-poor regions. This is probably the reason of sharp decline in the viscosity of pure ionic liquids when water or any solvent is added. Water molecules with high relative permittivity weaken electrostatic forces operating between ions. However, methanol or
dichloromethane when added to pure ionic liquid cannot fully dissociate the cations and anions due their lower relative permittivity.

The viscosity of phosphonium based ionic liquids with amino acid as anions has been studied in our group (Fig. 4). It is observed that on addition of water to [TBP][Ala] and [TBP][Val], the viscosity decreases by 35 % and 42 % respectively, while in the case of addition of methanol the decrease in viscosity was 31 % and 40 %, respectively. The viscosities were also measured in the presence of dichloromethane. However, the viscosities of ionic liquids did not decrease sharply upon addition of dichloromethane. This decrease in the viscosity value was about 15 % from the viscosity data except for [TBP][Val], where the viscosity of pure ionic liquids declined by about 22 %.

Fig. 4 — The ln $\eta$ - $V_{f,2}$ plots for the mixtures of [TBP][Ala] with water (○), methanol (○), dichloromethane (Δ) at 298.15 K. [Figure taken from ref. 33].

Effect of temperature on viscosity

Temperature dependent studies of binary mixtures of ionic liquids

The viscosity data of binary mixtures of ionic liquids with solvents over a wide temperature range has been studied many times. The viscosity of binary mixture of ionic liquid [BMIM][BF$_4$] with water in the temperatures range of 303.15–353.15 K shows that sensitivity of viscosity towards the composition of the mixture decreases with temperature. Data are also available for the binary mixtures of [EMIM][C$_2$H$_5$SO$_4$] with water and ethanol over a wide temperature range. The binary mixtures of [BMIM][ClO$_4$] and [OMIM][BF$_4$] with ethanol are also studied at atmospheric pressure and temperatures at 278.15–363.15 K. Viscosity measurements have also been made for the system of [3-MEP][EtSO$_4$] with water and ethanol at different temperatures.

The temperature dependent viscosity data for these ionic liquids cannot be represented by the Arrhenius equation. The modified Vogel-Fulcher-Tammann (VFT) equation was used to investigate the temperature dependence of the viscosities of ionic liquids. The temperature dependence of viscosity for pyridinium based ionic liquids is shown in Fig. 5. The deviations of the viscosity of the mixture from ideality are inversely related to temperature.

The modified VFT equation is of the form (Eq. 1),

$$\ln \eta = \ln A + 0.5 \ln T + k (T-T_o)$$  \hspace{1cm} (1)

where $T_o$ is glass transition temperature, $k$ and $A$ are adjustable parameters. Also, the viscosities of binary mixture of only one of the ionic liquids, [4-MBP][BF$_4$], with water has been depicted as a function of temperature at constant compositions in Fig. 6.

Fig. 5 — The ln $\eta$ -1000/T plots for ionic liquids. ([BP][BF$_4$](○), [3-MBP][BF$_4$](●), [4-MBP][BF$_4$] (△)). [Figure taken from ref. 33].

Fig. 6 — The plots of ln $\eta-V_{f,2}$ for aqueous [4-MBP][BF$_4$] ionic liquids at 298.15 K (○) and 323.15 K (○). [Figure taken from ref. 33].
Solvent Properties

Polarity
In order to use ionic liquids as solvents in chemical processes, it is necessary to determine their solvent properties. The polarity of several ionic liquids has been studied in terms of $E_T(30)$ (electronic transition energy in kilocalories/mole) and the Kamlet-Taft polarity parameters.\textsuperscript{40-44} Several recent publications have shown that the commonly used ionic liquids are reasonably polar solvents, having polarity greater than those of solvents like acetone, dimethyl sulfoxide, etc. but less than those of water and short-chain alcohols.\textsuperscript{45-47} A comprehensive account of the polarity of ionic liquids has been recently presented by Reichardt.\textsuperscript{40} The polarity data of ionic liquids have revealed many interesting characteristics in these novel media, which were not observed earlier or were too “weak” to be observed in conventional solvents. For example, ionic liquids show a strong tendency of preferential solvation for a probe molecule in their binary mixtures with water or organic cosolvents. Although preferential solvation was also observed in conventional binary mixtures, the effect was not as drastic as is seen in ionic liquid mixtures. The polarity studies on the binary mixture of tetraethylene glycol with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$], showed interesting synergistic effects, which was termed as “hyperpolarity”.\textsuperscript{48} It is believed that such phenomena arise due to the formation of highly ordered microsegregated phases in the binary mixtures of ionic liquids. Another interesting aspect is the substantial temperature dependence of polarity parameters or “thermosolvatochromism” observed in ionic liquids. The polarity of ionic liquids is known to be sensitive to the changes in temperature.\textsuperscript{46} Thermosolvatochromism of the probe molecule in solvents like cyclohexane, di-isopropyl ether and tetrahydrofuran was earlier reported by Suppan et al.\textsuperscript{49} There are reports available on thermosolvatochromism phenomena for Reichardt’s dye in aqueous alcohols and very recently El Seoud et al.\textsuperscript{50} studied the thermosolvatochromism in aqueous [BMIM][BF$_4$] and compared it with those of aqueous alcohols. However, the small magnitude of the temperature effect on polarity made it difficult to obtain reliable results. The temperature effect on the solvatochromic shift in ionic liquids was much more pronounced along with the influence of substituting alkyl length on the cation on polarity parameters as reported by Prausnitz et al.\textsuperscript{46} On the basis of temperature dependence of polarity of [BMIM][PF$_6$], Baker et al.\textsuperscript{51} had concluded that the hydrogen bond donor strength of the imidazolium cation was strongly temperature dependent, while the hydrogen bond accepting ability was a weak function of temperature. Weingartner et al.\textsuperscript{52} explained the polarity of ionic liquids with different cations by measuring a static dielectric constant using microwave dielectric spectroscopy. The polarities determined by microwave dielectric spectroscopy were lower than those obtained by using solvatochromic dyes.\textsuperscript{52} In spite of these interesting observations, systematic studies on the temperature dependence of polarity in ionic liquids have not been carried out. Also, the effect of cations and anions of ionic liquids on the thermosolvatochromism in ionic liquids has not been studied to date. We have embarked upon an extensive research program on investigating the physicochemical properties of ionic liquids and their implications on chemical and electrochemical process.\textsuperscript{53} As a part of this ongoing research program, we have investigated the thermal effect on solvatochromism of probe molecules in pyridinium-, pyrrolidinium- and phosphonium-based ionic liquids.\textsuperscript{54} To investigate the anionic effect on polarity of these ionic liquids, we had selected the anions, namely, bis(trifluoromethylsulfonyl) imide [NTf$_2$]$^-$, tetrafluoroborate [BF$_4$]$^-$ and [amino acid]-based species. The hydrogen bond donating property ($\alpha$), hydrogen bond accepting property ($\beta$), polarizability ($\pi^*$) and the electronic transition energy parameter ($E_T$) were determined for different combinations of cations and anions using three indicator dyes, viz., Reichardt’s dye (1), N,N-diethyl-4-nitroaniline (2) and 4-nitroaniline (3) (Fig. 7). Several reports are available for the measurement of $\lambda_{max}$ and calculation of polarity parameters.

![Fig. 7 — Reichardt’s dye (1), N,N-diethyl-4-nitroaniline (2) and 4-nitroaniline (3) used as probe molecules for polarity determination.](image-url)
The polarity parameters for pyrrolidinium ionic liquids follows the trends: \([\text{BMPy}]\text{[NTf}_2\text{]} > [\text{HMPy}]\text{[NTf}_2\text{]} > [\text{OMPy}]\text{[NTf}_2\text{]}\). However, in the case of the pyridinium ionic liquids the observed trend is \([\text{OP}]\text{[NTf}_2\text{]} > [\text{BP}]\text{[NTf}_2\text{]} > [\text{HP}]\text{[NTf}_2\text{]}\) at 25 °C. It is important to understand the solute-solvent interactions in ionic liquids that cause such drastic variations with temperature. The temperature-dependence of the polarity parameters or thermosolvatochromism for all the ionic liquids was then studied at 298–353 K. Depending on the cationic and anionic species, the polarity values showed either a direct or an inverse relation with the change in temperature. The \(E^N_T\) value decreases with temperature for the pyridinium-based (Fig. 8) and pyrrolidinium-based ionic liquids (Fig. 9), but increases with temperature for the phosphonium ionic liquids (Fig. 10). This indicates that the choice of the cation can determine the response of polarity to a change in temperature. The betaine dye systems are known to show a negative solvatochromism due to differential solvation of more polar ground state (dipole moment of ground state \(\mu_G = 15\) D) as compared to the less polar excited state (dipole moment of excited state \(\mu_E = 6\) D). This explains the blue shift of absorption maxima for betaine dye with increasing solvent polarity. In polar solvents, the ground state is stabilized due to stronger solute-solvent interaction as compared to the excited state. When the temperature is increased, the ground state solvent interactions are weakened, thus reducing the energy gap between the ground state and the excited state of the betaine molecule. As a result, an increase in temperature should cause a red shift in the absorption maximum of betaine dye in polar solvents. This is precisely the case observed for the pyridinium and pyrrolidinium-based ionic liquids. The opposite effect of temperature in the case of the phosphonium-based ionic liquids may then be explained along similar lines. The blue shifts in the solvatochromism indicate that the phosphonium ionic liquids solvate the excited state of betaine dye more efficiently as compared to the ground state. The greater stabilization of the excited state is also reflected in lower \(E^N_T\) value at 303 K in phosphonium-based ionic liquids as compared to the pyrrolidinium ionic liquids when the temperature increases.
The weakening of stabilizing excited state-solvent interactions should lead to an increase in energy gap between the ground state and excited state of betaine molecules. This causes the observed blue shift in the thermosolvatochromism. The results present an interesting contrast to Suppan’s generalization that “absorption bands which give solvatochromic blue shifts are expected, on this basis to show thermochromic red shift”. The present line of reasoning implies that while pyridinium- and pyrrolidinium-based ionic liquids are perceived as “polar” solvent by the betaine molecule, the phosphonium-based ionic liquids acts as “nonpolar” solvents for the same probe molecule. It would be interesting to validate this implication further by analyzing the reasons for the apparent contrast. Since the betaine dye is neither a hydrogen bond donor nor a Lewis acid, it is reasonable to assume that there is no direct interaction of the molecule with the anions of the ionic liquids. The betaine dye is capable of exhibiting strong dipole-dipole, dipole-induced dipole and H-bond acceptor and dispersion interactions (due to large polarizability). The cation-betaine molecule interaction should then be the primary interaction, while the influence of the anion is accounted for only in an indirect manner. An increase of solvent polarity for probe (2) leads to a bathochromic shift of $\nu_{\text{max}}$. This is consistent with series of $\pi^* - \pi$ transitions, which go from a relatively charge diffused ground state to an excited state, wherein electronic charges are more concentrated and charge centers are more separated. Hence, more polar solvents stabilize the electronic ground state with the effect of shifting $\nu_{\text{max}}$ to lower energy. As the temperature increases, the solute-solvent interactions are weakened. In the case of dye (2), this entails that the relative stabilization of the excited state decreases as the temperature increases.

Increase in excited energy is reflected by decreasing $\pi^*$ value with temperature for all the ionic liquids studied. It is difficult to discuss the variation in $\alpha$ and $\beta$ parameters along similar lines since these parameters are determined by the combination of responses of two or more solute probes. A thorough computational investigation into the interesting variations in thermochromic behavior of the dye molecules with the structure of the ionic liquids would be desirable in the future.

Applications

Chemical processes

Ionic liquids are found to be promising solvents in many of the organic reaction such as Diels-Alder, Bails-Hillman, Heck Reaction, esterification, isomerization reactions and many coupling reaction.\textsuperscript{55,56} Pressure, temperature and concentrations of reactants govern the progress of the reaction. However, it has been observed that viscosity can also play an important role in reaction kinetics. The rates of Diels-Alder reaction increase with an increase in viscosity up to $\sim$1 cP. A sharp downfall in the rates of these reactions is witnessed in solvents possessing viscosities greater $\sim$1 cP. The increase in the rates was attributed to the gain of vibrational mode at the expense of translational modes up to $\sim$1 cP, thus facilitating the bond formation.\textsuperscript{57} However, the reactions slow down considerably in viscous solvents owing to the diffusion problems in highly viscous environment thus causing retardation in the reaction rates. Reports are available on the rate of reaction being faster in the ionic liquids possessing higher viscosities than in the ones with lower viscosities.\textsuperscript{58} This means that the high viscosity favors the above reaction. In another study, the rate constants for a diffusion-controlled reaction involving neutral reactants were measured in ionic liquids with different viscosities at varying temperatures. The overall bimolecular rate constant, $k_2$, was noted to increase with an increase in the viscosities of ionic liquids. However, the data reported in the work appeared to be insufficient for conclusive evidence of the role of viscosity in Diels-Alder reactions.

In our laboratory, we discovered that the $k_2$ values for a number of Diels-Alder reactions in ionic liquids with varying viscosities were inhibited in the ionic liquids with high viscosities. The observations were attributed to the diffusion problems arising out of high viscosities. However, efforts to correlate $k_2$ values with different properties such as surface tension, solvent properties, etc., of ionic liquids, were not successful. The results were interpreted in terms of the restricted diffusion of reactants in the encounter-controlled regime. The order for the rates of reaction of cyclopentadiene with the three acrylates used was as follows: methyl acrylate > ethyl acrylate > butyl acrylate. The difference may arise due to the different microviscosity experienced by each of these acrylate molecules, which will be a complex function of the viscosity of the medium, the molecular volume of the reacting moiety and the viscosity of the acrylate itself. The enhanced steric effect will also play an important role in governing the reactions.

The reaction of cyclopentadiene with methyl acrylate showed Arrhenius behavior as evident from
the temperature dependence of rate constants in [BMIM][PF₆] and [EMIM][BF₄]. The activation energy, \( E_o \), was reported to be 63.4 kJ mol\(^{-1}\) and 57.7 kJ mol\(^{-1}\) for the reaction of cyclopentadiene with methyl acrylate in [BMIM][PF₆] and [EMIM][BF₄] respectively. However, any change in temperature led to a change in the \( \eta \) values of the ionic liquids, which affected the rate of the reaction. The “intrinsic” activation energy, \( E_o \), was reported to be 51.8 kJ mol\(^{-1}\) implying a difference \( (E_o - E_a) \) of 5.9 kJ mol\(^{-1}\) for [EMIM][BF₄] and of 11.6 kJ mol\(^{-1}\) for [BMIM][PF₆]. These values were in agreement with the qualitative prediction that the reactants would have to overcome a “higher barrier” in a more viscous medium, leading to a decrease in the rate of the reaction. A detailed study of the isoviscosity relationships, Arrhenius parameters and determination of microviscosity are some of the most challenging problems one needs to address in this area.

The effect of a “viscosity reducer” in the presence of ionic liquid was also checked on the rates of reaction. For this purpose, the reaction of cyclopentadiene with methyl acrylate was carried out at 298 K in a mixture of [BMIM][BF₄] with dichloromethane (45 mol % of [BMIM][BF₄] in 55 mol % of dichloromethane). Here, dichloromethane was used as a “viscosity reducer”, with \( \eta = \sim 18 \) cP as compared to the value of \( \eta = 233 \) cP for [BMIM][BF₄]. The resulting rate constant, \( k_2 \), was much higher than that in pure [BMIM][BF₄] or dichloromethane alone. Although a simple correlation between a given solvent property and the magnitude of a particular rate constant does not conclusively imply a dependence of rate on that solvent property, the evidences do merit further investigation.

It is important to understand the structure-property correlations with reference to their effects on the chemical processes. The highly viscous nature of ionic liquid can slow down the rate of a bimolecular Diels-Alder reaction by an order of magnitude as compared to that in water. However, there have been very few attempts to correlate the physico-chemical properties of ionic liquids with the kinetic and stereochemical outcome of the reactions. Towards this end, an extensive collection of kinetic data for a variety of organic reactions carried out in a range of ionic liquids and subsequent comparison of the results with theoretical models is essential. In this context, our group studied the kinetic studies of an intramolecular Diels-Alder (IMDA) reaction of (E)-1-phenyl-4-[2-(3-methyl-2-butenyloxy) benzylidene]–5-pyrazolone in a series of pyridinium-based ionic liquids. The IMDA reactions were carried out in different pyridinium based ionic liquids. The alkyl substituents on the pyridinium cation were varied to give different cations, viz., 1-butyl, 1-hexyl and 1-octyl. The anions used were \([\text{BF}_4]^–\) and \([\text{NTf}_2]^–\). The use of two anions resulted in a homologous series of ionic liquids, differing only with respect to the alkyl substituent on the pyridinium cations. Changing the alkyl substituents, the anion or the temperature, could thus vary the viscosity of the ionic liquids (Fig. 11). The rate constants within the \([\text{BF}_4]^–\) series of ionic liquids show a definite correlation with the viscosity of the medium. The rate of reaction decreased from \( 4.45 \times 10^5 \) s\(^{-1}\) in [BP][BF₄] to \( 1.68 \times 10^5 \) s\(^{-1}\) in [3MOP][BF₄] for a corresponding change in viscosity from 175.4 cP to 66.1 cP at 308 K. The correlation between \( k \) and \( \eta \) was not very obvious for the \([\text{NTf}_2]^–\) series. Surprisingly, the magnitude of \( k \) in the \([\text{NTf}_2]^–\) ionic liquids was very close to that in \([\text{BF}_4]^–\) based ionic liquids. If the rate constants are indeed dependent on the viscosity of the medium, then the lower viscosity of the \([\text{NTf}_2]^–\) based ionic liquids should have led to higher rates.

In order to access the correlation between the rates and viscosity in greater detail, temperature dependent studies were carried out in different ionic liquids. The variation in temperature served to control the

Fig. 11 — Plot of \( \ln k \) for the IMDA reaction against the viscosity, \( \eta \), of pyridinium ionic liquids with \([\text{BF}_4]^–\) anion (○) and \([\text{NTf}_2]^–\) anion (□) at different temperatures. [Figure taken from ref. 53a].
viscosity of the medium and the results plotted are a compilation of the rates in different ionic liquids at different temperatures. For the $[\text{BF}_4^-]$ series of ionic liquids, the uniform variation in the experimental data showed that the rate constants at the same viscosity were nearly the same (independent of the means by which that viscosity value was attained) on changing the alkyl substituent or the temperature. The rate constants decreased uniformly with increasing viscosity, thus indicating “universal” viscosity dependence. It was obvious however, that this “universal” trend failed to extend to the $[\text{NTf}_2^-]$ series. The $[\text{NTf}_2^-]$ based ionic liquids also showed a similar but independent trend with the changing viscosity; in fact, the decrease in rates was sharper for $[\text{NTf}_2^-]$ ionic liquids for a similar magnitude of increase in viscosity. At a given value of viscosity, the rate of the IMDA reaction in $[\text{NTf}_2^-]$ was much lower than that in the $[\text{BF}_4^-]$ ionic liquid. The rate constant decreased from $\sim13 \times 10^{-5}$ s$^{-1}$ to $\sim3 \times 10^{-5}$ s$^{-1}$ when the viscosity increased from 50 cP to 100 cP for the $[\text{BF}_4^-]$ based ionic liquids, i.e., a decrease to one-fourth of the original rate constant. For a viscosity of 100 cP for $[\text{NTf}_2^-]$ ionic liquids, the rate decreased to one-tenth of its value at 50 cP, i.e., from $\sim2.10 \times 10^{-5}$ s$^{-1}$ to $\sim0.21 \times 10^{-5}$ s$^{-1}$.

The results indicate that in addition to viscosity, the rates are also influenced by a solvent property that varied, independent of viscosity, on changing from one anion series to another. Within the homologous series, this effect might still be operative but was either masked by a greater competing influence of viscosity or it changed in proportion to the viscosity.

**Electrochemical devices**

Excellent reviews are published demonstrating the applications of ionic liquids to electrochemical devices such as super capacitors, lithium ion batteries, polymer-electrolyte fuel cells and dye-sensitized solar cells. In an electrochemical device, an ionic liquid acts as electrolyte. $^{60-64}$ Ionic liquids should be resistant to any electrochemical reduction and oxidation. Two main advantages of using ionic liquids in electrochemical devices include non-volatility and prevention of electrolytes from drying during the operation. The transport properties, like viscosity, conductance and diffusion gain significance when one considers diffusion process or conductivity for making an effective electrochemical device. However, the fundamental requirement for an ionic liquid to be useful in developing applications in electrochemistry is that it should be able to offer a wide electrochemical window. While aqueous systems possess about 1.23 V as the electrochemical window, propylene carbonate and acetonitrile can offer an electrochemical window as high as 4 V. Almost many the ionic liquids offer electrochemical window in the range of 4-5 V, while the most common and popular ionic liquid, $[\text{BMIM}][\text{BF}_4]$, possesses an electrochemical window as high as 6 V as shown in Fig. 12. Another ionic liquid, $[\text{BMP}][\text{CF}_3\text{SO}_3]$, is reported to have an electrochemical window of 6 V.

One notes that the selection of reference electrode can be very important criteria in enhancing electrochemical stability. Ionic liquids have been found to be useful for electric double layer capacitors.$^{65,66}$ Several applications in this regard have been critically examined. For example, many ionic liquids composed of $[\text{EMIM}]$ cation with a variety of anions have been found effective. Another popular ionic liquid, $[\text{BMIM}][\text{BF}_4]$, with quite a high electrochemical window is also very useful for this application. In general, the capacitance changes in the order: aqueous solutions > ionic liquids > organic solutions.

The high viscous ionic liquid has also been mixed with propylene carbonate to decrease the viscosity and to provide output data better than conventional systems. Another important area of application of ionic liquids is lithium batteries. The main interest in using ionic liquids for this application has been to find

![Fig. 12 — Electrochemical window of $[\text{BMIM}][\text{BF}_4]$ measured by linear sweep voltammetry using W, Pt electrodes which require a high conductivity and a wide electrochemical window.](image-url)
substitutes for organic solvents. Also, if ionic liquids are used instead of organic solvents, the batteries will be safer to use. Chloroaluminate ionic liquids have been used from the very beginning in lithium batteries. In fact, this is the reason that one finds a large number of data on physico-chemical and electrochemical properties of chloroaluminates. Normally, a combination of two species has been employed for this work. Also, ionic liquids with [BF$_4$]$^-$ and [NTf$_2$]$^-$ anions coupled with lithium salts of the same anion have been frequently employed for this purpose. For example, [EMIM][BF$_4$] mixed with LiBF$_4$ acts as a good substance for lithium battery with LiCoO$_2$ as a cathode material. Also, one gets good results with LiCoO$_2$ and Li-Al as cathode and anode materials, respectively with the same ionic liquid. In order to avoid cathodic reduction, pyrrolidinium and piperidinium based ionic liquids are preferable. Interestingly, some additives like water and SOCl$_2$ in traces with ionic liquids have been reported to be effective for this application. Also, ionic liquids based on guanidinium cation with [NTf$_2$]$^-$ anion are found to be potential electrolytes for electrochemical devices. Though exhaustive reports are available, reviewing the use of ionic liquids in lithium batteries, a greater need exists to develop a model to predict the composition of a mixture of ionic liquids with some solvent that will provide the optimum results on lithium batteries. It is now certain that ionic liquids with sufficient conductivity and cycle stability in the lithium deposition/dissolution process can be designed by introducing appropriate functional groups. Ionic liquids are non-volatile due to their insignificant vapor pressure. This property of ionic liquid renders them a potential candidate for solar cell. An important point has emerged in this regard. Ionic liquids based on [HMIM] cation and [NTf$_2$]$^-$ anion are noted to be effective in solar cells. Further, addition of a dye in ionic liquid system has been noted to enhance the efficiency of a solar cell. Ionic liquids have appeared to be potential substitute for smooth operation of polymer electrolyte membrane fuel cell at high temperatures. A mixture of ionic liquids with additives like amines is the most promising candidate for this work. Proton conducting gelatinous electrolyte with [BMIM][BF$_4$] are thermally mechanically stable up to 300 °C. It is now possible to transport hydrogen via fluorohydrogenate conduction in ionic liquids system. Quite interestingly, ionic liquids have found a useful role in actuators. The research group of Asaka$^{67}$ has shown that a dry actuator can be fabricated layer to layer casting using bucky gel, which is a gelatinous room temperature ionic liquids containing single wall carbon nanotubes. The solid polymer electrolyte layer is sandwiched between polyaniline (PANI) and polypyrrole (PPY), etc. Unfortunately, the solid polymer electrolyte layer possessing low ionic conductivity leads to slow response system. The electrolyte solution gives rise to swelling polymer electrolyte thereby leading to poor performance of the system. Figure 13 depicts a cross section of PPy double sided actuators with ionic liquids. [BMIM][PF$_6$] showed PPy was stable and was able to withstand continuous functioning for more than 3600 cycles without degradation.$^{68}$

**Extraction technology**

Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, processing of perfumes and other industries. The use of ionic liquids to separate toxic metal ions and organic molecules has been investigated.$^{69,70}$ At present, ionic liquids have been used as extraction solvents for the separation of metal ions by crown ethers. Hence, ionic liquids have got much more attention towards their use in extraction processes. Earlier, crown ethers found use in designing novel solvent extraction systems that are selective for certain metal ions which are based on the size of the crown-ether rings. Crown ether extract metal ions from aqueous solutions by complexation. The efficiency of such extraction processes is strongly dependent not only on cations but also on counter anions. The extraction process is more favored by hydrophobic counter anions in aqueous solutions than

![Fig. 13 — Cross-section of PPy double sided PVDF electrochemical actuator using polymer in ionic liquids as electrolyte. [Published from ref. 69, with copyright permission from Elsevier Limited, UK.]](image-url)
with hydrophilic anions. Due to low efficiency in using crown ether for extraction, ionic liquids have been used as extraction solvents to remove strontium nitrate from aqueous phase into ionic liquids by crown ether.\textsuperscript{71} The distribution coefficients for the ionic liquid extraction systems are higher than extraction systems based on organic solvents. Successful extraction of organic acids from aqueous solutions into an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, has been reported. The solvation of ionic species (such as crown-ether complexes, NO\textsubscript{3} and SO\textsubscript{4}) in the ionic liquids is more favored thermodynamically than in conventional solvent extractions. The unique solvation capability of the room-temperature ionic liquid has not been used to full advantage.

In many nuclear plants, large volumes of liquid waste are produced, called “tank waste.” This liquid waste, which may be acidic or basic depending on the treatment process, contains many long-lived radioactive products, including \(^{137}\)Cs, \(^{129}\)I, \(^{90}\)Sr and \(^{99}\)Tc and a variety of transuranic elements, which are normally \(\alpha\)-emitters.\textsuperscript{72} The \(^{137}\)Cs\(^{+}\) and \(^{90}\)Sr\(^{2+}\) in tank waste are normally present at low concentrations in a large volume of liquid and any treatment process for this waste must therefore produce a significant reduction in the volume of this liquid. So to extract these radioactive products, ionophores such as calix[4]arene-bis(octylbenzocrown-6), BOBCalixC-6 and dicyclohexano-18-crown-6, dissolved in hydrophobic solvents, including hydrophobic ionic liquids have been used.\textsuperscript{73} Hence, electrochemistry can play a useful role in this recycling process. This proposed electrochemical process for remediation of the extraction solvent preserves both the ionophore and ionic liquids.

**Conclusions**

From the above discussion, it is clear that ionic liquids can be very effective solvent media for obtaining optimum output in several applications with minimum possible environment pollution. It is hoped that demerits of ionic liquids such as high viscosity will be tackled by chemical or physical means to enable them to emerge as very powerful solvents. It is also hoped that simple semi-empirical models if developed, will be able to help many chemical engineers to predict thermal and transport properties of ionic liquids on the basis of the information on the structures of ionic liquids.

**Acknowledgement**

NDK thanks CSIR, New Delhi, for providing a research fellowship to carry out this work. AK thanks DST, New Delhi, for providing financial assistance in the form of many research grants-in-aid during which this work was carried out.

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MMIM]</td>
<td>1,3-Dimethyl imidazolium</td>
</tr>
<tr>
<td>[EMIM]</td>
<td>1-Ethyl-3-methyl imidazolium</td>
</tr>
<tr>
<td>[BMIM]</td>
<td>1-Butyl-3-methyl imidazolium</td>
</tr>
<tr>
<td>[HMIM]</td>
<td>1-Hexyl-3-methyl imidazolium</td>
</tr>
<tr>
<td>[OMIM]</td>
<td>1-Octyl-3-methyl imidazolium</td>
</tr>
<tr>
<td>[BMPyr]</td>
<td>1-Butyl-1-methyl pyrrolidinium</td>
</tr>
<tr>
<td>[HMPyr]</td>
<td>1-Hexyl-1-methyl pyrrolidinium</td>
</tr>
<tr>
<td>[OMPyr]</td>
<td>1-Octyl-1-methyl pyrrolidinium</td>
</tr>
<tr>
<td>[BP]</td>
<td>1-Butyl-pyridinium</td>
</tr>
<tr>
<td>[HP]</td>
<td>1-Hexyl-pyridinium</td>
</tr>
<tr>
<td>[OP]</td>
<td>1-Hexyl-pyridinium</td>
</tr>
<tr>
<td>[4-MBP]</td>
<td>1-Butyl-4-methyl pyridinium</td>
</tr>
<tr>
<td>[TBP]</td>
<td>Tetrahexyl phosphonium</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>Tetrafluoroborate</td>
</tr>
<tr>
<td>PF(_6)</td>
<td>Hexafluorophosphate</td>
</tr>
<tr>
<td>NTF(_3)</td>
<td>Bis(trifluoromethane sulfonyl)jiimide</td>
</tr>
<tr>
<td>C(_2)H(_3)SO(_3)</td>
<td>Ethyl sulfate</td>
</tr>
<tr>
<td>CF(_3)CO(_2)</td>
<td>Trifluoromethyl acetate</td>
</tr>
<tr>
<td>CF(_3)SO(_3)</td>
<td>Trifluoromethyl sulfate</td>
</tr>
<tr>
<td>(C(_2)F(_3)SO(_2))(_2)N</td>
<td>Bis(pentafluoroethanesulfonyl)jiimide</td>
</tr>
<tr>
<td>[Ala]</td>
<td>Alanate</td>
</tr>
<tr>
<td>[Val]</td>
<td>Valinate</td>
</tr>
<tr>
<td>ClO(_4)</td>
<td>Perchlorate</td>
</tr>
<tr>
<td>(\Delta\eta)</td>
<td>Excess viscosity</td>
</tr>
<tr>
<td>(V/\rho)</td>
<td>Volume fraction of ionic liquids</td>
</tr>
</tbody>
</table>

**References**
