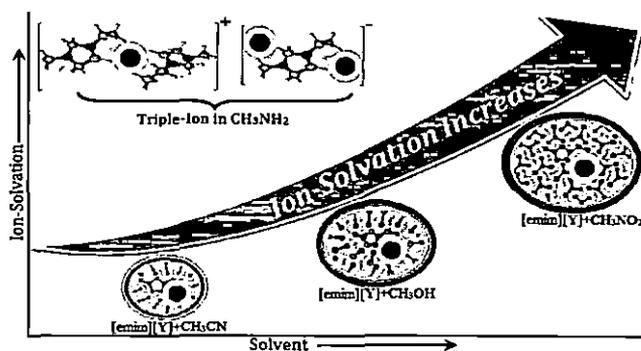


# CHAPTER - V

## Quantitative and Qualitative Analysis of Ionic Solvation of Individual Ions of Imidazolium Based Ionic Liquids in Significant Solution Systems by Conductance and FTIR Spectroscopy

Analysis of molecular interactions quantitatively by precise measurement of conductance ( $\Lambda$ ) and qualitatively by the FTIR spectroscopy, in the solution systems between some imidazolium based ionic liquids



[[emim]NO<sub>3</sub>, [emim]CH<sub>3</sub>SO<sub>3</sub>, [emim]Tos) and non-aqueous solvents (acetonitrile, methanol, nitromethane, methylamine solution) have been reported at 298.15K. Fuoss conductance equation (1978) and Fuoss-Kraus theory, for ion-pair and triple-ion formations respectively have been used for analysing the conductance data. Using the appropriate division of the limiting molar conductivity value of [Bu<sub>4</sub>NBPh<sub>4</sub>] as "reference electrolyte", the limiting ionic conductances ( $\lambda_0^\pm$ ) for individual ions have been calculated and reported. Dipole-dipole interaction, hydrogen bonding formation, structural aspect, and configurational theory are the driving forces, have been employed for discussion of the results. FTIR spectroscopic studies of variational intensity of characteristic bands of the studied solvents have been undertaken and the solvation phenomenon is manifested by the change of these band intensities in the presence of ionic liquids.

## V.1 INTRODUCTION

Ionic liquids (ILs) have been actively tested as innovative non volatile compound and they are used in many academic and industrial research areas. Most of the ionic liquids are good examples of neoteric solvents (new types of solvents, or older materials that are finding new applications as solvents), which is environmentally friendly (or eco-friendly) because they are less hazardous for human body as well as less toxic for living organisms. Room-temperature ionic liquids (RTILs) are salts in liquid state with relatively low melting points (below 100°C) that usually consist of an organic cation or anion and a counter-ion. Generally, an ideal electrolyte should have high ionic conductivity ( $>10^{-4}$  S cm<sup>-1</sup>), fast ion mobility ( $>10^{-14}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), large electrochemical potential windows ( $>1$  V), and low volatility. RTILs exhibit most of these properties and characteristics. Recently, ionic liquids (ILs) have been well thought-out as the innovative compound, owing to their inimitable inherent characteristics, such as negligible vapour pressure, large liquid range, ability of dissolving a variety of chemicals, non-volatility, high thermal stability, large electrochemical window and their potential as 'designer solvents' and 'green' replacements for volatile organic solvents.<sup>[V.1]</sup> They have been intensively investigated for various applications such as recyclable solvents for organic reactions and separation processes,<sup>[V.2]</sup> lubricating fluids,<sup>[V.3]</sup> heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in the field of electrochemistry (batteries and solar cells)<sup>[V.4, V.5]</sup> and so forth. By modifying the cations and anions, the physical properties (such as the melting point, viscosity, density, hydrophobicity, or hydrophilicity) of ionic liquids can be customized.<sup>[V.6]</sup> In the modern technology, industry, and also in academic research field, the vast application of the ILs is frequently increases, and this is well understood by studying the ionic solvation or ion-association.

ILs can be classified into two groups: protic ILs (PILs) and aprotic ILs (AILs).<sup>[V.7]</sup> Generally, PILs are synthesized with equimolar amounts of a Brønsted acid and a Brønsted base.<sup>[V.8]</sup> Because of the recent interest in proton-conducting electrolytes,<sup>[V.8]</sup> PILs appear as promising materials for aqueous batteries, fuel cells, double-layer capacitors, solar cells, or actuators.<sup>[V.9]</sup> The selected ionic liquids are one of the AILs.

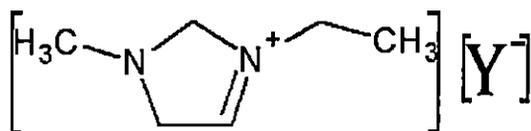
There are several imidazolium, pyridinium, ammonium and phosphonium based cation ionic liquids commercially available. Ionic liquids based on imidazolium cations have been demonstrated to exhibit AILs and has greater thermal stability and are commercially available in large quantity.<sup>[V.10]</sup>

The ionic liquids with functional groups or polar anions (here,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ , and  $\text{Tos}^-$ ) are capable for additional interactions with polar solvents. Given their structure and diversity of functionality, they are capable of most types of interactions (*i.e.*, hydrogen bonding, ion-dipole, dipole-dipole, van der Waal forces etc).<sup>[V.11, V.12]</sup>

A plenty of works in conductometric<sup>[V.13, V.14]</sup> and allied study of potential electrolytes in non-aqueous common solvents have been equipped for their supreme use in high-energy batteries<sup>[V.15]</sup> and for furthermore understanding organic reaction mechanisms.<sup>[V.16, V.17]</sup> Ionic level of association of the individual ions of the electrolytes in studied solution systems depends on the manner of solvation of its ions, which in turn depends on the characteristics of the solvent or solvent mixtures. The solvent properties such as viscosity and the relative permittivity have been taken into deliberation as these properties are excellently assist in determining the extent of ion-solvent interaction as well as the ion association occurring in the solution systems. On the other hand the non-aqueous solution systems have also been of massive importance<sup>[V.18]</sup> to the industrialist, technologist and theoretician (in industry as well as academic chemistry), to examine the nature, mode and magnitude of ion-ion and ion-solvent interactions, for the reason that many chemical processes take place in these systems.

As the literature review divulge that very scant work have been accomplished in studied binary solution systems and keeping in mind the vast application of the studied systems; in continuation of the present study on electrical conductance, an endeavour has been made to explore the nature of ion-solvation of 1-ethyl-3-methylimidazolium based ionic liquids {1-ethyl-3-methylimidazolium nitrate [emim] $\text{NO}_3$ , 1-ethyl-3-methylimidazolium methanesulfonate [emim] $\text{CH}_3\text{SO}_3$ , and 1-ethyl-3-methylimidazolium tosylate [emim] $\text{Tos}$  (Scheme V.1) in non-aqueous polar solvents, acetonitrile ( $\text{CH}_3\text{CN}$ ), methanol ( $\text{CH}_3\text{OH}$ ), nitromethane ( $\text{CH}_3\text{NO}_2$ ), and methylamine solution ( $\text{CH}_3\text{NH}_2$ ). The solvation phenomenon is evident by the shifting of the vibrational intensity of characteristic bands (functional group) of the

studied solvents in FTIR spectroscopy due to the presence of the ionic liquids in the solution.



**Scheme V.1:** 1-ethyl-3-methylimidazolium based ionic liquids;  
(where Y= NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> and Tos<sup>-</sup>)

## V.2 EXPERIMENTAL

### V.2.1 Source and purity of materials

The RTILs selected for the present work puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of [emim]NO<sub>3</sub>, [emim]CH<sub>3</sub>SO<sub>3</sub>, and [emim]Tos} was ≥ 0.99, 0.98, and 0.98 respectively.

All the solvents of spectroscopic grade were procured from Sigma-Aldrich, Germany and were used as procured. The purities of acetonitrile, methanol, nitromethane, and methylamine solution were 99.8%, ≥99.8%, ≥98.5%, and ≥40% wt. in water respectively. The purity of the solvents were checked by measuring their density, viscosity and conductivity values, which were in good agreement with the literature values<sup>[V.19]</sup> as shown in Table V.1.

### V.2.2 Apparatus and Procedure

Prior of the start of the experimental work we have been precisely checked, the solubility of the selected ionic liquids; the selected room temperature ionic liquids (RTILs) were liberally soluble in all proportion of the solvents. All the mother solutions of the electrolytes (ILs) in studied solvents were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003g). For the conductance data the working solutions, were obtained by mass dilution of the prepared mother solutions.

The specific conductance data have been measured by means of a Systronics-308 conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately (0.1±0.001) cm<sup>-1</sup>. The

measurements have been made in a thermostat water bath maintained at the experimental temperature  $T = (298.15 \pm 0.01)$  K. The cell was calibrated by the method proposed by Lind et al.<sup>[V.20]</sup> and cell constant was measured based on 0.01 M aqueous KCl solution. The conductance data have been reported at a frequency of 1 kHz and the accuracy was  $\pm 0.3\%$ . During all the measurements, uncertainty of temperatures was  $\pm 0.01$  K.

For analysing the conductance data, the density and viscosity of the solvents are required. So, the densities ( $\rho$ ) of the solvents were measured by means of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with a precision of  $\pm 0.00005\text{g cm}^{-3}$  maintained at  $\pm 0.01\text{K}$  of the desired temperature. It was calibrated by triply-distilled water and passing dry air.

The viscosities ( $\eta$ ) were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The viscosities were obtained using the following equation

$$\eta = \left( \frac{100}{RPM} \right) \times TK \times torque \times SMC$$

where  $RPM$ ,  $TK$  (0.09373) and  $SMC$  (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous  $\text{CaCl}_2$  solutions.<sup>[V.21]</sup> The temperature was maintained to within  $\pm 0.01^\circ\text{C}$  using Brookfield Digital TC-500 thermostat bath. The viscosities were measured with an accuracy of  $\pm 1\%$ . Each measurement reported herein is an average of triplicate reading with a precision of 0.3 %.

Infrared spectra have been recorded in 8300 FTIR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described.<sup>[V.22]</sup> The concentration of the studied solutions used in the IR study is 0.05M.

## V.3 RESULTS AND DISCUSSION

### V.3.1 Ion-pair formation from electrical conductance

In comparison with the literature data, the experimentally measured physicochemical properties of the pure solvents at 298.15 K are reported in Table V.1, where appropriate corrections were made by the specific conductance of the solvents at desired temperature and apt precaution has been taken during the measurement.

The experimentally measurable quantity specific conductance ( $\kappa$ ,  $\mu\text{S cm}^{-1}$ ) of the electrolytes (ILs) solutions in chosen solvents were measured by Systronics-308 Conductivity Bridge. The measurement have been made within a molar concentration range of  $1.13 \times 10^{-4}$  –  $1.04 \times 10^{-3}$  (M) at the experimental temp. Using the specific conductance data, the molar conductances ( $\Lambda$ ) for all studied solution systems (ionic liquid + solvent) have been calculated by the appropriate equation.<sup>[V.23]</sup>

The determined molar conductances ( $\Lambda$ ) values of the solutions of studied ionic liquids in different chosen solvents (IL+solvent) at the corresponding molar concentrations ( $c$ ) were represented in Table V.2. The linear variation of the molar conductance data against the square root of concentration ( $\Lambda$  versus  $\sqrt{c}$ ) have been found for the range of higher to moderate relative permittivity for the solvents acetonitrile ( $\epsilon_r = 35.95$ ), methanol ( $\epsilon_r = 32.70$ ), and nitromethane ( $\epsilon_r = 35.87$ ) and depicted in Figure V.1. The extrapolation of  $\sqrt{c} = 0$  (i.e; at the infinite dilution), it appraise the starting limiting molar conductance for the electrolytes. However, the non-linearity in Figure V.2 has been found in the conductance curves vs square root of concentration, in case of the low relative permittivity ( $\epsilon_r < 10$ ) solvent (methylamine solution,  $\epsilon_r = 9.10$ ). The Fuoss conductance equation (1978)<sup>[V.24, V.25]</sup> has been used for analyze the linear variation conductance data in higher or moderate relative permittivity solvents. For a given set of conductivity values ( $c_j, \Lambda_j, j=1, \dots, n$ ), for each of the electrolyte in the solvents, the three adaptable parameters, the limiting molar conductance ( $\Lambda_0$ ), the association constant ( $K_A$ ), and the distance of closest approach of ions ( $R$ ) are derived from the following set of equations

$$\Lambda = P\Lambda_0[(1+R_x) + E_L] \tag{V.1}$$

$$P = 1 - \alpha(1 - \gamma) \tag{V.2}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{V.3}$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)} \tag{V.4}$$

$$\beta = \frac{e^2}{(\epsilon_r k_B T)} \tag{V.5}$$

$$K_A = \frac{K_R}{(1 - \alpha)} = \frac{K_R}{(1 + K_S)} \tag{V.6}$$

where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current,  $k^{-1}$  is the radius of the ion atmosphere,  $\epsilon_r$  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,  $K_A$  is the overall pairing constant,  $K_S$  is the association constant of the contact-pairs,  $K_R$  is the association constant of the solvent-separated pairs,  $\gamma$  is the fraction of solute present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $f$  is the activity coefficient,  $T$  is the absolute temperature and  $\beta$  is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss.<sup>[V.25]</sup> The introductory values of the limiting molar conductance  $\Lambda_0$ , for the iteration procedure were obtained from Shedlovsky extrapolation of the conductance data. Input for the program is the set  $(c_j, \Lambda_j, j = 1, \dots, n), n, \epsilon_r, \eta, T$ , initial values of  $\Lambda_0$ , and an instruction to cover a pre-selected range of  $R$  values.

The best value of the observable parameters have been taken those one, when the equations is best fitted to the experimental data corresponding to minimum standard deviation  $\delta$  for a sequence of predetermined  $R$  values. The standard deviation  $\delta$  was calculated by the following equation

$$\delta^2 = \sum \frac{[\Lambda_j(cal) - \Lambda_j(obs)]^2}{(n - m)} \tag{V.7}$$

where  $n$  is the number of experimental points and  $m$  is the number of fitting parameters. The conductance data were evaluated by fixing the distance of closest approach  $R$  of ions with fitting two parameter (*i.e.*;  $m = 2$ ). No significant minima were found in the curve of  $\delta$  versus  $R$  for the studied ionic liquids (ILs) in the

solvents (acetonitrile, methanol, nitromethane), whereas the  $R$  values were arbitrarily preset at the centre to centre distance of solvent-separated ion pair. Thus, theoretically the  $R$  values are assumed to be  $R = (a + d)$ ; where  $a = (r_+ + r_-)$  is the sum of the crystallographic radii of the cation ( $r_+$ ) and anion ( $r_-$ ) and  $d$  is the solvent effect parameter, which is the average distance corresponding to the side of a cell occupied by a solvent molecule. The average distance,  $d$  is given by<sup>[V.26]</sup>

$$d(\text{\AA}) = 1.183 \left( \frac{M}{\rho} \right)^{1/3} \quad (\text{V.8})$$

where  $M$  and  $\rho$  is the molar mass and density of the solvent respectively.

The programmable values of  $\Lambda_0$ ,  $K_A$ , and  $R$  obtained by this procedure for all the studied ionic liquids in selected solvents are represented as a tabular form in Table V.3. Perusal of Table V.3 discloses that the observed limiting molar conductances ( $\Lambda_0$ ) for each of the electrolytes (ILs) gradually decrease from acetonitrile to nitromethane among the studied solvents. Thus the observed trend of the  $\Lambda_0$  values is;

$$\Lambda_0(\text{CH}_3\text{CN}) > \Lambda_0(\text{CH}_3\text{OH}) > \Lambda_0(\text{CH}_3\text{NO}_2)$$

The order is the converse of the order of the viscosities of these solvents. As expected, limiting molar conductance values should decrease when the viscosity of the solvents increases, because the ionic mobility is diminished in viscous medium. Interestingly, it is seen from Figure V.3, a linear relationship exists between the limiting molar conductivities for each of ILs and the reciprocal of the viscosity ( $1/\eta$ ) (or the fluidity,  $\eta^{-1}$ ) for the solvents. From the Table V.1 and Table V.3, we have seen that the association constant ( $K_A$ ) as well as the  $\log(K_A)$  values were linearly vary with the viscosity values of the solvents; which also shows that the viscous medium diminished fluidity of the ion, and this is obviously due to the association of the ions as well as electrolyte by the solvent molecules in the solution systems. This suggests that the fluidity ( $\eta^{-1}$ ) of the solvents played a predominant role in the limiting molar conductivities, in addition to the association of the ILs. The similar observation has been observed by Huiyong Wang and co-workers.<sup>[V.27]</sup>

From the willpower of ion-association constants ( $K_A$ ) of the studied ILs, some characteristics may be concluded from the present results. We have examined the

consequence of the solvent properties on the ion-association behaviour of the selected ILs. It is interesting to note from Table V.3 that the association constant ( $K_A$ ) of the ionic liquids (ILs) is just inverse of the limiting molar conductance, (i.e.,  $K_A \propto \frac{1}{\Lambda_0}$ ). The magnitudes of the  $K_A$  are lower in acetonitrile and higher in case of nitromethane for each of the electrolyte, which is in following order;

$$K_A(\text{CH}_3\text{NO}_2) > K_A(\text{CH}_3\text{OH}) > K_A(\text{CH}_3\text{CN})$$

As the idea, literature inspection and experimental results indicates that the association constant ( $K_A$ ) are represent the ion-solvent interaction or ion-association. The interactions between the electrolytes (as well as ions) and solvent molecules in the binary solutions, are increases from acetonitrile to nitromethane among the chosen solvents, leading to a lower conductance of ionic liquids. In comparison between the Table V.1 and V.3, we can see that the association constant values follow the same trend as viscosity value of the solvents. Thus the viscosity values also support the above facts, i.e. the electrolytes (ILs) in the lower viscous solvent, the  $\Lambda_0$  value should increase or mobility of the ion should increase. But the fact is not in line with the relative permittivity ( $\epsilon_r$ ) of the solvents. Although the decreasing trend of viscosity for the solvents suggests concomitant increase in limiting molar conductances<sup>[V.28, V.29]</sup> for the electrolytes. The trend suggest the solvents viscosity ( $\eta_0$ ) is predominance over the relative permittivity ( $\epsilon_r$ ), in effecting both of the electrolytic conductance and association constant of the electrolytes (ILs) under the studied solution media. This also suggests that the solvent effect for ion-association of ILs is similar to that of typical electrolytes, and electrostatic interaction between the cation and anion is mainly responsible for their association. The data in Table V.3 allow us to evaluate the ion-association ability of anions of the ILs with comparison of  $K_A$  values for [emim] $\text{NO}_3$ , [emim] $\text{CH}_3\text{SO}_3$ , and [emim]Tos in chosen solvents. It is clear that the anion species dependence of the association constants for the common imidazolium based ionic liquids, is of the following order:



This trend suggests that the high solvation of the  $\text{Tos}^-$  anion significantly enhance its association relative to  $\text{CH}_3\text{SO}_3^-$  and  $\text{NO}_3^-$  in the molecular solvents, which concordat the similar shape observed experimentally. Therefore, it is apt to state that

the net result of good alliance between the intrinsic interactions of cations with anions and the ion-solvation.

The Walden product ( $\Lambda_0\eta$ ) (product of the limiting molar conductance and solvent viscosity) and it is a constant under normal condition, is the another characteristic function for discussion and validating the trend obtained in limiting molar conductance ( $\Lambda_0$ ) and ion-association and given in Table V.3. From Table V.3 and Figure V.4, the falling trend of Walden product from acetonitrile to nitromethane, is excellent agreement with the concomitant raise in the solvents viscosity and falling limiting molar conductance of the electrolytes (ILs) in the studied solvents. This is warranted as the Walden product of an ion or solute is inversely proportional to the effective solvated radius ( $r_{eff}$ ) of the ion or solute in a particular solvent<sup>[V.30]</sup> and have been estimated from the following equation;

$$\Lambda_0\eta = \frac{1}{6\pi r_{eff}T} \quad (V.9)$$

The variation of the Walden product reflects on the degree of solvation.<sup>[V.12]</sup> It is difficult to interpret quantitatively the variation of the Walden product with solvent composition. However, the part of a set of information arise from the results that the electrostatic ion-solvent interactions or ion-associations is stronger in these cases. The variation with solvent composition the solvation phenomenon can be explained by the following aspect:

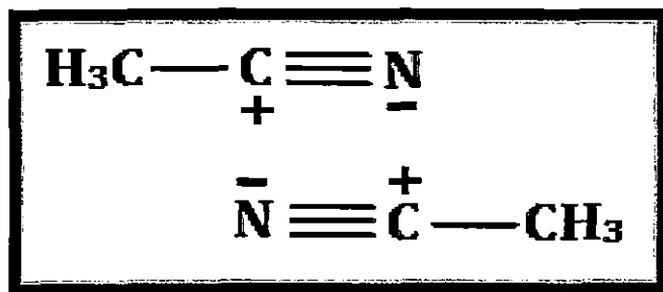
- (i) Preference of solvation of the electrolytes (ILs) for solvent molecules. Taking into consideration of the conductance and association constant value of ionic liquids in deferent solvents, we can say that the studied ILs mostly prefer the nitromethane compared to the other two solvents and the order of preference of solvation by the ILs in the chosen solvents is as follows:

**nitromethane > methanol > acetonitrile**

- (ii) With considering the structural aspect of the solvents,

- (a) In case of acetonitrile ( $\text{CH}_3\text{CN}$ ), the interaction present between negatively charged nitrogen atom of acetonitrile and positively charged N atom of  $[\text{emim}]^+$  moiety, shown in (I) of Scheme V.2, i.e., the interaction occurs through the ion-dipole interaction. Dimerization of acetonitrile, in  $\text{CH}_3\text{C}^+\text{N}^-$  most of the positive charge is on the nitrile carbon, i.e., "inside" the

molecule, evidence that acetonitrile tends to associate and forming the antiparallel dimer<sup>[V.31]</sup> represent in **Scheme V.3**. The existence of antiparallel dimerization in acetonitrile or interaction of the acetonitrile molecules itself (solvent-solvent interaction), leads to the formation of less ion-solvent interaction with the ionic liquids.



**Scheme V.3: Antiparallel dimerization of acetonitrile (CH<sub>3</sub>CN)**

- (b) The interaction of the ionic liquids is present in case of methanol are shown in (II), where the interaction is more intense due to the presence of more negative oxygen atom in molecular structure of methanol, making it stronger interaction with ILs either it interact with electrostatic, ion-dipole interaction between negatively charge oxygen atom and the positively charged nitrogen atom of the imidazole centre of the [emim]<sup>+</sup> moiety or H-bond interaction of methanol and NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup>.
- (c) In case of nitromethane, where three nucleophilic centres are present (two electronegative oxygen atoms and one nitrogen), show in (III); gives the more number of interacting centre to interact with the studied ionic liquids. Thus in the solution of ILs+nitromethane, the nitromethane strongly interact with more number of attacking centres with the ionic liquids through H-bond/ion-dipole interaction etc. Hence gives the highest value of ion-association constant as well as higher aggregation.

The schematic representation of plausible ion-solvent interaction, for the particular ion in the studied solvents (*i.e.*; ILs+solvents), in view of various derived parameters is depicted in **Scheme V.2**.

To investigate the role of the individual ions of the ILs in the ion-solvation phenomenon, we have to split the limiting molar conductance values into their ionic

contributions. The ionic conductances  $\lambda_o^\pm$  for the [emim]<sup>+</sup> cation and NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup> anion in different solvents, were calculated using tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>) as a 'reference electrolyte' using the following scheme as suggested by B. Das et al.<sup>[V.32]</sup> We have premeditated the ionic limiting molar conductances  $\lambda_o^\pm$ , in studied solvents by interpolation of conductance data from the literature<sup>[V.33]</sup> using cubic spline fitting. The determined ionic conductance values are given in Table V.4. Perusal of Table V.4 illustrates that the degree of ionic conductance is higher for [emim]<sup>+</sup> ion than that of the NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup>, which suggested the greater share in the ionic association come out from the anions (NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup>) than the common imidazolium cation [emim]<sup>+</sup>. The prime clue for the most part estimation of ionic contribution in the conductance came out from the Stokes' law, which provide the valuable inkling about limiting ionic Walden product. The law states that the limiting ionic Walden product ( $\lambda_o^\pm\eta$ ), (the product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function of the ionic radius (crystallographic radius) and thus under normal condition, is a constant. The contribution of anions (NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup>) for the common cation [emim]<sup>+</sup>, in both the limiting ionic conductance ( $\lambda_o^\pm$ ), and limiting ionic Walden product ( $\lambda_o^\pm\eta$ ) are shown in Figure V.5. From the Figure V.5, it has been seen that both the  $\lambda_o^\pm$ , and  $\lambda_o^\pm\eta$ , are decreases from acetonitrile to nitromethane for each of the studied ionic liquids (ILs), which also implied that ion-solvent interaction of ions increases from acetonitrile to nitromethane. For a particular solvent the order of limiting ionic conductance of anions are as follow:



This indicates the greater shape of Tos<sup>-</sup> ion, in the interaction with solvent molecules than other two ions. Since the intrinsic radius of a given anion is constant in the different solvents, a smaller value of the limiting molar conductivity of an anion in a solvent suggests enhanced solvation of this anion in that medium. Therefore, it may be possible to state that the degree of solvation of the anions in the solvents is as following order:



The stronger solvation of the anions in nitromethane is believed to be attributable to the stronger hydrogen-bonding interaction between the anions and the nitromethane molecules relative to methanol, whereas the difference in the degree of solvation of the anions in acetonitrile is attributed to the difference in dipole moment of the solvents. The ion–dipole interactions decrease with an increase of the intrinsic radius of the anions because of their much decreased charge densities. This result is supported by the molecular dynamic simulation result that in hydrogen bonding solvents; ILs was mainly solvated by the hydrogen bonding interactions between the anion and the solvent molecules.<sup>[V.34]</sup>

The  $\lambda_o^\pm$  values were in turn utilized for the calculation of Stokes' radii ( $r_s$ ) according to the classical expression<sup>[V.35]</sup>

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^\pm r_c} \quad (\text{V.10})$$

where the symbols are usual meanings. The limiting ionic Walden products ( $\lambda_o^\pm \eta$ ), Stokes' radii ( $r_s$ ), and crystallographic radii ( $r_c$ ) are presented in Table V.4. The trends in Walden products ( $\lambda_o \eta$ ) and ionic Walden products ( $\lambda_o^\pm \eta$ ) for the selected electrolytes (ILs) in the chosen solvents are depicted in Table V.3 and V.4 and in Figure V.4 and V.5 respectively. It shows that both the Walden products ( $\lambda_o \eta$ ) and ionic Walden products ( $\lambda_o^\pm \eta$ ) for the ionic liquids (ILs) approximately linear variation from acetonitrile to nitromethane. For the employed ions i.e; [emim]<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and Tos<sup>-</sup> ions, the determined Stokes' radii ( $r_s$ ) are higher than their crystallographic radii ( $r_c$ ); this suggests that the ion are comparatively more solvated due to its intrinsic surface charge density. These results also support the fact of higher association of the ions by the solvent molecules in the experimental solutions. The distance parameter  $R$ , shown in Table V.3, is the least distance that two free ions can approach before they merge into an ion-pair in the studied media. The marked characteristic behaviours in the association constant ( $K_A$ ) values, which generally increase from acetonitrile to nitromethane; indicates that the thermal motion of the ions were probably destroy in the solvents. However, from the Table V.3 and Figure V.6, as increasing trend of  $K_A$  values, ion-association for the electrolytes (ILs) increases from acetonitrile to nitromethane among the studied solvents.

The Gibbs energy changes is also a key parameter to interpretation of the nature of ion-pair formation, if we inspect the  $\Delta G^\circ$ , we can be able to clearly forecasts the propensity for ion-pair formation taking place in the solution systems. The association constant ( $K_A$ ) values have been utilized to calculating the Gibbs energy change  $\Delta G^\circ$ , by the following relationship<sup>[V.36]</sup> and are arranged in Table V.3.

$$\Delta G^\circ = - RT \ln K_A \quad (V.11)$$

It has been found the negative values of  $\Delta G^\circ$  for all the electrolytes in solvents, and the observed results can be explicated in view of the participation of definite interaction in the ion-association phenomena. It is observed from the Table V.3 and Figure V.6 that the values of the Gibbs free energy are negative, entire all over the solutions and the negativity increases from acetonitrile to nitromethane for each electrolyte: The increasing negativity in the value of  $\Delta G^\circ$  of ionic liquids leads to the more feasible in the ion-solvent interaction. This result indicates the extent of solvation of selected ionic liquids by the following order:



There have another distinguishing factor, which is  $A$ -coefficient. The significance of the term had since then been realized due to the development Debye-Hückel theory<sup>[V.37]</sup> of inter-ionic attractions in 1923. The  $A$ -coefficient depends on the ion-ion interactions (self interaction of the employed ions in solution) and can be calculated from interionic attraction theory as given by the Falkenhagen and Vernon<sup>[V.38]</sup> equation:

$$A_{Theo} = \frac{0.2577 \Lambda_o}{\eta_o (\epsilon_r T)^{0.5} \lambda_+^\circ \lambda_-^\circ} \left[ 1 - 0.6863 \left( \frac{\lambda_+^\circ \lambda_-^\circ}{\Lambda_o} \right)^2 \right] \quad (V.12)$$

where the symbols have their usual significance.  $A$ -coefficient suggesting that should be calculated from conductivity measurements and given in the Table V.5. From the table  $A$ -coefficient is negative and very small, shows that the existence of the ion-ion interactions is negligible, as compared to the ion-solvent interactions for all the selected ionic liquids in the studied solvents. Consequently, it is very clear to declare that the ion-solvent interactions dominant over the ion-ion interactions; the similar shape has been established in our previous paper,<sup>[V.14]</sup> by Banik and Roy,<sup>[V.17]</sup> and Wang and co-worker.<sup>[V.27]</sup>

Various types of interactions exist between the ions and solvent molecules in solutions. These interactions result in the orientation of the solvent molecules towards the effective ions. The greater number of the solvent molecules oriented sequentially around the effective ion, increases the ion-solvation. The number of solvent molecules that are involved in the solvation is called solvation number ( $n_s$ ). Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the molecule, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion as well as electrolyte (ionic liquid).

If the limiting conductance of the ions ( $\lambda_o^\pm$ ) of charge  $Z_i$  is known, the effective radius of the solvated ion can be determined from Stokes' law and the volume of the solvation shell is given by the equation.

$$V_s = \left( \frac{4\pi}{3} \right) (r_s^3 - r_c^3) \quad (\text{V.13})$$

where  $r_c$  and  $r_s$  is the crystallographic and Stokes' radius of the ions. The solvation number  $n_s$  would then be obtained from

$$n_s = \frac{V_s}{V_o} \quad (\text{V.14})$$

where  $V_o$  is the volume of the solvent molecules. The solvation number  $n_s$  is given in the Table V.5. From the table we have seen that the order of the solvation number is

**methanol > nitromethane > acetonitrile**

suggests that the number of solvent molecules which are aligned in the force field is increases, which leads to the increasing trend of ion-solvent interaction.

Using the solvent viscosity and the estimated Stokes' radii, the diffusion coefficient ( $D_\pm$ ) of the ions can be determined by the Stokes-Einstein relation:

$$D_\pm = \frac{k_B T}{6\pi\eta_o r_s} \quad (\text{V.15})$$

where  $k_B$  is the Boltzmann's constant,  $T$  is the temperature.

The diffusion coefficient ( $D_\pm$ ) in turn utilized to obtained the ionic mobility ( $i_\pm$ ) for the individual ions using the following equation

$$i_{\pm} = \frac{z_{\pm} F}{R_g T} D_{\pm} \quad (\text{V.16})$$

where  $z_{\pm}$ ,  $F$ ,  $R_g$ ,  $T$  and  $D_{\pm}$  is the ionic charge, Faraday constant, universal gas constant, temperature and diffusion co-efficient respectively. Diffusion co-efficient ( $D_{\pm}$ ) and ionic mobility ( $i_{\pm}$ ) for the individual ions [emim]<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and Tos<sup>-</sup> in the studied solvents is given in Table V.6. Scrutiny of Table V.6 reveals that the contribution of diffusion coefficient of the anions (NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, Tos<sup>-</sup>) is less than the cation [emim]<sup>+</sup> in all the studied solvents, which indicates that [emim]<sup>+</sup> ions diffuses more through the solvents. If we see for the each of ions in solvents, we observed that the diffusion coefficient decrease from acetonitrile to nitromethane. As indicated in Table V.6, the employed [emim]<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and Tos<sup>-</sup> ions showing the greater diffusion in acetonitrile. Table V.6, also shows that the mobility of anions (NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and Tos<sup>-</sup>) is lower than [emim]<sup>+</sup> in all the investigated solvents, indicating greater share of conductance by [emim]<sup>+</sup> ions mentioned earlier in conductance measurement. The observation indicates the diffusion coefficient ( $D_{\pm}$ ) is directly proportional to the ionic mobility ( $i_{\pm}$ ) and these are the driving force to conduct electricity by ILs or ions in solutions. From the same table we have seen that the diffusion as well as mobility the ions decrease from acetonitrile to nitromethane, and the decreasing order in ionic mobility of the anions are as follow:



The results are reciprocal to the density and viscosity of the solvents.<sup>[V.39]</sup> Lower the diffusivity and mobility is obviously higher the ion-solvent interaction or ion-solvation, which is evident from the association constant values, and reported in Table V.3. A graphical comparison of diffusion coefficient ( $D_{\pm}$ ) and ionic mobility ( $i_{\pm}$ ), for anions (NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and Tos<sup>-</sup>) is given in Figure V.7. These findings may find applications in the modulation of the conductance performance of the ILs by using solvents.

### V.3.2 Triple-ion formation from electrical conductance

The graphical representation of molar conductance corresponding to the square root of concentration ( $\Lambda$  vs  $\sqrt{c}$ ) of the selected ionic liquids in methylamine solution (CH<sub>3</sub>NH<sub>2</sub>) have been presented Figure V.2. The figure show that the

electrolytes (IL) follows the same sketch, i.e. the conductance value gradually decreases with increasing concentration, reach a minima and then increases. Due to the deviation of the conductometric curves from linearity in case of ionic liquids (ILs) in methylamine solution ( $\epsilon_r = 9.10$ ), the conductance data have been analyzed to determine the limiting molar conductance and triple ion conductance by the classical Fuoss-Kraus theory of triple-ion formation<sup>[V.26, V.36]</sup> in the form

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (V.17)$$

where  $g(c)$  is a factor that lumps together all the intrinsic interaction terms and is defined by

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\} (1 - \Lambda / \Lambda_0)^{0.5}} \quad (V.18)$$

$$\beta' = \frac{1.8247 \times 10^6}{(\epsilon_r T)^{1.5}} \quad (V.19)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon_r T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon_r T)^{0.5}} \quad (V.20)$$

In all the above usable equations, the  $\Lambda_0$  term signify the sum of the molar conductance of the simple ions at infinite dilution, the  $\Lambda_0^T$  is the sum of the conductance value of the two possible formation of triple-ions  $[(emim)_2]^+[Y]$  and  $[emim][Y_2]^-$  for the imidazolium ionic liquids,  $[emim][Y]$  (where  $Y = NO_3^-, CH_3SO_3^-$  and  $Tos^-$ ). Where the constants as  $K_P \approx K_A$  and  $K_T$  are implies that the ion-pair and triple-ion formation constants respectively and  $S$  is the limiting Onsager coefficient. On employing the applicability of the equation (V.17), the symmetrical approximation of

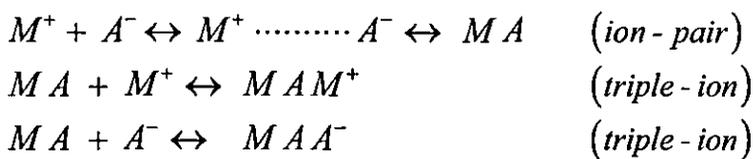
the two possible formation of triple-ions constants,  $K_{T1} = \frac{[(emim)_2]^+[Y]}{\{[(emim)^+][emim][Y]\}}$  and

$K_{T2} = \frac{[(emim)][Y_2]^-}{\{[Y]^- [emim][Y]\}}$  equal to each other has been assumed as  $K_{T1} = K_{T2} = K_T$ .<sup>[V.40]</sup>

The  $\Lambda_0$  values for the studied electrolytes in methylamine solution have been determined using the scheme as recommended by Krumgalz in 1983.<sup>[V.41]</sup> The values of  $\Lambda_0^T$  have been calculated with the help of  $\Lambda_0$  values by fitting the triple-ion

conductance equal to  $\frac{2}{3}\Lambda_0$ .<sup>[V.42]</sup> Thus the ratio  $\frac{\Lambda_0^T}{\Lambda_0}$  was set equal to 0.667 during linear regression analysis of equation (V.17).

The obtained limiting molar conductance of simple ion ( $\Lambda_0$ ), limiting molar conductance of triple ion ( $\Lambda_0^T$ ), slope and intercept of equation (V.17) for selected ionic liquids (ILs) in methylamine solution at 298.15 K are represented in Table V.7. The intercept and slope have been obtained by employing the linear regression analysis of equation (V.17) for the electrolytes with an average regression constant,  $R^2 = 0.9989$ . Thereafter these values utilized to calculation of other derived parameters such as  $K_P$  and  $K_T$  and listed in Table V.8. Read-through of Table V.8 demonstrates that the degree of ion-pair constant  $K_P$  is larger than that of the triple-ion formation constant  $K_T$ , which indicates the major portion of the electrolytes (ILs) exists as ion-pair with a minor portion as triple-ion. This is due to the fact that the electrolytes is exist as ion-pair with a major portion in with the interaction of water molecules and as triple-ion with a minor portion interacting with methylamine molecules of methylamine solution (40% wt. methylamine +60% wt. water). The propensity of triple ion formation with respect to ion-pair, can also be judged from the ratio of  $\left(\frac{K_T}{K_P}\right)$  and the values of  $\log\left(\frac{K_T}{K_P}\right)$ ; which are shown in Table V.8. The ratios and logarithm values recommend that strong ion-association between the ions and solvent molecules are owing to the coulombic interactions in addition to covalent forces in the solution. The observed grades are in excellent accord with those obtained by Hazra et al.<sup>[V.43]</sup> We know that the electrostatic ionic interactions are very large due to the higher force field effect, for very low relative permittivity solvents, i.e.,  $\epsilon_r < 10$ . Therefore the formed ion-pairs were attracted by the free movable cations or anions 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 acquires the charge of the respective ions, attracted from the solution bulk<sup>[V.33, V.36]</sup> i.e.;



where the symbols  $M^+$  and  $A^-$  are implies for the  $[emim]^+$  and  $Y^-$  (where  $Y= NO_3^-$ ,  $CH_3SO_3^-$  and  $Tos^-$ ) ions respectively. The effect of ternary association<sup>[V.44]</sup> thus clearly explained the non-linearity of the conductometric curve. According to the consequence of this ternary association, some formative non-conducting species MA, removed from solution and replaces by triple-ions which increase the conductance values evident by non-linearity observed in conductance curves for the ionic liquids in methylamine solution. The pictographic depiction of triple-ion formations for the selected ionic liquids(ILs) in methylamine solution has been depicted in **Scheme V.4**.

Additionally, the ion-pair and triple-ion concentrations,  $C_P$  and  $C_T$ , respectively, at the minimum molar concentration of the salt solution have also been calculated using the  $K_P$  and  $K_T$  value by following set of equations<sup>[V.42]</sup>

$$\alpha = \frac{1}{(K_P^{1/2} \cdot C^{1/2})} \tag{V.21}$$

$$\alpha_T = \left( \frac{K_T}{K_P^{1/2}} \right) C^{1/2} \tag{V.22}$$

$$C_P = C(1 - \alpha - 3\alpha_T) \tag{V.23}$$

$$C_T = \left( \frac{K_T}{K_P^{1/2}} \right) C^{3/2} \tag{V.24}$$

At this point, the fraction of ion-pairs ( $\alpha$ ) and triple-ions ( $\alpha_T$ ), present in the salt-solutions are shown in Table V.9. The calculated values of  $C_P$  and  $C_T$  are also presented in Table V.9. From the appraisal of comparison of the  $C_P$  and  $C_T$  values, it's found that the  $C_P$  is higher with respect to  $C_T$ ; which indicates that the major portion of ions are present as ion-pair even at high concentration and a small fraction exist as triple-ion. The conductance value decreases with increasing concentration, reach a minimum is called  $\Lambda_{min}$ , and the concentration at which the conductance value reach minimum is termed as  $C_{min}$ ; after the  $C_{min}$ , fraction of the triple-ions in the solution increases with the increasing concentration, in the studied solution media  $\{[emim][Y]+methylamine\}$  solution.

Using the  $K_P$  values, the interionic distance parameter  $a_{IP}$  has been calculated with the aid of the Bjerrum's theory of ionic association<sup>[V.44]</sup> in the form

$$K_P = \frac{4\pi N_A}{1000} \left[ \frac{e^2}{\epsilon_r KT} \right]^3 Q(b) \quad (V.25)$$

$$Q(b) = \int_2^b y^{-4} \exp(y) dy \quad (V.26)$$

$$b = \frac{e^2}{a_{IP} \epsilon_r KT} \quad (V.27)$$

The  $a_{IP}$  values obtained are given in Table V.10. The  $Q(b)$  and  $b$  values have been calculated by the literature procedure.<sup>[V.45]</sup> The Table reveals the  $a_{IP}$  values for all the ionic liquids (ILs) lies within the range the actual ionic sizes (or crystallographic radii) varied by (3.33 to 4.49) Å. This may be due to easy penetration by the anions ( $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$  and  $\text{Tos}^-$ ) to some extent into the void spaces between the alkyl chain of the  $[\text{emim}]^+$ , as suggested by Abbott and Schiffrin.<sup>[V.46]</sup> Again, the  $a_{IP}$  values have found within the crystallographic radii ( $r_c$ ), suggesting probable contact ion-pair formation in solution.<sup>[V.28]</sup> This will cause a decrease in the degree of freedom for the ions in the ion-pair formation, which results in their loss of configurational entropy of the contact-pair. Generally,  $K_P$  values do not change significantly for imidazolium ionic liquids with the alkyl chain consisting of less carbon atoms. The small changes in the  $K_P$  may thus be related to entropic contributions.

The interionic distance  $a_{TI}$  for the triple ion can be calculated using the expressions<sup>[V.33]</sup>

$$K_T = \frac{2\pi N_A a_{IP}^3}{1000} I(b_3) \quad (V.28)$$

$$b_3 = \frac{e^2}{a_{TI} \epsilon_r KT} \quad (V.29)$$

$I(b_3)$  is a double integral tabulated in the literature<sup>[V.36]</sup> for a range of values of  $b_3$ . Since  $I(b_3)$  is a function of  $a_{TI}$ , the  $a_{TI}$  values have been calculated by an iterative computer program. From Table V.10, the  $a_{TI}$  values for the ionic liquids (ILs) are greater than the corresponding  $a_{IP}$  values but are much less than the expected theoretical value  $1.5a_{IP}$ . This is probably due to repulsive forces between the two anions or cations in the triple ions  $[\text{Bu}_4\text{P}(\text{MS})_2]^-$  and  $[(\text{Bu}_4\text{P})_2^+\text{MS}]$  as suggested by

Hazra et al.<sup>[V.43]</sup> These values also suggested the small fraction exist as triple-ion formation compared to the ion-pair.

### V.3.3 FTIR Spectroscopic Study

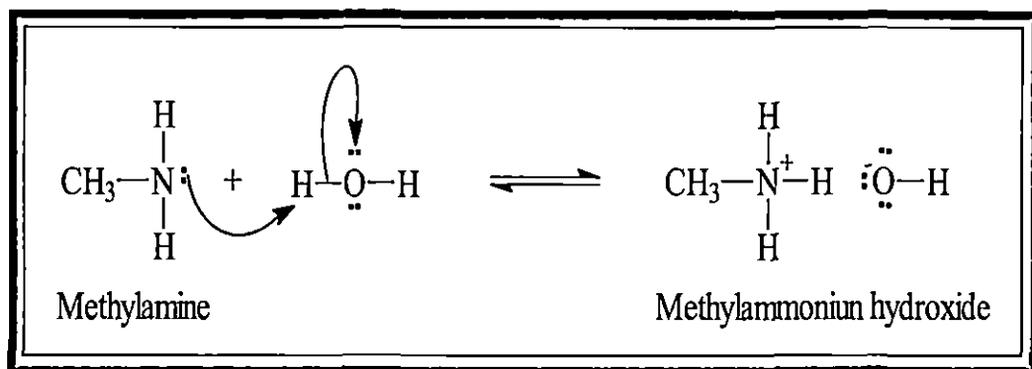
With the help of FTIR spectroscopy the molecular interaction existing between the ionic liquid and the solvents have been presented qualitatively and used as supportive evidence for the study of bond breaking and bond formation (electrostatic bond) due to the ion-solvent and solvent-solvent interactions. The IR spectra of the pure solvents as well as the solutions of {[emim][Y]+Solvents} have been studied and the stretching frequencies of the functional groups and mixed with ionic liquids are given in Table V.11 and Figure V.8- V.11 within the range of wave number 400-4000  $\text{cm}^{-1}$ .

The IR spectra of acetonitrile show a sharp peak at  $\nu_0 = 2253.8 \text{ cm}^{-1}$  which is attributed to the  $\text{C}\equiv\text{N}$  stretching vibration range (2210-2260  $\text{cm}^{-1}$ ). When the ionic liquids (ILs) is added to acetonitrile (i.e; [emim][Y]+ $\text{CH}_3\text{CN}$ ), the peak shifts to  $\nu_s = 2278.9 \text{ cm}^{-1}$ , 2291.2  $\text{cm}^{-1}$ , and 2307.6  $\text{cm}^{-1}$  for [emim] $\text{NO}_3$ , [emim] $\text{CH}_3\text{SO}_3$ , and [emim]Tos respectively. This is due to the disruption of dipole-dipole interaction present in acetonitrile<sup>[V.31]</sup> leading to the formation of ion-dipole interaction between [emim]<sup>+</sup>,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ , Tos<sup>-</sup> ions with  $\text{C}\equiv\text{N}$  bond leading to the shift in the  $\text{C}\equiv\text{N}$  stretching frequency. Negligible change in stretching frequency of C-H bond (3.6 $\text{cm}^{-1}$ , 4.2  $\text{cm}^{-1}$ , 4.6  $\text{cm}^{-1}$ ) of  $\text{CH}_3\text{CN}$ , shows that C-H bond does not contribute in interaction.

In case of methanol, a broad peak is obtained at  $\nu_0 = 3384.7 \text{ cm}^{-1}$  which is attributed to hydrogen bonded (H-bond) O-H stretching vibration (within the range 3200-3600  $\text{cm}^{-1}$ ). But when the IR spectra of {[emim][Y]+ $\text{CH}_3\text{OH}$ } solutions was taken, the broad peak are shifted to  $\nu_s = 3418.5 \text{ cm}^{-1}$ , 3430.8  $\text{cm}^{-1}$ , 3447.1  $\text{cm}^{-1}$ . This indicates that the H-bonding existing between the methanol molecule<sup>[V.47]</sup> is disrupted by the addition of the ionic liquids [emim][Y]. This is due to the interaction of ions ([emim]<sup>+</sup>,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ , Tos<sup>-</sup>) of the studied ionic liquids with the -OH gr of  $\text{CH}_3\text{OH}$  leading to the shift in the O-H bond stretching frequency. Negligible change in stretching frequency of C-H bond (2.7  $\text{cm}^{-1}$ , 3.4  $\text{cm}^{-1}$ , 4.1  $\text{cm}^{-1}$ ) of  $\text{CH}_3\text{OH}$  shows negligible contribution C-H group.

In case of nitromethane, two bands are obtained in the regions  $\nu_o = 1564.1 \text{ cm}^{-1}$  and  $1362.9 \text{ cm}^{-1}$ , former for the asymmetric stretching vibration ( $\nu_{as}$ ) of N-O ( $1500\text{-}1570 \text{ cm}^{-1}$ ) and the latter for symmetric stretching vibration ( $\nu_s$ ) of N-O ( $1300\text{-}1370 \text{ cm}^{-1}$ ) respectively shown in Table V.11. When we added ionic liquids in nitromethane, the asymmetric stretching vibration ( $\nu_{as}$ ) of N-O shift to  $1604.7 \text{ cm}^{-1}$ ,  $1619.9 \text{ cm}^{-1}$ ,  $1634.0 \text{ cm}^{-1}$  and symmetric stretching vibration ( $\nu_{as}$ ) shift to  $1401.9 \text{ cm}^{-1}$ ,  $1411.7 \text{ cm}^{-1}$ ,  $1430.5 \text{ cm}^{-1}$ , for the ionic liquids [emim] $\text{NO}_3$ , [emim] $\text{CH}_3\text{SO}_3$ , and [emim]Tos respectively. The shift in the bands is due to the rupture of the H-bonding interaction present in the  $\text{CH}_3\text{NO}_2$  molecules.<sup>[V.48]</sup> The ionic liquids also interact via ion-dipole interaction with the solvent molecules. The C-H stretching of the  $-\text{CH}_3$  group in  $\text{CH}_3\text{NO}_2$  occurs at  $2961.4 \text{ cm}^{-1}$  attributing to asymmetric vibration ( $\nu_{as}$ ) and  $2872.9 \text{ cm}^{-1}$  attributing to symmetric vibration ( $\nu_s$ ). From the same Table V.11, negligible change in asymmetric or symmetric stretching frequency of C-H bond in  $\text{CH}_3\text{NO}_2$ , when the ionic liquids (ILs) is added to it, shows the interaction is negligible between C-H and ions of ionic liquids (ILs).

The higher interaction is seen between [emim][Y] (Y=  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$  and Tos $^-$ ) and methylamine solution as evident from the values of the  $K_A$  obtained from the conductivity study as described above. Here the peaks for hydroxyl -OH, C-N, and C-H bonds of methylamine solution were at  $3446.3 \text{ cm}^{-1}$ ,  $1283.4$  ( $1000\text{-}1360 \text{ cm}^{-1}$ ), and  $2914.9$  ( $2850\text{-}2950 \text{ cm}^{-1}$ ) respectively. The peak is shifts to  $3492.6 \text{ cm}^{-1}$ ,  $3503.1 \text{ cm}^{-1}$  and  $3521.0 \text{ cm}^{-1}$  for -OH group, respectively when [emim] $\text{NO}_3$ , [emim] $\text{CH}_3\text{SO}_3$ , and [emim]Tos is added to methylamine solution. The shifting figure has been given in the Table V.11. This is due to the disruption of weak H-bonding interaction present in  $\text{CH}_3\text{NH}_2$ <sup>[V.49]</sup> and  $\text{H}_2\text{O}$  molecules of methylamine solution and formation of ion-dipole interaction with the [emim] $^+$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ , Tos $^-$  ions. In the aqueous solutions of amines are basic; and the -NH groups less interact because the protons attached to nitrogen are less acidic than the  $\text{H}_2\text{O}$ . In methylamine solution ( $pK_b=3.36$ ) the unshared pair of electrons on nitrogen forms a new covalent bond with hydrogen and displaces hydroxyl ion.



It should be recognized at this point that the presence of ILs, leads to the generation of considerable intensity increases and that increases is due to occurrence in association of  $\text{CH}_3\text{NH}_3^+$ ,  $-\text{OH}$  and additional  $[\text{emim}]^+$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{Tos}^-$  ions. Figure V.11 summarizes results for the  $-\text{OH}$  intensity increases for all the electrolytes in the methylamine solution. The shifting of the C-N and C-H bonds in the (ILs+solvents) mixture is negligible.

The overall schematic representation of the interaction or ion-solvation occurring in studied solution systems  $\{[\text{emim}][\text{Y}]+\text{Solvent}\}$  have been represented in Scheme V.5 in view of the observed derived parameters.

## V.4 CONCLUSIONS

The extensive qualitative and quantitative analysis on the ion-solvation phenomenon of the typical 1-ethyl-3-methylimidazolium based ionic liquids  $\{[\text{emim}][\text{Y}]; \text{ where } \text{Y} = \text{NO}_3^-, \text{CH}_3\text{SO}_3^- \text{ and } \text{Tos}^-\}$  in industrially important non-aqueous polar solvents acetonitrile ( $\text{CH}_3\text{CN}$ ), methanol ( $\text{CH}_3\text{OH}$ ), nitromethane ( $\text{CH}_3\text{NO}_2$ ), methylamine solution ( $\text{CH}_3\text{NH}_2$ ) with the help of conductometric and FTIR measurements. Precise examine on all the observed conductometric consequence, it has been obvious that studied ionic liquids (ILs) exists as ion-pair in acetonitrile, methanol, nitromethane, and as triple-ion in methylamine solution. The ionic size, the charge distribution of the anions ( $\text{NO}_3^-$ ,  $\text{CH}_3\text{SO}_3^-$  and  $\text{Tos}^-$ ) for the common cation ( $[\text{emim}]^+$ ), and structural aspects, i.e: functional group of the solvents, are the key factor in formation of ion-pair and triple-ion. The decreasing tendency of the transport properties as fluidity, diffusion coefficient ( $D_2$ ) and ionic mobility ( $i_2$ ) from acetonitrile to nitromethane for ions  $\{[\text{emim}]^+, \text{NO}_3^-, \text{CH}_3\text{SO}_3^- \text{ and } \text{Tos}^-\}$ , suggests the

greater extent of ion-solvent interaction or ion-association in nitromethane than the other two studied solvents. For a particular solvent the order of ion-association of anions for the common cation [emim]<sup>+</sup> are as follow:



In all the chosen solvents, the selected ionic liquids interact with hydrogen bonding and ion-dipole interactions as evident from the FTIR spectroscopic studies.

After all, it is very clear to state that the ion-solvent interactions dominant over the ion-ion interactions. All the derived parameters determined by analyzing different valid equations enhancement with experimental data uphold the same climax as discussed and explained in this text, which challenging the distinctiveness of the effort and such information is particularly pertinent to the design of the appropriate (IL+molecular solvent) binary system for a diligent application.

## REFERENCES

- [V.1] Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071-2084.
- [V.2] Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123-150.
- [V.3] Ye C, Liu W, Chen Y, Yu L. Room-temperature ionic liquids: a novel versatile lubricant. *Chem. Commun.* **2001**, 2244-2245.
- [V.4] Endres F, El Abedin SZ. Air and water stable ionic liquids in physical chemistry, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101-2116.
- [V.5] Wang P, Zakeeruddin SM, Moser JE, Grätzel M. A New Ionic Liquid Electrolyte Enhances the Conversion Efficiency of Dye-Sensitized Solar Cells. *J. Phys. Chem. B.* **2003**, *107*, 13280-13285.
- [V.6] Dupont J, de Souza RF, Suarez PAZ. Ionic Liquid (Molten Salt) Phase organometallic, Catalysis. *Chem. Rev.* **2002**, *102*, 3667-3692.
- [V.7] Greaves TL, Drummond CJ. Protic ionic liquids: Properties and applications. *Chem. Rev.* **2008**, *108*, 206-237.
- [V.8] Greaves TL, Weerawardena A, Fong C, Krodkiewska I, Drummond CJ. Protic Ionic Liquids: Solvents with Tunable Phase Behavior and Physicochemical Properties. *J. Phys. Chem. B.* **2006**, *110*, 22479-22487.
- [V.9] Timperman L, Anouti M. Transport Properties of Tributylphosphonium Tetrafluoroborate Protic Ionic Liquid. *Ind. Eng. Chem. Res.* **2012**, *51*, 3170-3178
- [V.10] Zhang S, Sun N, He X, Lu X, Zhang X. Physical Properties of Ionic Liquids: Database and Evaluation. *J. Phys. Chem. Ref. Data.* **2006**, *35*, 1475-1517.
- [V.11] Crosthwaite JM, Aki SNVK, Maginn EJ, Brennecke JF. Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols. *J. Phys. Chem. B.* **2004**, *108*, 5113-5119.
- [V.12] Cadena C, Anthony JL, Shah JK, Morrow TI, Brennecke JF, Maginn EJ. Why Is CO<sub>2</sub> So Soluble in Imidazolium-Based Ionic Liquids? *J. Am Chem. Soc.* **2004**, *126*, 5300-5308.
- [V.13] Janz CG, Tomkins RPT. *Non-aqueous Electrolytes Handbook*, Academic Press: New York, **1973**, Vol. 2.

- [V.14] Ekka D, Roy MN. Conductance, a Contrivance to Explore Ion Association and Solvation Behavior of an Ionic Liquid (Tetrabutylphosphonium Tetrafluoroborate) in Acetonitrile, Tetrahydrofuran, 1,3-Dioxolane, and Their Binaries. *J. Phys. Chem B*, **2012**, *116*, 11687-11694.
- [V.15] Aurbach D. *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, **1999**.
- [V.16] Krom JA, Petty JT, Streitwieser A. Lithium and Cesium Ion-Pair Acidities of Diphenylamine in Tetrahydrofuran. The Aggregation of Lithium and Cesium Diphenylamide. A New Method for the Determination of Aggregation Constants in Dilute Solution. *J. Am. Chem. Soc.* **1993**, *115*, 8024-8030.
- [V.17] Banik I, Roy MN. Probing subsistence of ion-pair and triple-ion of an ionic salt in liquid environments by means of conductometric contrivance, *J. Chem. Thermodynamics*, **2013**, *63*, 52-59.
- [V.18] Popvykh O, Tomkins RPT. *Nonaqueous Solution Chemistry*, Wiley-Interscience: New York, **1981**, Chapter 4.
- [V.19] Covington AK, Dickinson T. *Physical chemistry of organic solvent systems*, Plenum: New York, **1973**.
- [V.20] Lind Jr JE, Zwolenik JJ, Fuoss RM. Calibration of conductance cells at 25° with aqueous solutions of potassium chloride. *J. Am. Chem. Soc.* **1959**, *81*, 1557-1559.
- [V.21] Abdulagatov IM, Azizov ND. Viscosity of aqueous calcium chloride solutions at high temperatures and high pressures. *Fluid Phase Equilibria*, **2006**, *240*, 204-219.
- [V.22] Sinha A, Bhattacharjee A, Roy MN. Ion-Solvent Interactions in Acrylonitrile Solutions of Some Tetraalkylammonium Halides Using FTIR Spectroscopy. *J. Disp. Sc. and Techn.* **2009**, *30*, 1003-1007.
- [V.23] El-Dossoki FI. Effect of hydrogen bond, relative permittivity and temperature on the transport properties and the association behavior of some 1:1 electrolytes in some binary mixed solvents. *J. Mol. Liquids.* **2010**, *151*, 1-8.

- [V.24] Fuoss RM. Paired ions: Dipolar pairs as subset of diffusion pairs, *Proc. Natl. Acad. Sci., U.S.A.* **1978**, *75*, 16-20.
- [V.25] Fuoss RM. Conductance-concentration function for the paired ion model, *J. Phys. Chem.* **1978**, *82*, 2427-2440.
- [V.26] Fuoss RM, Accascina F. *Electrolytic Conductance*, Interscience: New York, 1959.
- [V.27] Wang H, Wang J, Zhang S, Pei Y, Zhuo K. Ionic association of the ionic liquids [C<sub>4</sub>mim][BF<sub>4</sub>], [C<sub>4</sub>mim][PF<sub>6</sub>], and [C<sub>n</sub>mim]Br in molecular solvents. *ChemPhysChem*, **2009**, *10*, 2516 – 2523.
- [V.28] Bester-Rogac M, Hunger J, Stoppa A, Buchner R. 1-ethyl-3-methylimidazolium Ethylsulfate in water, acetonitrile, and dichloromethane: molar conductivities and association constants. *J. Chem. Eng. Data*, **2011**, *56*, 1261-1267.
- [V.29] Bockris JO, Reddy AN. *Modern Electrochemistry*, 2<sup>nd</sup> Ed. Plenum Press: New York, 1998, p 552.
- [V.30] Bhat JI, Bindu P. Effect of temperature on the conductance of chloramine-T and bromamine-T in different compositions of solvent mixtures. *J. Ind. Chem. Soc.* **1995**, *72*, 783-790.
- [V.31] Yamdagni R, Kebarle P. Solvation of negative ions by protic and aprotic solvents. Gas-phase solvation of halide ions by acetonitrile and water molecules. *J. Am. Chem. Soc.* **1972**, *94*(9), 2940-2943.
- [V.32] Chakraborty JM, Das B. Electrical conductances and viscosities of tetrabutylammonium thiocyanate in acetonitrile in the temperature range 25-45°C. *Z. Phys. Chem.* **2004**, *218*, 219-230.
- [V.33] Fuoss RM, Hirsch E. Single ion conductances in non-aqueous solvents. *J. Am. Chem. Soc.* **1960**, *82*, 1013-1017.
- [V.34] Hanke CG, Atamas NA, Lyndcn-Bell RM, Solvation of small molecules in imidazolium ionic liquids: a simulation study, *Green Chem.* **2002**, *4*, 107–111.
- [V.35] Robinson RA, Stokes RH. *Electrolyte Solutions*, Butterworth: London, 1959, Ch 6, p 130.

- [V.36] Fuoss RM, Kraus CA. Properties of electrolytic solutions. iv. the conductance minimum and the formation of triple ions due to the action of coulomb forces. *J. Am. Chem. Soc.* **1933**, *55*, 2387-2399.
- [V.37] Debye P, Hückel E. Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen. *Phys. Z.* **1923**, *24*, 185-206.
- [V.38] Falkenhagen H, Vernon EL. The viscosity of strong electrolyte solutions according to electrostatic theory, *Phil. Mag.* **1983**, *14*, 537-565.
- [V.39] Roy MN, Dewan R, Ekka D, Banik I. Probing molecular interactions of ionic liquid in industrially important solvents by means of conductometric and spectroscopic approach. *Thermochimica Acta* **2013**, *559*, 46-51.
- [V.40] Harada Y, Salamon M, Petrucci S. Molecular dynamics and ionic associations of LiAsF<sub>6</sub> in 4-butyrdactone mixtures with 2-methyltetrahydrofuran. *J. Phys. Chem.* **1985**, *89*, 2006-2010.
- [V.41] Krumgalz BS. Separation of limiting equivalent conductances into ionic contributions in non-aqueous solutions by indirect methods. *J. Chem. Soc., Faraday Trans. I.* **1983**, *79*, 571-587.
- [V.42] Delsignore M, Farber H, Petrucci S. Ionic Conductivity and Microwave Dielectric Relaxation of LiAsF, and LiClO, in Dimethyl Carbonate, *J. Phys. Chem.* **1985**, *89*, 4968-4973.
- [V.43] Nandi D, Roy MN, Hazra DK. Electrical conductances for tetraalkylammonium bromides, LiBF<sub>4</sub> and LiAsF<sub>6</sub> in tetrahydrofuran at 25°C. *J. Indian Chem. Soc.* **1993**, *70*, 305-311.
- [V.44] Sinha A, Roy MN. Conductivity studies of sodium iodide in pure tetrahydrofuran and aqueous binary mixtures of tetrahydrofuran and 1,4-dioxane at 298.15 K. *Phys. Chem. Liq.* **2007**, *45*, 67-77.
- [V.45] Fuoss RM, Krauss CA. Properties of electrolytic solutions. III. The dissociation constant. *J. Am. Chem. Soc.* **1933**, *55*, 1019-1028.
- [V.46] Abbott AP, Schiffrin DJ. Conductivity of tetra-alkylammonium salts in polyaromatic solvents. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1453-1459.
- [V.47] Pagliai M, Cardini G, Righini R, Schettino V. Hydrogen bond dynamics in liquid methanol. *J. Chem. Phys.* **2003**, *119*, 6655-6662.

- [V.48] Li J, Zhao F, Jing F. *An ab initio* study of intermolecular interactions of nitromethane dimer and nitromethane trimer. *J. Comp. Chem.* **2003**, *24*, 345-252.
- [V.49] Cabaleiro-Lago EM, Ríos MA. *Ab initio* study of interactions in methylamine clusters. The significance of cooperative effects. *J. Chem. Phys.* **2000**, *112*, 2155-2163.
- [V.50] Saha N, Das B. Apparent molar volumes of some symmetrical tetraalkylammonium bromides in acetonitrile at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data.* **1997**, *42*, 227-229.
- [V.51] Catalogue of the product from Sigma Aldrich.
- [V.52] Stairs RA. Viscosity of associated liquids. 2. Methylamine. *J. Chem. Eng. Data.* **1980**, *25*, 379-379.
- [V.53] Ramana CVV, Kiran Kumar ABV, Moodley MK. *Journal of Chemistry*, <http://dx.doi.org/10.1155/2013/687106>.

## TABLES

**Table V.1: Values of density ( $\rho$ ), viscosity ( $\eta$ ) and relative permittivity ( $\epsilon_r$ ) of studied solvents at  $T = 298.15 \text{ K}^a$**

Solvents	$\rho \times 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$\eta / \text{mPa} \cdot \text{s}$		$\epsilon_r$
	Expt	Lit	Expt	Lit	
CH <sub>3</sub> CN	0.77668	0.77667 <sup>[V.50]</sup>	0.35	0.3446 <sup>[V.50]</sup>	35.95 <sup>[V.19]</sup>
CH <sub>3</sub> OH	0.78661	0.78660 <sup>[V.19]</sup>	0.55	0.545 <sup>[V.19]</sup>	32.70 <sup>[V.19]</sup>
CH <sub>3</sub> NO <sub>2</sub>	1.13015	1.13015 <sup>[V.20]</sup>	0.62	0.614 <sup>[V.20]</sup>	35.87 <sup>[V.20]</sup>
CH <sub>3</sub> NH <sub>2</sub>	0.89703	0.89700 <sup>[V.51]</sup>	0.18	0.178 <sup>[V.52]</sup>	9.10 <sup>b</sup>

<sup>a</sup>standard uncertainties  $u$  are:  $u(\rho) = 2 \times 10^{-6} \text{ kg m}^{-3}$ ,  $u(\eta) = 0.02 \text{ mPa s}$ , and  $u(T) = 0.01 \text{ K}$ .

<sup>b</sup>Assume and extrapolation of the values of the Ref. [V.53]

**Table V.2: Molar conductance ( $\Lambda$ ) and the corresponding concentration ( $c$ ) of the studied ILs in different solvents at  $T = 298.15 \text{ K}^a$** 

$c \times 10^4$ /mol·dm <sup>-3</sup>	$\Lambda \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$c \times 10^4$ /mol·dm <sup>-3</sup>	$\Lambda \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$c \times 10^4$ /mol·dm <sup>-3</sup>	$\Lambda \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$c \times 10^4$ /mol·dm <sup>-3</sup>	$\Lambda \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>
[emim]NO <sub>3</sub>							
CH <sub>3</sub> CN		CH <sub>3</sub> OH		CH <sub>3</sub> NO <sub>2</sub>		CH <sub>3</sub> NH <sub>2</sub>	
10.39	154.51	7.26	82.53	6.53	76.82	1.13	16.30
19.05	151.33	12.11	80.42	13.48	73.11	2.08	14.17
26.37	149.08	17.22	79.21	19.60	71.43	2.88	12.67
32.65	147.32	22.80	77.82	24.94	68.81	3.56	11.50
38.09	145.91	29.16	76.14	29.61	67.42	4.15	10.75
44.09	144.43	35.40	74.72	33.73	66.30	4.67	10.25
50.84	143.04	41.81	73.21	37.39	65.23	5.13	9.91
59.86	141.22	47.06	72.43	43.59	63.72	5.90	9.35
68.57	139.41	53.73	71.22	52.81	62.01	6.80	8.80
77.42	137.61	63.52	69.71	59.34	60.84	7.84	8.52
84.98	136.34	75.00	68.04	66.20	59.42	8.90	8.61
92.72	135.23	85.93	66.72	77.13	58.33	9.86	9.06
[emim]CH <sub>3</sub> SO <sub>3</sub>							
CH <sub>3</sub> CN		CH <sub>3</sub> OH		CH <sub>3</sub> NO <sub>2</sub>		CH <sub>3</sub> NH <sub>2</sub>	
9.62	148.93	6.76	74.04	8.01	65.53	1.25	14.03
17.64	145.26	11.29	71.72	12.89	63.64	2.08	12.00
24.42	141.97	17.14	69.43	19.01	61.72	2.79	10.89
30.24	140.24	22.75	67.61	24.50	59.81	3.45	9.86
35.28	138.27	27.35	66.51	29.16	58.43	4.07	9.28
43.58	135.85	32.95	65.44	34.81	57.02	4.72	8.63
50.13	134.12	39.82	63.52	41.60	55.21	5.57	8.05
57.72	132.07	47.06	61.43	49.42	53.44	6.35	7.73
65.12	130.64	55.80	60.04	58.83	51.57	7.06	7.64
72.76	128.84	65.45	58.82	68.89	49.73	7.85	7.65
80.63	127.01	75.17	57.43	76.74	47.52	8.70	7.81
86.93	125.64	84.46	54.41	82.08	46.73	9.68	8.30

## [emim]Tos

CH <sub>3</sub> CN		CH <sub>3</sub> OH		CH <sub>3</sub> NO <sub>2</sub>		CH <sub>3</sub> NH <sub>2</sub>	
9.62	116.22	7.84	59.50	8.70	51.04	1.18	11.70
17.64	109.32	14.38	57.11	14.98	48.81	1.94	9.91
24.42	106.14	19.91	54.92	21.16	47.12	2.63	8.57
30.24	103.56	24.65	53.30	28.62	44.93	3.33	7.80
35.28	101.67	28.76	52.22	34.57	43.82	3.94	7.35
43.58	98.40	32.36	51.08	41.06	42.84	4.62	6.71
50.13	96.57	38.35	50.03	48.67	40.51	5.39	6.65
55.43	95.20	43.14	48.45	54.75	39.23	6.23	6.40
61.73	93.61	48.77	48.06	61.89	38.04	6.94	6.58
68.03	92.02	55.47	46.32	68.95	36.82	7.78	6.80
74.70	90.67	62.32	45.64	77.30	36.01	8.59	6.87
80.63	89.71	66.68	44.74	85.17	34.03	9.60	7.53

<sup>a</sup>standard uncertainties  $u$  are:  $u(c) = 2 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ ,  $u(\Lambda) = 1 \times 10^{-6} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ , and  $u(T) = 0.01 \text{ K}$

**Table V.3: Limiting molar conductivity ( $\Lambda_0$ ), the association constant ( $K_A$ ), the distance of closest approach of ions ( $R$ ), standard deviations  $\delta$  of experimental  $\Lambda$ , Walden product ( $\Lambda_0\eta$ ) and Gibb's energy change ( $\Delta G^\circ$ ) of ILs in different studied solvents at  $T = 298.15 \text{ K}$**

Solvents	$\Lambda_0 \times 10^4$ / $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A$ / $\text{dm}^3 \cdot \text{mol}^{-1}$	$R$ / $\text{\AA}$	$\delta$	$\Lambda_0\eta \times 10^4$ / $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$	$\text{Log}(K_A)$	$\Delta G^\circ$ / $\text{kJ} \cdot \text{mol}^{-1}$
[emim]NO <sub>3</sub>							
CH <sub>3</sub> CN	162.17	28.6	8.26	0.18	55.85	3.35	-0.83
CH <sub>3</sub> OH	87.53	59.0	7.89	0.21	47.66	4.08	-1.01
CH <sub>3</sub> NO <sub>2</sub>	82.34	98.5	8.29	0.27	50.56	4.59	-1.14
[emim]CH <sub>3</sub> SO <sub>3</sub>							
CH <sub>3</sub> CN	157.35	42.9	9.10	0.18	54.19	3.76	-0.93
CH <sub>3</sub> OH	79.78	96.2	8.73	0.22	43.44	4.57	-1.13
CH <sub>3</sub> NO <sub>2</sub>	73.23	128.1	9.13	0.31	44.96	4.85	-1.20
[emim]Tos							
CH <sub>3</sub> CN	125.62	90.8	9.43	0.14	43.26	4.51	-1.12
CH <sub>3</sub> OH	66.17	135.2	9.06	0.27	36.03	4.91	-1.21
CH <sub>3</sub> NO <sub>2</sub>	58.85	169.7	9.46	0.33	36.13	5.13	-1.27

**Table V.4: Limiting ionic conductance ( $\lambda_o^\pm$ ), ionic Walden product ( $\lambda_o^\pm\eta$ ), Stokes' radii ( $r_s$ ) and crystallographic radii ( $r_c$ ) of imidazolium based ionic liquids in different studied solvents at  $T = 298.15$  K**

Solvents	$\lambda_o^\pm \times 10^4$		$\lambda_o^\pm\eta \times 10^4$		$r_s$		$r_c$		$t_\pm$	
	/S·m <sup>2</sup> ·mol <sup>-1</sup>		/S·m <sup>2</sup> ·mol <sup>-1</sup> ·mPa·s		/Å		/Å			
	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>
CH <sub>3</sub> CN	97.20	64.97	33.48	22.37	2.45	3.66	1.33	1.99	0.599	0.401
CH <sub>3</sub> OH	52.47	35.06	28.57	19.09	2.87	4.29	1.33	1.99	0.599	0.401
CH <sub>3</sub> NO <sub>2</sub>	49.35	32.99	30.30	20.25	2.70	4.05	1.33	1.99	0.599	0.401
	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
CH <sub>3</sub> CN	107.04	50.31	36.87	17.33	2.22	4.73	1.33	2.83	0.680	0.320
CH <sub>3</sub> OH	54.27	25.51	29.55	13.89	2.77	5.90	1.33	2.83	0.680	0.320
CH <sub>3</sub> NO <sub>2</sub>	49.82	23.41	30.59	14.38	2.68	5.70	1.33	2.83	0.680	0.320
	[emim] <sup>+</sup>	Tos <sup>-</sup>	[emim] <sup>+</sup>	Tos <sup>-</sup>	[emim] <sup>+</sup>	Tos <sup>-</sup>	[emim] <sup>+</sup>	Tos <sup>-</sup>	[emim] <sup>+</sup>	Tos <sup>-</sup>
CH <sub>3</sub> CN	88.41	37.21	30.45	12.82	2.69	6.39	1.33	3.16	0.704	0.296
CH <sub>3</sub> OH	46.57	19.60	25.36	10.67	3.23	7.68	1.33	3.16	0.704	0.296
CH <sub>3</sub> NO <sub>2</sub>	41.42	17.43	25.43	10.70	3.22	7.66	1.33	3.16	0.704	0.296

**Table V.5: A-coefficient and solvation number ( $n_s$ ) of ionic liquids in different studied solvents at 298.15K**

Solvents	A-coefficient		A-coefficient		A-coefficient	
	$/(\text{mPa}\cdot\text{s}\cdot\text{K}^{1/2}$	$n_s$	$/(\text{mPa}\cdot\text{s}\cdot\text{K}^{1/2}$	$n_s$	$/(\text{mPa}\cdot\text{s}\cdot\text{K}^{1/2}$	$n_s$
	$\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1})^{-1}$		$\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1})^{-1}$		$\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1})^{-1}$	
	[emim]NO <sub>3</sub>		[emim]CH <sub>3</sub> SO <sub>3</sub>		[emim]Tos	
CH <sub>3</sub> CN	-0.19	5.23	-0.17	6.67	-0.13	7.28
CH <sub>3</sub> OH	-0.07	9.03	-0.06	8.06	-0.05	13.34
CH <sub>3</sub> NO <sub>2</sub>	-0.05	7.40	-0.04	7.17	-0.03	13.22

**Table V.6: Diffusion coefficient ( $D_{\pm}$ ) and ionic mobility ( $i_{\pm}$ ) of ionic liquids in different studied solvents at 298.15K**

Solvents	$D_{\pm}\cdot 10^{15}/\text{m}^2\cdot\text{s}^{-1}$		$i_{\pm}\cdot 10^{14}/\text{m}^2\cdot\text{s}^{-1}\cdot\text{volt}^{-1}$	
	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>
CH <sub>3</sub> CN	2.59	1.73	10.07	6.74
CH <sub>3</sub> OH	1.40	0.93	5.43	3.63
CH <sub>3</sub> NO <sub>2</sub>	1.32	0.88	5.13	3.42
	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[emim] <sup>+</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
CH <sub>3</sub> CN	2.85	1.34	11.11	5.21
CH <sub>3</sub> OH	1.45	0.68	5.63	2.64
CH <sub>3</sub> NO <sub>2</sub>	1.33	0.62	5.16	2.43
	[emim] <sup>+</sup>	Tos <sup>-</sup>	[emim] <sup>+</sup>	Tos <sup>-</sup>
CH <sub>3</sub> CN	2.35	0.99	9.17	3.86
CH <sub>3</sub> OH	1.24	0.52	4.83	2.03
CH <sub>3</sub> NO <sub>2</sub>	1.10	0.46	4.30	1.81

**Table V.7:** The calculated limiting molar conductance of ion-pair ( $\Lambda_0$ ), limiting molar conductance of triple-ion ( $\Lambda_0^T$ ), slope and intercept of equation (V.17) of ionic liquids in methylamine solution ( $\text{CH}_3\text{NH}_2$ ) at  $T = 298.15 \text{ K}$

Ionic liquids	$\Lambda_0 \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$\Lambda_0^T \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	Slope	Intercept
[emim]NO <sub>3</sub>	53.78	35.87	36.17	0.18
[emim]CH <sub>3</sub> SO <sub>3</sub>	44.17	29.47	39.44	0.16
[emim]Tos	30.39	20.27	61.68	0.12

**Table V.8:** Salt concentration at the minimum conductivity ( $c_{\min}$ ) along with the ion-pair formation constant ( $K_P$ ), triple-ion formation constant ( $K_T$ ) for ionic liquids in methylamine solution ( $\text{CH}_3\text{NH}_2$ ) at  $T = 298.15 \text{ K}$

Ionic liquids	$c_{\min} \times 10^4$ /mol·dm <sup>-3</sup>	$\log c_{\min}$	$K_P \times 10^{-3}$ /m <sup>3</sup> ·mol <sup>-1</sup>	$K_T \times 10^{-2}$ /m <sup>3</sup> ·mol <sup>-1</sup>	$\left(\frac{K_T}{K_P}\right) \times 10^4$	$\log\left(\frac{K_T}{K_P}\right)$
[emim]NO <sub>3</sub>	7.84	-3.11	84.23	2.93	34.74	-2.46
[emim]CH <sub>3</sub> SO <sub>3</sub>	7.06	-3.15	78.25	2.80	47.85	-2.32
[emim]Tos	6.23	-3.21	63.80	2.53	120.48	-1.92

**Table V.9:** Salt concentration ( $c_{\min}$ ) at the minimum conductivity ( $\Lambda_{\min}$ ), the ion-pair fraction ( $\alpha$ ), triple-ion fraction ( $\alpha_T$ ), ion-pair concentration ( $C_P$ ) and triple-ion concentration ( $C_T$ ) of ionic liquids in methylamine solution ( $\text{CH}_3\text{NH}_2$ ) at  $T = 298.15 \text{ K}$

Ionic liquids	$c_{\min} \times 10^4$ /mol·dm <sup>-3</sup>	$\Lambda_{\min} \times 10^4$ /S·m <sup>2</sup> ·mol <sup>-1</sup>	$\alpha \times 10^2$	$\alpha_T \times 10^2$	$C_P \times 10^5$ /mol·dm <sup>-3</sup>	$C_T \times 10^5$ /mol·dm <sup>-3</sup>
[emim]NO <sub>3</sub>	7.84	8.52	12.30	2.82	75.44	2.22
[emim]CH <sub>3</sub> SO <sub>3</sub>	7.06	7.64	13.46	3.56	68.59	2.51
[emim]Tos	6.23	6.40	15.87	7.59	66.55	4.73

**Table V.10: Interionic distance parameter for ion-pair ( $a_{IP}$ ) and for triple-ion ( $a_{TI}$ ) in methylamine solution ( $\text{CH}_3\text{NH}_2$ ) at  $T = 298.15$  K**

Ionic liquids	$a_{IP}/\text{\AA}$	$a_{TI}/\text{\AA}$	$1.5a_{IP}/\text{\AA}$
[emim] $\text{NO}_3$	3.44	4.01	5.16
[emim] $\text{CH}_3\text{SO}_3$	3.48	3.98	5.22
[emim]Tos	3.50	3.96	5.24

**Table V.11: Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of ILs in the solvents.**

Solvents	Functional Group	Stretching frequencies			
		Pure Solvent ( $\nu_0$ $\text{cm}^{-1}$ )	[emim] $\text{NO}_3$ ( $\nu_{IL}$ $\text{cm}^{-1}$ )	[emim] $\text{CH}_3\text{SO}_3$ ( $\nu_{IL}$ $\text{cm}^{-1}$ )	[emim]Tos ( $\nu_{IL}$ $\text{cm}^{-1}$ )
$\text{CH}_3\text{CN}$	$\text{C}\equiv\text{N}$	2253.8	2278.9	2291.2	2307.6
	C-H	2915.7	2919.3	2919.9	2920.3
$\text{CH}_3\text{OH}$	O-H	3384.7	3418.5	3430.8	3447.1
	C-H	2916.6	2919.3	2920.0	2920.7
$\text{CH}_3\text{NO}_2$	N-O	1564.1 ( $\nu_{as}$ )	1604.7 ( $\nu_{as}$ )	1619.9 ( $\nu_{as}$ )	1634.0 ( $\nu_{as}$ )
		1362.9 ( $\nu_s$ )	1401.9 ( $\nu_s$ )	1411.7 ( $\nu_s$ )	1430.5 ( $\nu_s$ )
	C-H	2961.4 ( $\nu_{as}$ )	2963.5 ( $\nu_{as}$ )	2964.3 ( $\nu_{as}$ )	2964.9 ( $\nu_{as}$ )
		2872.9 ( $\nu_s$ )	2874.0 ( $\nu_s$ )	2874.8 ( $\nu_s$ )	2875.4 ( $\nu_s$ )
$\text{CH}_3\text{NH}_2$	-OH	3446.3	3492.6	3503.1	3521.0
solution	C-N	1283.4	1285.5	1286.7	1287.9
	C-H	2914.9	2917.2	2919.0	2920.3

## FIGURES

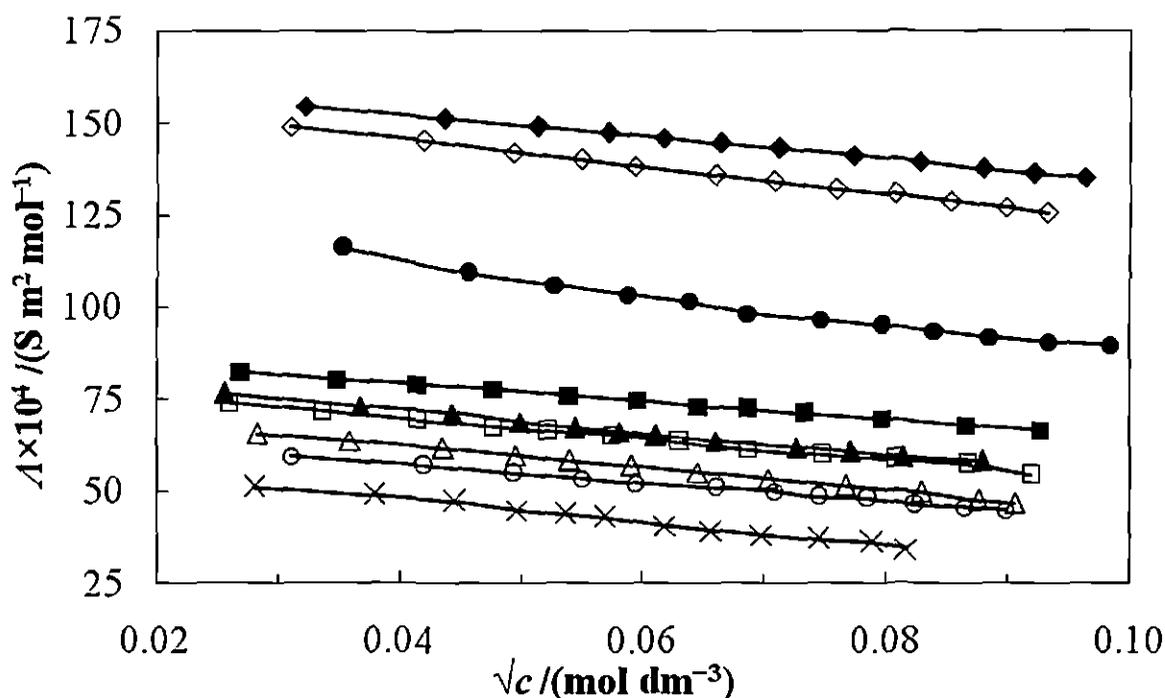


Figure V.1: Plot of molar conductance ( $\Lambda$ ) and the square root of molar concentration ( $\sqrt{c}$ ) for [emim]NO<sub>3</sub> in CH<sub>3</sub>CN (♦), CH<sub>3</sub>OH (■), CH<sub>3</sub>NO<sub>2</sub> (▲), for [emim]CH<sub>3</sub>SO<sub>3</sub> in CH<sub>3</sub>CN (◇), CH<sub>3</sub>OH (□), CH<sub>3</sub>NO<sub>2</sub> (△), for [emim]Tos in CH<sub>3</sub>CN (●), CH<sub>3</sub>OH (○), CH<sub>3</sub>NO<sub>2</sub> (×) respectively at  $T = 298.15\text{K}$

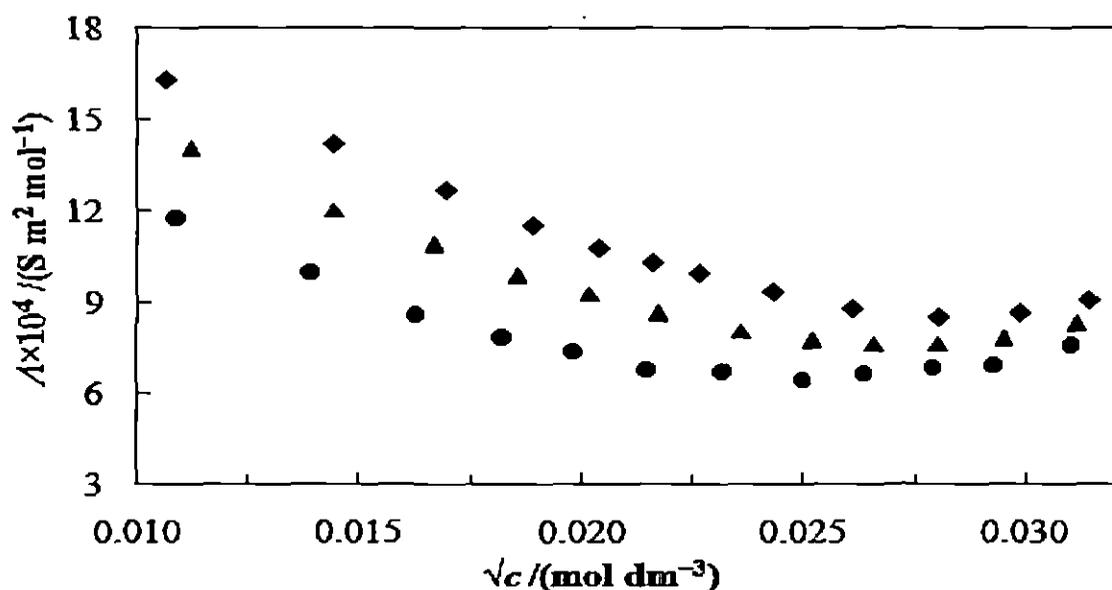


Figure V.2: Plot of molar conductance ( $\Lambda$ ) and the square root of molar concentration ( $\sqrt{c}$ ) of [emim]NO<sub>3</sub> (♦), [emim]CH<sub>3</sub>SO<sub>3</sub> (▲), [emim]Tos (●) in CH<sub>3</sub>NH<sub>2</sub> respectively at  $T = 298.15\text{K}$

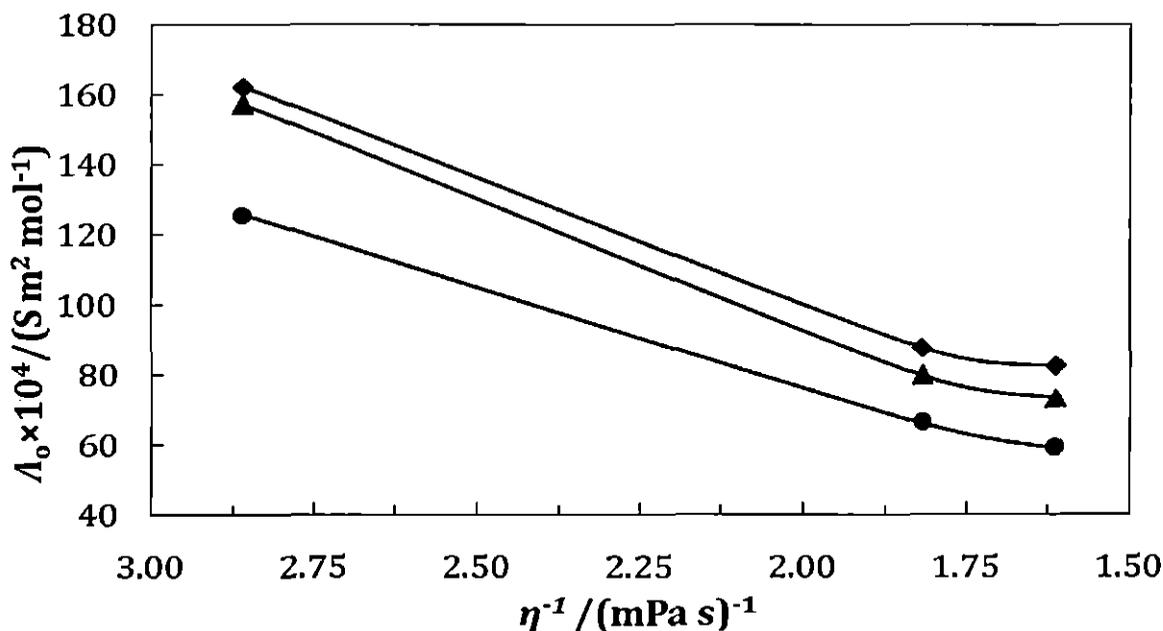


Figure V.3: Plot of limiting molar conductance ( $\Lambda_0$ ) for [emim]NO<sub>3</sub> (♦), [emim]CH<sub>3</sub>SO<sub>3</sub> (▲), [emim]Tos (●) and fluidity ( $\eta^{-1}$ ) of the solvents CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>3</sub>NO<sub>2</sub> respectively at  $T = 298.15\text{K}$

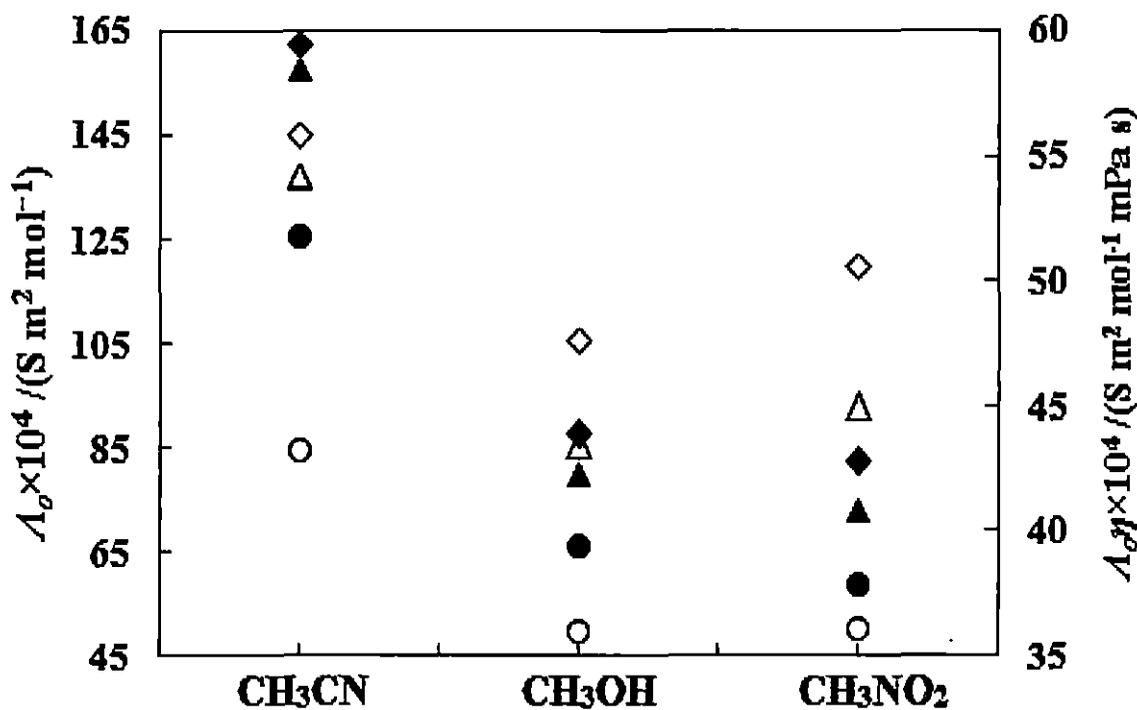


Figure V.4: Plot of limiting molar conductance ( $\Lambda_0$ ) for [emim]NO<sub>3</sub> (♦), [emim]CH<sub>3</sub>SO<sub>3</sub> (▲), [emim]Tos (●) and Walden Product ( $\Lambda_0\eta$ ) for [emim]NO<sub>3</sub> (♦), [emim]CH<sub>3</sub>SO<sub>3</sub> (▲), [emim]Tos (●) in CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>3</sub>NO<sub>2</sub> respectively at  $T = 298.15\text{K}$

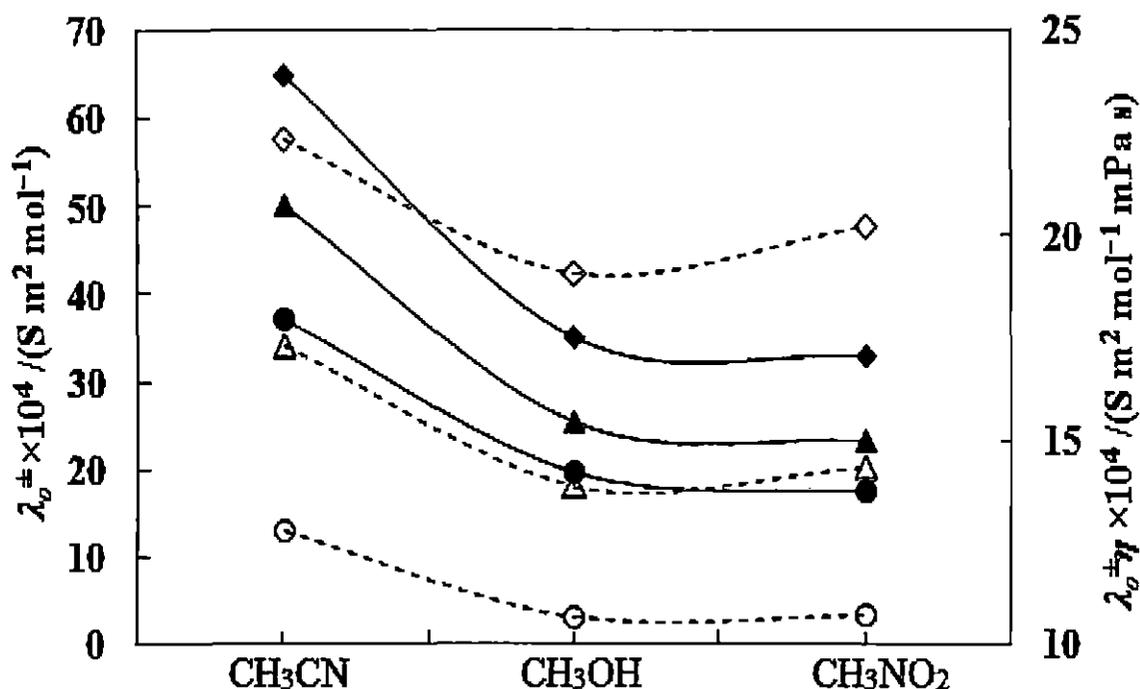


Figure V.5: Plot of limiting ionic conductance ( $\lambda_o^+$ ) for NO<sub>3</sub><sup>-</sup> (♦), CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> (▲), Tos<sup>-</sup> (●) and ionic Walden Product ( $\lambda_o^+\eta$ ) for NO<sub>3</sub><sup>-</sup> (◊), CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> (△), Tos<sup>-</sup> (○) in CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>3</sub>NO<sub>2</sub> respectively at  $T = 298.15\text{K}$

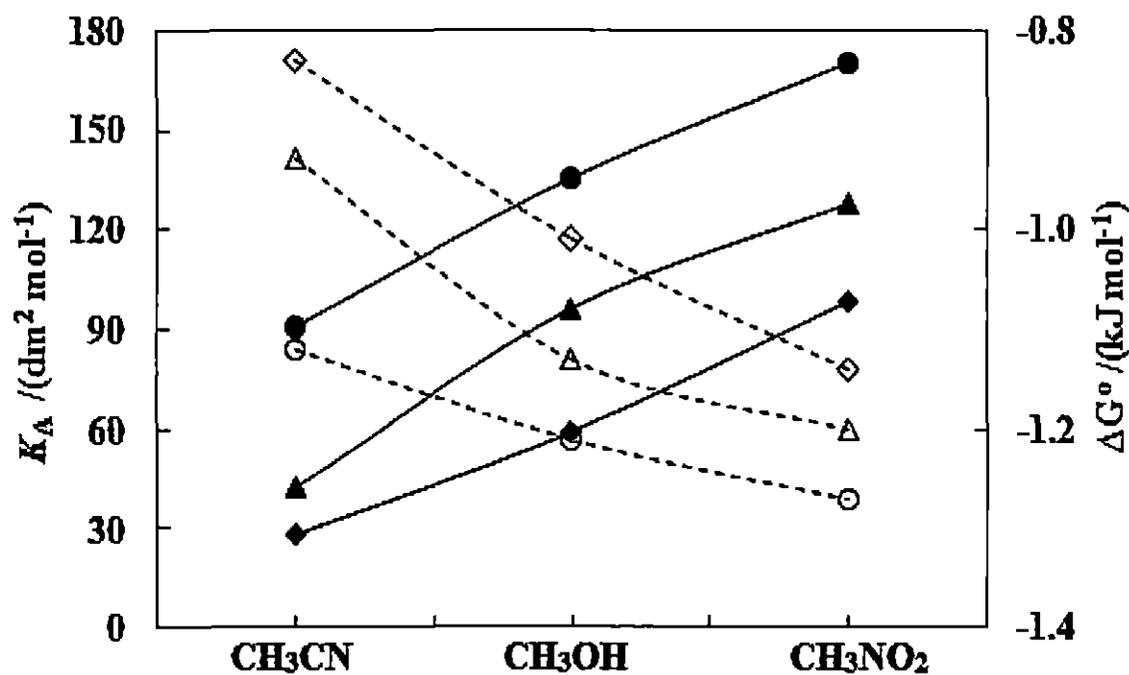


Figure V.6: Plot of association constant ( $K_A$ ) for [emim]NO<sub>3</sub> (♦), [emim]CH<sub>3</sub>SO<sub>3</sub> (▲), [emim]Tos (●) and Gibbs's energy change ( $\Delta G^\circ$ ) for [emim]NO<sub>3</sub> (◊), [emim]CH<sub>3</sub>SO<sub>3</sub> (△), [emim]Tos (○) in CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>3</sub>NO<sub>2</sub> respectively at  $T = 298.15\text{K}$

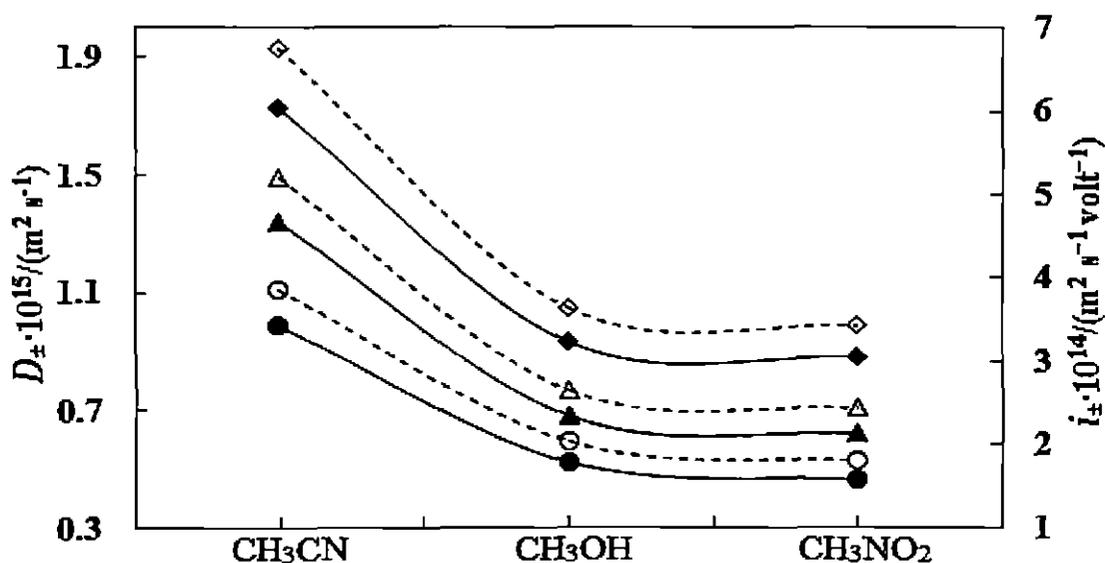


Figure V.7: Plot of diffusion coefficient ( $D_{\pm}$ ) for for  $\text{NO}_3^-$  ( $\blacklozenge$ ),  $\text{CH}_3\text{SO}_3^-$  ( $\blacktriangle$ ),  $\text{Tos}^-$  ( $\bullet$ ) and ionic mobility ( $i_{\pm}$ ) for  $\text{NO}_3^-$  ( $\diamond$ ),  $\text{CH}_3\text{SO}_3^-$  ( $\Delta$ ),  $\text{Tos}^-$  ( $\circ$ ) in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{NO}_2$  respectively at  $T = 298.15\text{K}$

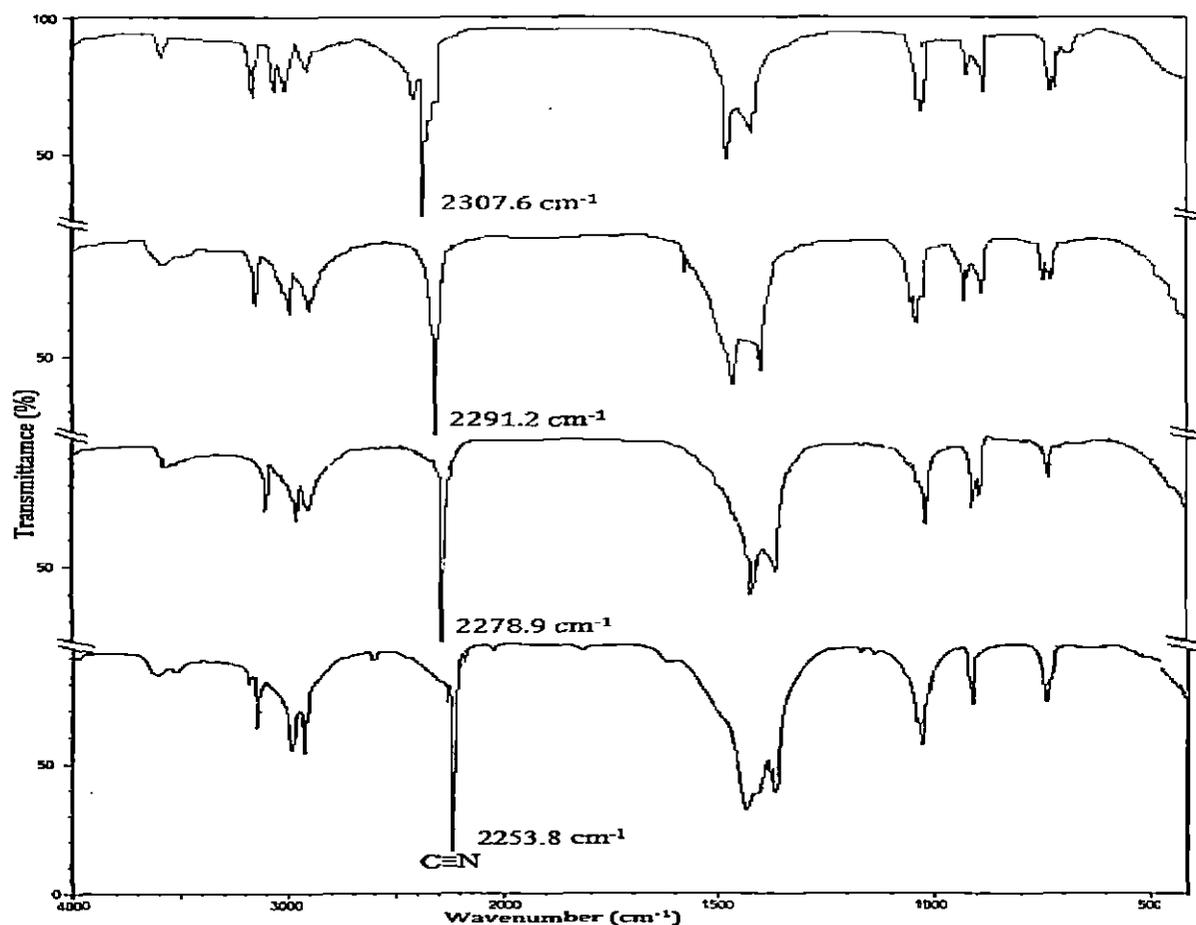


Figure V.8: Stretching frequency of  $-\text{C}\equiv\text{N}$  in acetonitrile (black solid line), in  $\{[\text{emim}]\text{NO}_3+\text{CH}_3\text{CN}\}$  (red solid line), in  $\{[\text{emim}]\text{CH}_3\text{SO}_3+\text{CH}_3\text{CN}\}$  (violet solid line), in  $\{[\text{emim}]\text{Tos}+\text{CH}_3\text{CN}\}$  (blue solid line).

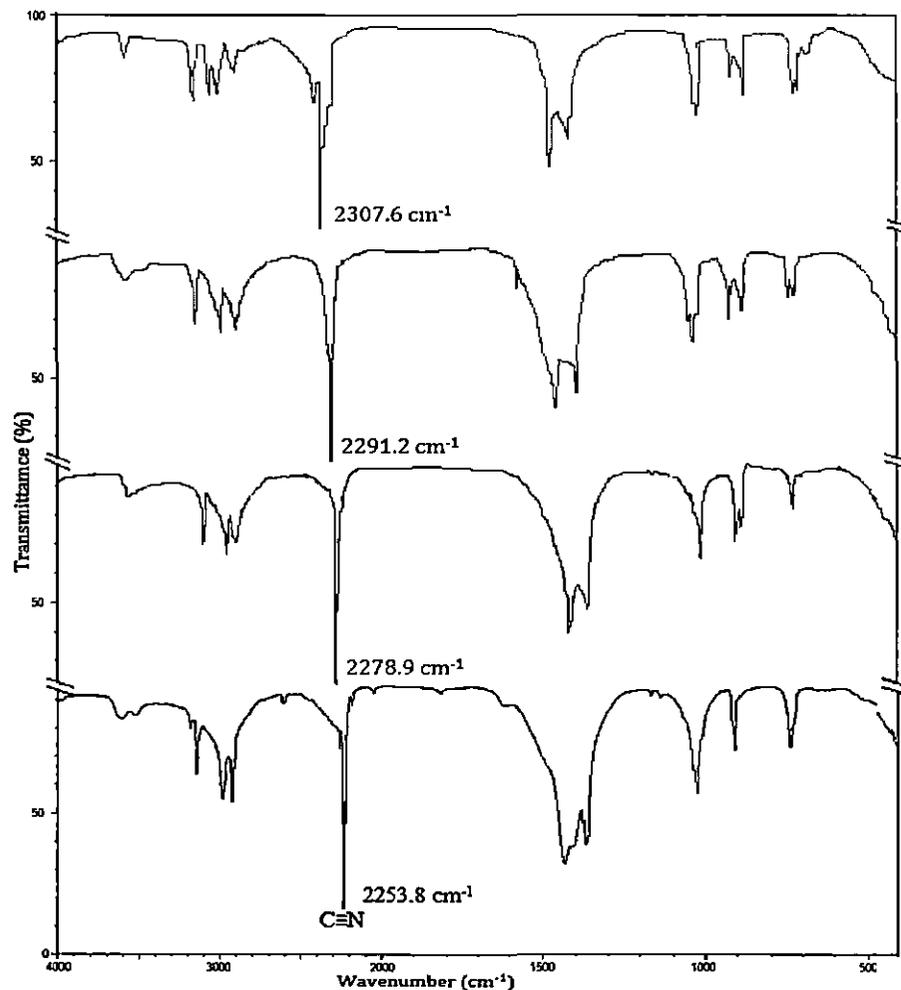


Figure V.9: Stretching frequency of -O-H in methanol (black solid line), in  $\{[emim]NO_3+CH_3OH\}$  (red solid line), in  $\{[emim]CH_3SO_3+CH_3OH\}$  (violet solid line), in  $\{[emim]Tos+CH_3OH\}$  (blue solid line).

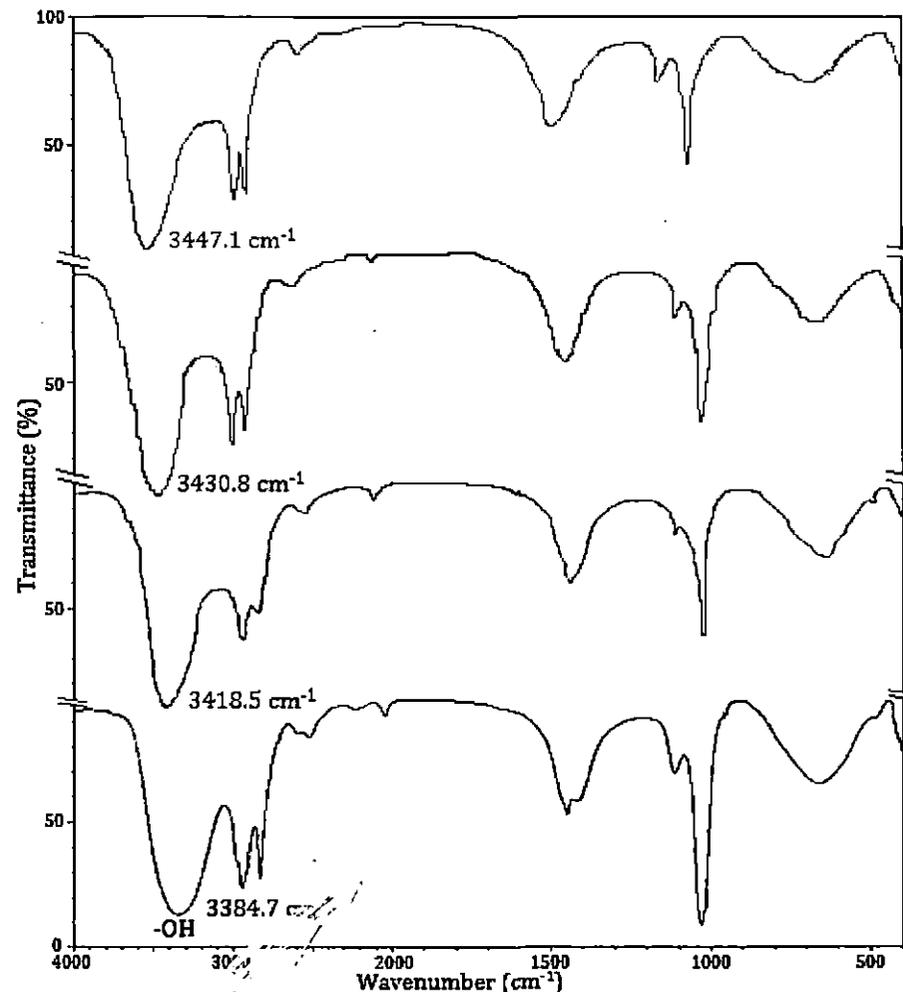


Figure V.10: Stretching frequency of -N-O in nitromethane (black solid line), in  $\{[emim]NO_3+CH_3NO_2\}$  (red solid line), in  $\{[emim]CH_3SO_3+CH_3NO_2\}$  (violet solid line), in  $\{[emim]Tos+CH_3NO_2\}$  (blue solid line).

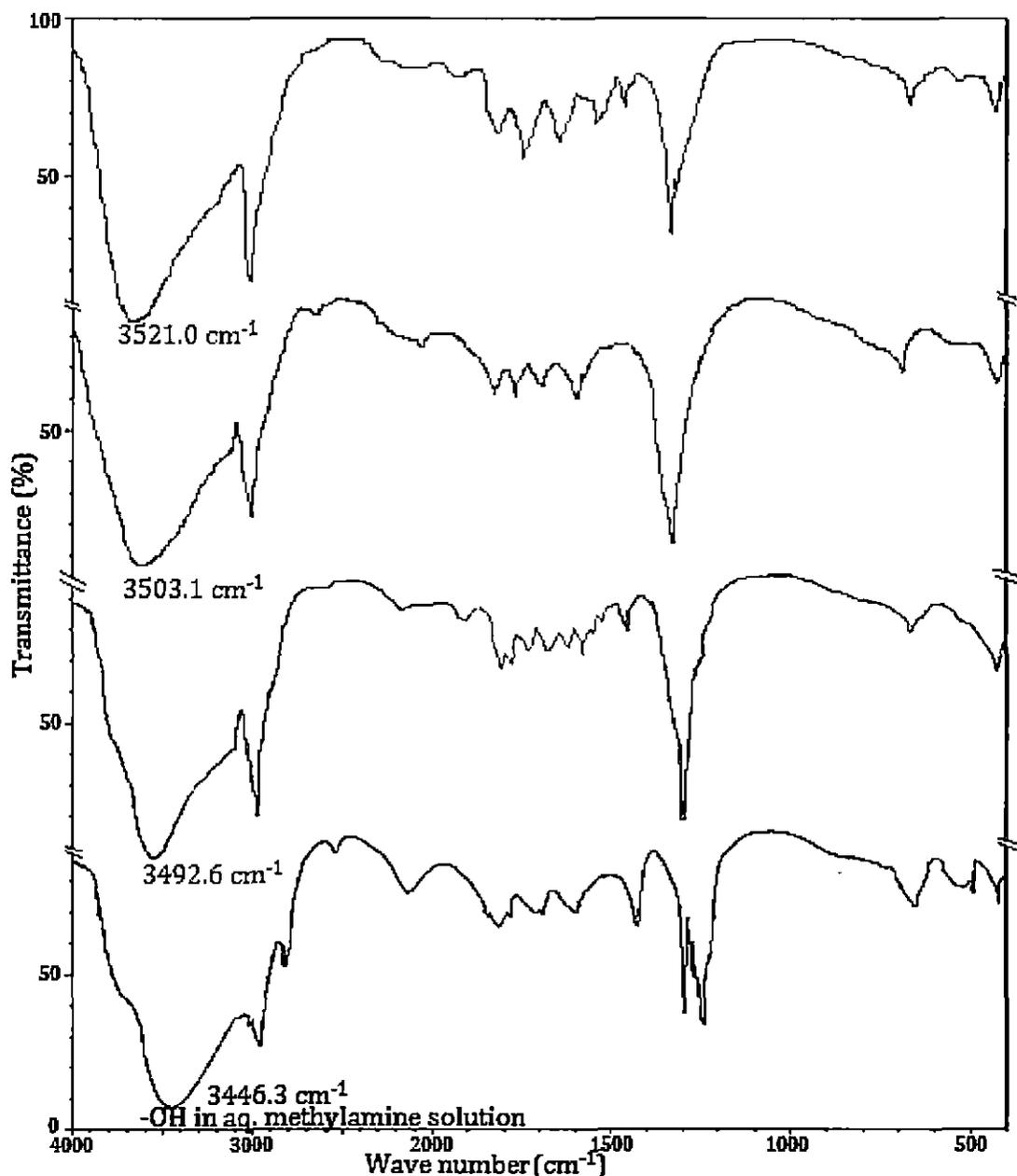
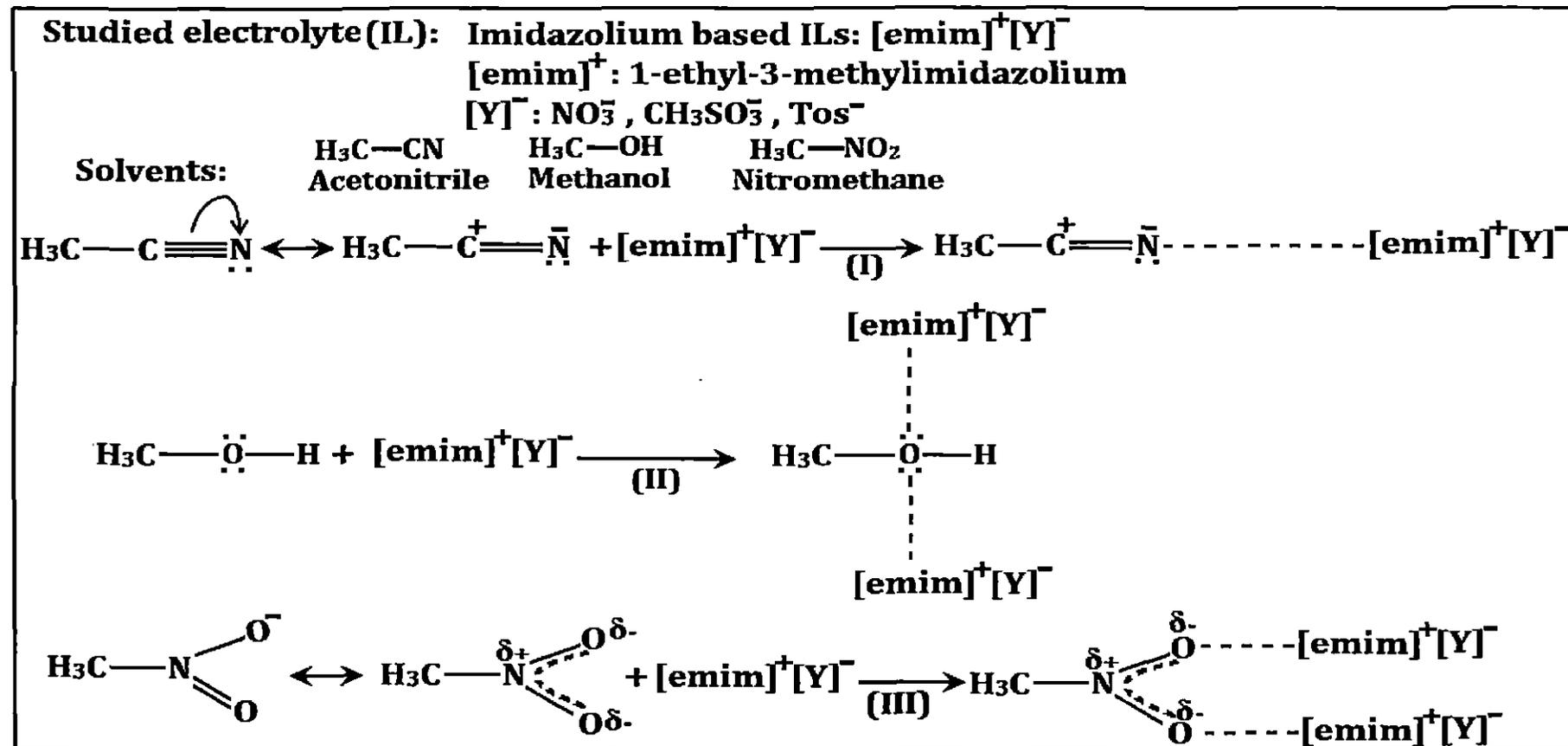
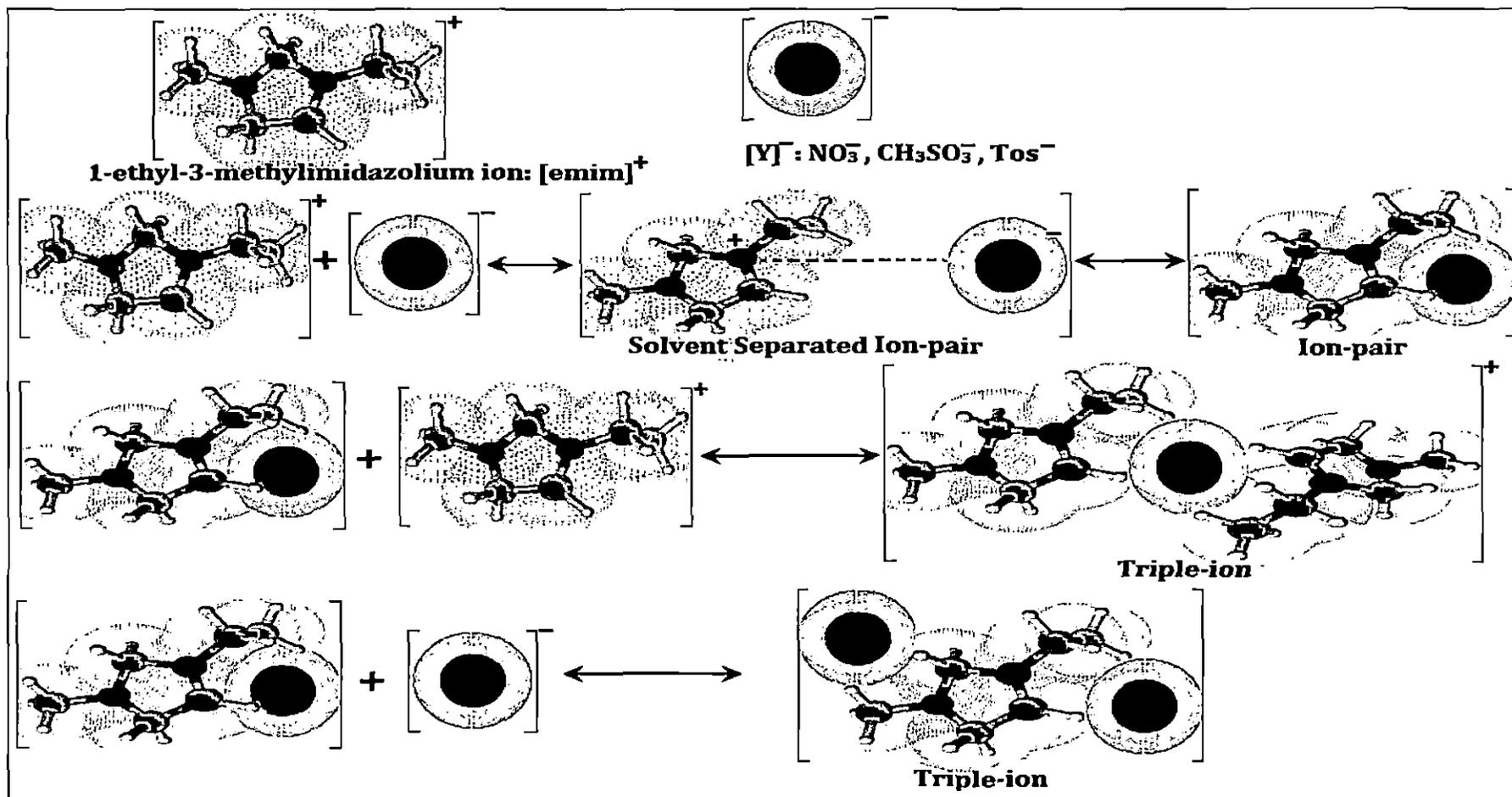


Figure V.11: Stretching frequency of -N-H in methylamine solution (black solid line), in  $\{[\text{emim}]\text{NO}_3 + \text{CH}_3\text{NH}_2\}$  (red solid line), in  $\{[\text{emim}]\text{CH}_3\text{SO}_3 + \text{CH}_3\text{NH}_2\}$  (violet solid line), in  $\{[\text{emim}]\text{Tos} + \text{CH}_3\text{NH}_2\}$  (blue solid line).

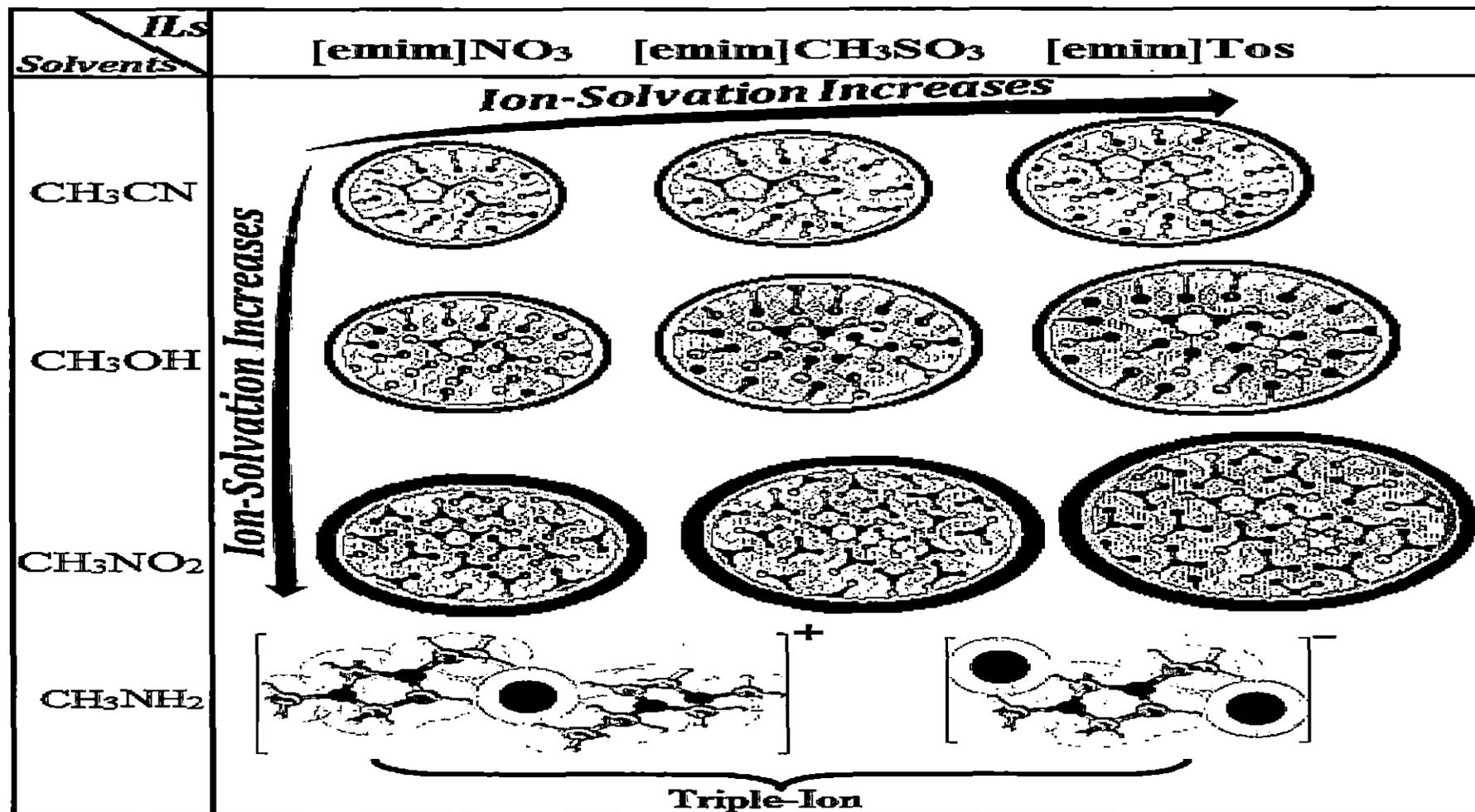
## SCHEMES



Scheme VI.2: The schematic representation of ion-solvation, for the particular ion in the studied solutions {[emim][Y]+solvents}



Scheme VI.4: The pictorial representation of triple-ion formations for the electrolyte (IL), as an example in methylvamine solution



Scheme VI.5: Schematic representation of the interaction or ion-solvation occurring in studied solution systems {[emim][Y]+Solvent}; in view of the observed derived parameters.