RSC Advances

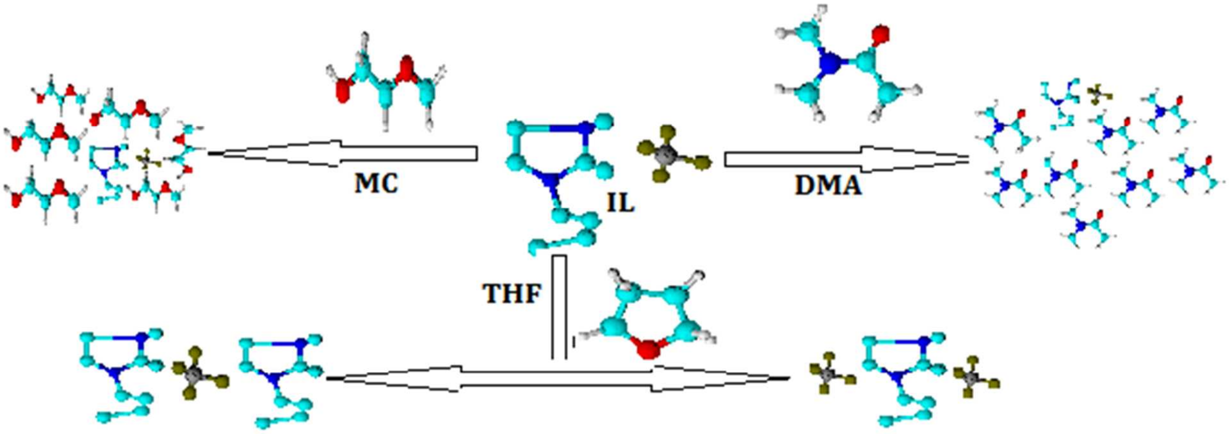
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Graphical Abstract

Subsistence of Ion-Pair and Triple-Ion Origination of an Ionic Liquid, ([bmmim][BF$_4$]) Predominant in Solvent Systems

Mahendra Nath Roy*, Tanusree Ray, Milan Chandra Roy and Biswajit Dutta



Subsistence of Ion-Pair and Triple-Ion Origination of an Ionic Liquid, ([bmmim][BF_4]) Predominant in Solvent Systems

Mahendra Nath Roy*, Tanusree Ray, Milan Chandra Roy and Biswajit Datta
Department of Chemistry, University of North Bengal, Darjeeling-734013, India

Abstract

Electrolytic conductivities, densities, viscosities, and FT-IR studies of 1-butyl-2,3 dimethylimidazolium tetrafluoroborate ([bmmim][BF_4]) have been studied in Tetra hydro furan, Dimethyl acetamide and Methyl Cellosolve at different temperatures. The limiting molar conductivities, association constants, and the distance of closest approach of the ion have been evaluated using the Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs and triple ion formation. Ion–solvent interactions have been interpreted in terms of apparent molar volumes and viscosity B-coefficients which are obtained from the results supplemented with densities and viscosities, respectively. The limiting apparent molar volumes, experimental slopes derived from the Masson equation and viscosity A and B coefficients using the Jones–Dole equation have been interpreted in terms of ion–ion and ion–solvent interactions respectively. However, the deviation of the conductometric curves (Λ vs $\sqrt{c}$) from linearity in tetrahydrofuran indicated triple-ion formation and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple-ion. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate as the "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T). The FT-IR spectra for the solvents as well as the solute in solvent have also been studied. The results have been discussed in terms of ion-dipole interactions, hydrogen bonds formation, structural aspect, and configurational theory.

Keywords: Ion-Pair and Triple-Ion Formation, Solvation consequence, Viscosity, Density, Conductance, FT-IR spectra

Author information: *corresponding author's e-mail: ***mahendraroy2002@yahoo.co.in***
Tel: +91-353-2776381, Fax: +91 353 2699001

1. Introduction

In general, ionic liquids (ILs) are liquid electrolytes that consist of combinations of organic–organic or organic–inorganic cation /anions. Because of their unique physicochemical properties, such as the favourable solubility of organic and inorganic compounds, low vapour pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest in a wide range of industrial applications.

The solvents used in this study find wide industrial usage. N,N-dimethylacetamide (DMA) is commonly used as a solvent for fibres and in the adhesive industry, in the production of pharmaceuticals and plasticizers as a reaction medium, in the manufacture of adhesives, synthetic leathers, fibres, films, and surface coatings. Tetrehydrofuran (THF) is used as a precursor to polymers. The other main application of THF is an industrial solvent for PVC and in vernishes. 2-methoxy ethanol or methyl cellosolve (MC) is used as a solvent for many different purposes such as varnishes, dyes, and resins.

In continuation of our earlier investigations[1-5], we have studied here density, viscosity, conductance and FT-IR of an ionic liquid (1-butyl-2,3-dimethyl imidazolium tetrafluoroborate)([bmmim][BF_4]) in assorted solvents to investigate the solvation consequences analysed by different appropriate equations.

2. Experimental

2. 1 Source and purity of samples

The RTIL selected for the present work puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of the ILs was ≥ 0.99.

All the solvents of spectroscopic grade were procured from Sigma-Aldrich, Germany and were used as procure. The mass fraction of purity of the solvents was 0.995. The purity of the liquids were checked by measuring their density, viscosity and conductivity values, which were in good agreement with the literature values as shown in Table 1.

2. 2 Apparatus and Procedure

All the stock solutions of the electrolyte (IL) in studied solvents were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003g). For conductance the working solutions, were obtained by mass dilution of the stock solutions.

The densities of the solvents and experimental solutions (ρ) were measured by means of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with a precision of ±0.00005g cm^{-3} maintained at ±0.01K of the desired temperature. It was calibrated by triply-distilled water and passing dry air.

The viscosities were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42 fitted to a Brookfield digital bath TC-500. The viscosities were obtained using the following equation

$$\eta = (100 / RPM) \times TK \times \text{torque} \times SMC$$

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 $CaCl_2$ solutions.[17] Temperature of the solution was maintained to within ± 0.01°C using Brookfield Digital TC-500 temperature thermostat bath. The viscosities were measured with an accuracy of ± 1 %. Each measurement reported herein is an average of triplicate reading with a precision of 0.3 %.

The conductance measurements were carried out in 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^{-1}. Measurements were made in a thermostat water bath maintained at T = (298.15 ± 0.01) K. The cell was calibrated by the method proposed by Lind et al. and cell constant was measured based on 0.01 M aqueous KCl solution. During the conductance measurements, cell constant was maintained within the range 1.10–1.12 cm^{-1}. The conductance data were reported at a frequency of 1 kHz and the accuracy was ±0.3%. During all the measurements, uncertainty of temperatures was ±0.01 K.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described.[5]

3. Results and Discussion

The solvent properties are given in Table 1. The concentrations and molar conductances (Λ) of IL in Methyl Cellosolve, Dimethyl Acetamide and Tetrahydrofuran at different temperatures are given in Table 2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation.

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

Linear conductance curve (Λ versus $\sqrt{c}$) were obtained for the electrolyte in Methyl Cellosolve and DMA extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductance for the electrolyte.

3.1 Ion-pair Formation

The ion-pair formation in case of conductometric study of [bmmim][BF_4] in Methyl cellosolve and DMA are analysed using the Fuoss conductance equation[6]. With a given set of conductivity values (c_j, Λ_j; j = 1…….n), three adjustable parameters, i.e., Λ_0, K_A and R have been derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method[7] for determining the R value but in order to treat the data in our system, R value is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by[8]

$$d = 1.183\ (M / \rho)^{1/3} \tag{2}$$

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

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

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \tag{3}$$

$$P = 1-\alpha(1-\gamma) \tag{4}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{5}$$

$$-\ln f = \beta\kappa / 2(1+\kappa R) \tag{6}$$

$$\beta = e^2 / (\varepsilon_r k_B T) \tag{7}$$

$$K_A = K_R / (1-\alpha) = K_R / (1+K_S) \tag{8}$$

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

The computations were performed using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data[9]. Input for the program is the no. of data, n, followed by ε, η (viscosity of the solvent mixture), initial Λ_0 value, T, ρ (density of the solvent mixture), mole fraction of the first component, molar masses, M_1 and M_2 along with c_j, Λ_j values where $j = 1, 2$…….n and an instruction to cover preselected range of R values.

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

$$\delta^2 = \sum[\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n-m) \tag{9}$$

for a sequence of R values and then plotting δ against R, the best- fit R corresponds to the minimum of the δ–R versus R curve. So, an approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minima is found in the δ - R curves, thus R values is assumed to be $R = a + d$, with terms having usual significance. Finally, the corresponding limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for [bmmim][BF$_4$] in methyl cellosolve and DMA at 298.15 K, 303.15 K and 308.15 K respectively are given in table 3.

Table 3 shows that K_A values increase with increasing temperature in case of MC and DMA. As in case of MC and DMA, with increasing temperature the number of free ions per unit volume decreases and hence the tendency of ion pair formation enhances.

The standard Gibbs free energy change of solvation, ΔG^o, for [bmmim][BF$_4$] in methyl cellosolve and DMA is given by the following equation[10]

$$\Delta G^o = -RTlnK_A \tag{10}$$

It is observed from the Table 4 that the value of the Gibbs free energy is entirely negative for methyl cellosolve and DMA at all temperatures and it can be explained by considering the participation of specific covalent interaction in the ion-association process.

Table 5 shows the value of ionic conductance ($\lambda_0^{\pm}$) and ionic Walden product ($\lambda_0^{\pm}\eta$) (product of ionic conductance and viscosity of the solvent) along with Stokes' radii (r_S) and Crystallographic Radii (r_c) of [bmmim][BF$_4$] in methyl cellosolve and DMA at different temperatures.

3.2 **Triple-ion Formation**

But for the electrolyte in THF, a deviation in the conductance curve was obtained and shows a decrease in conductance values up to a certain concentration reaches a minimum and then increases indicating triple-ion formation.

The conductance data for the electrolyte in THF have been analysed using the classical Fuoss-Kraus equation[11] for triple-ion formation

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \tag{11}$$

$$g(c) = \frac{\exp\{-2.303\ \beta^{/}(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \tag{12}$$

$$\beta^{/} = 1.8247\times10^6/(\varepsilon T)^{1.5} \tag{13}$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204\times10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \tag{14}$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; Λ_0^T is the sum of the conductances of the two triple ions bmmim$^+$BF$_4^-$ and bmmim$^+$(BF$_4$)$_2^-$. $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make equation (2) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted[12] and Λ_0 values for the studied electrolytes have been calculated[13]. Λ_0^T is calculated by setting the triple ion conductance equal to 2/3Λ_0[14].

The ratio Λ_0^T/Λ_0 was thus set equal to 0.667 during linear regression analysis of equation (2). Limiting molar conductance of triple-ions (Λ_0^T), slope and intercept of Eq. (2) for [bmmim][BF_4]in THF at different temperatures are given in Table 6.

Linear regression analysis of equation (2) for the electrolytes with an average regression constant, R^2 = 0.9653, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_P and K_T listed in Table 7. It is observed that Λ passes through a minimum as c increases. The K_P and K_T values predict that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles).

At very low permittivity of the solvent (ε<10) electrostatic ionic interactions are very large. So the ion-pairs attract the free $_+$ve and -ve ions present in the solution medium as the distance of the closest approach of the ions become minimum. This results in the formation of triple-ion, which acquire the charge of the respective ions in the solution[15] i.e.

$$M^+ + A^- \leftrightarrow M^+\cdots\cdots\cdots A^- \leftrightarrow MA \qquad \text{(ion-pair)} \qquad (15)$$

$$MA + M^+ \leftrightarrow MAM^+ \qquad \text{(triple-ion)} \qquad (16)$$

$$MA + A^- \leftrightarrow MAA^- \qquad \text{(triple-ion)} \qquad (17)$$

where M^+ and A^- are respectively bmmim$^+$ and BF_4^-. The effect of ternary association thus removes some non-conducting species, MA, from solution, and replaces them with triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolyte in THF.

Furthermore, the ion-pair and triple-ion concentrations, c_P and c_T respectively of the electrolyte have also been calculated at the minimum conductance concentration of [bmmim][BF_4] in THF using the following relations:[16]

$$\alpha = 1 / (K_P^{1/2}\cdot c^{1/2}) \qquad (18)$$

$$\alpha_T = (K_T/ K_P^{1/2})\, c^{1/2} \qquad (19)$$

$$c_P = c(1- \alpha-3\alpha_T) \qquad (20)$$

$$c_T = (K_T / K_P^{1/2})\, c^{3/2} \qquad (21)$$

Here α and α_T are the fractions of ion-pairs and triple-ions present in the salt-solutions respectively and are given in Table 8. Thus, the values of C_P and C_T also given in table 5 indicate that the ions are mainly present as ion-pairs even at high concentration and a small fraction existing as triple-ions. The ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) have also been calculated over the whole concentration range of [bmmim][BF_4] in THF and are provided in table 5.

From Table 7, it has been observed with increasing temperature the number of free ions per unit volume decreases resulting in the increase of K_P and K_T values. Interactions between ionic liquid and different solvents are represented in scheme 1.

4. Apparent molar volume

The measured values of densities of [bmmim][BF$_4$] in MC, DMA and THF 298.15, 303.15 and 308.15 K are reported in Table1 . The densities of the electrolytes in different solvents increase linearly with the concentration at the studied temperatures. For this purpose, the apparent molar volumes ϕ_V were determined from the solutions densities using the following equation and the values are given in Table 9.

$$\phi_V = M/\rho - (\rho - \rho_o)/m\rho_o\rho \qquad (22)$$

where *M* is the molar mass of the solute, *m* is the molality of the solution, $\rho$and ρ_0 are the densities of the solution and solvent, respectively. The apparent molar volumes ϕ_V were found to decrease with increasing molality (*m*) of IL in different solvents and increase with increasing temperature for the system under study. The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_V versus $\sqrt{c}$ using the following Masson equation[17]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \qquad (23)$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope.

The plots of ϕ_V against the square root of the molar concentration $\sqrt{c}$ were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 9. From Table 3 it is observed that ϕ_V^0 values for this electrolyte are generally positive for all the solvents and is highest in case of [bmmim][BF$_4$] in MC. This indicates the presence of strong ion–solvent interactions and the extent of interactions increases from THF to MC.

On the contrary, the S_V* indicates the extent of ion-ion interaction. The values of S_V* shows that the extent of ion-ion interaction is highest in case of THF and is lowest in MC. Owing to a quantitative comparison, the magnitude of ϕ_V^0 are much greater than S_V*, in every solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that higher ion-solvent interaction in MC, leads to lower conductance of [bmmim][BF$_4$] in it than DMA and THF, discussed earlier.

4.1 Temperature dependent limiting apparent molar volume:

The variation of ϕ_V^0 with the temperature of the IL in different solvents can be expressed by the general polynomial equation as follows,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \tag{24}$$

where a_0, a_1, a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the cosolute IL, and T is the temperature range under study in Kelvin. The values of these coefficients of the above equation for the IL in THF, DMA and MC are reported in Table 10.

The limiting apparent molar expansibilities, ϕ_E^0, can be obtained by the following equation,

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T\right)_P = a_1 + 2 a_2 T \tag{25}$$

The limiting apparent molar expansibilities, ϕ_E^0, change in magnitude with the change of temperature. The values of ϕ_E^0 for different solutions of the studied IL at (298.15, 303.15, and 308.15) K are reported in Table 11. The table reveals that ϕ_E^0 is positive for IL in all the studied solvents and studied temperatures. This fact can ascribed to the absence of caging or packing effect for the IL in solutions.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or -breaking nature of any solute. Hepler[18] developed a technique of examining the sign of $\left(\delta \phi_E^0 / \delta T\right)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$\left(\delta \phi_E^0 / \delta T\right)_P = \left(\delta^2 \phi_V^0 / \delta T^2\right)_P = 2 a_2 \tag{26}$$

If the sign of $\left(\delta \phi_E^0 / \delta T\right)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker[19]. As is evident from Table 7 the $\left(\delta \phi_E^0 / \delta T\right)_P$ values for IL in all the solvents are positive under investigation are predominantly structure makers in all of the experimental solutions.

5. Viscosity calculation

Another transport property of the solution is viscosity has been studied for comparison and conformation of the solvation of the electrolyte in the chosen solvents. The viscosity data has been analyzed using Jones-Dole equation.[20]

$$\left(\eta / \eta_0 - 1\right) / \sqrt{c} = A + B \sqrt{c} \tag{27}$$

where η and η_0 are the viscosities of the solution and solvent respectively. The values of *A*-coefficient and *B*-coefficient are obtained from the straight line by plotting $\left(\eta / \eta_0 - 1\right) / \sqrt{c}$

against $\sqrt{c}$ which are reported in Table 12. The viscosity *B*-coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 12 it is evident that the values of the *B*-coefficient are positive, thereby suggesting the presence of strong ion-solvent interactions, and strengthened with an increase the solvent viscosity value, are agreement with the results obtained from ϕ_V^0 values discussed earlier. The values of the *A*-coefficient are found to increases slightly with temperature and with the increase in mass of IL in the solvent mixture. These results designate the presence of very weak solute-solute interactions. These results are in excellent arrangement with those obtained from S_V^* values.

The extent of solute-solvent interaction in the solution calculated from the viscosity *B*-coefficient[21] gives valuable information regarding the solvation of the solvated solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules in the solutions. From Table 12 it is evident that the values of the *B*-coefficient are positive and much higher than *A*-coefficient, thereby suggesting the solute-solvent interactions are dominant over the solute-solute interactions. The higher *B*-coefficient values for higher viscosity values is due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature. These results are in good agreement with those obtained from ϕ_V^0 values discussed earlier.

Thus, the trend of ion-solvent interaction is MC >DMA>THF. The viscosity *A*- and *B*-coefficients are in excellent agreement with the results drawn from the volumetric studies.

6. FT-IR Spectroscopy

With the aid of FT-IR spectroscopy the molecular interaction existing between the solute and the solvent can be studied. At first the IR spectra of the pure solvents were studied. The stretching frequencies of the key groups are given in Table 8 and Figure 1, 2 and 3.

In case of THF a sharp peak is obtained at 1084.4cm^{-1} for C-O which shifts to 1098.2 cm^{-1}, due to the addition of 0.05M of the electrolyte [bmmim]BF4, due to the interaction of [bmmim]$^{+}$ with the C-O dipole showing ion-dipole interaction which is formed due to the disruption of H-bonding interaction in THF molecules.

Similar types of interactions are observed in case of DMA where the sharp peak for C=O shifts from 1670.2cm^{-1} to 1698.1 cm^{-1} in case of [bmmim]BF4 due to ion-dipole interaction between [bmmim]$^{+}$ and C=O dipole.

The FT-IR spectra of the ionic liquids in MC show that the peak for C-O at 1060 cm^{-1} shifts to 1071.5 cm^{-1}, for [bmmim]BF4 due to the disruption of weak H-bonding interaction between the two MC molecules[22] leading to the formation of ion-dipole interaction between [bmmim]$^+$ and C-O dipole.

7. Conclusion

The extensive study of IL, [bmmim][BF_4]in MC, DMA and THF leads to the conclusion that, the salt is more associated in MC than the other two solvents. It can also be seen that in the conductometric studies in THF the [bmmim][BF_4]mostly remains as triple-ions than ion-pairs but in MC and DMA the [bmmim][BF_4] remains as ion-pairs. There is more ion-solvent interaction in MC than DMA. The experimental values obtained from the volumetric, viscometric studies suggest that in solution there is more ion–solvent interaction than the ion–ion interaction and the extent of ion–solvent interaction of [bmmim][BF_4] in MC, DMA and THF, respectively.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme, Department of Chemistry, NBU under the University Grants Commission, New Delhi (No. 540/27/DRS/2007, SAP-1) for financial support and instrumental facilities in order to continue this research work.

Tanusree Ray is also thankful to ''Rajiv Gandhi National Fellowship,'' UGC, New Delhi Ref UGC Letter No. F1-17.1/2013-14/RGNF-2013-14-SC-WES-52926, for sanctioning research fellowship and financial assistance.

Milan Chandra Roy is also thankful to ''UGC Research Fellowship in Science for Meritorious Students'' Ref UGC Letter No. F.4-1/2006(BSR)/7-133/2007(BSR) under SAP, for sanctioning research fellowship and financial assistance.

One of the authors, Prof. M. N. Roy is thankful to University Grant Commission, New Delhi, Government of India for being awarded one time Grant under Basic Scientific Research via the Grant-in-Aid No. F.4-10/2010 (BSR) regarding his active service for augmenting of research facilities to facilitate further research work.

Reference:

1. D. Ekka and M. N. Roy, *RSC Adv*., 2014, **4**, 19831-19845.
2. A. Bhattacharjee and M. N. Roy, *Phys. Chem. Chem. Phys* 2010,**12**, 14534-14542.
3. D. Ekka and M. N. Roy, *J. Phys. Chem. B* 2012, **116**, 11687−11694.
4. D. Ekka and M. N. Roy, *Amino Acids* 2013, **45**, 755–777.
5. M. N. Roy, D. Ekka, S. Saha and M. C. Roy, *RSC Adv*., 2014, *DOI: 10.1039/c4ra07877b*.
6. R. M. Fuoss., J. Phys. Chem. 1978, **82**, 2427-2440.
7. B. Per, ***Acta Chem. Scand***., **1977,** 31(A), 869-876.

8. R. Dewan and M.N. Roy, *J. Chem. Thermodynamics.*, 2012, **54**, 28–34.
9. D. S. Gill and M. S. Chauhan, *Z. Phys. Chem. NF.* ,1984, **140**, 139-148.
10. J. Barthel, M. B. Rogac and R. Neueder, *J. Solution Chem.*, 1999, **28**, 1071-1086.
11. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.*, 1933, **55**, 2387-2399.
12. Y. Harada, M. Salamon and S. Petrucci, *J. Phys. Chem.*,1985, **89**, 2006-2010.
13. B.S. Krumgalz, *J. Chem. Soc. Faraday. Trans I.*, 1983, **79**, 571-587.
14. M. Delsignore and H. Farber, *J. Phys. Chem.*, 1985, **89**, 4968-4973.
15. M. N. Roy, R. Chanda and A. Bhattacharjee, *Fluid Phase Equilibria*, 2009, **280**, 76-83.
16. M. N. Roy and R. Chanda, *Fluid Phase Equilibria*, 2008, **269**, 134–138.
17. M. N. Roy, D. Ekka and R. Dewan, *Acta Chimica Slovenica,* 2011, **58,** 792-796.
18. L. G. Helper, *Can J Chem.* 1969, **47**, 4613-4618.
19. M. N. Roy, Dakua, V. K. Dakua and B. Sinha, *Int J Thermophys*. 2007, **28**, 1275-1284.
20. G. Jones and M. Dole, *Journal of American Chemical Society*, 1929**, 51,** 2950-2964.
21. F. J. Millero, *Chem Rev*. 1971, **71**, 147-176.
22. K. Rubesova, T. Hlasek, V. Jakes, P. Matejka, J. Oswald and P. Holzhauser, *J.Sol-Gel Sci Technol*, 2014, **70,** 142-148.

Tables:

Table 1. Density (ρ), viscosity (η) and relative permittivity (ε) of the different solvents dimethyl acetamide (DMA), tetrahydrofuran (THF) and methyl cellusolve (MC) at different temperatures.

Solvents	Temp (K)	$\rho \cdot 10^{-3}$/kg m^{-3}	η/mPa s	E
DMA	298.15	0.93680	0.923	37.78
	303.15	0.93343	0.871	-
	308.15	0.92908	0.7262	-
THF	298.15	0.88074	0.463	7.58
	303.15	0.87731	0.381	-
	308.15	0.87179	0.369	-
MC	298.15	0.96002	1.541	15.4
	303.15	0.95836	1.522	-
	308.15	0.95374	1.509	-

Table 2. The concentration (c) and molar conductance (Λ) of [bmmim][BF_4] in Methyl Cellosolve, Dimethyl acetamamide and Tetrahydrofuran at 298.15, 303.15, 308.15 K respectively.

$c\cdot10^4$/ mol·dm^{-3}	$\Lambda\cdot10^4$/ S·m^2·mol^{-1}	$c\cdot10^4$/ mol·dm^{-3}	$\Lambda\cdot10^4$/ S·m^2·mol^{-1}	$c\cdot10^4$/ mol·dm^{-3}	$\Lambda\cdot10^4$/ S·m^2·mol^{-1}
298.15K					
Methyl Cellosolve		Dimethyl acetamamide		Tetrahydrofuran	
3.3672	141.54	3.5044	92.82	3.97	52.31
3.9641	141.50	4.4521	92.77	4.74	51.21
4.7350	141.46	5.1938	92.72	5.52	50.31
5.7600	141.41	5.8081	92.69	6.21	49.50
6.6203	141.37	6.2001	92.68	6.82	49.20
7.3984	141.33	6.9169	92.64	7.21	48.90
8.2254	141.29	7.7841	92.60	7.84	48.50
9.0721	141.27	8.7557	92.55	8.28	48.00
10.1188	141.25	9.6534	92.51	9.00	46.40
11.1422	141.25	10.6406	92.48	9.45	45.50
11.9578	141.25	11.8542	92.44	10.24	44.70
13.2642	141.27	13.3810	92.40	11.02	43.11
14.2129	141.28	15.0777	92.38	11.90	42.90
15.5000	141.31	16.4106	92.39	12.90	42.80
16.4106	141.34	17.7241	92.42	14.98	42.00
303.15K					
Methyl Cellosolve		Dimethyl acetamamide		Tetrahydrofuran	
3.3672	144.54	3.5044	94.82	3.97	56.31
3.9641	144.50	4.4521	94.77	4.74	54.21
4.7350	144.46	5.1938	94.72	5.52	52.31
5.7600	144.41	5.8081	94.69	6.21	51.50
6.6203	144.37	6.2001	94.68	6.82	50.20
7.3984	144.33	6.9169	94.64	7.21	49.90
8.2254	144.29	7.7841	94.60	7.84	48.50
9.0721	144.27	8.7557	94.55	8.28	48.00
10.1188	144.25	9.6534	94.51	9.00	46.40
11.1422	144.25	10.6406	94.48	9.45	45.50
11.9578	144.25	11.8542	94.44	10.24	44.70
13.2642	144.27	13.3810	94.40	11.02	43.11
14.2129	144.28	15.0777	94.38	11.90	42.90
15.5000	144.31	16.4106	94.39	12.90	42.80
16.4106	144.34	17.7241	94.42	14.98	42.00
308.15K					
Methyl Cellosolve		Dimethyl acetamamide		Tetrahydrofuran	
3.3672	148.54	3.5044	98.82	3.97	58.31
3.9641	148.50	4.4521	98.77	4.74	58.21

4.7350	148.46	5.1938	98.72	5.52	58.31
5.7600	148.41	5.8081	98.69	6.21	58.50
6.6203	148.37	6.2001	98.68	6.82	58.20
7.3984	148.33	6.9169	98.64	7.21	48.90
8.2254	148.29	7.7841	98.60	7.84	48.50
9.0721	148.27	8.7557	98.55	8.28	48.00
10.1188	148.25	9.6534	98.51	9.00	48.40
11.1422	148.25	10.6406	98.48	9.45	48.50
11.9578	148.25	11.8542	98.44	10.24	48.70
13.2642	148.27	13.3810	98.40	11.02	48.11
14.2129	148.28	15.0777	98.38	11.90	48.90
15.5000	148.31	16.4106	98.39	12.90	48.80
16.4106	148.34	17.7241	98.42	14.98	48.00

Table 3. Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in Methyl cellosolve and DMA at 298.15, 303.15, 308.15 K respectively.

Solvent	$\Lambda_o\cdot10^4$/S·m²·mol⁻¹	K_A/ dm³·mol⁻¹	R/Å	Δ
		298.15K		
Methyl cellosolve	23.29	422.24	7.44	0.25
DMA	24.27	421.14	6.83	0.14
		303.15K		
Methyl cellosolve	23.49	423.24	7.54	0.26
DMA	24.67	422.14	6.93	0.15
		308.15K		
Methyl cellosolve	33.29	453.24	8.54	0.16
DMA	34.67	443.14	8.23	0.14

Table 4. walden product ($\Lambda_o \cdot \eta$) and Gibb's energy change (ΔG°) of 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in Methyl cellosolve and DMA at 298.15 K, 303.15 K and 308.15 K respectively are given below.

Solvent	$\Lambda_o \cdot \eta \cdot 10^4$/ $S \cdot m^2 \cdot mol^{-1} mPa$	ΔG°/ $kJ \cdot mol^{-1}$
	298.15 K	
Methyl cellosolve	94.44	-30.31
DMA	86.94	-29.21
	303.15 K	
Methyl cellosolve	95.44	-31.31
DMA	85.94	-30.21
	308.15 K	
Methyl cellosolve	105.44	-32.31
DMA	104.24	-30.11

Table 5. Limiting Ionic Conductance ($\lambda_0^{\pm}$), Ionic Walden Product ($\lambda_0^{\pm}\eta$) , Stokes' Radii (r_s), and Crystallographic Radii (r_c) of 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in Methyl cellosolve and DMA at 298.15 K, 303.15 K and 308.15 K respectively are given below.

.

Solvent	ion	$\lambda_0^{\pm}$ ($S \cdot m^2 \cdot mol^{-1}$)	$\lambda_0^{\pm}\eta$ ($S \cdot m^2 \cdot mol^{-1} mPa$)	r_s (Å)	Z
298.15					
Methyl cellosolve	$Bmmim^+$	10.05	21.51	3.44	5.78
	BF_4-	21.01	42.15	1.50	2.06
DMA	$Bmmim^+$	10.15	22.51	3.64	5.88
	BF_4-	21.71	48.15	1.70	2.16
303.15					
Methyl cellosolve	$Bmmim^+$	10.15	22.51	3.54	5.78
	BF_4-	21.71	46.15	1.50	2.06
DMA	$Bmmim^+$	10.15	23.11	3.74	5.88
	BF_4-	21.71	47.05	1.70	2.12
308.15K					
Methyl cellosolve	$Bmmim^+$	9.15	20.51	3.24	5.87
	BF_4-	20.71	48.15	1.70	2.15

DMA	Bmmim$^+$	8.25	22.51	3.11	5.42
	BF$_4$-	19.71	48.15	1.70	2.12

Table 6. The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductances of triple ion Λ_0^T, experimental slope and intercept obtained from Fuoss-Kraus Equation for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in THF at 298.15 K, 303.15 K and 308.15 K respectively.

Solvents	$\Lambda_0 \cdot 10^4$ /$S \cdot m^2 \cdot mol^{-1}$	$\Lambda_o^T \times 10^4$ /$S \cdot m^2 \cdot mol^{-1}$	Slope×10^{-2}	Intercept ×10^{-2}
		298.15K		
THF	55.34	38.25	0.09	0.42
		303.15 K		
THF	60.34	40.25	0.11	0.45
		308.15 K		
THF	61.34	41.25	0.14	0.48

Table 7. Salt concentration at the minimum conductivity ($C_{\min}$) along with the ion-pair formation constant (K_P), triple ion formation constant (K_T) for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in THF at 298.15 K.

Solvents	$c_{\min} \cdot 10^4$/ $mol \cdot dm^{-3}$	log $c_{\min}$	$K_P \cdot 10^{-5}$/ $(mol \cdot dm^{-3})^{-1}$	K_T/ $(mol \cdot dm^{-3})^{-1}$	K_T / K_P $\cdot 10^5$	log K_T / K_P
			298.15 K			
THF	8.14	-2.8343	1.76	63.33	35.9	-2.83425
			303.15 K			
THF	8.24	-2.9343	1.86	65.33	36.9	-2.93425
			308.15 K			
THF	8.34	-2.9353	1.96	66.33	38.9	-2.83425

Table 8. Salt concentration at the minimum conductivity (c_{min}), the ion pair fraction (α), triple ion fraction (α_{T}), ion pair concentration (c_{P}) and triple-ion concentration (c_{T}) for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in THF at 298.15 K, 303.15 K and 308.15 K respectively.

Solvents	$c_{\text{min}}\cdot10^{4}$/ mol·dm^{-3}	$\alpha\cdot10^{-5}$	$\alpha_{\text{T}}\cdot10^{3}$	$c_{\text{P}}\cdot10^{-4}$/ mol·dm^{-3}	$c_{\text{T}}\cdot10^{-6}$/ mol ·dm^{-3}
298.15 K					
THF	8.14	6.61	4.82	9.01	4.2
303.15 K					
THF	8.24	6.71	4.92	9.11	4.4
308.15 K					
THF	8.34	6.83	4.87	9.35	4.6

Table 9. Concentration, c, density, ρ, apparent molar volume, ϕ_V, limiting apparent molar volume ϕ_{V}^{0} and experimental slope for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in Methyl Cellosolve, Dimethyl Acetamide and Tetrahydrofuran at 298.15 K, 303.15 K and 308.15 K respectively.

Solvents	c/ mol·dm^{-3}	$\rho\cdot10^{-3}$/ kg m^{-3}	$\phi_{\text{V}}\cdot10^{6}$/ m^{3}·mol^{-1}	$\phi_{\text{V}}^{0}\cdot10^{6}$/ m^{3}·mol^{-1}	$S_{\text{V}}^{*}\cdot10^{6}$/ m^{3} · mol$^{-3/2}$ ·dm$^{3/2}$
298.15 K					
Methyl Cellosolve				67.38	-98.01
	0.010	0.99849	440.58		
	0.025	1.00000	438.58		
	0.040	1.00155	437.15		
	0.055	1.00312	436.17		
	0.070	1.00472	435.19		

	0.085	1.00634	434.32		
Dimethyl acetamamide				55.70	-91.58
	0.010	0.87629	449.65		
	0.025	0.87854	444.51		
	0.040	0.88086	441.49		
	0.055	0.88324	438.91		
	0.070	0.88566	436.82		
	0.085	0.88814	434.66		
Tetrahydrofuran	0.010	1.16303	219.191	35.31	-78.46
	0.025	1.16328	216.48		
	0.040	1.16369	214.67		
	0.055	1.16421	213.24		
	0.070	1.16484	212		
	0.085	1.16550	210.9		
303.15 K					
Methyl Cellosolve				70.14	-128.31
	0.010	0.99849	440.58		
	0.025	1.00000	438.58		
	0.040	1.00155	437.15		
	0.055	1.00312	436.17		
	0.070	1.00472	435.19		
	0.085	1.00634	434.32		
Dimethyl acetamamide				62.02	-122.04
	0.010	0.87629	449.65		
	0.025	0.87854	444.51		
	0.040	0.88086	441.49		
	0.055	0.88324	438.91		
	0.070	0.88566	436.82		
	0.085	0.88814	434.66		
Tetrahydrofuran	0.010	1.16303	457.18	40.20	-86.78
	0.025	1.16328	450.30		
	0.040	1.16369	445.39		
	0.055	1.16421	441.53		
	0.070	1.16484	438.00		
308.15 K					
Methyl Cellosolve				73.03	-158.57
	0.010	0.99849	440.58		

	0.025	1.00000	438.58		
	0.040	1.00155	437.15		
	0.055	1.00312	436.17		
	0.070	1.00472	435.19		
	0.085	1.00634	434.32		
Dimethyl acetamamide				69.07	-151.78
	0.010	0.87629	449.65		
	0.025	0.87854	444.51		
	0.040	0.88086	441.49		
	0.055	0.88324	438.91		
	0.070	0.88566	436.82		
	0.085	0.88814	434.66		
Tetrahydrofuran	0.010	1.16303	457.18	47.92	-108.51
	0.025	1.16328	450.30		
	0.040	1.16369	445.39		
	0.055	1.16421	441.53		
	0.070	1.16484	438.00		

Table 10. Values of empirical coefficients (a_0, a_1, and a_2) of Equation 4 for IL in different solvents (MC, DMA, THF) at 298.15K to 308.15K respectively

solvent mixture	$a_0 \cdot 10^6$ /$m^3 \cdot mol^{-1}$	$a_1 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-1}$	$a_2 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-2}$
THF+IL			
298.15	4859.46	-33.050	0.0566
303.15	4859.46	-33.050	0.0566
308.15	4859.46	-33.050	0.0566
DMA+IL			
298.15	998	-7.515	0.0146
303.15	998	-7.515	0.0146
308.15	998	-7.515	0.0146

MC+IL			
298.15	137.80	-1.011	0.0026
303.15	137.80	-1.011	0.0026
308.15	137.80	-1.011	0.0026

Table 11. Limiting apparent molal expansibilities (ϕ_E^0) for IL in different solvents (THF, DMA, THF) at 298.15K to 308.15K respectively

solvent mixture	$\phi_E^0 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-1}$			$\left(\partial\phi_E^0/\partial T\right)_P \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-2}$
THF+IL				
T/K	298.15	303.15	308.15	
	0.701	1.267	1.833	0.113
DMA+IL				
T/K	298.15	303.15	308.15	
	1.191	1.337	1.483	0.269
MC+IL				
T/K	298.15	303.15	308.15	
	0.539	0.565	0.591	0.309

Table 12. Concentration, *c*, viscosity, *η*, $\frac{(\eta_r - 1)}{\sqrt{c}}$**,** viscosity *A* and *B* coefficients for 1-butyl-2,3-dimethylimidazoliun tetrafluoroborate in Methyl Cellosolve, Dimethyl Formamide and Tetrahydrofuran at 298.15 K, 303.15 K and 308.15 K respectively.

Salts	c /mol·dm^{-3}	η/mPa · s	$\frac{(\eta_r - 1)}{\sqrt{c}}$	*B* /dm^{3} · mol^{-1}	*A* /dm$^{3/2}$ · mol$^{-1/2}$
298.15 K					
Methyl Cellosolve	0.010	1.57	0.186	2.2891	0.1701
	0.025	1.62	0.323		
	0.040	1.65	0.352		
	0.055	1.69	0.411		
	0.070	1.73	0.462		
	0.085	1.78	0.531		
Dimethyl acetamamide	0.010	0.91	0.225	2.1324	0.1528
	0.025	0.93	0.284		
	0.040	0.95	0.337		
	0.055	0.97	0.383		
	0.070	0.99	0.425		
	0.085	1.02	0.501		
Tetrahydrofuran	0.005	0.48	0.324	1.9876	0.1448
	0.020	0.50	0.505		
	0.035	0.51	0.508		
	0.050	0.53	0.617		
	0.065	0.55	0.686		
	0.080	0.56	0.711		

303.15 K					
Methyl Cellosolve				2.3535	0.2086
	0.010	1.53	0.052		
	0.025	1.55	0.116		
	0.040	1.57	0.157		
	0.055	1.59	0.190		
	0.070	1.61	0.218		
	0.085	1.66	0.311		
Dimethyl acetamamide				2.2154	0.1954
	0.010	0.89	0.218		
	0.025	0.91	0.283		
	0.040	0.92	0.281		
	0.055	0.94	0.338		
	0.070	0.95	0.343		
	0.085	0.98	0.429		
Tetrahydrofuran	0.010	0.40	0.394	2.0734	0.1831
	0.025	0.41	0.498		
	0.040	0.43	0.617		
	0.055	0.44	0.649		
	0.070	0.46	0.744		
	0.085	0.47	0.783		

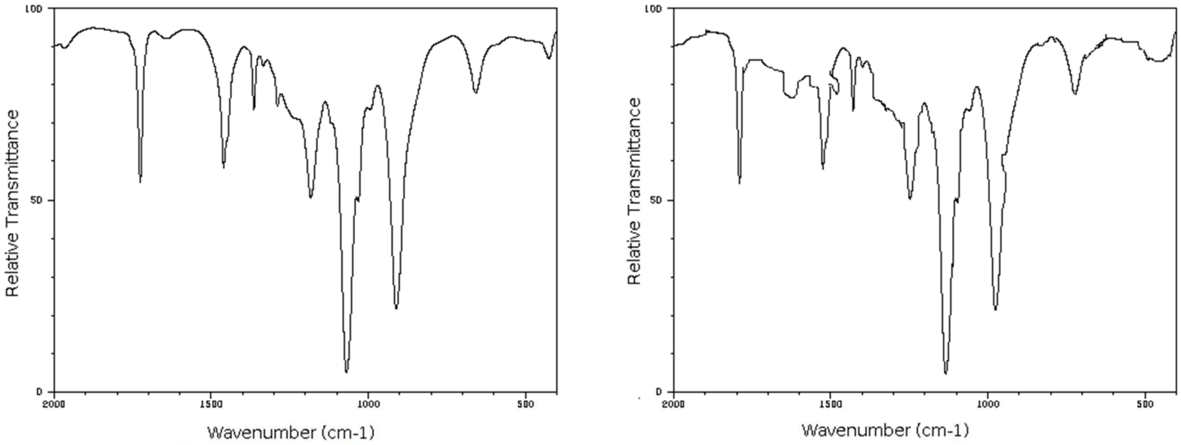
308.15 K					
Methyl Cellosolve				2.4329	0.2313
	0.010	1.52	0.073		
	0.025	1.55	0.172		
	0.040	1.58	0.235		
	0.055	1.63	0.342		
	0.070	1.67	0.403		
	0.085	1.73	0.502		
Dimethyl acetamamide				2.3015	0.2214
	0.010	0.75	0.331		
	0.025	0.76	0.296		
	0.040	0.78	0.372		
	0.055	0.80	0.440		
	0.070	0.82	0.489		
	0.085	0.83	0.491		

Tetrahydrofuran	0.010	0.38	0.298	2.2007	0.2119
	0.025	0.40	0.548		
	0.040	0.41	0.556		
	0.055	0.42	0.589		
	0.070	0.44	0.727		
	0.085	0.45	0.753		

Table 13. Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of 0.05(M) concentration of [bmmim][BF_4] in THF, DMA and MC.

	Stretching frequencies(cm^{-1})	
Solvents	Pure Solvent	Solvent + [bmmim][BF_4]
THF	C-O (1084)	C-O (1098.2)
DMA	C=O (1670)	C=O (1695.4)
MC	C-O (1060)	C-O (1071.5)

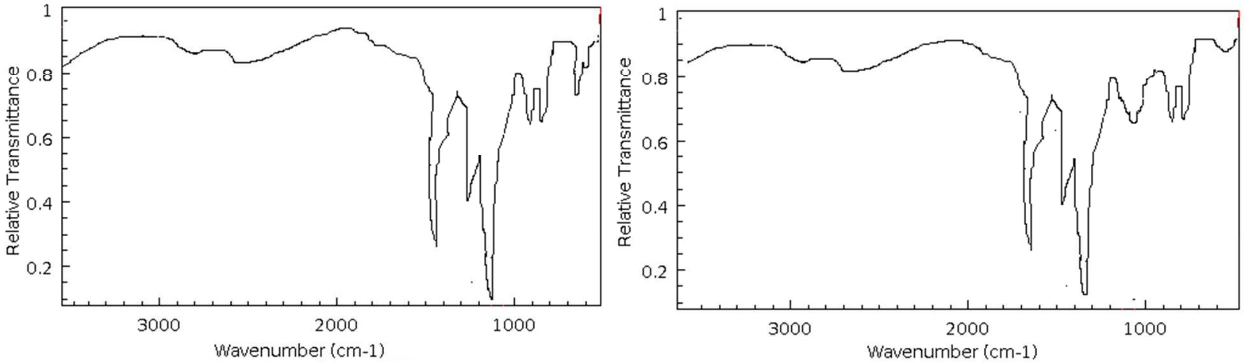
Figures:



IR spectra of pure THF

IR spectra of THF+IL

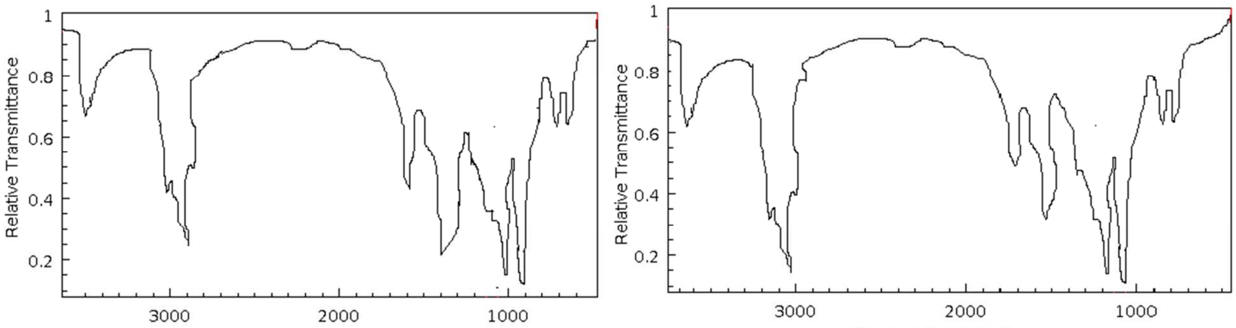
Figure 1: IR spectra of pure THF and its binary mixture with ionic liquid.



IR spectra of pure DMA

IR spectra of DMA+IL

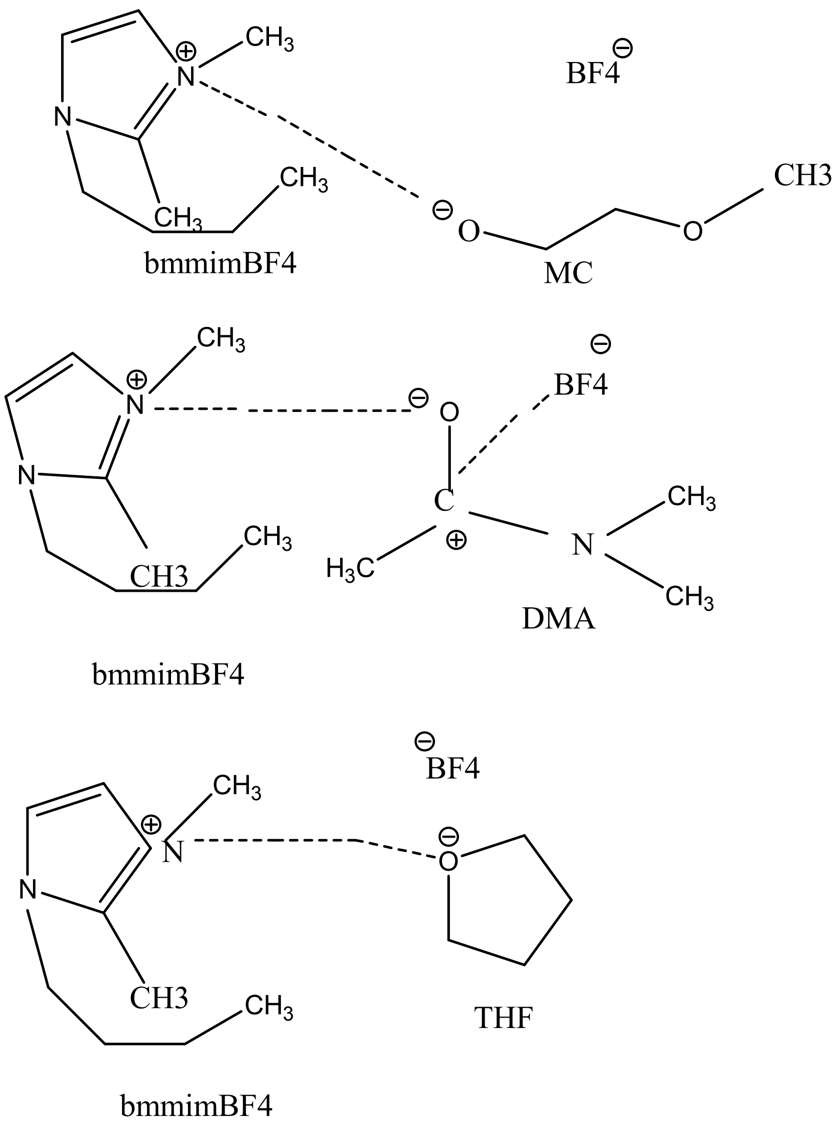
Figure 2: IR spectra of pure DMA and its binary mixture with ionic liquid.



IR spectra of pure Methyl Cellosolve

IR spectra of Methyl Cellosolve+IL

Figure 3: IR spectra of pure Methyl Cellosolve and its binary mixture with ionic liquid.



Scheme 1: Solvation Consequence between ionic liquid and diverse solvents