

## CHAPTER IX

### **ROLE OF ANIONS (TETRAFLUOROBORATE, PERCHLORATE) OF TETRABUTYLAMMONIUM SALTS IN DETERMINING SOLVATION EFFECTS PREVAILING IN INDUSTRIALLY ESSENTIAL SOLVENTS PROBED BY CONDUCTANCE AND FT-IR SPECTRA**

#### **9.1. INTRODUCTION**

Studies of the transport properties of electrolytes in different solvent media are very useful to gain information on the behavior of ions in solution. In the modern technology, the study of ion solvation is very helpful in knowing any salt's application. Therefore, a number of conductometric [1] and related studies of electrolytes in nonaqueous common solvents have been done for their optimal use in high-energy batteries [2] and understanding organic reaction mechanisms [3]. The nature of the solvent/solvent mixtures plays an important role in the mode of solvation of the electrolyte in solution, which in turn dictates its ionic association. Solvent properties such as viscosity and the relative permittivity have been taken into consideration in order to determine the extent of ion association and the ion-solvent interactions. Technologist and theoretician find the nonaqueous solution systems [4] very useful, as many chemical processes occur in these systems, whose nature and magnitude of ion-ion and ion-solvent interactions can be examined.

The excellent solubility characteristic of tetraalkylammonium salts in aqueous as well as non-aqueous solvents makes it very suitable. These salts find its application in trace analysis (of metals and organic compounds), environmental analytical chemistry, pharmaceutical and medicinal chemistry. Both the thermodynamics and kinetics of reactions carried out in electrolytes are different from those in conventional molecular solvents, which make it very interesting for the chemist. The usage of aqueous solutions of symmetrical tetraalkylammonium ions, particularly those with large alkyl groups, has played a significant role in revealing hydrophobic interaction and hydration behavior through various experimental approaches, because of the high solubility of the salts and the simple geometrical structures [5]. Another benefit for their use is the possibility of systematically changing the ionic

size by the proper choice of an alkyl group without a nonuniform charge in the distribution on the ionic surface.

Keeping in mind the use of electrolytes in battery industries we have here studied the thermodynamic and the transport properties of electrolytes in industrially important solvents, which will provide significant information about the nature and strength of intermolecular forces operating between components of mixture. As Fourier transform infrared (FT-IR) measurements is one of the most convenient methods for investigating the molecular interactions in electrolytic solutions, so it has also been done [6-8].

In continuation with our investigation on understanding the behaviour of electrolytes in organic solvents by physicochemical techniques, we have studied the conductance and FT-IR measurements of tetrabutylammonium tetrafluoroborate  $[\text{Bu}_4\text{NBF}_4]$  and tetrabutylammonium perchlorate  $[\text{Bu}_4\text{NClO}_4]$  in nitromethane (NM), N-methylformamide (NMF), and formamide (FA) at 298.15 K.

## 9.2. EXPERIMENTAL SECTION

### 9.2.1. Source and purity of samples

Tetrabutylammonium tetrafluoroborate  $[\text{Bu}_4\text{NBF}_4]$  and Tetrabutylammonium perchlorate  $[\text{Bu}_4\text{NClO}_4]$  of puriss grade were obtained from Aldrich, Germany and was used as purchased. The mass fraction purity for  $[\text{Bu}_4\text{NBF}_4]$  was 0.99 and for  $[\text{Bu}_4\text{NClO}_4]$  was  $\geq 0.98$ .

All the solvents of spectroscopic grade were procured from Thomas Baker, India, and were rid of impurities using standard methods [9]. The mass fraction of purity found was  $\geq 0.99$ .

### 9.2.2. Apparatus and Procedure

Stock solutions for the two electrolytes in three different solvents were made by mass (Mettler Toledo AG285 with uncertainty  $\pm 0.0003$  g), and mass dilution was employed to obtain the working solutions at 298.15 K. The uncertainty of molality of different solutions was estimated to  $\pm 0.0001$  mol.kg<sup>-1</sup>. The density ( $\rho$ ) was determined using vibrating-tube Anton Paar density-meter (DMA 4500M) with an accuracy of  $\pm 0.00005$  g.cm<sup>3</sup>. The calibration was carrying out by triply-distilled water and passing dry air.

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500. The viscosities were determined using the following equation:

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

where RPM, TK (0.09373) and SMC (0.327) indicates the speed, viscometer torque constant, and spindle multiplier constant, respectively. The calibration of instrument was done using the standard viscosity samples supplied with the instrument, water, and aqueous CaCl<sub>2</sub> solution [10]. Temperature of the solution was kept within  $\pm 0.01$  °C with the help of Brookfield Digital TC-500 temperature thermostat bath. The viscosities were calculated with an accuracy of  $\pm 1$  %. Each measurement given here is an average of triplicate reading with a precision of 0.3 %.

All the conductance measurements were carried out in a Systronic-308 conductivity bridge (accuracy  $\pm 0.01$ ) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately  $(0.1 \pm 0.001)$  cm<sup>-1</sup>. A water bath maintained within  $T = (298.15 \pm 0.01)$  K was used, and the method proposed by Lind et al. [11] was used to calibrate the cell and cell constant was calculated based on 0.01 M aqueous KCl solution. The conductance data was obtained at a frequency of 1 kHz. Throughout each and every one measurement, uncertainty of temperatures was  $\pm 0.01$  K.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described [8].

### 9.3. RESULTS AND DISCUSSION

#### 9.3.1. *Electrical Conductance*

The selected electrolytes were freely soluble in all proportion of the solvents. The experimental values of physical properties of the pure solvents obtained were almost same as the values found in the literature, given in Table 1.

The molar conductances ( $\Lambda$ ) for all studied solution systems have been calculated with the help of the following equation [12]:

$$\Lambda = 1000 \kappa / c \quad (1)$$

where  $c$  and  $\kappa$  denote the molar concentration and specific conductance of the studied solutions respectively. The molar conductances ( $\Lambda$ ) of the solutions of studied electrolytes with the corresponding molar concentrations ( $c$ ) in different solvents (nitromethane, N-methylformamide, and formamide) are represented in Table 2. Linear conductance curves ( $\Lambda$  versus  $\sqrt{c}$ ) were obtained, and with the extrapolation of  $\sqrt{c} = 0$ , the starting limiting molar conductances for the electrolytes were evaluated. Fuoss conductance equation [13, 14] was used to analyze the ion-pair formation from conductance data.

The following set of equations were used to derive the three adjustable parameters, namely, the limiting molar conductance ( $\Lambda_0$ ), the association constant ( $K_A$ ), and the distance of closest approach of ions ( $R$ ) from a given set of conductivity values ( $c_j, \Lambda_j; j = 1 \dots n$ )

$$\Lambda = P\Lambda_0[(1+R_x)+E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

Where  $R_x$  denotes the relaxation field effect,  $E_L$  denotes the electrophoretic counter current,  $k$  is the radius of an ionic atmosphere, and  $e$  is the electron charge,  $\epsilon$  is the relative permittivity of the solvent mixture,  $c$  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 analyzed by Fuoss program. The initial  $\Lambda_0$  values for the iteration procedure are obtained from the Shedlovsky extrapolation of the data. Input for the program is the no. of data,  $n$ , followed by  $\epsilon, \eta, T$ , initial values of  $\Lambda_0$ , along with  $c_j, \Lambda_j$  values, where  $j = 1, 2, \dots, n$  and an instruction to cover a pre-selected range of  $R$  values.

The computations along with calculations have been determined supplemented with the values of  $\Lambda_0$  and  $\alpha$  which minimization the standard deviation,  $\delta$ , whereby

$$\delta^2 = \sum [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n - m) \quad (8)$$

where  $n$  is the number of experimental points and  $m$  is the number of fitting parameters. The conductance data have been explained and discussed by fixing the distance of closest approach  $R$  with two parameter fit ( $m = 2$ ). From a graphical representation of  $\delta$  against  $R$  the minimum of the  $\delta$ - $R$  versus  $R$  curve predicts the best-fit  $R$ . Through the iteration and running of the computer program with small

increments of the data of the studied electrolytes in nitromethane, N-methylformamide and formamide, the  $R$  values assumed to be as follows:

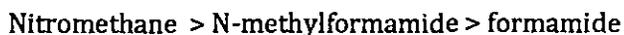
$$R = a + d \quad (9)$$

Where  $a = (r_+ + r_-)$  represents the sum of the crystallographic radii of the ions and the average distance corresponding to the side of a cell occupied by a solvent molecule is denoted by  $d$ . The distance,  $d$  is given by [15]

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (10)$$

where  $M$  and  $\rho$  are molar mass and density of the solvents, respectively. The values of  $\Lambda_0$ ,  $K_A$  and  $R$  obtained by this procedure are given in Table 3 along with  $\delta$  for the all the solutions.

Inspection of Table 3 and Figure 1 shows that the limiting molar conductance ( $\Lambda_0$ ) of the electrolytes among the studied solvents is highest in the case of nitromethane (NM) and lowest in case of formamide (FA). The trend of the  $\Lambda_0$  value of the electrolytes in the studied solvents is as follows:



This illustrates that the electrolytes are solvated more by formamide, due to its highest viscosity value among the studied solvents. It is also seen that with an increase in the size of the anion, the extent of solvation also increase.

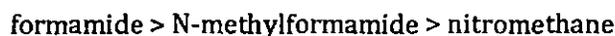
Table 3 and Figure 4 also show that the association constant ( $K_A$ ) of the electrolytes is greater in FA than in NMF and NM. Hence, the ion-solvent interaction is greater in FA than in NMF and NM, which results in lower conductance of the electrolytes in the former than in the latter two. The above observation is also supported by the higher viscosity of FA because with the increase in viscosity the  $\Lambda_0$  value decreases. The maximum ion-solvent interaction leading to very high solvation is observed in the case of  $[\text{Bu}_4\text{NBF}_4]$  and FA, which is evident from the  $K_A$  values given in Table 3 and Figure 4. The weakest ion-solvent interaction is between  $[\text{Bu}_4\text{NClO}_4]$  and the lowest viscous solvent NM.

The observed order of  $\Lambda_0$  values can be confirmed through another characteristic function called the Walden product,  $\Lambda_0\eta$  (Product of the limiting molar conductance and solvent viscosity), given in Table 3. Figure 2 demonstrates that the increasing order of Walden product is mainly in agreement with the associated increase of solvent viscosity and decrease of limiting molar conductance for the electrolytes in the studied solvents. This same observation is also justified as the Walden product of an ion or solute is inversely proportional to the radius of the ion or solute in a particular solvent [16]

$$\Lambda_0\eta = \frac{1}{6\pi r_{eff} T} \quad (11)$$

This shows that the electrostatic ion-solvent interaction or ion-association is strong in these cases. The deviation of the Walden product reflects the change of solvation [17] though the deviation of the Walden product with solvent composition is difficult to understand quantitatively, but its deviation with solvent composition can still be explained by

- (i) Preferential solvation [18] of the electrolyte by solvent molecules. Considering the conductance and association constant values of electrolytes in different solvents, we can say that the studied electrolytes mostly prefer the formamide among the solvents and the order of preferential solvation by the electrolytes is as follows:



- (ii) With considering the structural aspect of the solvents,
- (a) In case of nitromethane, where the two electronegative oxygen atoms are present with nitrogen, resulting in more ion-solvent interaction, shown in (I). Thus in the solution of electrolytes and nitromethane, the nitromethane interact with the electrolytes through ion-dipole interaction. The interaction is between negatively charged O atom (single bonded with N) in NM with

positive species of electrolyte, positively charged N atom in NM and negative species of electrolyte, and between lone pair of electron of O atom (doubly bonded with N) in NM and positive species of electrolyte.

(b) From the structure of N-methylformamide, there are three possibilities of interaction of solvent with solute: ion-dipole interaction of lone pair(s) of electron present in O atom and N atom, and H-bonding with H atom attached with electronegative N atom shown in (II) of Scheme 1. Thus in the solution of electrolytes and N-methylformamide, the N-methylformamide strongly interact with the electrolytes with H-bond/ion-dipole interactions. The lone pairs of electron in electronegative carbonyl oxygen stabilizes the positive species of the electrolytes through ion-dipole interaction; the lone pair of electron in N also stabilizes the positive species of the electrolytes, whereas the H-atom attached to nitrogen forms hydrogen bonds with negative species of the electrolyte. As N-methylformamide is the derivative of formamide, where an H-atom attached to nitrogen in formamide is replaced by a methyl group, the hydrogen bonding ability of N-methylformamide is less than that of formamide.

(c) From the structure of formamide, there are three possibilities of interaction of solvent with solute: ion-dipole interaction of lone pair(s) of electron present in O atom and N atom, and H-bonding with H atom attached with electronegative N atom shown in (III) of Scheme 1. Thus in the solution of electrolytes and formamide, the formamide strongly interact with the electrolytes with H-bond/ion-dipole interactions. The lone pair of electron in electronegative carbonyl oxygen stabilizes the positive species of the electrolyte through ion-dipole interaction; the lone pair of electron in N also stabilizes the positive species of the electrolytes, whereas H-atom attached to nitrogen forms H bonds with negative species of the electrolyte. Also the respective average number of hydrogen-bonds was found to be higher in the

case of formamide as compared to N-methylformamide, as one H atom in formaldehyde is replaced by methyl group in N-methylformamide.

The values of conductance shows that the solution of electrolytes ([Bu<sub>4</sub>NBF<sub>4</sub>] and [Bu<sub>4</sub>NClO<sub>4</sub>]) in solvents is in the following order:

formamide (FA) < N-methylformamide (NMF) < nitromethane (NM)

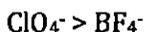
The electrolytic solution of nitromethane is more conducting than N-methylformamide, which in turn is greater than formamide. As we know, the greater the conductance, the lesser is the ion-solvent interaction in the solution. Therefore the interaction between the electrolytes and solvents will follow the reverse trend

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

This observation implies that the degree of interaction (ion-dipole) also obeys the above order. Therefore, formamide stabilizes the electrolytes ([Bu<sub>4</sub>NBF<sub>4</sub>] and [Bu<sub>4</sub>NClO<sub>4</sub>]) to a greater degree than N-methylformamide, which in turn that stabilizes same to a greater degree than nitromethane.

The schematic representation of plausible ion-solvent interaction, for the particular ion in the studied solvents (i.e; electrolytes in solvents), in view of various derived parameters is represented in Scheme 1.

Stokes' law is considered to be the starting point for most evaluations of ionic conductance, and it states that the limiting ionic Walden product ( $\lambda_0^{\pm}\eta$ ), (the product of the limiting ionic conductance and solvent viscosity) for any singly charged spherical ion is a function only of the ionic radius (crystallographic radius) and thus, under normal conditions, is a constant. The ionic conductances  $\lambda_0^{\pm}$  for the [Bu<sub>4</sub>N]<sup>+</sup> cation and BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> anion in different solvent arrangements, were computed as described in the literature values [19] The ionic limiting molar conductances  $\lambda_0^{\pm}$ , in investigated solvents were determined by interpolation of conductance data from the literature [20] using cubic spline fitting. A perusal of Table 4 and Figure 3 shows that the anion (BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) holds the greater share of the conductance value than the common cation [Bu<sub>4</sub>N]<sup>+</sup>. For a particular solvent, the order of limiting ionic conductance of anion is as follow:



The  $\lambda_o^\pm$  values were utilized for the calculation of Stokes' radii ( $r_s$ ) according to the classical expression.<sup>21</sup>

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^\pm r_c} \quad (12)$$

where,  $r_s$  and  $r_c$  are the Stokes' radii and crystallographic radii respectively,  $N_A$  is the Avogadro's no.,  $\lambda_o^\pm$  is the limiting ionic conductance and  $F$  is the Faraday Constant.

Ionic Walden products  $\lambda_o^\pm \eta$ , Stokes' radii  $r_s$ , and crystallographic radii  $r_c$  are represented in Table 4. The Walden products ( $\Lambda_o \eta$ ) and ionic Walden products ( $\lambda_o^\pm \eta$ ) for the electrolytes in different solvents are reported in Tables 3 and 4 and Figures 2 and 3, respectively, indicating that both the ionic Walden products  $\lambda_o^\pm \eta$  and Walden products  $\Lambda_o \eta$  for the electrolytes are higher in the case of FA than NMF and NM. For  $\text{Bu}_4\text{N}^+$ ,  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  ion, the Stokes' radii  $r_s$  are either lower or comparable to their crystallographic radii  $r_c$ ; this implies that the ion is relatively less solvated due to its intrinsic low surface charge density. The distance parameter  $R$ , is the least distance that two free ions can move towards together before they merge into an ion pair which was shown in Table 3.

The graphical representation of the 'Gibbs free energy' for ion-pair formation,  $\Delta G^\circ$ , categorically interprets the tendency for ion-pair formation where 'Gibbs free energy'  $\Delta G^\circ$ , is derived by analyzing the following equation [22] and given in Table 3.

$$\Delta G^\circ = -RT \ln K_A \quad (13)$$

The negative values of  $\Delta G^\circ$  can give explanation of considering the participation of specific covalent interaction in the ion-association process. It is evident from the Table 3 and Figure 4 that the values of the 'Gibbs free energy' are all negative entirely all over the solutions and the negativity increases from nitromethane to formamide. The negative value of  $\Delta G^\circ$  is highest for electrolytes in FA than NFM and NM, shows that the highest degree of association in FA. This result indicates that the extent of solvation is in the following order:

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

The same type of observation was established from the conductance data elaborated and explained earlier in this paper.

The significance of the term (*A*-coefficient) has since then been realized due to the development Debye-Hückel theory [23] of inter-ionic attractions in 1923. The *A*-coefficient depends on the ion-ion interactions and can be determined from interionic attraction theory and analyzed by the Falkenhagen and Vernon [24] equation:

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[ 1 - 0.6863 \left( \frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (13a)$$

where the symbols have their usual significance. *A*-coefficient should be calculated from conductivity measurements and given in the Table 3. Table 3 shows that *A*-coefficient is negative and very small, shows that the existence of the ion-ion interaction is negligible, as compared to the ion-solvent interaction for all the chosen electrolytes in the studied solvents.

Stokes-Einstein Relation was used to obtain the diffusion coefficient (*D*):

$$D = \frac{k_B T}{6\pi\eta_o r_s} \quad (14)$$

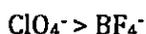
where  $k_B$  is the Boltzmann's constant, *T* is the temperature,  $\eta$  is the solvent viscosity and  $r_s$  denotes Stoke's radii.

The ionic mobility was obtained using the following equation:

$$i = \frac{z^+ F}{RT} D \quad (15)$$

where  $z_+$ , *F*, *R*, *T* and *D* is the ionic charge, Faraday constant, universal gas constant, temperature, and diffusion co-efficient respectively. Table 5 depicts that the contribution of diffusion coefficient of the anions ( $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) is greater than the cation  $[\text{Bu}_4\text{N}]^+$  in all the investigated solvents, which indicates that ( $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ )

diffuses greater in the solvents. The diffusion coefficient decrease from nitromethane to formamide as indicated in Table 5 for both  $[\text{Bu}_4\text{N}]^+$  and  $(\text{BF}_4^-, \text{ClO}_4^-)$  ions showing larger diffusion of the ions in nitromethane. Table 5 also illustrates that the mobility of anions  $(\text{BF}_4^-, \text{ClO}_4^-)$  are higher than that of cation  $[\text{Bu}_4\text{N}]^+$  in all the studied solvents, which indicates that greater share of conductance by  $(\text{BF}_4^-, \text{ClO}_4^-)$  mentioned earlier i.e; the diffusion coefficient is directly proportional to the ionic mobility, and these are the driving force to conduct electricity by electrolyte or ions in solutions. The trend of the anions is enhanced by the following order, which was derived from the same observation.



This is because of the increase in solvent's viscosity and the increase in the ion-solvent interaction or ion-solvation, which is evident from the association constant values, given in Table 3. A graphical comparison of diffusion coefficient ( $D_{\pm}$ ) and ionic mobility ( $i_{\pm}$ ), for anions  $(\text{BF}_4^-$  and  $\text{ClO}_4^-)$  is given in Figure 5.

### 9.3.2. FT-IR Spectroscopic Study

FT-IR spectroscopy was used to present the molecular interaction existing between the electrolytes and the solvents qualitatively and also used as supportive evidence to study the bond formation due to the ion-solvent and solvent-solvent interactions. The IR spectra of the pure solvents as well as the solutions of  $\{[\text{Bu}_4\text{N}][\text{Y}]$  and Solvents $\}$  have been studied, and the stretching frequencies of the functional groups and mixed with electrolytes are given in Table 6 and Figure 6-8 within the range of wavenumber  $400\text{-}4000\text{ cm}^{-1}$ .

Table 6 shows that presence of strong bands at  $1564.8\text{ cm}^{-1}$  and  $1363.3\text{ cm}^{-1}$  attributed to asymmetric stretching vibration ( $\nu_{as}$ ) of N-O ( $1500\text{-}1570\text{ cm}^{-1}$ ), and symmetric stretching vibration ( $\nu_s$ ) of N-O ( $1300\text{-}1370\text{ cm}^{-1}$ ), respectively, in nitromethane. When the IR spectra of  $\{[\text{Bu}_4\text{N}][\text{Y}]$  and nitromethane $\}$  solution was taken, the asymmetric stretching vibration ( $\nu_{as}$ ) of N-O got shifted to  $1601.7\text{ cm}^{-1}$  and  $1614.7\text{ cm}^{-1}$  for the electrolytes  $[\text{Bu}_4\text{NClO}_4]$  and  $[\text{Bu}_4\text{NBF}_4]$  respectively. The

symmetric stretching vibration ( $\nu_s$ ) got shifted to  $1388.8\text{ cm}^{-1}$  and  $1402.3\text{ cm}^{-1}$  for the electrolytes  $[\text{Bu}_4\text{NClO}_4]$  and  $[\text{Bu}_4\text{NBF}_4]$ , respectively. The shift resulted due to the strengthening of N-O bond [25] because of the reduction in the resonance effect in NM. The reduction in resonance is due to the presence of ionic interaction between negatively charged oxygen atom of NM and positive part of  $\{[\text{Bu}_4\text{N}][\text{Y}]\}$ . Because of the reduction in the resonance effect, the negative charge in oxygen atom gets somewhat localized, therefore, the other oxygen atom has more double bond characteristic with nitrogen atom than in the NM in idle case. Therefore, due to the increase in double bond characteristic in N-O bond, the IR spectra of N-O got shifted to increased wavenumber.

In case of N-methylformamide, the IR spectra shows a sharp peak at  $1679.8\text{ cm}^{-1}$  for C=O stretching vibration. The peak got shifted to  $1721.9\text{ cm}^{-1}$  and  $1734.5\text{ cm}^{-1}$  in the solution of N-methylformamide with  $[\text{Bu}_4\text{NClO}_4]$  and  $[\text{Bu}_4\text{NBF}_4]$  respectively, due to the reduction in resonance effect in N- methylformamide, which results in strengthening of C=O bond. As the lone pair of electron-present N atom of N-methylformamide is involved in ion-dipole interaction with the positive part of  $\{[\text{Bu}_4\text{N}][\text{Y}]\}$ , the delocalization of electron pair from N atom to O atom is reduced; thus the double bond characteristic of C=O bond is somewhat increased. This results in the shift of IR spectra of C=O bond in N- methylformamide to higher wavenumber, when  $\{[\text{Bu}_4\text{N}][\text{Y}]\}$  is added to it.

Greatest interaction is seen between  $[\text{Bu}_4\text{N}][\text{Y}]$  ( $\text{Y} = \text{BF}_4^-$  and  $\text{ClO}_4^-$ ) and formamide, as obvious from the values of the  $K_A$  obtained from the conductivity study as described earlier. The IR spectra of formamide shows a sharp peak at  $1692.9\text{ cm}^{-1}$  for C=O stretching vibration. When the IR spectra of  $[\text{Bu}_4\text{NY}]$  and formamide solution were taken, the peak moved to  $1740.6\text{ cm}^{-1}$  ( $\nu_1$ ) and  $1754.1\text{ cm}^{-1}$  ( $\nu_2$ ) for  $[\text{Bu}_4\text{NClO}_4]$  and  $[\text{Bu}_4\text{NBF}_4]$  respectively showing the presence of ion-dipole interaction. The shift is the result of the strengthening of C=O in formamide<sup>26</sup> due to reduction in the resonance effect in it. The reason for reduction in resonance effect in formamide is same as that in the case of N-methylformamide. The greater

reduction in resonance effect in formamide than that of N-methylformamide is because of the presence of H atom in place of methyl group. The ion-dipole interaction between the lone pair of electron-present N atom and the positive part of  $\{[Bu_4N][Y]\}$  is somewhat hindered because of the presence of methyl group in N-methylformamide, but this hindrance is not present in the case of formamide because of the absence of methyl group. Therefore, because of the greater reduction in resonance effect, the ion-dipole interaction is more in the case of formamide than that of N-methylformamide. Thus, the shift in IR spectra of C=O bond in formamide is greater than N- methylformamide.

From Table 6 we can see that shift in IR vibration data of C-H bond in nitromethane; and N-H and C-N bond in N-methylformamide and formamide is negligible when the electrolytes are added to it.

The shift in IR vibration is caused due to the weakening of solvent-solvent interaction. Therefore, more the shift toward higher frequency, better the interaction. The order of magnitude of shift in case of both  $[Bu_4NBF_4]$  and  $[Bu_4NClO_4]$  is in the following order

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

This implies that the degree of interaction (ion-dipole) also obeys the same order. Therefore formamide stabilizes the electrolytes (ion-solvent association) to a greater extent than N-methylformamide, which in turn stabilizes the same greater than nitromethane.

#### 9.4. CONCLUSION

Precise electrical conductivity study of  $[Bu_4NBF_4]$  and  $[Bu_4NClO_4]$  in nitromethane, N-methylformamide, and formamide confirms that the conductance for the electrolytes is highest in the case of nitromethane and lowest in the case of formamide. Among the two electrolytes,  $[Bu_4NBF_4]$  is associated most with the studied solvents, and the highest association is seen between  $[Bu_4NBF_4]$  and

formamide. The greater share of the conductance holds the  $[Y]^-$  ion than the  $[Bu_4N]^+$  as clear from their ionic conductance values. In all of the investigated solvents, the electrolytes shows ion-dipole interactions observed from the FT- IR and conductance studies. The derived parameters obtained by analyzing various equations supplemented with experimental data predict the same conclusion as discussed and described in this manuscript, demanding the individuality of the work.

## REFERENCES

- [1].G.J. Janz, R.P.T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 1 Academic Press: New York, (1972).
- [2].D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, (1999).
- [3].J. A. Krom, J. T. Petty, A. J. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [4].O. Popvyeh, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Chapter 4, Wiley-Interscience: New York, (1981).
- [5].W.Y. Wen, *Water and Aqueous Solutions. Structure, Thermodynamics, and Transport Process*, R. A. Horne, ed. Chapter 15, Wiley-Interscience: New York, (1971).
- [6].R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation, Part B, Spectroscopy Solvation*, Elsevier: Amsterdam, (1986).
- [7].A. Sinha, G. Ghosh, M. N. Roy, *J. Phys. Chem. Liq.* 48 (2010) 62.
- [8].A. Sinha, A. Bhattacharjee, M. N. Roy, *J. Disp. Sc. and Techn.* 30 (2009) 1003.
- [9].D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press: Oxford, (1988).
- [10]. I. M. Abdulagatov, N. D. Azizov, *Fluid Phase Equilibria.* 240 (2006) 204.
- [11]. J. E. Lind Jr, J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [12]. F. I. El-Dossoki, *J. Mol. Liquids.* 151 (2010) 1.
- [13]. R. M. Fuoss, *Proc. Natl. Acad. Sci., U.S.A.* 75 (1978) 16,
- [14]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [15]. R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience: New York, (1959).
- [16]. J. I. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [17]. C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press: New York, (1973).

- [18]. R. Yamdagni, P. Kebarle, *J. Am. Chem. Soc.* 94(9) (1972) 2940.
- [19]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [20]. R. M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1013.
- [21]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Chapter 6, p 130, Butterworth: London, (1959).
- [22]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [23]. P. Debye, E. Hückel, *Phys. Z.* 24 (1923) 185.
- [24]. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* 14 (1932) 537.
- [25]. J. Li, F. Zhao, F. Jing, *J. Comp. Chem.* 24 (2003) 345.
- [26]. P. G. Jasien, W. J. Stevens, *J. Chem. Phys.* 84 (1986) 3271.
- [27]. M. N. Roy, D. Ekka, R. Dewan, *Fluid Phase Equilibria.* 314 (2012) 113.
- [28]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum: New York, (1973).
- [29]. W. Libus, B. Chachulski, L. Fraczyk, *J. Sol. Chem.* 9 (5) (1980) 355.
- [30]. O. N. Kalugin, S.M. Gubsky, I.N. Vyunnik, *J. Chem. Soc. Faraday Trans.* 87 (1991) 63.

## TABLES

**Table 1. Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Relative Permittivity ( $\epsilon_r$ ) of Studied Pure Solvents at  $T = 298.15$  K and  $P = 0.1$  MPa<sup>a</sup>**

solvents	$\rho^b \cdot 10^{-3} (\text{kg} \cdot \text{m}^{-3})$		$\eta^c (\text{mPa} \cdot \text{s})$		$\epsilon_r$
	expt	lit	expt	lit	
nitromethane	1.13015	1.13015 [27]	0.62	0.614 [27]	35.87 [27]
N-methylformamide	0.99761	0.99760 [28]	1.65	1.650 [28]	182.40 [28]
formamide	1.12922	1.12920 [28]	3.30	3.302 [28]	109.50 [28]

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.01$  K,  $u(P) = 0.1$  MPa, <sup>b</sup>  $u(\rho) = 0.00005$  g  $\cdot$  cm<sup>-3</sup>,  
<sup>c</sup>  $u(\eta) = 0.03$  mPa.s

**Table 2. Molar Conductance ( $\Lambda$ ) and the Corresponding Concentration ( $c$ ) of the Studied Electrolytes in Different Solvents at  $T = 298.15$  K and  $T = 0.1$  MPa<sup>a</sup>**

$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
<b>[Bu<sub>4</sub>NBF<sub>4</sub>] in Nitromethane</b>		<b>[Bu<sub>4</sub>NBF<sub>4</sub>] in N-Methylformamide</b>		<b>[Bu<sub>4</sub>NBF<sub>4</sub>] in Formamide</b>	
7.73	83.32	7.95	35.23	8.29	21.50
13.03	79.43	15.13	33.07	14.52	20.30
17.31	76.51	20.25	31.43	20.25	19.20
23.72	73.50	27.35	29.93	26.32	18.30
29.27	70.93	32.95	28.64	31.81	17.50
35.76	68.40	39.56	27.52	37.82	16.70
41.34	65.96	48.02	26.15	45.70	15.80
49.14	63.97	53.88	25.28	52.91	15.02
56.55	61.75	60.53	23.97	61.31	14.30
65.77	59.35	73.27	22.34	70.56	13.44
75.69	56.84	78.32	21.59	79.21	12.49
85.56	54.33	87.98	20.45	84.82	11.90
<b>[Bu<sub>4</sub>NClO<sub>4</sub>] in Nitromethane</b>		<b>[Bu<sub>4</sub>NClO<sub>4</sub>] in N-Methylformamide</b>		<b>[Bu<sub>4</sub>NClO<sub>4</sub>] in Formamide</b>	

8.64	100.53	7.95	44.93	8.07	31.23
13.47	98.03	15.13	42.34	14.98	29.01
18.06	95.45	20.25	40.73	20.61	27.83
24.30	92.71	27.35	38.88	26.73	26.43
29.92	89.94	32.95	37.14	32.38	25.54
35.28	87.93	39.56	35.77	38.56	24.44
41.86	85.42	48.02	34.24	46.65	23.12
49.98	83.08	53.88	33.34	52.42	22.39
57.15	80.89	60.53	32.27	62.09	21.17
66.42	77.67	68.23	30.86	71.57	20.24
76.39	75.26	78.32	29.26	80.10	19.59
86.68	73.06	87.98	27.94	86.12	18.95

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.01$  K,  $u(P) = 0.1$  MPa, <sup>d</sup>  $u(m) = 0.0001$  mol.kg<sup>-1</sup>. <sup>e</sup> The relative standard uncertainty  $u_r$  is  $u_r(A) = 0.01$ .

**Table 3. Limiting Molar Conductivity ( $\Lambda_0$ ), the Association Constant ( $K_A$ ), the Distance of Closest Approach of Ions ( $R$ ), Standard Deviations  $\delta$  of Experimental  $\Lambda$  from Eq 1, Walden Product ( $\Lambda_0\eta$ ), Gibb's energy change ( $\Delta G^\circ$ ) and  $A$ -coefficient of Electrolytes in Different Studied Solvents at  $T = 298.15$  K**

Solvents	$\Lambda_0 \cdot 10^4$ ( $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ )	$K_A$ ( $\text{dm}^3 \cdot \text{mol}^{-1}$ )	$R$ ( $\text{\AA}$ )	$\delta$	$\Lambda_0\eta \cdot 10^4$ ( $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$ )	$\text{Log}(K_A)$	$\Delta G^\circ$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$A \cdot 10^4$ ( $\text{mPa} \cdot \text{K}^{1/2} \cdot \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ )
[Bu <sub>4</sub> NBF <sub>4</sub> ]								
NM	94.60±0.12	182.09±0.01	12.69	0.58	58.08	2.26	-1.29	-3.93
NMF	41.04±0.14	203.76±0.01	12.83	0.57	67.72	2.31	-1.32	-1.72
FA	26.18±0.06	265.96±0.01	12.26	0.47	86.44	2.42	-1.38	-2.17
[Bu <sub>4</sub> NClO <sub>4</sub> ]								
NM	111.42±0.07	114.15±0.02	12.31	0.67	68.41	2.06	-1.17	-3.75
NMF	50.55±0.04	154.56±0.01	12.45	0.45	83.41	2.19	-1.25	-0.73
FA	35.94±0.08	195.88±0.01	11.88	0.27	118.67	2.29	-1.31	-1.20

**Table 4. Limiting Ionic Conductance ( $\lambda_o^\pm$ ), Ionic Walden Product ( $\lambda_o^\pm\eta$ ), Stokes' Radii ( $r_s$ ) and Crystallographic Radii ( $r_c$ ) of Ammonium Based Electrolytes in Different Studied Solvents at  $T = 298.15$  K**

solvents	$\lambda_o^\pm \cdot 10^4$ (S .m <sup>2</sup> .mol <sup>-1</sup> )		$\lambda_o^\pm\eta \cdot 10^4$ (S .m <sup>2</sup> .mol <sup>-1</sup> mPa. s)		$r_s$ (Å)		$r_c$ (Å)	
	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>
NM	34.07	60.53	20.92	37.17	3.92	2.20	4.94	2.78
NMF	14.78	26.26	24.38	43.33	3.36	1.89	4.94	2.78
FA	9.43	16.75	31.13	55.31	2.63	1.48	4.94	2.78
	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>
NM	36.43	74.99	22.37	46.04	3.66	1.78	4.94	2.40
NMF	16.53	34.02	27.27	56.14	3.00	1.46	4.94	2.40
FA	11.75	24.19	38.80	79.87	2.11	1.03	4.94	2.40

<sup>a</sup> Crystallographic radii for cation from ref [28] and for anion calculated and judged from refs [29] and [30] respectively.

**Table 5. Diffusion Coefficient ( $D_\pm$ ) and Ionic Mobility ( $i_\pm$ ) of Electrolytes in Different Studied Solvents at 298.15 K**

solvents	$D_\pm \cdot 10^9 / (\text{m}^2 \cdot \text{s}^{-1})$		$i_\pm \cdot 10^8 / (\text{m}^2 \cdot \text{s}^{-1} \cdot \text{volt}^{-1})$	
	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	BF <sub>4</sub> <sup>-</sup>
NM	0.91	1.62	3.53	6.29
NMF	0.39	0.70	1.53	2.72
FA	0.25	0.45	0.98	1.74
	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	[Bu <sub>4</sub> N] <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>
NM	0.97	1.99	3.78	7.78
NMF	0.44	0.91	1.72	3.53
FA	0.31	0.64	1.22	2.50

**Table 6. IR Vibration Data of the Functional Groups Present in the Pure Solvent and Change of Frequency after Addition of Electrolytes [Bu<sub>4</sub>NClO<sub>4</sub>] and [Bu<sub>4</sub>NBF<sub>4</sub>] in the Solvents.**

solvents	functional group	IR vibration data		
		pure solvent ( $\nu_0$ cm <sup>-1</sup> )	[Bu <sub>4</sub> N]ClO <sub>4</sub> ( $\nu_1$ cm <sup>-1</sup> )	[Bu <sub>4</sub> N]BF <sub>4</sub> ( $\nu_2$ cm <sup>-1</sup> )
NM	N-O	1564.8 ( $\nu_{as}$ )	1601.7 ( $\nu_{as}$ )	1614.7 ( $\nu_{as}$ )
		1363.3 ( $\nu_s$ )	1388.8 ( $\nu_s$ )	1402.3 ( $\nu_s$ )
	C-H	2960.9 ( $\nu_{as}$ )	2963.1 ( $\nu_{as}$ )	2964.5 ( $\nu_{as}$ )
		2872.5 ( $\nu_s$ )	2873.9 ( $\nu_s$ )	2874.1 ( $\nu_s$ )
NMF	C=O	1679.8	1721.9	1734.5
	N-H	1543.3	1545.5	1546.2
	C-N	1400.1	1401.6	1403.9
FA	C=O	1692.9	1740.6	1754.1
	N-H	1578.2	1579.5	1582.9
	C-N	1401.8	1403.0	1404.2

## FIGURES

Figure 1. Plot of molar conductance ( $\Lambda$ ) and the square root of molar concentration ( $\sqrt{c}$ ) for  $[\text{Bu}_4\text{NBF}_4]$  in nitromethane ( $\blacklozenge$ ), N-methylformamide ( $\blacksquare$ ), formamide ( $\blacktriangle$ ), for  $[\text{Bu}_4\text{NClO}_4]$  in nitromethane ( $\diamond$ ), N-methylformamide ( $\square$ ), and formamide ( $\triangle$ ) respectively, at  $T = 298.15$  K.

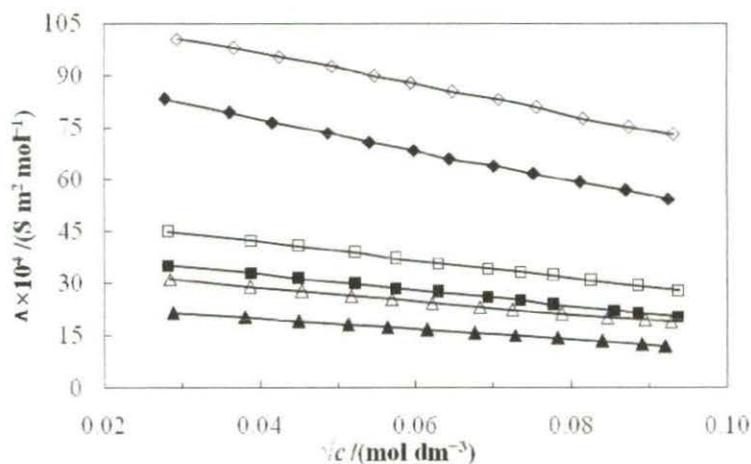


Figure 2. Plot of limiting molar conductance ( $\Lambda_0$ ) for  $[\text{Bu}_4\text{NBF}_4]$  ( $\blacklozenge$ ),  $[\text{Bu}_4\text{NClO}_4]$  ( $\blacktriangle$ ), and Walden Product ( $\Lambda_0\eta$ ) for  $[\text{Bu}_4\text{NBF}_4]$  ( $\diamond$ ),  $[\text{Bu}_4\text{NClO}_4]$  ( $\triangle$ ), in nitromethane, N-methylformamide and formamide respectively at  $T = 298.15$  K

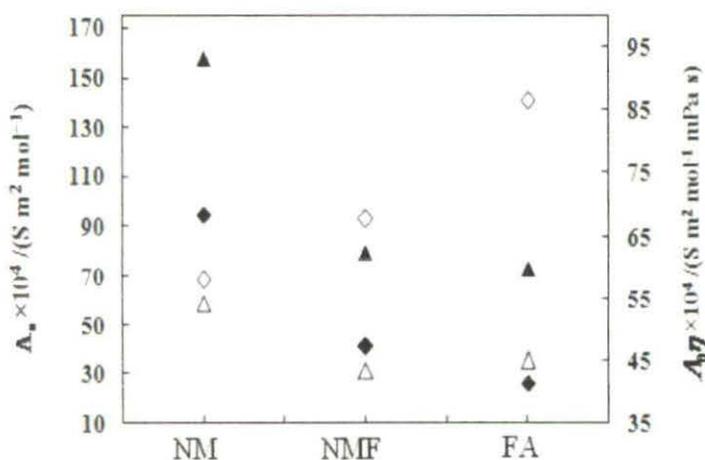


Figure 3. Plot of limiting ionic conductance ( $\lambda_o^\pm$ ) for  $\text{BF}_4^-$  ( $\blacksquare$ ),  $\text{ClO}_4^-$  ( $\blacktriangle$ ) and ionic Walden Product ( $\lambda_o^\pm \eta$ ) for  $\text{BF}_4^-$  ( $\square$ ),  $\text{ClO}_4^-$  ( $\triangle$ ) in nitromethane, N-methylformamide and formamide respectively at  $T = 298.15$  K.

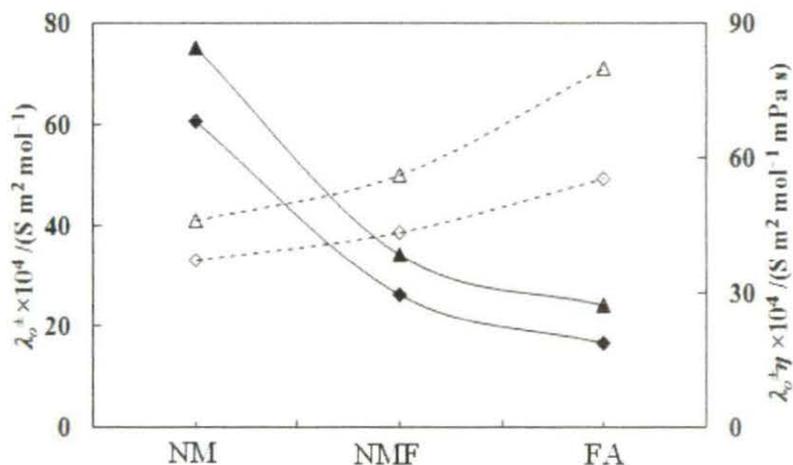


Figure 4. Plot of association constant ( $K_A$ ) for  $[\text{Bu}_4\text{NBF}_4]$  ( $\blacklozenge$ ),  $[\text{Bu}_4\text{NClO}_4]$  ( $\blacktriangle$ ), and Gibb's energy change ( $\Delta G^\circ$ ) for  $[\text{Bu}_4\text{NBF}_4]$  ( $\diamond$ ) and  $[\text{Bu}_4\text{NClO}_4]$  ( $\triangle$ ), in nitromethane, N-methylformamide, and formamide respectively at  $T = 298.15$  K.

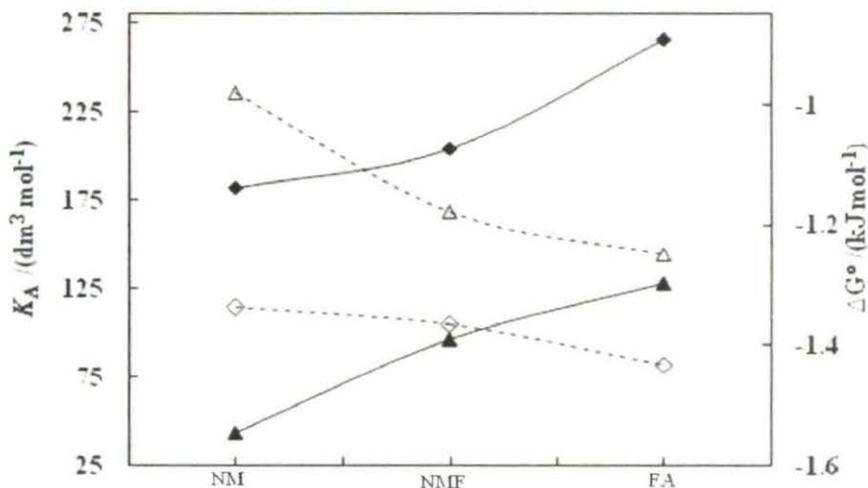


Figure 5. Plot of diffusion coefficient ( $D_{\pm}$ ) for  $\text{BF}_4^-$  (■),  $\text{ClO}_4^-$  (▲) and ionic mobility ( $i_{\pm}$ ) for  $\text{BF}_4^-$  (□),  $\text{ClO}_4^-$  (Δ), in nitromethane, N-methylformamide, and formamide, respectively, at  $T = 298.15$  K.

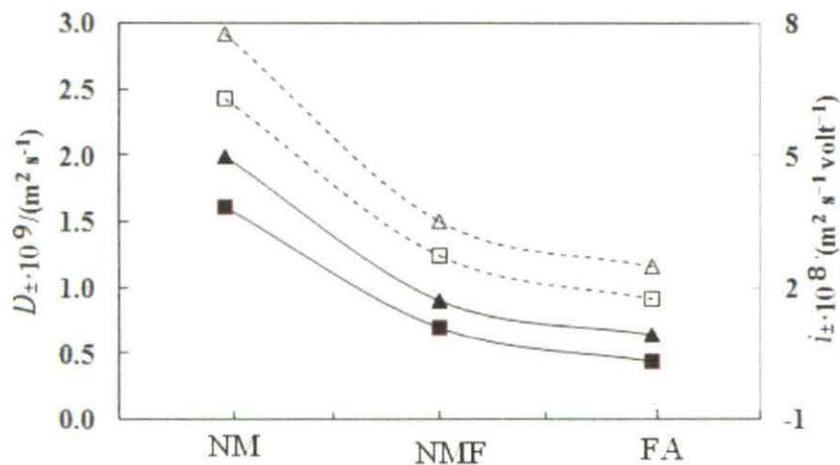
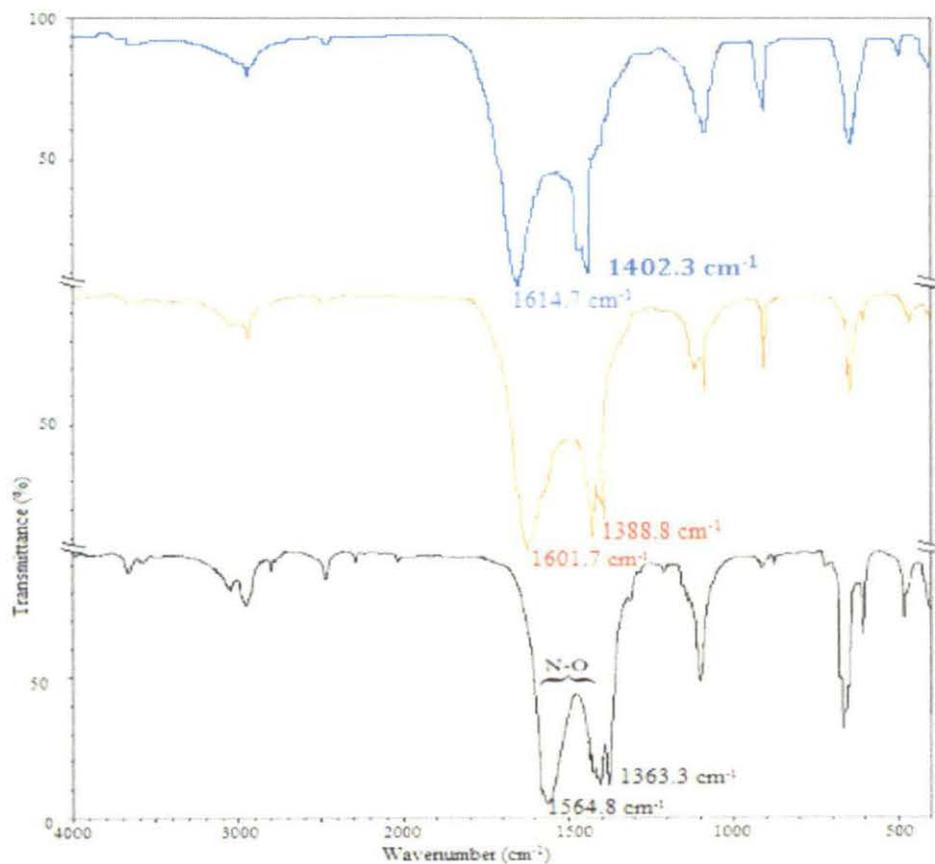


Figure 6. IR vibration data of -N-O in nitromethane (black solid line) and in {[Bu<sub>4</sub>NClO<sub>4</sub>] and nitromethane} (red solid line), {[Bu<sub>4</sub>NBF<sub>4</sub>] and nitromethane} (blue solid line)



**Figure 7.** IR vibration data of C=O in N-methylformamide (black solid line) and in {[Bu<sub>4</sub>NClO<sub>4</sub>] and N-methylformamide} (red solid line) and {[Bu<sub>4</sub>NBF<sub>4</sub>] and N-methylformamide} (blue solid line).

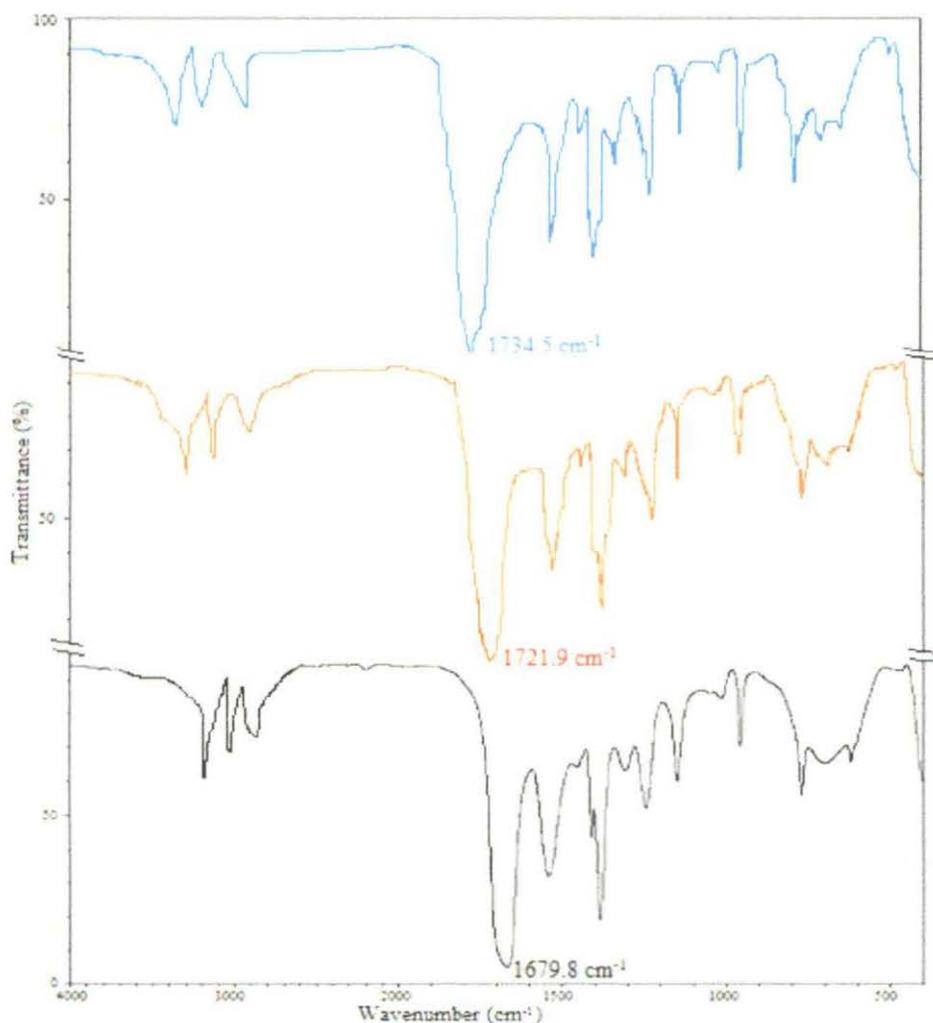
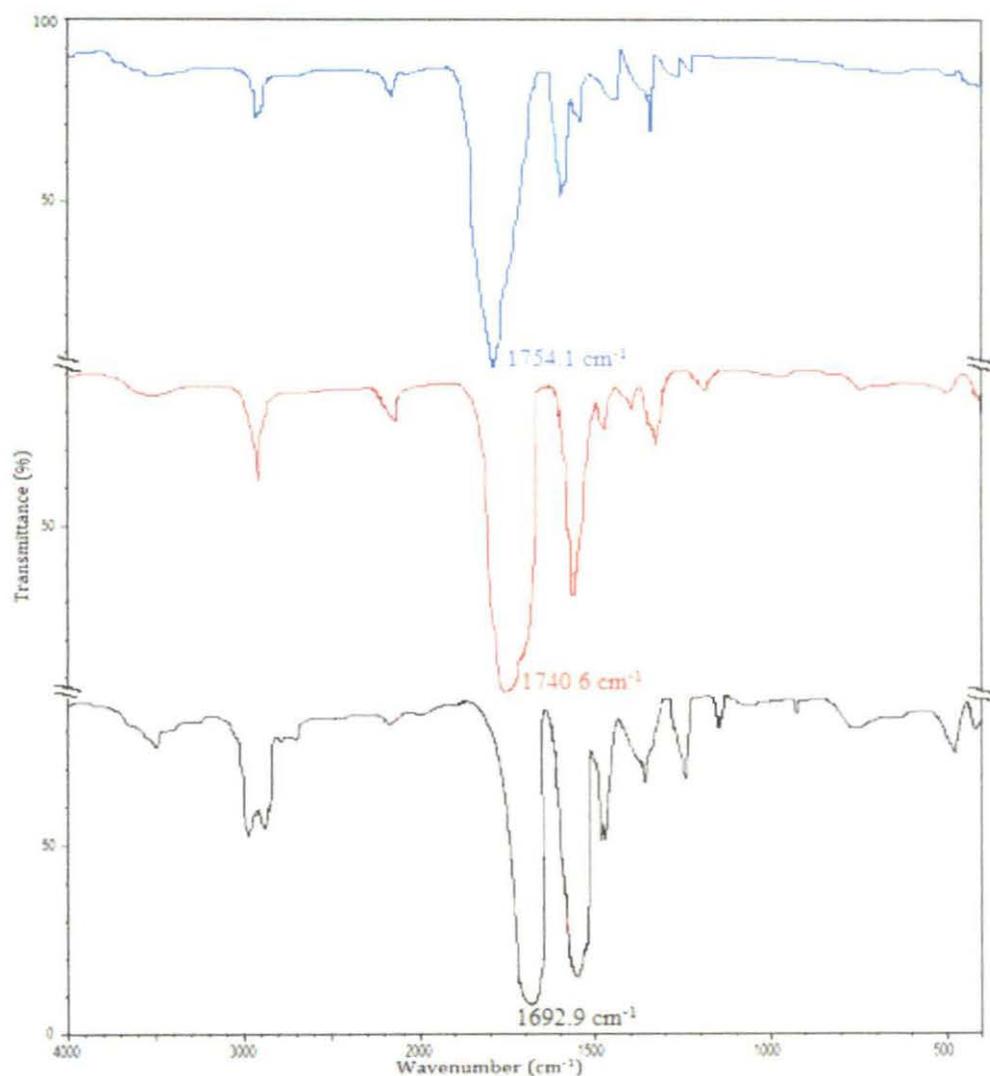


Figure 8. IR vibration data of C=O in formamide (black solid line) and in {[Bu<sub>4</sub>NClO<sub>4</sub>] and formamide} (red solid line) and {[Bu<sub>4</sub>NBF<sub>4</sub>] and formamide} (blue solid line).



## SCHEMES

Scheme 1. Two Dimensional Representation of the Plausible Interaction Occurring in  $\{[Bu_4N][Y]$  and Solvent $\}$  Together with the Trend in the Ion-Solvation in the Studied Solvents, Which Is Given Below:  $I < II < III$

