

## CHAPTER VIII

# PROBING SUBSISTENCE OF ION-PAIR AND TRIPLE-ION OF AN IONIC SALT IN LIQUID ENVIRONMENTS BY MEANS OF CONDUCTOMETRIC CONTRIVANCE

### 8.1. INTRODUCTION

The exploration of molecular interaction existing in solution is always of interest to chemists. Molecular interaction can be studied in the solution phase by studying its thermodynamic and transport properties. These properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Study on the transport properties of electrolytes in different solvent media is of great importance to obtain information as to the solvation and association behavior of ions in solutions. In the modern technology the application of the salt is well understood by studying the ion solvation. A number of conductometric [1] and related studies of electrolytes in non-aqueous solvents have been done in relation to the use of these types of electrolytes in high-energy batteries [2] and for further understanding of organic reaction mechanisms [3]. Tetraalkylammonium salts are very suitable due to the excellent solubility characteristics in aqueous/non-aqueous solvents. Tetraalkylammonium salts have a broad range of applications that includes trace analysis (of metals and organic compounds), environmental analytic chemistry pharmaceutical and medicinal.

The solvents chosen for the study are all polar aprotic except methanol ( $\text{CH}_3\text{OH}$ ) which is polar protic. The solvents used in this study find wide industrial usage. Industrially important acetonitrile ( $\text{CH}_3\text{CN}$ ) is predominantly used in the manufacture of pharmaceutical and in battery industries.

Alcohols have varied applications in chemical and cosmetic industries. Methanol ( $\text{CH}_3\text{OH}$ ) is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc.

Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and non polar groups is used in veterinary medicine, in organic synthesis and as an antifreeze agent of living cells [4]. It is widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology and microbiology [5].

1, 3-Dioxolane is cyclic diether and it figures prominently in the high energy battery technology [6] and has also found application in organic synthesis as manifested from the physico-chemical studies in this media. The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents. Even though these solvents have drawn much focus in recent years as solvents for physico-chemical investigations, still a lot remains to be explored.

In continuation of our investigation on electrical conductances [7,8] an attempt has been made in the present study, to ascertain the nature of ion-solvent interactions of tetrabutylammonium tetrafluoroborate [ $Bu_4NBF_4$ ] in acetonitrile ( $CH_3CN$ ), methanol ( $CH_3OH$ ), dimethyl sulfoxide (DMSO) and 1,3-dioxolane(1,3-DO) at 298.15 K. The conductometric studies have been done for the electrolyte in the studied solvents and the obtained results have been discussed for the formation of ion-pairs and triple-ions. In the solvents, viz.  $CH_3CN$ ,  $CH_3OH$  and DMSO; ion-pairs are formed due to the high/moderate dielectric constant of the solvents. However, in case of 1, 3-DO triple-ions are formed due to its low dielectric constant ( $\epsilon < 10$ ). Different thermodynamic parameters such as association constant ( $K_A$ ), and Gibbs energy change of solvation ( $\Delta G^\circ$ ), have been evaluated and discussed.

## 8.2. EXPERIMENTAL

### 8.2.1. *Source and purity of samples*

[ $Bu_4NBF_4$ ] of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of [ $Bu_4NBF_4$ ] was  $\geq 0.99$ .

The solvents CH<sub>3</sub>CN, CH<sub>3</sub>OH, DMSO and 1,3-DO were procured from Merck, India. These were further purified by standard methods [9]. The values of purity obtained were  $\geq 0.99$ . See Table 1.

### 8.2.2. Apparatus and Procedure

A stock solution of the electrolyte [Bu<sub>4</sub>NBF<sub>4</sub>] was prepared by mass (Mettler Toledo AG-285 with uncertainty  $\pm 0.0003$  g) and the working solutions were obtained by mass dilution at 298.15 K and atmospheric pressure.

The densities of the solvents ( $\rho$ ) were measured by means of vibrating-tube Anton Paar density-meter (DMA 4500 M) with a precision of  $\pm 0.00005$  g·cm<sup>-3</sup> maintained at  $\pm 0.01$ K of the desired temperature. Adequate precautions were taken to minimize evaporation loses during the actual measurements. The precision of density measurements was  $\pm 3.10^{-5}$  g·cm<sup>-3</sup>. It was calibrated by double-distilled water and dry air. Measurement of solvent viscosities was carried out by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [10-12]. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt., Ltd.) and maintained the temperature to  $\pm 0.01$  K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to  $\pm 0.1$  s. At least three repetitions of each datum reproducible to  $\pm 0.1$  s were taken to average the flow times.

Viscosity of the solution is evaluated using the following equation [13];

$$\eta = \left( Kt - \frac{L}{t} \right) \rho \quad (1)$$

where  $K$  and  $L$  are the viscometer constants,  $t$  is the efflux time of flow in seconds and  $\rho$  is the density of the experimental liquid. The uncertainty in viscosity measurements is within  $\pm 0.003$  mPa·s.

The conductance measurements were carried out in a Systronics-308 conductivity bridge of 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 $^{-1}$ . Measurements were carried out in a thermostat water bath maintained at  $T = (298.15 \pm 0.01)$  K. The cell was calibrated by the method proposed by Lind et al. [14]. During the conductance measurements, cell constant was maintained within the range 1.10 to 1.12 cm $^{-1}$ . The conductance data were reported at a frequency of 1 kHz and the accuracy was  $\pm 0.3\%$ . During the measurements, uncertainty of temperatures was  $\pm 0.01$  K.

### **8.3. RESULTS AND DISCUSSION**

#### **8.3.1. Electrical Conductance**

##### **8.3.1.1. Ion-pair formation**

The electrolyte was freely soluble in all proportions of the solvent. The physical properties of the pure solvents were in good agreement with values found in the literature, as reported in Table 2, where appropriate corrections were made by the specific conductance of the solvents at that temperature.

The molar conductance ( $\Lambda$ ) for all studied system was calculated using following equation. [15]

$$\Lambda = 1000 \kappa / c \quad (2)$$

where  $c$  is the molar concentration and  $\kappa$  is the measured specific conductance of the studied solution. The experimental values of molar conductances ( $\Lambda$ ) of electrolyte  $[Bu_4NBF_4]$  measured at the corresponding molar concentrations ( $c$ ) in CH<sub>3</sub>CN, CH<sub>3</sub>OH, DMSO and 1,3-DO are given in Table 3. The conductance data for  $[Bu_4NBF_4]$  in the studied solvents have been analyzed using the Fuoss conductance equation [16]. So with a given set of conductivity values ( $c_j, \Lambda_j, j = 1, \dots, n$ ) three adjustable parameters, i.e.  $\Lambda_0$ ,  $K_A$  and  $R$  have been derived from the Fuoss equation. Here,  $\Lambda_0$  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 [17] 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  $a = (r_+ + r_-)$  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 [18]:

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

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

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

$$\Lambda = P \Lambda_o [(1 + R_x) + E_L] \quad (4)$$

$$P = 1 - \alpha(1 - \gamma) \quad (5)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (6)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (7)$$

$$\beta = e^2 / (\varepsilon k_B T) \quad (8)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (9)$$

where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current,  $k^{-1}$  is the radius of the ion atmosphere,  $\varepsilon$  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 paring 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 the program suggested by Fuoss. The initial  $\Lambda_o$  values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [19]. Input for the program is the set  $(c_j, \Lambda_j, j=1, \dots, n), n, \varepsilon, \eta, T$ , initial values of  $\Lambda_o$ , and an instruction to cover a pre-selected range of  $R$  values.

The best value of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation  $\delta$  for a sequence of predetermined  $R$  values, and standard deviation  $\delta$  was calculated by the following equation

$$\delta^2 = \sum [A_j(\text{cal}) - A_j(\text{obs})]^2 / (n-m) \quad (10)$$

where  $n$  is the number of experimental points and  $m$  is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach  $R$  with two parameter fit ( $m = 2$ ). For a sequence of  $R$  values and then plotting  $\delta$  against  $R$ , the best-fit  $R$  corresponds to the minimum of the  $\delta$ - $R$  versus  $R$  curve. So, approximate runs are made over a fairly wide range of  $R$  values using 0.1 increments to locate the minimum, but no significant minima were found in the  $\delta$ - $R$  curves for the electrolyte in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$  and DMSO.

The values of  $A_0$ ,  $K_A$ , and  $R$  obtained by this procedure are represented in Table 4. Perusal of Table 4 and Figure 1 reveals that the limiting molar conductance  $A_0$  of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$  is greater than that in  $\text{CH}_3\text{OH}$  and DMSO which is in the order  $\text{CH}_3\text{CN} > \text{CH}_3\text{OH} > \text{DMSO}$ . Table 3 and Figure 2 also imply that the association constant ( $K_A$ ) of the  $[\text{Bu}_4\text{NBF}_4]$  is more in DMSO, than in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CN}$ . Hence, there is more ion-solvent interaction in DMSO than in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CN}$ ; leading to a lower conductance of  $[\text{Bu}_4\text{NBF}_4]$  in the former than in the latter two. The higher viscosity of DMSO also supports the above fact because with higher viscosity the  $A_0$  value should decrease.

Solvent polarity and dielectric constant play a very important role in determining the physico-chemical properties of solution. As all the solvents used are polar, dielectric constant becomes more important here because it is the ability of the solvent to stabilize the charges or dipoles. So, more the dielectric constant of the solvent more will be its ability to stabilize the charges or dipoles. Dielectric constant of DMSO,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$  is about 46.7, 35.94 and 32.7 respectively at 298.15 K. Therefore ion-solvent

interaction should have been in the following order DMSO> CH<sub>3</sub>CN> CH<sub>3</sub>OH. But our finding tells the order of ion-solvent interaction of [Bu<sub>4</sub>NBF<sub>4</sub>] to be DMSO> CH<sub>3</sub>OH> CH<sub>3</sub>CN.

Out of the three solvents used, DMSO and CH<sub>3</sub>CN are polar aprotic solvents whereas CH<sub>3</sub>OH is a polar protic solvent. Polar aprotic solvents, (*e.g.*, DMSO and CH<sub>3</sub>CN) dissolve ionic compounds and stabilize cations very well, but do not stabilize anions to any appreciable extent because they cannot form H-bonds and having positive centers are well shielded from any interaction with anions. On the other hand polar protic solvent (*e.g.*; CH<sub>3</sub>OH) dissolves ionic compounds by forming H-bonds [20], because they have an H atom attached to an atom of strong electronegative element. When the ionic compound [Bu<sub>4</sub>NBF<sub>4</sub>] is dissolved in the above mentioned polar aprotic and polar protic solvents, the following interaction may be observed.

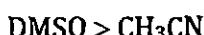
The schematic representation of ion-solvation, for the particular ion in the studied solvent is depicted in Scheme 1.

In case of solvent CH<sub>3</sub>CN, the only interaction present is between negatively charged N atom of CH<sub>3</sub>CN and positively charged N atom of [Bu<sub>4</sub>N]<sup>+</sup>, shown in (i). In case of DMSO as solvent, two types of interaction shown in (iii) are possible –

a) Between the negatively charged O atom of DMSO and positively charged N atom of [Bu<sub>4</sub>N]<sup>+</sup>.

b) Between positively charged S atom of DMSO and negatively charged species [BF<sub>4</sub>]<sup>-</sup>.

The interaction (b) is only possible because S atom is larger than C atom and is more electropositive than C atom present in CH<sub>3</sub>CN. For this reason conductance of [Bu<sub>4</sub>NBF<sub>4</sub>] is more in CH<sub>3</sub>CN than DMSO. Also higher dielectric constant of DMSO than CH<sub>3</sub>CN complies with the results. Hence, lower the conductance, more the interaction/association, which is in the following order-



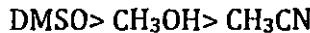
In case of solvent CH<sub>3</sub>OH, the H-bond interaction is present between F atom of negatively charged species [BF<sub>4</sub>]<sup>-</sup> and H atom of CH<sub>3</sub>OH. Also the free electron pairs present in O atom of CH<sub>3</sub>OH can stabilize positively charged N atom of [Bu<sub>4</sub>N]<sup>+</sup> as shown in (ii). Though dielectric constant of CH<sub>3</sub>CN is greater than CH<sub>3</sub>OH, ion-solvent interaction of CH<sub>3</sub>OH is more than CH<sub>3</sub>CN because it can stabilize both the charged species. Moreover CH<sub>3</sub>CN has the tendency to form anti-parallel dimer [21] shown in Scheme 2. The formation of anti-parallel dimer reduces the degree of ion-solvent interaction. So conductance of [Bu<sub>4</sub>NBF<sub>4</sub>] is more in CH<sub>3</sub>CN than in CH<sub>3</sub>OH. Hence, lower the conductance, more the interaction/association, which is in the following order-



As dielectric constant of DMSO is much higher than CH<sub>3</sub>OH, and it can stabilize both the positively charged species [Bu<sub>4</sub>N]<sup>+</sup> and negatively charged species [BF<sub>4</sub>]<sup>-</sup> as CH<sub>3</sub>OH does. So ion-solvent interaction is more in DMSO compared to CH<sub>3</sub>OH. Hence, lower the conductance, more the interaction/association, which is in the following order-



Thus, the overall ion-solvent interaction of electrolyte [Bu<sub>4</sub>NBF<sub>4</sub>] in the three solvents DMSO, CH<sub>3</sub>CN and CH<sub>3</sub>OH is of the order



The results are in accordance with the obtained data.

The above trend in  $\Lambda_0$  values can be verified through another characteristic function called the Walden product,  $\Lambda_0 \eta_0$  given in Table 4. From Table 4 and Figure 3 the increasing trend of Walden product is mainly in agreement with the concomitant increase of solvent viscosity and decrease of limiting molar conductance for the electrolyte in the studied solvents. This 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 [22]

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting ionic Walden product ( $\lambda_v^\pm \eta_o$ ), (product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions is a constant. The ionic conductances  $\lambda_o^\pm$  (for  $[Bu_4N]^+$  cation and  $[BF_4]^-$  anion) in different solvents  $CH_3CN$ ,  $CH_3OH$  and DMSO, were calculated using tetrabutylammonium tetraphenylborate ( $Bu_4NBPh_4$ ) as a 'reference electrolyte' following the scheme as suggested by B. Das et al.[23] The  $\lambda_o^\pm$  values were in turn utilized for the calculation of Stokes' radii ( $r_s$ ) according to the classical expression [24]

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^\pm r_c} \quad (11)$$

Ionic Walden products  $\lambda_v^\pm \eta_o$ , Stokes' radii  $r_s$ , and crystallographic radii  $r_c$  are presented in Table 5. The trends in Walden products  $\lambda_o \eta_o$  and ionic Walden products  $\lambda_v^\pm \eta_o$  for the electrolytes in the solvents  $CH_3CN$ ,  $CH_3OH$  and DMSO, are depicted in Tables 4 and 5 and Figures 3 and 5 respectively. It shows that both the ionic Walden products  $\lambda_v^\pm \eta_o$  and Walden products  $\lambda_o \eta_o$  for the electrolyte are higher in the case of DMSO than  $CH_3OH$  and  $CH_3CN$ . For  $Bu_4N^+$  and  $BF_4^-$  ion, the Stokes' radii  $r_s$  are either lower or comparable to their crystallographic radii  $r_c$ , this suggests that the ion is comparatively less solvated than alkali metal ions due to its intrinsic low surface charge density. The distance parameter  $R$ , shown in Table 3, is the least distance that two free ions can approach together before they merge into an ion pair.  $R$  values have been found to be greater in case of DMSO than other two solvents.

The nature of the curve for the Gibbs energy changes for ion-pair formation,  $\Delta G^\circ$ , which clearly predicts the tendency for ion-pair formation. The Gibbs energy change  $\Delta G^\circ$  is calculated by the following relationship [25] and is given in Table 3.

$$\Delta G^\circ = -RT \ln K_A \quad (12)$$

where  $K_A$  is the association constant. The negative values of  $\Delta G^\circ$  can be explained by considering the participation of specific covalent interaction in the ion-association process. The lower value of  $\Delta G^\circ$  for  $[Bu_4NBF_4]$  electrolyte in DMSO than  $CH_3OH$  and  $CH_3CN$  indicates the highest degree of association in DMSO. This result indicates the extent of solvation enhanced by the following order:



This is an excellent agreement with the observation obtained from conductance values discussed earlier in this paper.

There are marked characteristic behaviors in the  $K_A$  values, which are highest in case of DMSO than  $CH_3OH$  and  $CH_3CN$ . So, ion-association for the electrolyte increases in case of DMSO.

### 8.3.1.2. Triple-ion formation

Figure 4 present the graphical representation of  $A$  vs.  $\sqrt{c}$ , which shows that, the electrolyte follows the same trend, i.e. decreases with increasing concentration, reaches a minimum and then increases. Due to the deviation of the conductometric curves ( $A$  vs  $\sqrt{c}$ ) from linearity in case of  $[Bu_4NBF_4]$  in 1, 3- DO, the conductance data have been analyzed by using the classical Fuoss-Kraus theory of triple-ion formation in the form [18, 25]

$$A g(c) \sqrt{c} = \frac{A_0}{\sqrt{K_p}} + \frac{A_0^T K_T}{\sqrt{K_p}} \left( 1 - \frac{A}{A_0} \right) c \quad (13)$$

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

$$g(c) = \frac{\exp\{-2.303 \beta' (cA)^{0.5} / A_0^{0.5}\}}{\{1 - S(cA)^{0.5} / A_0^{1.5}\}(1 - A/A_0)^{0.5}} \quad (14)$$

$$\beta' = 1.8247 \times 10^6 / (\varepsilon T)^{1.5} \quad (15)$$

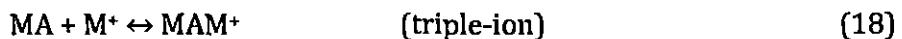
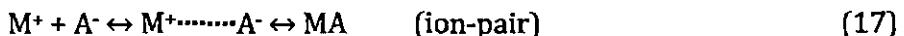
$$S = \alpha A_0 + \beta = \frac{0.8204 \times 10^6}{(\varepsilon T)^{1.5}} A_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \quad (16)$$

In the above equations,  $\Lambda_0$  is the sum of the molar conductance of the simple ions at infinite dilution,  $\Lambda_0^T$  is the sum of the conductance value of the two triple-ions  $[(\text{Bu}_4\text{N})_2]^+\text{BF}_4^-$  and  $\text{Bu}_4\text{N}[(\text{BF}_4)_2]^-$  for  $[\text{Bu}_4\text{NBF}_4]$  salt;  $K_P \approx K_A$  and  $K_T$  are the ion-pair and triple-ion formation constants respectively and  $S$  is the limiting Onsager coefficient. To make equation (13) applicable, the symmetrical approximation of the two possible formation constants of triple-ions,  $K_{T1} = [(\text{Bu}_4\text{N})_2]^+\text{BF}_4^- / \{[\text{Bu}_4\text{N}^+][\text{Bu}_4\text{NBF}_4]\}$  and  $K_{T2} = \text{Bu}_4\text{N}[(\text{BF}_4)_2]^- / \{[\text{BF}_4^-][\text{Bu}_4\text{NBF}_4]\}$  equal to each other has been adopted, *i.e.*  $K_{T1} = K_{T2} = K_T$  [26] and  $\Lambda_0$  values for the studied electrolyte in 1,3-DO have been calculated following the scheme as suggested by Krumgalz [27] [1983]. The calculated values are listed in Table 5.  $\Lambda_0^T$  has been calculated by setting the triple-ion conductance equal to  $2/3 \Lambda_0$  [28]

The ratio  $\Lambda_0^T / \Lambda_0$  was thus set equal to 0.667 during linear regression analysis of equation (13). Table 5 shows the calculated limiting molar conductance of simple ion ( $\Lambda_0$ ), limiting molar conductance of triple-ion ( $\Lambda_0^T$ ), slope and intercept of equation (13) for  $[\text{Bu}_4\text{NBF}_4]$  in 1, 3-DO at 298.15 K. The linear regression analysis of equation (13) for the electrolytes with an average regression constant,  $R^2 = 0.9889$ , gives intercepts and slopes. These values permit the calculation of other derived parameters such as  $K_P$  and  $K_T$  listed in Table 6. The value of  $\log (K_T/K_P)$  has also been reported. A perusal of Table 7 shows that the major portion of the electrolytes exists as ion-pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the  $K_T/K_P$  ratios and  $\log (K_T/K_P)$ . These ratios suggest that strong association between the ions is due to the coulombic interactions as well as to covalent forces in the solution. These results are in good agreement with those of Roy et al. [21]

At very low dielectric constant of the solvent, *i.e.*,  $\epsilon < 10$ , electrostatic ionic interactions are very large. So the ion-pairs attract the free cations or anions present in the solution medium as the distance of the closest approach of the ions becomes minimum. These

result in the formation of triple-ions, which acquires the charge of the respective ions, attracted from the bulk solution [25, 29] i.e;



where  $M^+$  and  $A^-$  are  $Bu_4N^+$  and  $BF_4^-$  respectively. The effect of ternary association [30] 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 1,3-DO. The Scheme 3 depicts the pictorial representation of triple-ion formations for the electrolyte, in 1,3-DO.

Furthermore, the ion-pair and triple-ion concentrations,  $C_P$  and  $C_T$ , respectively of the  $[Bu_4NBF_4]$  in 1,3-DO have also been calculated using the following equations [21]

$$\alpha = 1 / (K_P^{1/2} \cdot C^{1/2}) \quad (20)$$

$$\alpha_T = (K_T / K_P^{1/2}) C^{1/2} \quad (21)$$

$$C_P = C(1 - \alpha - 3\alpha_T) \quad (22)$$

$$C_T = (K_T / K_P^{1/2}) C^{3/2} \quad (23)$$

Here  $\alpha$  and  $\alpha_T$  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 8, 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 ( $\alpha$ ), triple-ion fraction ( $\alpha_T$ ), ion-pair concentration ( $C_P$ ) and triple-ion concentration ( $C_T$ ) have also been calculated over the whole concentration range of  $[Bu_4NBF_4]$  in 1, 3- DO and the data are provided in Table 8. It is observed that the amount of the triple-ions in the solution increases with the increase in concentration. (see Table 9)

The schematic representation of ion-solvation, for the particular ion in the studied solvent in view of various derived parameters is depicted in Scheme 4.

#### 8.4. CONCLUSIONS

The present work reveals an extensive study on the ion-solvation behavior of the tetrabutylammonium tetrafluoroborate  $[Bu_4NBF_4]$  in  $CH_3CN$ ,  $CH_3OH$ , DMSO and 1,3-DO through the conductometric measurements. From the study it becomes clear that the salt is more associated with DMSO than the other three solvents. It can also be seen that in the conductometric studies in  $CH_3CN$ ,  $CH_3OH$  and DMSO, the electrolyte remains as ion-pairs but in 1,3-DO it remains as triple-ions. The tendency of the ion-pair and triple-ion formation depends on the size and the charge distribution of the ions.

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**TABLES****Table 1. Sample description**

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity
[Bu <sub>4</sub> NBF <sub>4</sub> ]	Sigma-Aldrich, Germany	0.99	Used as procured	0.99
CH <sub>3</sub> CN	Merck, India	0.98	Purified by standard methods [9]	0.99
CH <sub>3</sub> OH	Merck, India	0.98	Purified by standard methods [9]	0.99
DMSO	Merck, India	0.98	Purified by standard methods [9]	0.99
1,3-DO	Merck, India	0.98	Purified by standard methods [9]	0.99

**Table 2. Values of density ( $\rho$ ), viscosity ( $\eta$ ) and dielectric constant ( $\epsilon$ ) of CH<sub>3</sub>CN, CH<sub>3</sub>OH, DMSO, and 1,3-DO at T = 298.15 K and atmospheric pressure**

Solvents	<sup>a</sup> $\rho$ (kg m <sup>-3</sup> )		<sup>b</sup> $\eta$ (mPa s)		$\epsilon$
	Expt	Lit	Expt	Lit	
CH <sub>3</sub> CN	776.74	776.70[31]	0.343	0.344[33]	35.94[21]
CH <sub>3</sub> OH	786.60	786.60[32]	0.545	0.545[32]	32.70[32]
DMSO	1096.00	1095.80[32]	1.948	1.960[32]	46.70[32]
1,3-DO	1058.70	1058.72[21]	0.592	0.597[21]	7.34[21]

<sup>a</sup> uncertainty in the density values:  $\pm 0.00003$  g. cm<sup>-3</sup>.<sup>b</sup> uncertainty in the viscosity values:  $\pm 0.003$  mPa. s.

**Table 3. Molar conductance ( $\Lambda$ ) and the corresponding concentration (c) of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ , DMSO and 1, 3-D0 at  $T = 298.15 \text{ K}$  and atmospheric pressure**

$C^{\text{c}} \times 10^4$ (mol dm $^{-3}$ )	$\Lambda^{\text{d}} \times 10^4$ (S m $^2$ mol $^{-1}$ )	$C^{\text{c}} \times 10^4$ (mol dm $^{-3}$ )	$\Lambda^{\text{d}} \times 10^4$ (S m $^2$ mol $^{-1}$ )
<b>Acetonitrile</b>		<b>Methanol</b>	
9.35	156.35	13.31	104.08
16.33	153.33	18.19	101.99
23.09	151.21	26.00	99.56
28.10	149.63	35.53	97.08
33.82	148.14	44.58	94.84
38.57	147.03	53.20	93.14
42.42	145.97	60.93	91.65
47.22	144.91	69.24	90.20
53.88	143.56	75.00	88.99
60.00	142.39	81.21	87.99
65.48	141.34	88.89	86.91
70.91	140.34	94.56	85.88
75.31	139.59	102.01	84.85
79.30	138.86	110.24	83.86
83.08	138.22	118.82	82.69
<b>Dimethylsulfoxide</b>		<b>1,3-Dioxolane</b>	
20.63	32.94	0.17	59.60
37.83	30.01	0.23	53.97
52.38	28.18	0.29	50.15
64.85	27.04	0.33	47.40
75.66	26.03	0.38	45.27
93.46q	24.24	0.44	42.25
107.52	23.05	0.50	39.80
118.89	21.96	0.57	37.95
132.40	20.99	0.63	35.88
142.91	20.31	0.69	34.05
151.32	19.80	0.77	33.26
158.19	19.29	0.84	32.68
168.78	18.59	0.93	33.09
176.54	17.99	1.00	34.63
187.85	17.12	1.05	35.71

<sup>c</sup> Uncertainty in the molarity:  $\pm 0.0002 \text{ mol. dm}^{-3}$ .<sup>d</sup> Uncertainty in the molar conductance:  $\pm 0.01 \text{ S. m}^2 \cdot \text{mol}^{-1}$

**Table 4.** 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 Equation (2), Walden product ( $\Lambda_0\eta_0$ ) and Gibbs energy change ( $\Delta G^\circ$ ) of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$  and DMSO at  $T = 298.15 \text{ K}$  and atmospheric pressure

Solvents	$\Lambda_0 \times 10^4$ ( $\text{S m}^2 \text{ mol}^{-1}$ )	$K_A$	$R$ ( $\text{\AA}$ )	$\delta$	$\Lambda_0\eta_0$ ( $\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}$ )	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )
$\text{CH}_3\text{CN}$	162.01	12.07	11.84	0.08	55.37	-0.62
$\text{CH}_3\text{OH}$	112.70	29.77	11.87	0.18	61.27	-0.84
DMSO	45.75	112.19	12.71	1.27	89.11	-1.17

**Table 5.** Limiting ionic conductance ( $\lambda_o^\pm$ ), ionic Walden product ( $\lambda_o^\pm\eta_o$ ), Stokes' radii ( $r_s$ ) and crystallographic radii ( $r_c$ ) of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ , and DMSO at  $T = 298.15 \text{ K}$  and atmospheric pressure

Solvents	Ion	$\lambda_o^\pm$ ( $\text{S m}^2 \text{ mol}^{-1}$ )	$\lambda_o^\pm\eta_o$ ( $\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}$ )	$r_s$ ( $\text{\AA}$ )	$r_c$ ( $\text{\AA}$ )
$\text{CH}_3\text{CN}$	$\text{Bu}_4\text{N}^+$	58.34	20.01	4.09	4.94
	$\text{BF}_4^-$	103.67	35.56	2.30	2.78
$\text{CH}_3\text{OH}$	$\text{Bu}_4\text{N}^+$	40.58	22.10	3.71	4.94
	$\text{BF}_4^-$	72.12	39.27	2.09	2.78
DMSO	$\text{Bu}_4\text{N}^+$	16.47	32.09	2.55	4.94
	$\text{BF}_4^-$	29.27	57.02	1.44	2.78

<sup>e</sup> Crystallographic radii of cation and anion from ref. [32, 34] respectively.

**Table 6.** The calculated limiting molar conductance of ion-pair ( $\Lambda_0$ ), limiting molar conductance of triple-ion ( $\Lambda_0^T$ ), slope and intercept of Equation (13) of  $[\text{Bu}_4\text{NBF}_4]$  in 1, 3-DO at  $T = 298.15$  K and atmospheric pressure

Solvents	$\Lambda_0 \times 10^4$ ( $\text{S m}^2 \text{mol}^{-1}$ )	$\Lambda_0^T \times 10^4$ ( $\text{S m}^2 \text{mol}^{-1}$ )	Slope	Intercept
1,3-DO	100.49	67.03	1.58	0.33

**Table 7.** Salt concentration at the minimum conductivity ( $c_{\min}$ ) along with the ion-pair formation constant ( $K_P$ ), triple-ion formation constant ( $K_T$ ) of  $[\text{Bu}_4\text{NBF}_4]$  in 1, 3-DO at  $T = 298.15$  K and atmospheric pressure

Solvent	$c_{\min} \times 10^4$ ( $\text{mol dm}^{-3}$ )	$\log c_{\min}$	$K_P \times 10^{-4}$	$K_T$	$(K_T/K_P) \times 10^{-5}$	$\log(K_T/K_P)$
1,3-DO	0.84	-4.08	9.51	7.25	7.62	-4.12

**Table 8.** 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  $[\text{Bu}_4\text{NBF}_4]$  in 1,3-DO at  $T = 298.15$  K and atmospheric pressure

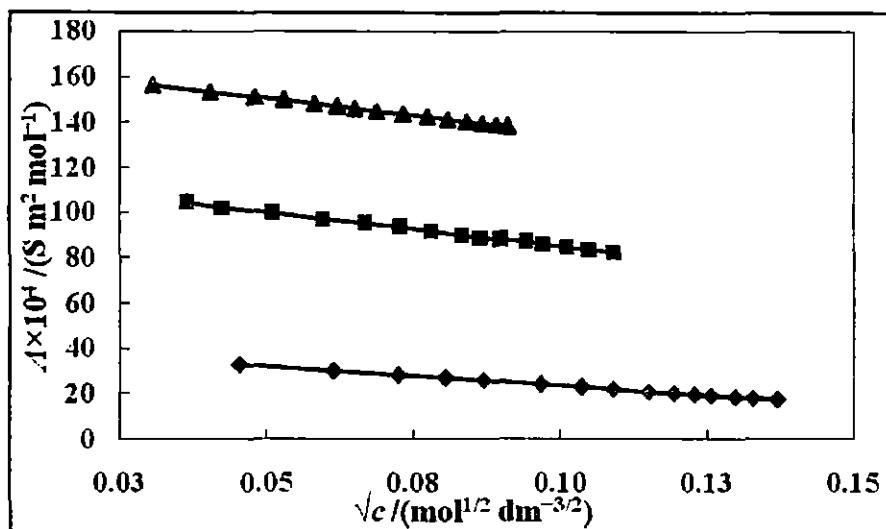
Solvent	$c_{\min} \times 10^4$ ( $\text{mol dm}^{-3}$ )	$\Lambda_{\min} \times 10^4$	$\Lambda$	$\alpha_T \times 10^4$	$C_P \times 10^5$ ( $\text{mol dm}^{-3}$ )	$C_T \times 10^8$ ( $\text{mol dm}^{-3}$ )
1,3-DO	0.84	32.68	0.35	2.16	5.44	1.81

**Table 9.** Salt concentration ( $c$ ), the ion-pair fraction ( $\alpha$ ), triple-ion fraction ( $\alpha_T$ ), ion-pair concentration ( $C_P$ ) and triple-ion concentration ( $C_T$ ) of  $[\text{Bu}_4\text{NBF}_4]$  in 1, 3-DO at 298.15 K and atmospheric pressure

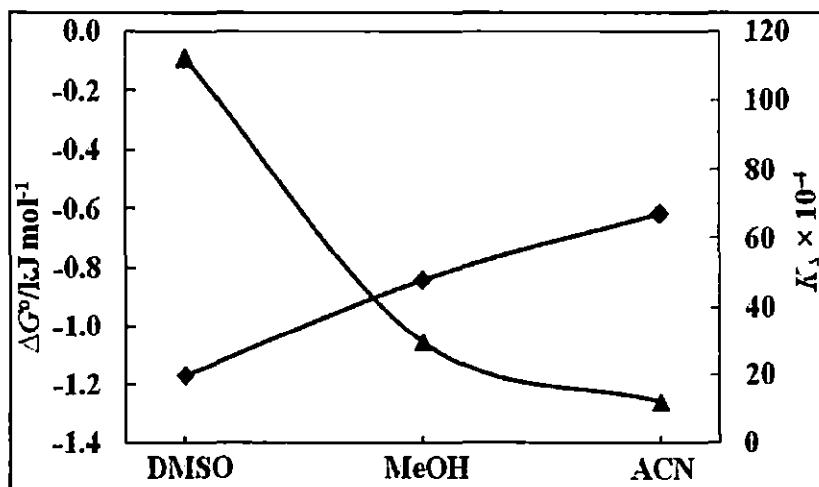
$c \times 10^4$ (mol dm $^{-3}$ )	$\alpha$	$\alpha_T \times 10^4$	$C_P \times 10^5$ (mol dm $^{-3}$ )	$C_T \times 10^8$ (mol dm $^{-3}$ )
0.17	0.79	0.96	0.34	0.16
0.23	0.67	1.13	0.75	0.26
0.29	0.61	1.26	1.13	0.36
0.33	0.56	1.36	1.46	0.45
0.38	0.53	1.44	1.77	0.54
0.44	0.49	1.57	2.29	0.70
0.50	0.46	1.66	2.71	0.83
0.57	0.43	1.77	3.22	1.00
0.63	0.41	1.87	3.73	1.17
0.69	0.39	1.96	4.27	1.37
0.77	0.37	2.06	4.84	1.58
0.84	0.35	2.16	5.44	1.81
0.93	0.34	2.27	6.19	2.11
1.00	0.32	2.35	6.78	2.36
1.05	0.31	2.41	7.18	2.53

**FIGURES**

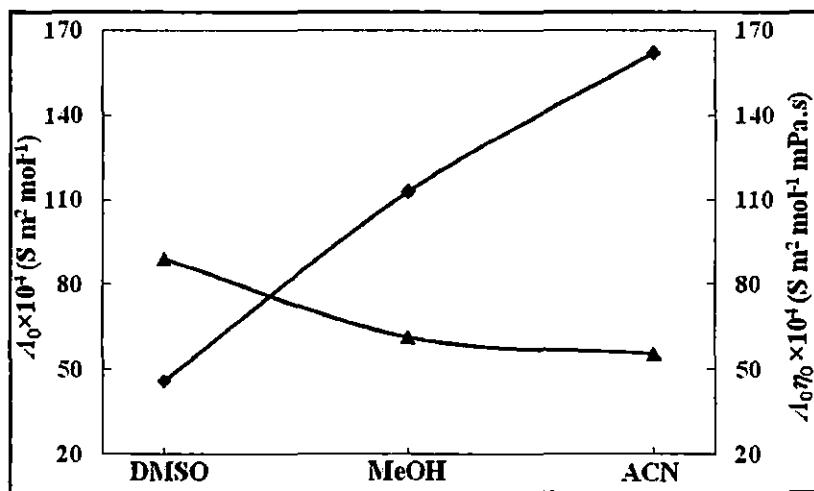
**Figure 1.** Plots of molar conductance,  $\Lambda$ , and the square root of concentration ( $\sqrt{c}$ ), of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$  (—▲—),  $\text{CH}_3\text{OH}$  (—■—), DMSO (—◆—) at  $T = 298.15$  K



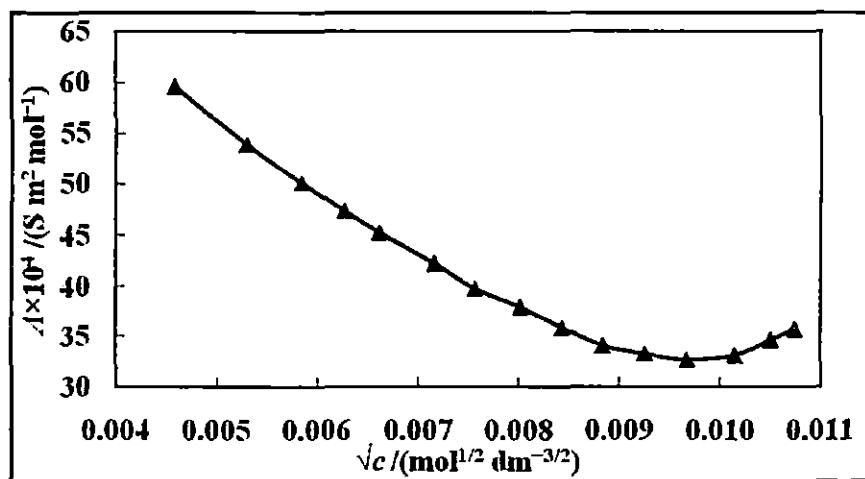
**Figure 2.** Plots of values of Gibbs energy change,  $\Delta G^\circ$ , (—◆—) and Association constant,  $K_A$ , (—▲—) of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$  and DMSO 298.15 K



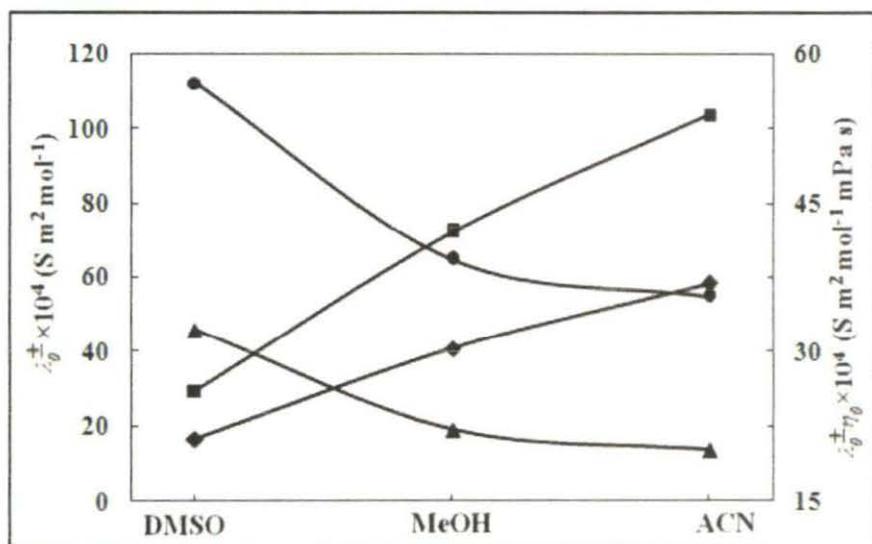
**Figure 3.** Plots of values of limiting molar conductivity,  $\Lambda_0$ , (—■—) and Walden Product,  $\Lambda_0\eta_0$ , (—▲—) of  $[\text{Bu}_4\text{NBF}_4]$  in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$  and DMSO at 298.15 K



**Figure 4.** Plot of values of Molar conductance ( $\Lambda$ ) and the square root of concentrations ( $\sqrt{c}$ ) of  $[\text{Bu}_4\text{NBF}_4]$  in 1,3- DO at 298.15 K

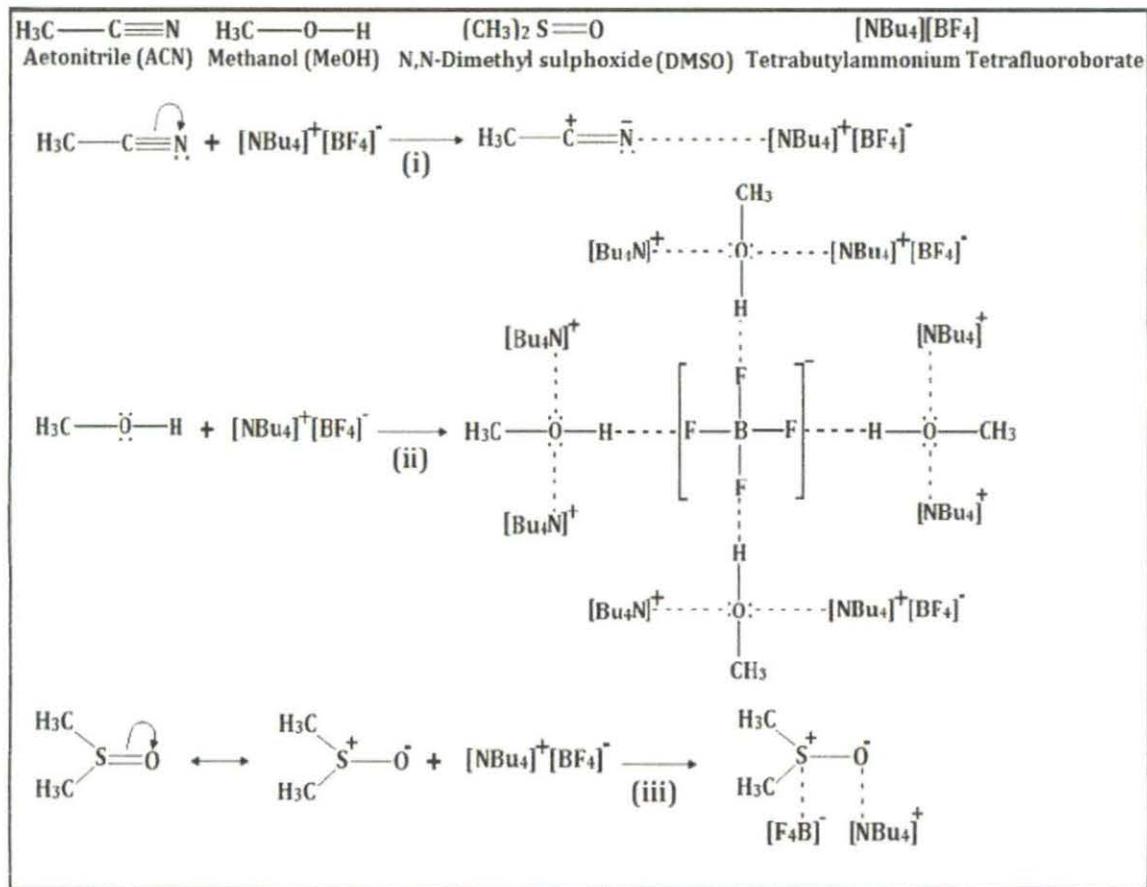


**Figure 5.** Plots of values of limiting ionic conductance,  $\lambda_0^\pm$ , for  $[\text{Bu}_4\text{N}]^+$  (—◆—), for  $[\text{BF}_4]^-$  (—■—) and ionic Walden product,  $\lambda_0^\pm \eta_0$ , for  $[\text{Bu}_4\text{N}]^+$  (—▲—), for  $[\text{BF}_4]^-$  (—●—), in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$  and DMSO at 298.15 K respectively.

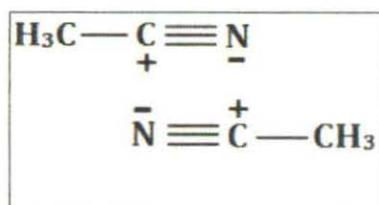


## SCHEMES

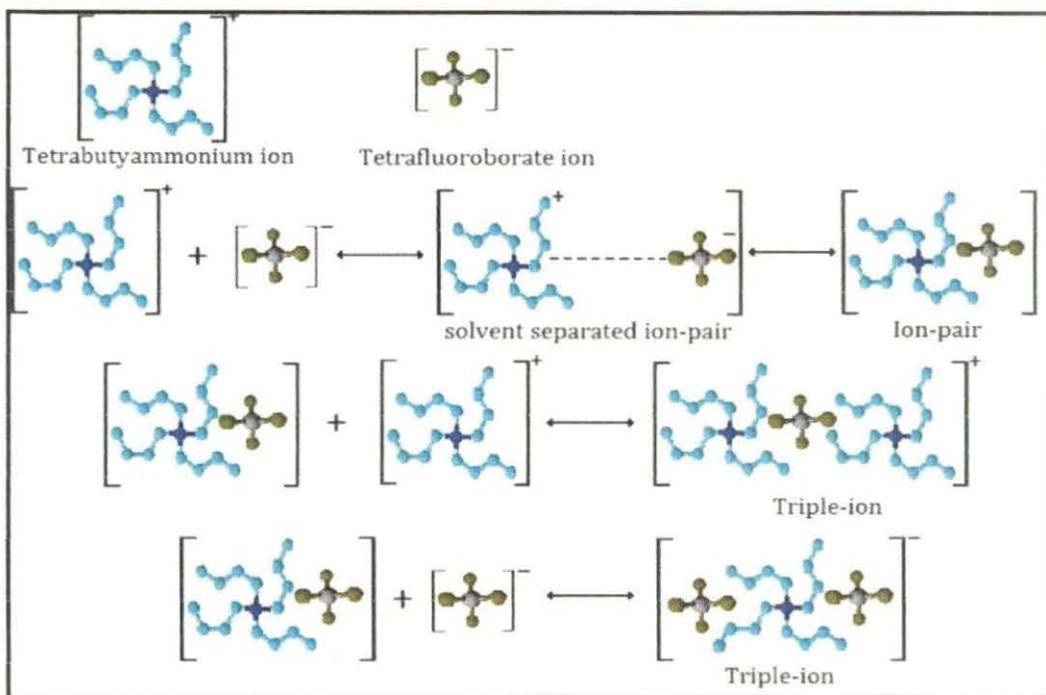
**Scheme 1.** The Schematic Representation of ion-solvation, for the particular ion in the studied solvents.



**Scheme 2.** Dimerization of Acetonitrile ( $\text{CH}_3\text{CN}$ ).



**Scheme 3.** The pictorial representation of triple-ion formations for the electrolyte in 1,3-DO.



**Scheme 4.** The schematic representation of ion-solvation, for the particular ion in the studied solvent in view of various derived parameters.

