

## CHAPTER IV

# CONDUCTANCE AND FTIR SPECTROSCOPIC STUDY OF TRIPLE-ION FORMATION OF TETRABUTYLPHOSPHONIUM METHANESULFONATE IN METHYLAMINE SOLUTION

---

### Abstract

Triple-ion formation of Tetrabutylphosphonium Methanesulfonate [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>] in methylamine solution has been reported quantitatively by conductometric study, and the observation is evident from the qualitative analysis of FT-IR spectroscopy. The ionic liquid exists as triple-ion state in low dielectric constant solution (methylamine solution having  $\epsilon_r < 10$ ). Thus, the conductance data have been analysed using the Fuoss-Kraus theory of triple-ion formation. After that, the results have been discussed in terms of driving forces *i.e.*, H-bond formation, dipole-dipole interactions, and structural aspects (functional group) of the ionic liquid and methylamine molecules. Shifting of the stretching frequency of functional group of the solvent in presence and absence of the ionic liquid has been taken into account in FTIR spectroscopic study, and then the solvation consequences have been manifested by the change of the intensity.

### Keywords:

Conductance, FT-IR spectroscopy, Tetrabutylphosphonium methanesulfonate, Methylamine solution.

## 1. Introduction

The electrolytic behaviour of the ionic liquid, Tetrabutylphosphonium Methanesulfonate in solvents of high and intermediate or moderate dielectric constant ( $\epsilon_r > 12$ ) have been studied extensively [1], but the behaviour of this ionic liquid in solvents of very low dielectric constant ( $\epsilon_r < 12$  or 10) have not been examined before. Normally, the ions/molecules in low dielectric constant solvents are poor conductor, and the ionic/molar conductance decreases gradually with increasing the molar concentration, because the ions or molecules become engaged with another ions or molecules, through the hydrogen bond, intermolecular attraction, Van der Waals bond, electrostatic interaction etc. On the other way, the influence of the dielectric constant on conductance of ionic liquids is satisfactorily accounted for by the inter ionic attraction theory in solvents of high dielectric constant, it is not completely known to what extent inter ionic forces are primarily concerned in solvents of low dielectric constant. There are some papers in low dielectric constant solvents. [2-5] Therefore, recently we are underway to investigate the behaviour of the ionic liquid in low dielectric constant solvents.

Ionic liquids (ILs) recently have been attracted as ground-breaking compounds. For their unique intrinsic properties [6], the application is also increasing exponentially in many academic, industrial, and research field. [7,8] The applications of individual ionic liquid may be understood clearly by investigation of their nature and mode of interaction with the solvent molecules. Imidazolium, Pyridinium, Ammonium and Phosphonium based ionic liquids are commercially available in the market. Among these ionic liquids, the phosphonium based ionic liquids exhibit high thermal stability. The chosen ionic liquid is also a phosphonium based ionic liquid having great thermal stability. We can apply this ionic liquid as conducting material if we closely study the conductometric behaviour and salvation consequences. The employed ionic liquid contain the functional anionic group ( $[\text{CH}_3\text{SO}_3]^-$ ), which are capable of interacting with polar solvents through the driving forces, like H-bonding, dipole-dipole interaction, dipolar ionic/charge-charge, Van der Waals forces etc. [9,10]

In continuation of our investigations on ionic conductance, in the present study, an attempt has been made to ascertain the nature of ion-association of

**\*Published in Chemical Methodologies 4 (2020) 55-67**

tetrabutylphosphonium methanesulfonate [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>] in methylamine solution. The solvation consequence have been explained with the evidence of shifting of the stretching frequency of characteristic bonds in FT-IR spectroscopy in presence and absence of the [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>].

## 2. Experimental Section

### 2.1 Materials

Tetrabutylphosphonium methanesulfonate [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>] was selected for the present work, puriss grade was procured from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of [Bu<sub>4</sub>PMS] was  $\geq 0.98$ . The methylamine solution is 40% wt. in H<sub>2</sub>O of spectroscopic grade was purchased from Sigma-Aldrich, Germany and used as purchased. The experimentally observed physical properties of methylamine solution are given in Table 1.

### 2.2 Apparatus and Procedure

Before the start of the experimental work we have checked the solubility of the chosen ionic liquid which was freely soluble in methylamine solution. The mother solution of the ionic liquid was prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003g), and then the specific conductance of the working solutions, was obtained by mass dilution method of the mother solution.

Instrumentally, the conductance measurements was carried out in a Systronics-308 conductivity bridge (accuracy  $\pm 0.01\%$ ), using a dip-type immersion conductivity cell (CD-10) having a cell constant of approximately  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . Measurements were carried out in a thermostat water bath by maintaining the temperature (T) =  $298.15 \pm 0.01\text{K}$ . The cell was calibrated by the method proposed by Lind et al.[11] and cell constant was measured based on 0.01M aqueous KCl solution. During the conductance measurements, cell constant was maintained within the range  $(1.10-1.12) \times 10^{-2} \text{ cm}^{-1}$ . The conductance data were reported at a frequency of 1 kHz and the accuracy of  $\pm 0.3\%$ .

For analysing the conductance data, the density and viscosity of the solvent mixture are required. Therefore, the density ( $\rho$ ) was measured with the help of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with a precision of  $\pm 0.00005 \text{ g cm}^{-3}$  maintained at  $\pm 0.01 \text{ K}$  of the desired temperature. It was calibrated by triply-distilled water and passing dry air. The viscosity ( $\eta$ ) was measured using Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The viscosities were obtained using the following relation

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

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  $\text{CaCl}_2$  solutions.[12] The temperature was maintained to within  $\pm 0.01^\circ\text{C}$  using Brookfield Digital TC-500 thermostat bath. The viscosity was measured with an accuracy of  $\pm 1 \%$ . The measurement reported is an average of triplicate reading with a precision of 0.3 %.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described. [13] The concentration of the studied solutions used in the IR study is 0.05M.

## 3. Results and Discussion

### 3.1 Conductance

The experimentally measured specific conductance ( $\kappa$ ) of the solutions have been utilized to determine the molar conductances ( $\Lambda$ ) by the equation (El-Dossoki, 2010),

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

The calculated values of molar conductances ( $\Lambda$ ) with corresponding molar concentrations ( $c$ ) are presented in Figure IV.1. However, the non-linearity in Figure 1, has been found in the conductance curves plotting with square root of molar concentration. In case of the solvent having low relative permittivity ( $\epsilon_r < 10$ ), as methylamine solution,  $\epsilon_r = 9.35$ , the ionic liquid showing the similar fashion of

**\*Published in Chemical Methodologies 4 (2020) 55-67**

conductivity curve, i.e., the conductance data gradually falling with rising the molar concentration; arrived at a minimum and then again increasing. The reason of the divergence of the conductometric curves from linearity, have been analysed by the classical Fuoss-Kraus theory of triple-ion formation [14-16] in the following form,

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (2)$$

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

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\} (1 - \Lambda / \Lambda_0)^{0.5}} \quad (3)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon_r T)^{1.5} \quad (4)$$

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon_r T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon_r T)^{0.5}} \quad (5)$$

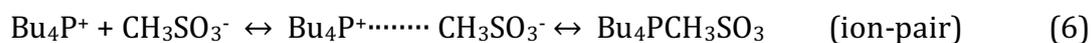
Where, the symbols have their usual meanings. In the above set of equations,  $\Lambda_0$  is representing the sum of the molar conductance of the simple ions at infinite dilution,  $\Lambda_0^T$  is the sum of the conductance value of the two existing triple-ions,  $[(\text{Bu}_4\text{P})_2(\text{CH}_3\text{SO}_3)]^+$  and  $[(\text{Bu}_4\text{P})(\text{CH}_3\text{SO}_3)_2]^-$  for the ionic liquid  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$ .  $K_p$  and  $K_T$  were the ion-pair and triple-ion formation constants respectively and  $S$  is the limiting Onsager coefficient. To make Equation (2) applicable, the symmetrical approximation of the two possible formation constants of triple-ions,

$$K_{T1} = \frac{[(\text{Bu}_4\text{P})_2(\text{CH}_3\text{SO}_3)]^+}{\{[\text{Bu}_4\text{P}^+][\text{Bu}_4\text{PCH}_3\text{SO}_3]\}} \quad \text{and,} \quad K_{T2} = \frac{[(\text{Bu}_4\text{P})(\text{CH}_3\text{SO}_3)_2]^-}{\{[\text{CH}_3\text{SO}_3^-][\text{Bu}_4\text{PCH}_3\text{SO}_3]\}}$$

equal to each other has been adopted, i.e.,  $K_{T1} = K_{T2} = K_T$  [17] and  $\Lambda_0$  values for the studied electrolyte have been calculated using the scheme as suggested by Krumgalz. [18]  $\Lambda_0^T$  has been calculated by setting the triple-ion conductance equal to  $(2/3) \cdot \Lambda_0$ . [19] The ratio  $\Lambda_0^T / \Lambda_0$  was thus set equal to 0.667 during linear regression analysis of

**\*Published in Chemical Methodologies 4 (2020) 55-67**

Equation (2). Table IV.3 showing the calculated limiting molar conductance of simple ion ( $\Lambda_0$ ), limiting molar conductance of triple ion ( $\Lambda_0^T$ ), slope and intercept from Equation (2) for  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  in methylamine solution at 298.15K. The linear regression analysis of Equation (2) for the ionic liquid with an average regression constant,  $R^2 = 0.9981$ , gives intercept and slope. These value permits to calculate the other derived parameters such as  $K_P$  and  $K_T$  listed in Table IV.4. A perusal of Table 4 and showing that the  $K_P$  is higher than  $K_T$ , indicating the major portion of the ionic liquid exists as ion-pair with a minor portion as triple-ions. The tendency of triple ion formation with respect to ion-pair, can be judged from the ratio of  $K_T/K_P$  and  $\log(K_T/K_P)$ . The ratios suggest that strong ion-association between the ions and solvent is due to the coulombic interactions as well as to covalent forces in the solution. These results are in good agreement with those of Hazra et al. [20] At very low permittivity of the solvent, i.e.,  $\epsilon_r < 10$ , electrostatic ionic interactions are very large. So, the ion-pairs attract the free cations or anions present in the solution medium and the distance of the closest approach of the ions become minimum. These results the formation of triple-ion, where the ion-pairs acquire a charged ion (cations or anions) from the solution bulk [16,21] as following,



And/or depicts as the pictorial representation in Scheme IV.1. Thus owing to the effect of ternary association [22] the non-conducting species,  $\text{Bu}_4\text{PCH}_3\text{SO}_3$ , removes some from the solution, and replaced into triple-ions that increase the conductance values; which is manifested by non-linearity observed in conductance curves.

Moreover, to understand clearly the nature of the formation of triple-ion from  $K_P$  and  $K_T$  values, we have calculated the concentration of ion-pair,  $C_P$ , and triple-ion,  $C_T$ , at minimum molar concentration ( $C_{\min}$ ) by means of the following set of equations [23],

$$\alpha = 1 / (K_P^{1/2} \cdot c^{1/2}) \quad (9)$$

$$\alpha_T = (K_T / K_P^{1/2}) c^{1/2} \quad (10)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \quad (11)$$

$$C_T = (K_T / K_P^{1/2}) c^{3/2} \quad (12)$$

Here,  $\alpha$  and  $\alpha_T$  are assigning the fraction of ion-pairs and triple-ions respectively, and  $c$  is the molar concentration. Thus, the observed values of  $C_P$ ,  $C_T$ ,  $\alpha$  and  $\alpha_T$  at minimum molar concentration ( $c_{\min}$ ) have been represented in Table IV.4. The concentration at which the conductance value reach minimum is termed as  $C_{\min}$  and the conductance value reach at  $C_{\min}$  is termed as  $\Lambda_{\min}$ . Initially, at very low concentration the free ions exists which are showing conductance value; after that on addition of ionic liquid into solvent the non-conducting ion-pair increases and the conductance values are gradually fallen. The certain concentration at which the fraction of non-conducting ion-pair species becomes maximum (i.e., all the ions are paired up) and the conductance value of ion-pair reach minimum  $\Lambda_{\min}$ . After that further addition of ionic liquid, the fraction of the triple-ion species in the solution becomes more by acquiring free movable ion by non-conducting species. As a result the values of conductance start increasing with growing up chargeable conducting triple-ion species in the studied solution media {[Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>]+methylamine solution}.

The  $K_P$  value is utilized to calculate the inter ionic distance ( $a_{IP}$ ) parameter with the aid of the Bjerrum's theory of ionic association [15,16] in the form,

$$K_P = \frac{4\pi N_A}{1000} \left[ \frac{e^2}{\epsilon_r K T} \right]^3 Q(b) \quad (13)$$

$$Q(b) = \int_2^b y^{-4} \exp(y) dy \quad (14)$$

$$b = \frac{e^2}{a_{IP} \epsilon_r K T} \quad (15)$$

Where, the symbols are of usual significance. The  $a_{IP}$  values obtained are given in Table 5. The  $Q(b)$  and  $b$  values have been calculated by the literature procedure. [15,16] The Table IV.6 reveals that the  $a_{IP}$  values for all the electrolyte lies within the range the actual ionic sizes (or crystallographic radii) varied by 2.83Å to 4.42Å. This may be due to easy penetration by the CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> ion to some extent into the void spaces between the

alkyl chain of the  $\text{Bu}_4\text{P}^+$ , as suggested by Abbott and Schiffrin. [24] Again, the  $a_{\text{IP}}$  are less in comparison with the crystallographic radii ( $r_c$ ) of  $\text{Bu}_4\text{P}^+$  is 4.42 [25] and of  $\text{CH}_3\text{SO}_3^-$  is 2.83 [26] of the  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$ , suggesting probable contact of ion-pair in solution. [27] This will cause a decrease in the degree of freedom for the cations in the ion-pair resulting in their loss of configurational entropy of the contact-pair. Generally,  $K_{\text{P}}$  values do not change significantly for quaternary phosphonium ions with the alkyl chain consisting of more than three carbon atoms. The small changes in the  $K_{\text{P}}$  may be to some extent due to the entropic contribution.

The inter ionic distance ( $a_{\text{TI}}$ ) for the triple ion can be calculated using the expressions [28],

$$K_T = \frac{2\pi N_A a_{\text{IP}}^3}{1000} I(b_3) \quad (16)$$

$$b_3 = \frac{e^2}{a_{\text{TI}} \epsilon_r K T} \quad (17)$$

$I(b_3)$  is a double integral tabulated in the literature [28] for a range of values of  $b_3$ . Since  $I(b_3)$  is a function of  $a_{\text{TI}}$ ; thus the  $a_{\text{TI}}$  values have been calculated by an iterative computer program. From Table IV.6 we can see that the  $a_{\text{TI}}$  values for the ionic liquid are greater than the corresponding  $a_{\text{IP}}$  values but are much less than the expected theoretical value  $1.5a_{\text{IP}}$ . This is probably due to repulsive forces between the two anions or cations in the triple ions  $[(\text{Bu}_4\text{P})(\text{CH}_3\text{SO}_3)_2]^-$  and  $[(\text{Bu}_4\text{P})_2(\text{CH}_3\text{SO}_3)]^+$  as suggested by Hazra et al. [23]

### 3.2 FT-IR Spectroscopy

The molecular interaction existing between the ionic liquid and the solvent molecules was qualitatively analysed with the help of FT-IR spectroscopy and used as supporting confirmation for examining bond formation (or bond breaking) owing to ion-solvent interaction. The IR spectra of the pure solvents as well as studied solutions of  $[(\text{Bu}_4\text{PCH}_3\text{SO}_3)+\text{Solvents}]$  have been studied, and the shifting of the stretching frequencies of the functional groups in presence and absence of ionic liquids within the range of wave number  $400\text{-}4000\text{ cm}^{-1}$  are given Figure IV.2. Higher interaction is seen between the molecules of  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  and methylamine in solution as evident from the values of the  $K_{\text{P}}$  obtained from the conductivity studies. Here the peaks for N-H, C-N,

**\*Published in Chemical Methodologies 4 (2020) 55-67**

and C-H bonds are at  $3448.5\text{ cm}^{-1}$  ( $3300\text{-}3500\text{ cm}^{-1}$ ),  $1285.6$  ( $1000\text{-}1360\text{ cm}^{-1}$ ), and  $2916.1$  ( $2850\text{-}2950\text{ cm}^{-1}$ ) respectively shifts to  $3553.8\text{ cm}^{-1}$ ,  $1287.3\text{ cm}^{-1}$  and  $2917.4\text{ cm}^{-1}$  when  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  is added to methylamine solution given in the Table 7.

This is due to the disruption of weak H-bonding interaction between the  $\text{CH}_3\text{NH}_2$  molecules [29] and formation of ion-dipole interaction between  $[\text{Bu}_4\text{P}]^+$  and/or  $\text{CH}_3\text{SO}_3^-$  and N-H. From the difference in shifting of frequency,  $\Delta\nu$ , in the Table IV.7, it is clear that the N-H bond of  $-\text{NH}_2$  group of  $\text{CH}_3\text{NH}_2$  is contributing to interact with the employed ions of the ionic liquid.

Thus, from the theoretical model of calculation and qualitative analysis of FT-IR spectroscopy, it is possible to state that the individual ions (central positive cation or outermost negatively charged anions) obviously interact with the methylamine solvent molecules in the studied ternary solutions.

## 4. Conclusions

The outstanding result of the triple-ion formation of the investigated ionic liquid, tetrabutylphosphonium methanesulfonate in methylamine solution ( $\text{CH}_3\text{NH}_2$ ) with the help of conductivity has been obtained. The tendency of the triple-ion formation depends on the size and the charge distribution of the ions, and functional group of the solvents. The qualitative analysis from FTIR spectroscopy has confirmed the same observation.

## Acknowledgement

The authors would like to thank Prof. M. N. Roy, Department of Chemistry, University of North Bengal for his valuable suggestions, encouragements; and Department of Chemistry, Siliguri College, for providing instrumental facilities to continue this research work.

## TABLES

■ **Table IV.1.** The density ( $\rho$ ), viscosity ( $\eta$ ) and relative permittivity ( $\epsilon_r$ ) value of methylamine solution at  $T = 298.15$  K<sup>a</sup>

$\rho \times 10^{-3}(\text{kg m}^{-3})$		$\eta$ (mPa s)		$\epsilon_r$
Expt	Lit	Expt	Lit	
0.89703	0.89700 <sup>b</sup>	0.59	-	9.35 <sup>c</sup>

<sup>a</sup>standard uncertainties  $u$  are  $u(\rho) = \pm 5 \times 10^{-5} \text{ kg m}^{-3}$ ,  $u(\eta) = \pm 0.02 \text{ mPa s}$ , and  $u(T) = \pm 0.01 \text{ K}$

<sup>b</sup>Catalogue of the product from Sigma Aldrich

<sup>c</sup>Ref. [30]

■ **Table IV.2.** Molar conductance ( $\Lambda$ ) with corresponding concentration ( $c$ ) of [Bu4PCH3SO3] in methylamine solution at  $T = 298.15$  K

$C \times 10^4 (\text{mol dm}^{-3})$	$\Lambda \times 10^4 (\text{S m}^2 \text{mol}^{-1})$
0.15	18.60
0.38	10.43
0.55	6.05
0.70	3.57
0.90	1.82
1.01	1.03
1.16	0.71
1.34	0.85
1.52	2.03
1.70	3.97
1.95	6.37
2.16	8.81

■ **Table IV.3.** The calculated limiting molar conductance of ion-pair ( $\Lambda_0$ ), limiting molar conductance of triple-ion ( $\Lambda_0^T$ ), slope and intercept of Eq. (2) for  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  in methylamine solution at  $T = 298.15$  K

$\Lambda_0 \times 10^4$ ( $\text{S m}^2 \text{ mol}^{-1}$ )	$\Lambda_0^T \times 10^4$ ( $\text{S m}^2 \text{ mol}^{-1}$ )	Slope $\times 10^{-2}$	Intercept
71.65	47.79	1.08	0.03

■ **Table IV.4.** The ion-pair  $K_P$ , and triple-ion  $K_T$  formation constant respectively corresponding to the minimum salt concentration ( $c_{\min}$ ) for  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  in methylamine solution at  $T = 298.15$  K

$c_{\min} \times 10^4$ ( $\text{mol kg}^{-1}$ )	$\log(c_{\min})$ / $\text{mol kg}^{-1}$	$K_P \times 10^{-4}$ ( $\text{mol m}^{-3}$ ) $^{-1}$	$K_T \times 10^{-4}$ ( $\text{mol m}^{-3}$ ) $^{-1}$	$(K_T/K_P) \times 10^4$	$\log(K_T/K_P)$
1.16	-3.94	442.20	0.47	10.72	-2.97

■ **Table IV.5.** 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  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  in methylamine solution at  $T = 298.15$  K

$c_{\min} \times 10^4$ ( $\text{mol kg}^{-1}$ )	$\Lambda_{\min} \times 10^4$	$\alpha \times 10^2$	$\alpha_T \times 10^2$	$C_P \times 10^6$ ( $\text{mol kg}^{-1}$ )	$C_T \times 10^6$ ( $\text{mol kg}^{-1}$ )
1.16	0.71	4.42	2.43	119.33	2.82

■ **Table IV.6.** Interionic distance parameter for ion-pair ( $a_{IP}$ ) and for triple-ion ( $a_{TI}$ ) in methylamine solution at  $T = 298.15$  K

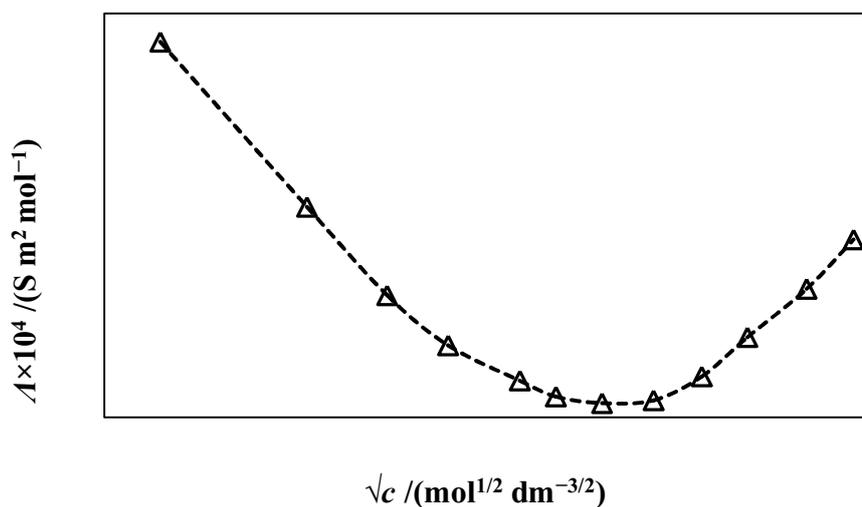
electrolyte	$a_{IP}/\text{Å}$	$a_{TI}/\text{Å}$	$1.5a_{IP}/\text{Å}$
[Bu <sub>4</sub> PCH <sub>3</sub> SO <sub>3</sub> ]	3.05	4.06	4.58

■ **Table IV.7.** Stretching frequency of the functional group of methylamine solution and change of frequency in addition of [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>]

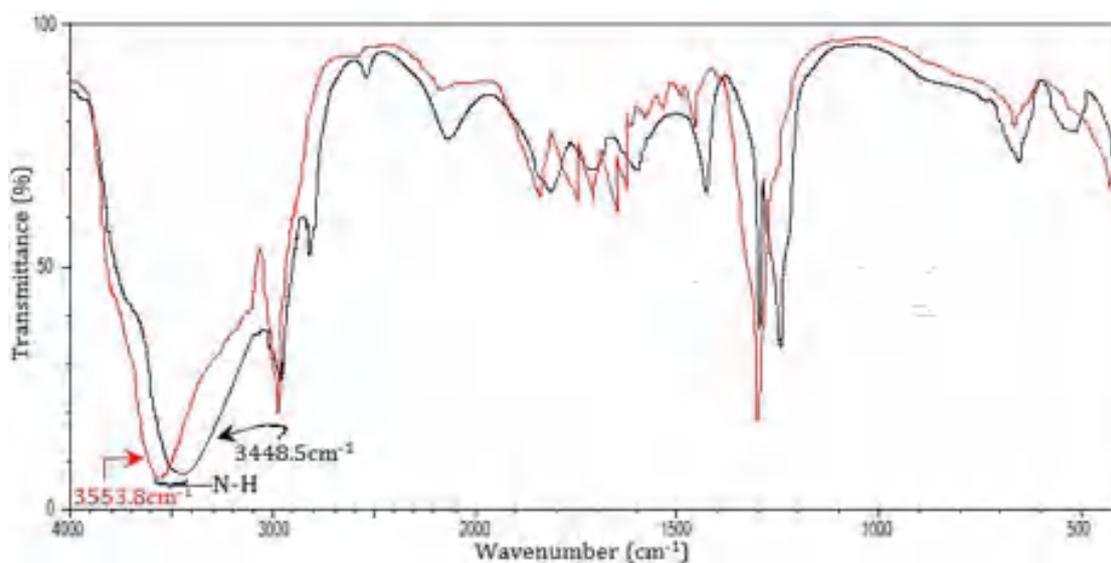
Functional Group	Range ( $\nu$ cm <sup>-1</sup> )	Pure Solvent ( $\nu_0$ cm <sup>-1</sup> )	[Bu <sub>4</sub> PMS]+Solvent ( $\nu_s$ cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )
N-H	3300-3500	3448.5	3553.8	105.3
C-N	1000-1360	1285.6	1287.3	1.7
C-H	2850-2950	2916.1	2917.4	1.3

**FIGURES**

- **Figure IV.1.** Plot of molar conductance ( $\Lambda$ ) and the square root of molar concentration ( $\sqrt{c}$ ) of  $[\text{Bu}_4\text{PCH}_3\text{SO}_3]$  in methylamine solution at  $T = 298.15\text{K}$

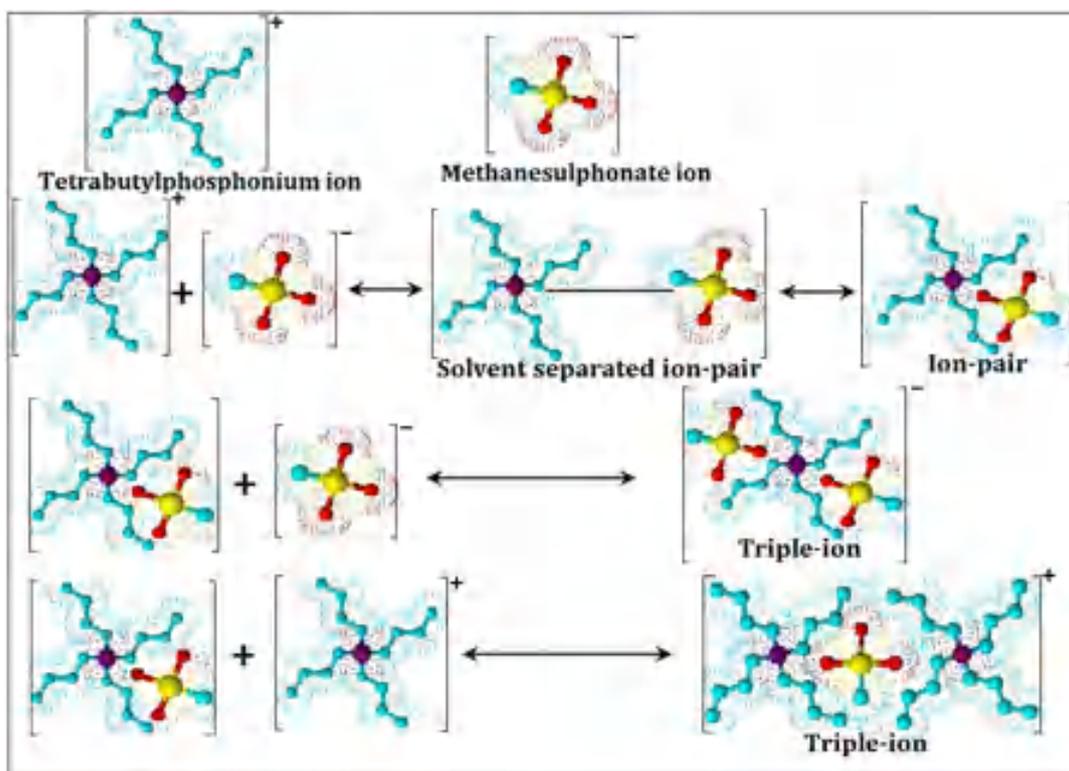


- **Figure IV.2.** Stretching frequency of N-H in methylamine solution (black solid line) and in  $\{[\text{Bu}_4\text{PMS}] + \text{CH}_3\text{NH}_2\}$  solution (red solid line) respectively

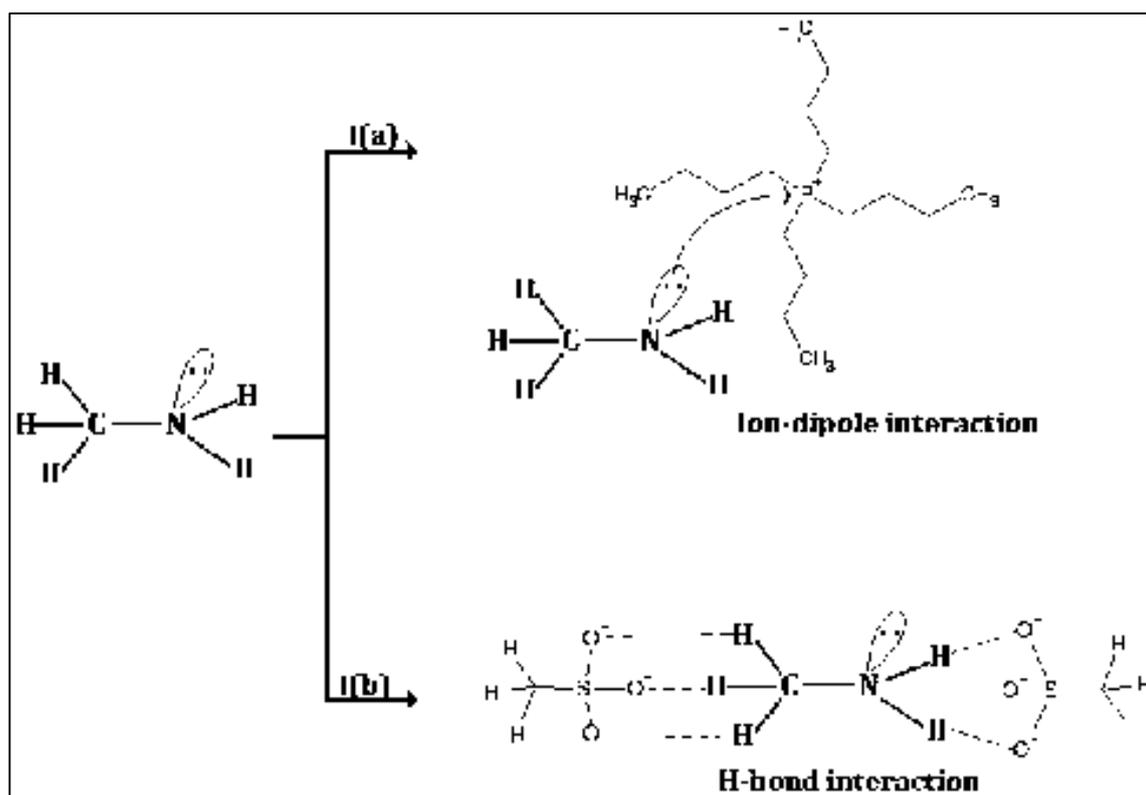


## SCHEMES

■ **Scheme IV.1.** The pictographic representation of triple-ion formations for the studied ionic liquid, as an example in methylamine solution



■ **Scheme IV.2.** The probable schematic representation of the interaction (ion-dipole, H-bond interaction) between ions of ionic liquid and methylamine molecule in solution system



### GRAPHICAL ABSTRACT

