

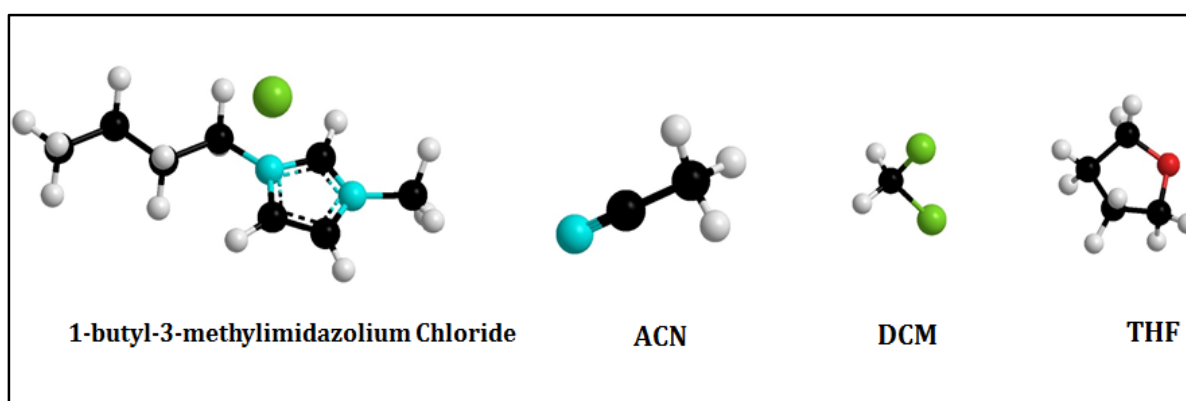
CHAPTER-VI

INVESTIGATION ON SOLVATION BEHAVIOR OF AN IONIC LIQUID (1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE) WITH THE MANIFESTATION OF ION ASSOCIATION PREVAILING IN DIFFERENT PURE SOLVENT SYSTEMS

VI.1. INTRODUCTION

Ionic liquids (IL) presently experience important consideration in many areas of chemistry. There is competition to find a proper niche for these materials, and also more insight is needed. The most attractive property is the “tunability” of the physical and chemical properties of ILs by varying structure. There are several reviews available on different aspects of ILs [1]. Ionic liquids (ILs) have attracted significant attention over the last two decades, as many of them have a negligible vapour pressure, exceptional thermal and electrochemical stability, favorable dissolution properties with many organic/inorganic compounds, and low flammability [2, 3]. ILs, which may consist of a diverse variety of cations and anions, have been widely investigated for a variety of applications including biphasic systems for separation, solvents for synthetic and catalytic applications [4], lubricants [5, 6], lithium batteries [7-9], supercapacitors [10–12], actuators [13,14], reaction media [15] replacement of conventional solvents [3], and active pharmaceutical ingredients [15]. Importantly, IL properties can be tailored for specific chemical or electrochemical applications by tuning the combination of cations and anions to achieve the desired thermodynamic, solvating, and transport properties, as well as safety. In the modern technology, the application of the ionic liquid is well understood by studying the ionic solvation or ion association. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions [16-19] which in turn depends on the solvent properties such as viscosity and the relative permittivity. These properties support in determining the extent of ion association and the solvent-solvent interactions. The non-aqueous arrangement has been of enormous prominence [20, 21] to the technologist and theoretician as numerous chemical processes ensue in these systems.

In this study, we have investigated on conductometric properties of the ionic liquid [IL] 1-butyl-3-methylimidazolium chloride [bmim][Cl] in polar aprotic solvents acetonitrile (ACN), tetrahydrofuran (THF), dichloromethane (DCM) at different temperatures 298.15 K, 303.15 K and 308.15 K. The experimental data was analyzed using Fuoss conductance equation and Fuoss–Kraus theory to calculate the ion pair formation constant K_p and triple ion formation constants K_T . The main purpose of this study is to obtain experimental and quantitative information for the interactions between the ions. Here the ion pair formation constants are expected to reflect strongly the direct interactions between the ions. The structure of the IL and solvents are presented in **Scheme VI.1**.



Scheme VI.1: Molecular structures of the IL and the solvents.

VI.2. EXPERIMENTAL SECTION

VI.2.1 Reagents

The IL [bmim][Cl] (purity $\geq 98\%$) was obtained from Sigma-Aldrich, Germany and the IL was preserved in vacuum desiccator containing anhydrous P_2O_5 and any water content of the solvents was removed by using molecular sieves.

The solvents ACN, THF, and DCM were procured from Merck, India. The solvents were further purified by standard methods [22]. The purity of the solvents were checked by measuring its density and viscosity which were in good agreement with the literature values [23, 24] as shown in **Table VI.1**. The purities of the solvents were $\geq 99.5\%$.

VI.2.2 Instrumentations

All the stock solutions of the IL in considered solvents were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003 g). In case of conductometric study the working solutions were achieved by mass dilution of the stock solutions.

Temperature of the solution was maintained to within ± 0.01 K using Brookfield Digital TC-500 temperature thermostat bath. The viscosities were measured with an accuracy of $\pm 1\%$. Each quantity reported herein is an average of triplicate reading with a precision of 0.3%.

The conductance values were obtained by using Systronics-308. Measurements were made 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. [25] and cell constant was calculated based on 0.01 (M) aqueous KCl solution. During the conductance measurements, cell constant was maintained within the range 1.10–1.12 cm^{-1} . The conductance data were reported at a frequency of 1 kHz and the accuracy was $\pm 0.3\%$. During all the measurements, uncertainty of temperatures were ± 0.01 K.

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

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

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

Where RPM= speed, TK (0.09373)= viscometer torque constant and SMC (0.327)= spindle multiplier constant, respectively. The instrument was standardized against the standard viscosity samples provided with the instrument, water and aqueous CaCl_2 solutions [26]. The viscosities were measured with an accuracy of $\pm 1\%$.

Fourier transform infrared spectra (FT-IR) were recorded in a Perkin Elmer FT-IR spectrometer. The spectra were acquired in the frequency range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with a total of 10 scans. The concentration of the studied solutions used in the IR study was 0.05 M.

VI.3. RESULTS AND DISCUSSION

VI.3.1 Electrical Conductance

VI.3.1.1 Ion-pair formation:

The formation of ion pair in ACN have been explored from the conductivity studies of [bmim][Cl] by using the Fuoss conductance equation [27]. The physical properties solvent are given in **Table VI.1**. The molar conductance (Λ) for all studied system was calculated using suitable equation [28].

Table VI.1: Density (ρ), viscosity (η) and relative permittivity (ϵ) of the different solvents Acetonitrile, Tetrahydrofuran and Dichloromethane.

Temp./K	$\rho^a \cdot 10^{-3}/\text{kg m}^{-3}$	$\eta^b/\text{mPa s}$	ϵ
Acetonitrile			
298.15	0.78597	0.36	35.94
303.15	0.78278	0.35	35.01
308.15	0.77996	0.34	34.30
Tetrahydrofuran			
298.15	0.88599	0.48	7.58
303.15	0.88591	0.45	7.24
308.15	0.88586	0.41	7.09
Dichloromethane			
298.15	1.32571	0.43	8.93
303.15	1.31852	0.41	8.84
308.15	1.30955	0.39	8.73

^a Uncertainty in the density values: $\pm 0.00001 \text{ g cm}^{-3}$

^b Uncertainty in the viscosity values: $\pm 0.03 \text{ mPa s}$

The plot of molal conductivity, Λ , versus the square root of the molal concentration, \sqrt{m} , gives a linear conductance curves for the solvent with higher to moderate relative permittivity ($\epsilon_r = 35.95$ to 14.47), shown in **Figure VI.1** and the values are listed in the **Table VI.2**. Extrapolation of $\sqrt{m} = 0$ evaluated the starting limiting molar conductances for the electrolyte [29].

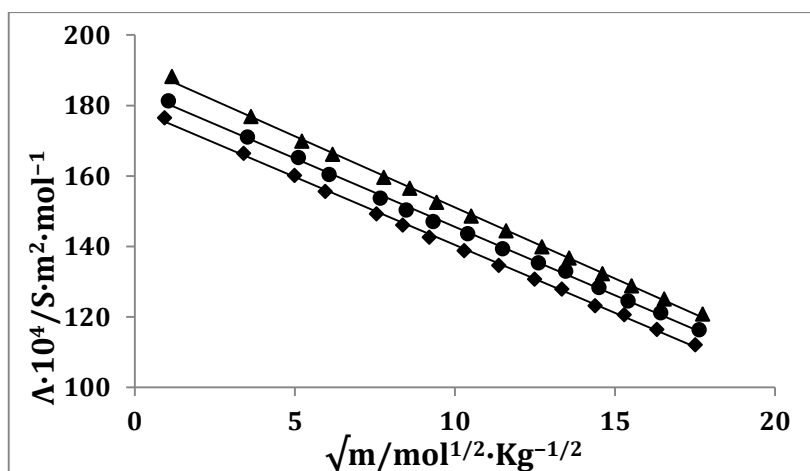


Figure VI.1: Plot of molar conductance (Λ) versus \sqrt{m} of [bmim][Cl] in ACN at 298.15 K (◆), 303.15 K (●) and 308.15 K (▲).

Table VI.2: The concentration (m) and molal conductance (Λ) of [bmim][Cl] in Acetonitrile, Dichloromethane and Tetrahydrofuran at 298.15 K, 303.15K and 308.15K respectively.

$m \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
Acetonitrile		Dichloromethane		Tetrahydrofuran	
298.15 K					
0.87	176.54	8.97	41.77	0.95	40.11
11.58	166.42	10.74	39.95	1.60	38.48
24.95	160.14	13.06	37.68	2.83	37.13
35.44	155.66	15.15	36.2	4.07	36.10
57.00	149.3	17.64	34.67	6.22	34.76
70.02	146.04	19.85	33.29	7.79	33.96
84.63	142.6	22.85	31.8	10.19	32.86
105.80	138.81	25.01	30.88	13.55	31.66
129.30	134.62	27.70	29.91	15.79	31.36
156.12	130.7	33.74	27.98	17.81	30.76
177.99	127.9	39.25	26.79	20.05	30.36
206.72	123.23	46.61	26.17	22.80	30.36
233.73	120.68	53.92	26.99	25.68	30.16
266.02	116.52	60.72	28.57	29.66	31.06

306.52	112.13	66.97	31.18	34.29	33.87
303.15K					
1.10	181.36	4.63	50.59	1.06	43.96
12.40	171.07	6.28	48.32	2.18	41.26
26.14	165.28	8.13	46.13	3.59	39.46
36.86	160.46	10.43	44.22	4.97	38.06
58.79	153.67	13.22	42.31	7.33	36.41
72.00	150.37	15.94	41.03	9.03	35.51
86.81	147.06	19.51	39.12	11.59	34.77
108.23	143.67	22.45	37.61	14.19	33.89
131.99	139.38	26.01	36.52	17.04	33.3
159.07	135.36	29.35	35.72	19.66	32.66
181.15	132.99	32.26	35.03	22.00	32.52
210.12	128.42	34.70	33.99	25.05	32.2
237.34	124.58	42.13	34.22	27.89	33.06
269.87	121.16	46.64	35.91	30.55	34.96
310.65	116.36	53.03	38.92	33.42	36.46
308.15 K					
1.34	188.20	9.09	52.14	1.43	49.66
13.18	176.91	11.09	50.22	2.70	47.56
27.27	169.90	13.94	48.54	4.25	45.86
38.20	166.20	17.04	46.62	6.34	44.06
60.49	159.61	21.29	44.93	8.26	42.67
73.87	156.51	23.94	43.84	10.06	41.69
88.87	152.51	28.20	42.53	12.75	40.61
110.53	148.64	31.74	41.37	16.49	39.38
134.52	144.42	35.92	40.73	18.95	38.4
161.85	139.90	39.74	40.06	22.09	37.96
184.12	136.73	45.02	39.26	23.59	37.56
213.32	132.26	47.84	38.88	25.72	37.66
240.74	128.82	54.21	38.56	29.68	37.96
273.49	125.10	60.05	39.74	32.43	39.46
314.53	120.82	64.25	42.32	35.37	41.36

The limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R) these three adaptable parameters are derived from the following set of equations (Fuoss equation) using a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) :

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

$$P = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A m \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (4)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (6)$$

Where R_X is the relaxation field effect, E_L is the electrophoretic counter current, α is the fraction of contact pairs, γ is the fraction of solute present as unpaired ion, K_A is the overall pairing constant, f is the activity coefficient, m is the molality of the solution, β is twice the Bjerrum distance, κ is the radius of the ion atmosphere, e is the electron charge, ϵ_r is the relative permittivity of the solvent mixture, k_B is the Boltzmann constant, T is the absolute temperature, K_R is the association constant of the solvent-separated pairs and K_S is the association constant of the contact-pairs.

The computations were performed using a program suggested by Fuoss [27]. The initial Λ_0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data [30]. Input for the program is the set ($m_j, \Lambda_j, j=1, \dots, n$), n, ϵ, η, T , initial Λ_0 value, and an instruction to cover a pre-selected range of R values. The best values of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation δ for a sequence of predetermined R values, and standard deviation δ was calculated by the following equation:

$$\delta^2 = \sum [A_j(cal) - A_j(obs)]^2 / (n - m) \quad (7)$$

Where n is the number of experimental points and m is the number of fitting parameters. The conductance data were examined by fixing the distance of closest approach (R) of ions with two fitting parameter ($m = 2$). No significant minima were detected in the δ vs. R curves, whereas the R values were arbitrarily preset at the center to center distance of solvent-separated ion pair [26, 29]. Thus, R values are

assumed to be $R = (a + d)$; where $a = (r_+ + r_-)$ is the sum of the crystallographic radii of the cation (r_+) and anion (r_-) and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by Fuoss and Accascina [31].

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (8)$$

Where M is the molar mass of the solvent and ρ is its density. The values of Λ_o , K_A and R obtained by using Fuoss conductance equation for [bmim][Cl] in ACN at 298.15 K, 303.15 K and 308.15 K are represented in **Table VI.3**. The values in table shows that the limiting molar conductances (Λ_o) of [bmim][Cl] is highest in ACN (**Table VI.3**) and lowest in case of THF (Table VI.7). Thus the observed trend of the Λ_o values is ACN > DCM > THF. The observed trend of solvent Λ_o is found to be the opposite of the viscosity trend. As expected, limiting molar conductance values decrease when the viscosity of the solvents increases because ionic mobility is diminished in viscous media.

Table VI.3: Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation of [bmim][Cl] in Acetonitrile at 298.15 K, 303.15 K and 308.15 K respectively.

T/K	$\Lambda_o \cdot 10^4 / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$K_A / \text{dm}^3 \cdot \text{mol}^{-1}$	$R / \text{\AA}$	δ
298.15	178.45	725.21	8.98	3.43
303.15	191.43	641.23	8.82	3.54
308.15	199.56	571.34	8.73	3.92

Ion-solvation can also be explained with the help of another characteristic property called the Walden product ($\Lambda_o \eta$) (**Table VI.4**) [32]. Λ_o increases for the IL in ACN with increasing temperature and the $\Lambda_o \eta$ also increases even though the viscosity of the solvent decreases. This fact indicates the prevalence of Λ_o over η .

Table VI.4: Walden product ($\Lambda_0 \cdot \eta$) and Gibb's energy change (ΔG°) of [bmim][Cl] in Acetonitrile at 298.15 K, 303.15 K and 308.15 K respectively.

T/K	$\Lambda_0 \cdot \eta \cdot 10^4 /$ $S \cdot m^2 \cdot mol^{-1} mPa$	$\Delta G^\circ /$ $kJ \cdot mol^{-1}$
298.15	64.24	-16.33
303.15	67.00	-16.29
308.15	67.85	-16.26

To investigate the role of the individual IL ions in ion-solvation, we have to split the limiting molar conductance values into their ionic contributions. The ionic conductances λ_0^\pm for the [bmim]⁺ cation and Cl⁻ anion in different solvents were calculated using tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) as a 'reference electrolyte' by the method of Das et al. [33]. The ionic limiting molar conductances λ_0^\pm values for [bmim]⁺ cation and [Cl]⁻ anion has been determined in ACN solvents by interpolating conductance data from the literature [34] using cubic spline fitting and the values are given in **Table VI.5**.

Table VI.5: Limiting Ionic Conductance (λ_0^\pm), Ionic Walden Product ($\lambda_0^\pm \eta$), Stokes' Radii (r_s), and Crystallographic Radii (r_c) of [bmim][Cl] in Acetonitrile at 298.15 K, 303.15 K and 308.15 K respectively.

T/K	ion	λ_0^\pm $/S \cdot m^2 \cdot mol^{-1}$	$\lambda_0^\pm \eta$ $/S \cdot m^2 \cdot mol^{-1} mPa$	$r_s / \text{Å}$	$r_c / \text{Å}$
298.15	bmim ⁺	87.41	31.47	3.15	2.25
	Cl ⁻	99.42	35.78	2.19	1.95
303.15	bmim ⁺	89.42	31.28	3.14	2.27
	Cl ⁻	103.31	36.15	2.16	1.98
308.15	bmim ⁺	93.24	31.70	3.12	2.28
	Cl ⁻	105.84	35.99	2.12	2.03

It is observed from **Table VI.5** that a smaller limiting molar conductivity value of the [bmim]⁺ than Cl⁻ in a solvent suggests enhanced solvation of the cation in that specific medium i.e., the [bmim]⁺ cation is responsible for a greater portion of ionic

association with the solvents. Estimation of the ionic contributions to conductance is based mostly on Stokes' law, which provides valuable insight for the limiting ionic Walden product. The law 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 of the ionic radius (crystallographic radius), and thus, is a constant under normal conditions. The values of ionic conductance λ_0^{\pm} and the product of ionic conductance and viscosity of the solvent named ionic Walden product ($\lambda_0^{\pm}\eta$) along with Stokes' radii (r_s) and Crystallographic Radii (r_c) of [bmim][Cl] in ACN at different temperatures are given in **Table VI.5**.

VI.3.1.2. Thermodynamic Parameters:

The Gibbs free energy change ΔG^0 is given by the following relationship [35] and is given in **Table VI.4**.

$$\Delta G^0 = -RT \ln K_A \quad (9)$$

The negative values of ΔG^0 can be explained by considering the participation of specific covalent interaction in the ion-association process.

The variation of conductance of an ion with temperature can be treated as similar to the variation of the rate constant with temperature which is given by the Arrhenius equation [27]:

$$\Lambda_0 = A e^{E_a/RT} \quad (10)$$

$$\log \Lambda_0 = \log A - \frac{E_a}{2.303RT} \quad (11)$$

Where A is an Arrhenius constant, E_a is the activation energy of the rate process which determines the rate of movement of ions in solution. The slope of the linear plot of $\log \Lambda_0$ versus $1/T$ gives the value of E_a (**Table VI.6**).

Table VI.6: Thermodynamic parameters for [bmim][Cl] in ACN.

$\Delta G_a^0 / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_a^0 / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S_a^0 / \text{J K}^{-1}\text{mol}^{-1}$	$E_a / \text{kJ}\cdot\text{mol}^{-1}$
-16.33	-18.22	-6.35	8.55

To have a better understanding of the thermodynamics of the ion-association process, it is beneficial to consider the contributions obtained from the thermodynamic parameters. The ΔH_a^0 and ΔS_a^0 values for the ion-association process

were evaluated by applying the linear least-squares analysis according to the equation:

$$\ln K_a = -\frac{\Delta H_a^\circ}{RT} + \frac{\Delta S_a^\circ}{R} \quad (12)$$

From the slopes and intercepts of linear Plots of $\ln K_a$ vs. $\frac{1}{T}$ (**Figure VI.2**) the values of enthalpy (ΔH_a°) and entropy (ΔS_a°) of ion association process were determined and the results are also included in **Table VI.6**. Both of these two parameters have negative values. The negative values of enthalpy confirm that when ion association occurs the overall energy of the system is decreased, i.e., there is some stabilization interaction in the system, whereas negative values of entropy factor indicate that there is an ordered arrangement, i.e., ion pair formation takes place. The negative value of entropy is unfavorable for the spontaneity of the system, but this effect is overcome by higher negative value of ΔH° . The value of ΔG_a° was calculated by using equation $\Delta G_a^\circ = \Delta H_a^\circ - T \Delta S_a^\circ$. The negative values of ΔG_a° (**Table VI.6**) suggests that the ion pair formation process proceeds spontaneously.

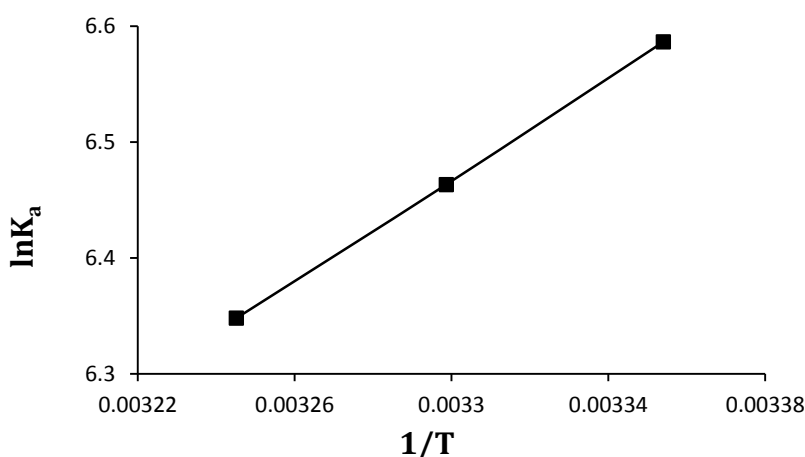


Figure VI.2: The linear relationships of $\ln K_a$ vs. $1/T$ for the ion pair formation in ACN.

VI.3.1.3 Triple-ion formation:

Figure VI.3 shows the deviations in the conductance curves from linearity which indicates the triple ion formation. The curves shows a decrease in conductance values with increasing concentration, reaches a minimum and then increases.

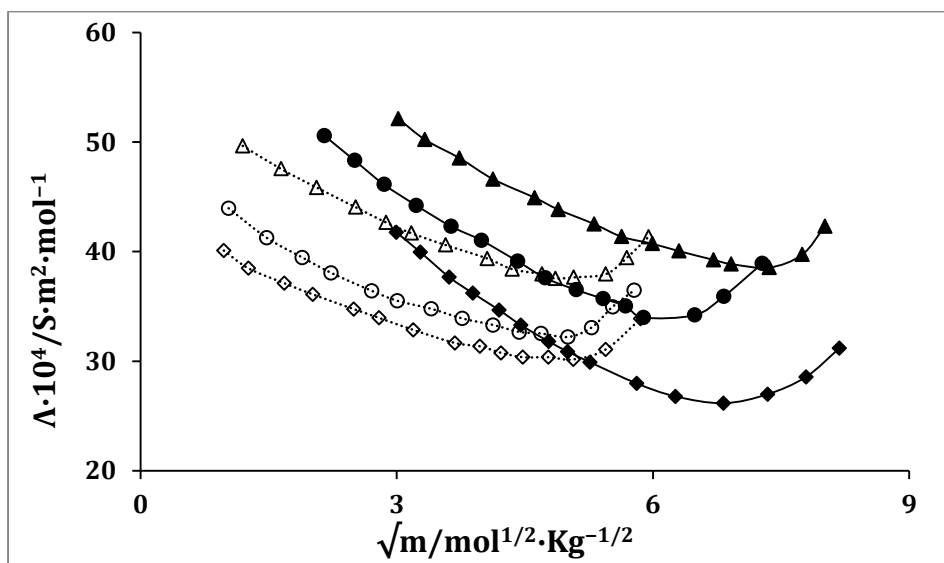


Figure VI.3: Plot of molar conductance (Λ) versus \sqrt{m} for [bmim][Cl] in DCM at 298.15 K (\blacklozenge), 303.15 K (\bullet) and 308.15 K (\blacktriangle) and in THF at 298.15 K (\diamond), 303.15 K (\circ) and 308.15 K (Δ).

The conductance data for the IL in THF and DCM have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation in the form [31, 35]:

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (13)$$

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

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\} (1 - \Lambda / \Lambda_0)^{0.5}} \quad (14)$$

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

$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta (\epsilon T)^{0.5}} \quad (16)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution, Λ_0^T is the sum of the conductance value of the two triple-ions [bmim⁺]₂Cl⁻ and bmim⁺[Cl⁻]₂. $K_P \approx K_A$ 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, $K_{T1} = \frac{[(\text{bmim}^+)_2][\text{Cl}^-]}{[\text{bmim}^+][\text{bmim}][\text{Cl}^-]}$ and $K_{T2} = \frac{[\text{bmim}][(\text{Cl}^-)_2]}{[\text{Cl}^-]}$

[[bmim][Cl]] equal to each other has been adopted, i.e. $K_{T1} = K_{T2} = K_T$ [36] and values for the studied electrolyte have been calculated following the scheme as suggested by Krumgalz [37]. Λ_0^T has been calculated by setting the triple-ion conductance equal to $\frac{2}{3} \frac{\Lambda_0^T}{\Lambda_0}$ [38].

Thus, the ratio $\frac{\Lambda_0^T}{\Lambda_0}$ was set equal to 0.667 during linear regression analysis of equation (13). The linear regression analysis of equation (13) for the electrolytes with an average regression constant, $R^2 = 0.9436$, gives intercepts and slopes. The calculated limiting molal conductance of simple ion (Λ_0), limiting molal conductance of triple ion (Λ_0^T), slope and intercept of equation (13) for [bmim][Cl] in DCM, THF at different temperature are given in **Table VI.7**.

Table VI.7: The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductances of triple ion Λ_0^T , experimental slope and intercept obtained from Fuoss-Kraus Equation for [bmim][Cl] in DCM and THF at 298.15 K, 303.15 K and 308.15 K respectively.

Solvents	$\Lambda_0 \cdot 10^4$ /S·m ² ·mol ⁻¹	$\Lambda_0^T \cdot 10^4$ /S·m ² ·mol ⁻¹	Slope × 10 ⁻²	Intercept × 10 ⁻²
298.15 K				
DCM	42.71	28.83	0.19	-5.21
THF	35.59	23.61	0.14	-6.83
303.15 K				
DCM	47.53	31.35	0.34	-5.27
THF	39.33	25.15	0.27	-6.91
308.15 K				
DCM	52.43	35.59	0.46	-5.53
THF	43.93	27.98	0.47	-7.83

We obtain K_P and K_T by applying the Fuoss-Kraus equation, the values are presented in **Table VI.8**.

Table VI.8: Salt concentration at the minimum conductivity (C_{\min}) along with the ion-pair formation constant (K_P), triple ion formation constant (K_T) for [bmim][Cl] in DCM and THF at 298.15 K, 303.15 K and 308.15 K respectively.

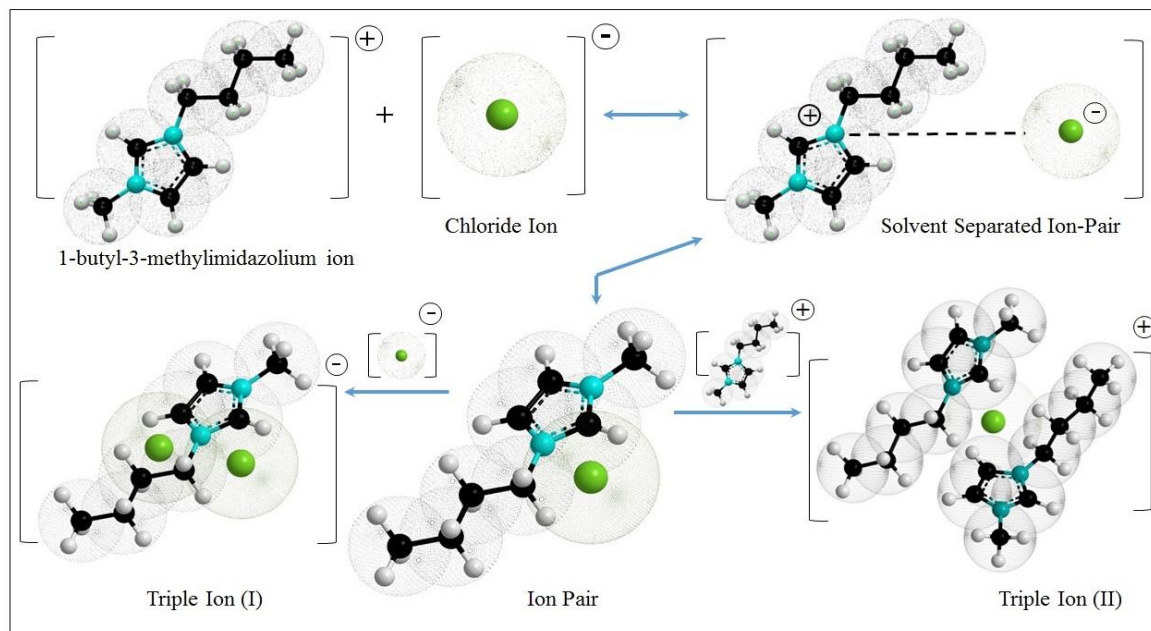
Solvents	$c_{\min} \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\log c_{\min}$	$K_P \cdot 10^2 /$ $(\text{mol} \cdot \text{dm}^{-3})^{-1}$	$K_T \cdot 10^3 /$ $(\text{mol} \cdot \text{dm}^{-3})^{-1}$	$K_T / K_P \cdot 10^5$	$\log K_T / K_P$
298.15 K						
DCM	5.31	0.7298	5.62	57.63	10.25	1.011
THF	5.25	0.7158	5.25	62.54	11.91	1.076
303.15 K						
DCM	6.36	0.8655	5.18	64.21	12.39	1.093
THF	5.38	0.7291	5.03	67.59	13.44	1.128
308.15 K						
DCM	7.12	0.8675	5.03	66.97	13.31	1.124
THF	5.51	0.7381	4.98	69.95	14.05	1.148

These values permit the calculation of other derived parameters such as K_P and K_T listed in **Table VI.8**. The values of K_P and K_T predicts that a 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 $\log (K_T/K_P)$, which are highest in THF. These ratios suggest that strong association between the ions is due to the coulombic interactions as well as covalent forces present in the solution. These results are in good agreement with those of Hazra et al. [39]. At very low permittivity of the solvent, i.e., $\epsilon < 10$, electrostatic ionic interactions are very large. So the ion-pairs attract the free cations (+ve) or anions (-ve) present in the solution medium as the distance of the closest approach of the ions becomes minimum resulting in the formation of triple-ions, which acquires the charge of the respective ions, attracted from the solution bulk [34, 35], i.e.,



Where M^+ is [bmim⁺] and A^- is [Cl⁻]. The effect of ternary association [40] 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 DCM, THF [Figure VI.3]. The pictorial representation of triple-ion formation for the selected ionic liquid ([bmim⁺][Cl⁻]) in DCM and THF solvents is depicted in Scheme VI.2.



Scheme VI.2: Pictorial representation of ion-pair and triple-ion formation for the electrolyte in diverse solvent systems.

The ion-pair and triple-ion concentrations, C_P and C_T , respectively of the IL in DCM, THF have also been calculated using the following set of equations [41]

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

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

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

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

The fraction of ion-pairs (α) and triple-ions (α_T) present in the salt-solutions are given in **Table VI.9**. The calculated values of C_P and C_T are also presented in **Table VI.9**. Comparison of the C_P and C_T values shows that the C_P is higher than C_T , indicating that the major portion of ions are present as ion-pairs even at high concentrations, and a small fraction exist as triple-ions. The conductance value decreases with increasing concentration and reach a minimum called Λ_{\min} . The concentration at

which the conductance value reaches a minimum is termed C_{\min} (**Table VI.9**); after that the fraction of triple-ions in the solution increases with the increasing concentration in the studied solution medium.

Table VI.9: Salt concentration at the minimum conductivity (c_{\min}), the ion pair fraction (α), triple ion fraction (α_T), ion pair concentration (c_P) and triple-ion concentration (c_T) for [bmim][Cl] in DCM and THF at 298.15 K, 303.15 K and 308.15 K respectively.

Solvents	$c_{\min} \cdot 10^4 / \text{mol} \cdot \text{dm}^{-3}$	$\alpha \cdot 10^{-2}$	$\alpha_T \cdot 10^2$	$c_P \cdot 10^{-3} / \text{mol} \cdot \text{dm}^{-3}$	$c_T \cdot 10^{-2} / \text{mol} \cdot \text{dm}^{-3}$
298.15 K					
DCM	6.89	14.98	57.34	0.96	3.43
THF	5.19	17.67	59.23	0.94	3.12
303.15 K					
DCM	6.86	15.21	65.24	1.56	5.45
THF	5.11	16.14	67.81	1.04	3.46
308.15 K					
DCM	6.84	18.34	71.26	1.61	5.97
THF	5.04	15.93	68.92	1.21	3.62

VI.3.2. Volumetric Properties:

The apparent molar volume (ϕ_V) and limiting apparent molar volume (ϕ_V^0) provide information regarding the solute-solvent interactions present in our systems. [42]. The apparent molal volume of the IL can be considered to be the sum of the geometric volume of the solute molecule [bmim][Cl] and changes in the solvent volume due to its interaction with the solute [43]. The values of ϕ_V of the IL (**Table VI.10**) at different concentrations were calculated using density data (**Table VI.11**) through the following equation:

$$\phi_V = M / \rho - (\rho - \rho_0) / m \rho_0 \rho \quad (24)$$

Where M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_0 are the densities of the solution and solvent, respectively.

Table VI.10: Density (ρ) and viscosity (η) of 1-butyl-3-methylimidazolium chloride in different mass fraction of Acetonitrile, Dichloromethane and Tetrahydrofuran at different temperatures.

molality/mol·kg ⁻¹	$\rho \cdot 10^{-3}/\text{kg m}^{-3}$		$\eta/\text{mPa s}$
	ACN	298.15 K	
0.0127		0.78713	0.38
0.0319		0.78893	0.40
0.0510		0.79078	0.42
0.0702		0.79267	0.43
0.0895		0.79460	0.45
0.1087		0.79656	0.46
303.15 K			
0.0128		0.78389	0.36
0.0320		0.78563	0.38
0.0513		0.78742	0.39
0.0705		0.78925	0.40
0.0899		0.79112	0.42
0.1092		0.79303	0.43
308.15 K			
0.0128		0.78101	0.35
0.0321		0.78266	0.36
0.0515		0.78437	0.38
0.0708		0.78613	0.39
0.0902		0.78792	0.40
0.1097		0.78975	0.42
DCM		298.15 K	
0.0076		1.32586	0.45
0.0189		1.32618	0.47
0.0303		1.32658	0.49
0.0417		1.32704	0.51
0.0532		1.32756	0.53
0.0647		1.32814	0.55

303.15 K		
0.0076	1.31863	0.42
0.0190	1.31890	0.44
0.0305	1.31924	0.46
0.0420	1.31965	0.47
0.0535	1.32012	0.49
0.0651	1.32074	0.51
308.15 K		
0.0076	1.30963	0.40
0.0192	1.30985	0.42
0.0307	1.31016	0.44
0.0423	1.31055	0.46
0.0539	1.31099	0.47
0.0655	1.31158	0.49
THF 298.15 K		
0.0113	0.88627	0.49
0.0283	0.88676	0.51
0.0454	0.88733	0.53
0.0626	0.88796	0.55
0.0799	0.88864	0.57
0.0972	0.88934	0.59
303.15 K		
0.0113	0.88616	0.47
0.0283	0.88662	0.50
0.0454	0.88715	0.52
0.0626	0.88774	0.55
0.0799	0.88839	0.57
0.0972	0.88907	0.59
308.15 K		
0.0113	0.88607	0.42
0.0283	0.88648	0.44
0.0455	0.88697	0.46
0.0627	0.88750	0.48
0.0799	0.88810	0.50
0.0973	0.88874	0.53

Table VI.11: Apparent molal volume (ϕ_V) and $\frac{(\eta_r - 1)}{\sqrt{m}}$ for 1-butyl-3-methylimidazolium Chloride ([bmim][Cl]) in different mass fraction of Acetonitrile, Dichloromethane and Tetrahydrofuran at different temperatures.

Molality /mol·kg ⁻¹	$\phi_V \cdot 10^6$ /m ³ ·mol ⁻¹	$\frac{(\eta_r - 1)}{\sqrt{m}}$	Molality /mol·kg ⁻¹	$\phi_V \cdot 10^6$ /m ³ ·mol ⁻¹	$\frac{(\eta_r - 1)}{\sqrt{m}}$	Molality /mol·kg ⁻¹	$\phi_V \cdot 10^6$ /m ³ ·mol ⁻¹	$\frac{(\eta_r - 1)}{\sqrt{m}}$
ACN			298.15 K			303.15 K		
0.0127	74.66	0.556	0.0128	81.35	0.286	0.0128	89.34	0.235
0.0319	71.61	0.703	0.0320	77.52	0.488	0.0321	85.49	0.409
0.0510	69.25	0.778	0.0513	74.96	0.571	0.0515	82.61	0.529
0.0702	67.26	0.829	0.0705	72.87	0.658	0.0708	80.13	0.627
0.0895	65.39	0.924	0.0899	70.95	0.756	0.0902	78.17	0.700
0.1087	63.73	0.953	0.1092	69.10	0.804	0.1097	76.29	0.807
DCM			298.15 K			303.15 K		
0.0076	120.45	0.465	0.0076	124.14	0.244	0.0076	127.28	0.256
0.0189	117.58	0.588	0.0190	120.95	0.463	0.0192	124.23	0.487
0.0303	115.36	0.698	0.0305	118.83	0.610	0.0307	121.74	0.641
0.0417	113.52	0.793	0.0420	116.90	0.666	0.0423	119.51	0.754
0.0532	111.83	0.879	0.0535	115.15	0.737	0.0539	117.68	0.804
0.0647	110.20	0.957	0.0651	113.65	0.837	0.0655	115.86	0.879
THF			298.15 K			303.15 K		
0.0113	165.55	0.208	0.0113	168.96	0.444	0.0113	173.48	0.244
0.0283	162.39	0.395	0.0283	165.12	0.675	0.0283	169.19	0.463
0.0454	159.35	0.521	0.0454	162.18	0.811	0.0455	165.86	0.610
0.0626	156.73	0.622	0.0626	159.62	0.919	0.0627	163.53	0.728
0.0799	154.43	0.709	0.0799	157.18	1.016	0.0799	161.06	0.830
0.0972	152.67	0.786	0.0972	155.21	1.075	0.0973	158.94	0.934

The values of the the apparent molar volume at infinite dilution (ϕ_V^0) and the experimental slopes (S_V^*) were determined by using leastsquares fitting of the linear plots of ϕ_V against the square root of the molar concentrations ($m^{1/2}$) using the Masson equation [44].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{m} \quad (25)$$

The calculated values of ϕ_V^0 and S_V^* are reported in **Table VI.12**.

Table VI.12: Limiting apparent molar volume (ϕ_V^0), experimental slope (S_V^*), viscosity *B*-and viscosity *A*- coefficient for [bmim[Cl] in ACN, DCM and THF at T= (298.15 to 308.15) K respectively.

Solvents	$\phi_V^0 \cdot 10^6$	$S_V^* \cdot 10^6$	<i>B</i>	<i>A</i>
	/m ³ ·mol ⁻¹	/m ³ ·mol ^{-3/2} ·kg ^{1/2}	/kg ^{1/2} ·mol ^{-1/2}	/kg ^{-1/2} ·mol ^{-1/2}
298.15 K				
ACN	80.511	-50.44	2.0710	+0.3593
DCM	125.89	-61.04	2.5905	+0.1910
THF	172.77	-64.16	3.0063	-0.0855
303.15 K				
ACN	87.607	-55.78	2.6746	+0.0371
DCM	129.6	-62.31	2.9687	-0.0252
THF	176.32	-67.25	3.3026	+0.1360
308.15 K				
ACN	96.189	-60.06	2.9162	-0.0555
DCM	133.46	-67.99	3.2438	-0.0381
THF	181.02	-70.56	3.5642	-0.1072

The plot of ϕ_V^0 values for the studied IL in different solvent systems at different temperatures has shown in **Figure VI.4**. The values of ϕ_V^0 are positive for all the systems and is highest in THF, suggesting presence of strong solute-solvent interactions in case of THF than in DCM than in ACN shown in the **Scheme VI.3**.

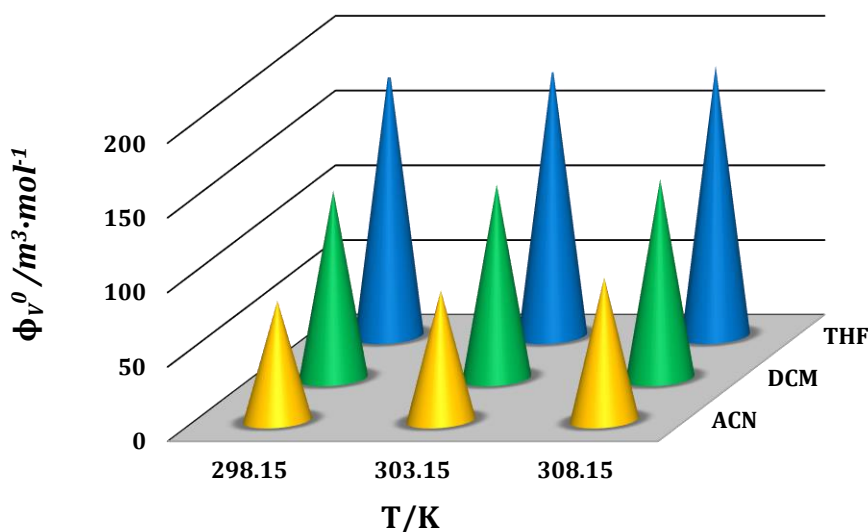
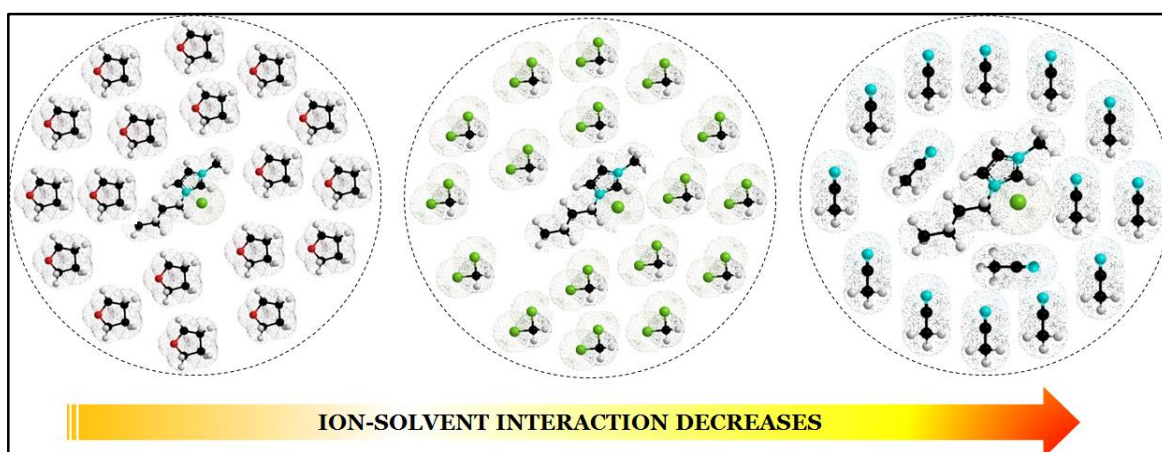


Figure VI.4: Plot of limiting apparent molal volume (ϕ_V^0) versus temperature for [bmim][Cl] in ACN (yellow), DCM (green) and THF (blue).

The values of ϕ_V^0 increases with an increase in temperature which indicates that stronger interaction occur between the IL and solvent at higher temperatures [45, 46]. Because of the release of some of the solvent molecules from loose solvation layers during the solute solvent interactions, the value of ϕ_V^0 increases with the increase in temperature.



Scheme VI.3: Extent of ion-solvent interaction of IL in various solvent systems.

The highest values of ϕ_V^0 in THF leads to lower conductance of [bmim][Cl] than in DCM and ACN as discussed in above section. The S_V^* values designate the extent of ion-ion interaction and the small values indicates the presence of less ion-ion interaction

in the medium. The degree of ion-ion interactions are highest in case of ACN and are lowest in THF. A quantitative comparison shows that the magnitude of ϕ_V^0 values is much greater than the magnitude of S_V^* values suggests that the ion-solvent interactions dominant over ion-ion interactions.

VI.3.3. Temperature dependent limiting apparent molal volume

The variation of ϕ_V^0 values with temperature can be expressed by the general polynomial equation as follows,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (26)$$

Where T is the temperature in degree kelvin and a_0 , a_1 , a_2 are the empirical coefficients and the values of these coefficients have been calculated by the least-squares fitting of apparent molar volume at different temperatures [Table VI.13].

Table VI.13: Values of empirical coefficients (a_0 , a_1 , and a_2) of Equation 26 of the [bmim][Cl] in ACN, DCM and THF.

Solvents	$a_0 \cdot 10^6$	$a_1 \cdot 10^6$	$a_2 \cdot 10^6$
	/m ³ ·mol ⁻¹	/m ³ ·mol ⁻¹ ·K ⁻¹	/m ³ ·mol ⁻¹ ·K ⁻²
ACN	2343.6	-16.451	0.0297
DCM	175.82	-1.062	0.0030
THF	2039.9	-13.12	0.0230

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

$$\phi_E^0 = (\delta\phi_V^0/\delta T)_P = a_1 + 2a_2T \quad (27)$$

Differentiation of equation 26 with respect to temperature gives the values of the limiting apparent molar expansibilities (ϕ_E^0) [Table VI.14]. These values are also employed in interpreting of the structure-making or breaking properties of various solutes. Positive expansivity i.e increasing volume with increasing temperature is a characteristic property of nonaqueous solutions of hydrophobic solvation [47].

Table VI.14: Limiting apparent molal expansibilities (ϕ_E^0) of [bmim][Cl] in ACN, DCM and THF at T= (298.15 to 308.15) K.

T/ K ^a	$\phi_E^0 \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻¹	$(\partial\phi_E^0/\partial T)_P \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻²
[bmim][Cl]+ ACN		
298.15	0.595	
303.15	0.825	0.046
308.15	1.055	
[bmim][Cl]+ DCM		
298.15	0.727	
303.15	0.757	0.006
308.15	0.787	
[bmim][Cl]+ THF		
298.15	1.259	
303.15	1.556	0.059
308.15	1.853	

^aStandard uncertainties in temperature (T) = ±0.01 K.

Hepler [48] developed a method of investigative the sign of $(\delta\phi_E^0/\delta T)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the solution using the general thermodynamic expression,

$$(\delta\phi_E^0/\delta T)_P = (\delta^2\phi_V^0/\delta T^2)_P = 2a_2 \quad (28)$$

If the sign of the second derivatives of the limiting apparent molal volume with respect to the temperature $(\delta\phi_E^0/\delta T)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [49]. It is evident from **Table VI.14** that the values for all the complexes are positive i.e. [bmim][Cl] is predominantly structure makers in all the solvent systems studied here.

VI.3.4. Viscosity B Coefficients

The experimental values of viscosity (η) measured at different temperatures for the studied systems under investigation are listed in **Table VI.11**. The relative viscosity (η_r) has been analyzed applying the Jones-Dole equation [50]

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \quad (29)$$

Where relative viscosity $\eta_r = \eta/\eta_0$, η_0 and η are the viscosities of the solvent and solution respectively, and m is the molality of the IL in the solutions. A and B are experimental constants known as viscosity A - and B -coefficients, which are specific to ion-ion and ion-solvent interactions, respectively. The values of A and B coefficients are obtained from the slope of linear plot of $(\frac{\eta}{\eta_0} - 1)/\sqrt{m}$ against \sqrt{m} (**Table VI.10**)

by least-squares method, and reported in **Table VI.12**.

The viscosity B coefficient is a measure of the effective solvodynamic volume of solvated species and depends on shape, size, and ion-ion interactions [51]. Positive values of the B -coefficient indicates the presence of strong ion-solvent interaction of the IL in the studied solvent system. This type of ion-solvent interaction arises mainly due to the hydrogen bonding of the solvent with the IL molecule and resulting in an increase in viscosity of the solution due to the large size of the moving molecules. The higher values of the B -coefficient are due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by ion-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature and follow the trend THF>DCM>ACN [**Figure VI.5**]. These observations are in excellent agreement with the conclusions drawn from the analysis of apparent molal volume, ϕ_V^0 discussed earlier.

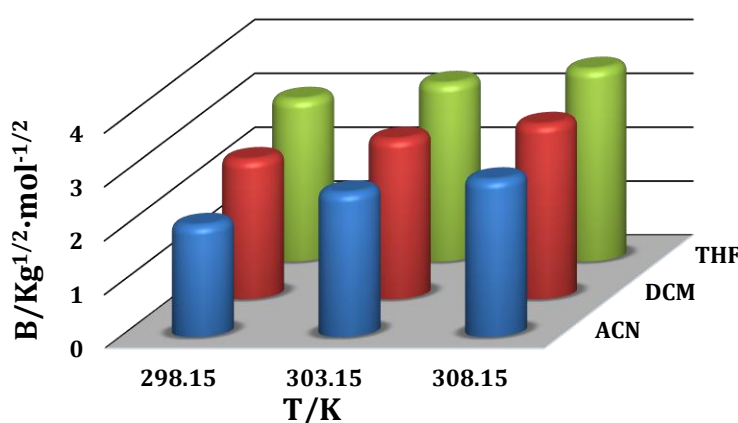


Figure VI.5: Plot of viscosity B -coefficient versus temperature for [bmim][Cl] in ACN (blue), DCM (red) and THF (green).

Thus, the volumetric and viscometric properties of the sulfa drug in the present work provide useful information in medicinal and pharmaceutical chemistry for the prediction of absorption and permeability of drug through membranes.

VI.3.5. Infrared Spectroscopy

Solvation is caused by specific interactions of functional groups. The FT-IR spectroscopy provide the supportive evidence for such type of ion-solvent interactions present in the studied solvent system. The IR spectra of the pure solvents as well as the solutions of {[bmim][Cl] + solvents} were investigated in the wave number range 400–4000 cm^{-1} and the stretching frequencies of the functional groups are given in **Table VI.15**.

Table VI.15: Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of [bmim][Cl] in the solvents.

Solvents	Functional Group	Stretching frequencies (cm^{-1})	
		Pure Solvents	Solvent + [bmim][Cl]
ACN	$\text{C}\equiv\text{N}$	2253.66	2290.64
DCM	C-Cl	746.54	736.00
THF	C-O	1069.30	1086.00

The $\nu(\text{C}\equiv\text{N})$ stretching vibrations of ACN is observed at 2253.66 cm^{-1} and this peak is shifted to 2290.64 cm^{-1} when the IL is added to ACN solvent. The shifts of the IR spectra occurs due to the disruption of the dipole–dipole interaction of acetonitrile [52] leading to the formation of ion–dipole interaction between the [bmim]⁺ ions and $\text{C}\equiv\text{N}$ bond. A sharp peak for C-O is obtained at 1069.30 cm^{-1} in case of THF and a peak for C-Cl is obtained at 746.54 cm^{-1} in DCM. After addition of IL to THF and DCM solvent these peaks are shifted to 1086 cm^{-1} and 736 cm^{-1} respectively. The observed shifts in the bands are due to the disruption of weak H-bonding interaction between the solvent molecules and formation of ion–dipole interaction between IL and solvent molecules [26].

VI.4. CONCLUSION

An extensive study was done on the ion-solvation behavioural aspect of the IL 1-butyl-3-methylimidazolium chloride in industrially-important non-aqueous polar solvents acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) with the help of conductometric, FTIR, density and viscosity measurements. From the conductometric measurements it becomes clear that the IL exists as ion-pairs in acetonitrile and as triple ions in tetrahydrofuran, dichloromethane solvents. The tendency of the ion-pair and triple-ion formation of $[\text{bmim}][\text{Cl}]$ depends on the dielectric constant of the medium. The present study revealed that this type of experimental study is being accompanied for a better understanding of the interionic interactions of ionic liquids. The evaluated values of thermodynamic functions of association suggest the spontaneity of the association process.