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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

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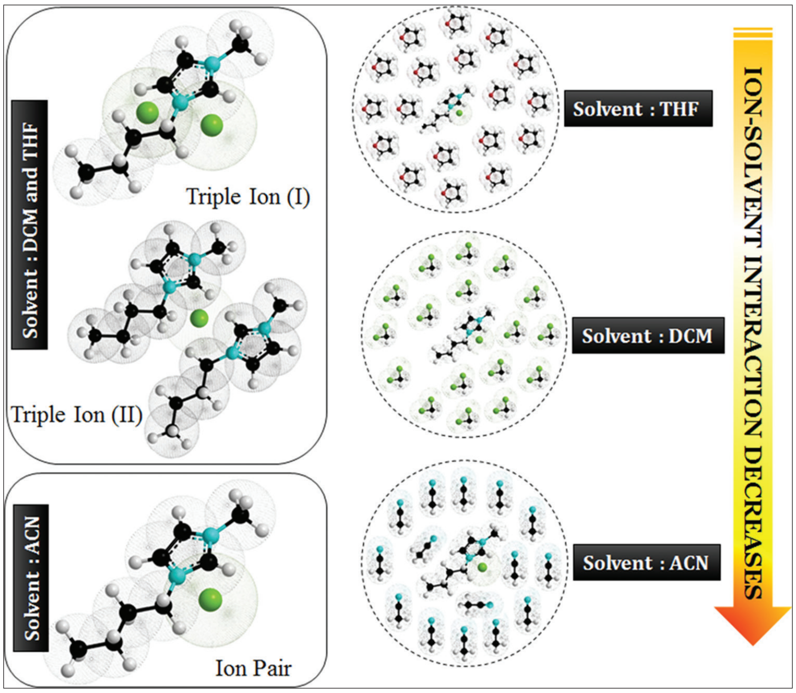
ABSTRACT

The ion-pair formation constant (K_P) and triple-ion formation constant (K_T) of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) have been determined conductometrically in different solvent media in the temperature range from 298.15 to 318.15 K. The Fuoss conductance equation (1978) for ion-formation and Fuoss–Kraus theory for triple-ion formations have been used for analyzing the conductance data. The Walden product is obtained and discussed. However, the deviation of the conductometric curves (Λ vs. $\sqrt{m}$) from linearity for the electrolyte in tetrahydrofuran and dichloromethane indicated/indicates triple-ion formation. Ion-solvent interactions have been studied with the help of density, viscosity, and Fourier transform infrared spectroscopic measurements. Apparent molar volume and viscosity B-coefficient have been calculated from experimental density and viscosity data, respectively. The limiting ionic conductances ($\lambda_o^{\pm}$) have been estimated from the appropriate division of the limiting molar conductance of tetrabutylammonium tetraphenylborate as "reference electrolyte" method.

Graphical abstract



Key words: *Ionic liquid, Ion-pair and triple-ion formation, Ion-solvent interaction, Thermodynamic parameters, Walden product.*

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1. INTRODUCTION

Ionic liquids (IL) or molten salts at room temperature presently experience significant attention 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]. ILs have attracted significant attention over the past two decades, as many of them have a negligible vapor 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 IL is well understood by studying the ionic solvation or ion association. Ionic association of electrolytes in solution depends on 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 help in determining the extent of ion association and the solvent-solvent interactions. The nonaqueous 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 IL1-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 were 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 is presented in Scheme 1.

2. EXPERIMENTAL

2.1. Materials

The IL [bmim][Cl] (purity ≥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 using molecular sieves.

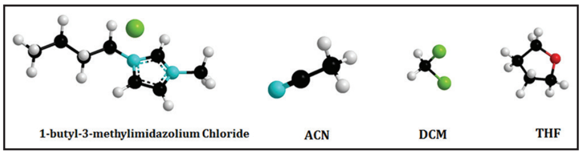
The solvents ACN, THF, and DCM were procured from Merck, India. The solvents were further purified by standard methods [22]. The purity of the solvents was checked by measuring its density and viscosity which were in good agreement with the literature values [23,24] as shown in Table 1. The purities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

2.2. Apparatus and Procedure

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 ±1%. Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.

The conductance measurements were carried out in a Systronics-308 conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity



Scheme 1: Molecular structures of the ionic liquids and the solvents.

Table 1: Density (ρ), viscosity (η) and relative permittivity (ε) of the different solvents acetonitrile, tetrahydrofuran, and dichloromethane.

Temp./K	ρ^a 10^{-3}/kg m^{-3}	η^b/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]Uncertainity in the density values: ±0.00001 g cm^{-3}.
[b]Uncertainity in the viscosity values: ±0.03 mPa s

cell, CD-10 having a cell constant of approximately (0.1±0.001) cm^{-1}. Measurements were made in a thermostat water bath maintained at T = (298.15 ± 0.01) K. The cell was calibrated by the method proposed by Lind *et al*. [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 ±0.3%. During all the measurements, uncertainty of temperatures was ±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

Table 2: The concentration (m) and molar conductance (Λ) of [bmim][Cl] in acetonitrile, dichloromethane and tetrahydrofuran at 298.15 K, 303.15 K and 308.15 K respectively.

$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·mol^{-1}	$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·mol^{-1}	$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·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
303.15 K					
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

(Contd...)

Table 2: (*Continued*).

$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·mol^{-1}	$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·mol^{-1}	$m\cdot10^4$/mol·dm^{-3}	$\Lambda\cdot10^4$/S·m^2·mol^{-1}
Acetonitrile		**Dichloromethane**		**Tetrahydrofuran**	
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

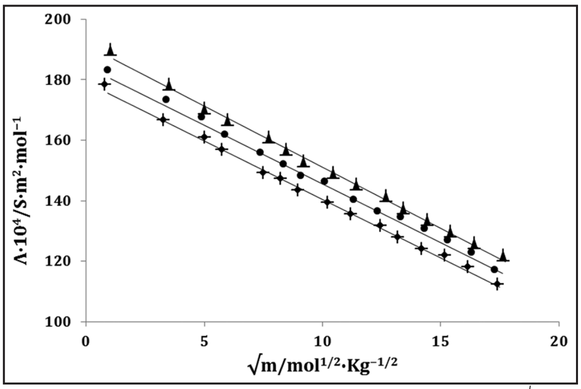


Figure 1: Plot of molar conductance (Λ) versus $\sqrt{m}$ of [bmim][Cl] in acetonitrile at 298.15 K (♦), 303.15 K (●) and 308.15 K (▲).

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.

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

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

Where RPM, TK (0.09373), and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous $CaCl_2$ solutions [26]. The viscosities were measured with an accuracy of ±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 at a resolution of 4/cm with a total of 10 scans. The concentration of the studied solutions used in the IR study was 0.05 M.

3. RESULTS AND DISCUSSION

3.1. Electrical Conductance

3.1.1. Ion-pair formation

The formation of ion-pair in ACN has been explored from the conductivity studies of [bmim][Cl] using the Fuoss conductance equation [27]. The physical properties solvent are given in Table 1. The molar conductance (Λ) for all studied system was calculated using suitable equation [28]. 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 (ε_r=35.95-14.47), shown in Figure 1, and the values are listed in Table 2. Extrapolation of $\sqrt{m}$=0 evaluated the starting limiting molar conductances for the electrolyte [29].

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, Λ_j, $j=1,\ldots,n$):

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

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

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

$$-\ln f=\beta k/2(1+kR) \quad (4)$$

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

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

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 paring 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, Λ_j, $j=1,...n$), n, ε, η, T, initial Λ_0 value, and an instruction to cover a preselected range of R values. The best values of a parameter are the one when equations are 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:

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

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 parameters (m=2). No significant minima were detected in the δ versus 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].

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

Where M is the molar mass of the solvent and ρ is its density. The values of Λ_0, 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 3. The values in Table 3 shows that the limiting molar conductances (Λ_0) of [bmim][Cl]] is highest in ACN (Table 3) and lowest in case of THF (Table 4). Thus, the observed trend of the Λ_0 values is ACN>DCM> THF. The observed trend of solvent Λ_0 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.

Ion-solvation can also be explained with the help of another characteristic property called the Walden product ($\Lambda_0\eta$) (Table 5) [32]. Λ_0 increases for the IL in ACN with increasing temperature, and the $\Lambda_0\eta$ also increases even though the viscosity of the solvent decreases. This fact indicates the prevalence of Λ_0 over η.

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 $\lambda_0^{\pm}$ for the $[bmim]^+$ cation and Cl^- anion in different solvents were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a "reference electrolyte" by the method of Das *et al.* [33]. The ionic limiting molar conductances $\lambda_0^{\pm}$ 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 6. It is observed from Table 6 that a smaller limiting molar conductivity value of the $[bmim]^+$ than Cl^- in

Table 3: Limiting molar conductance (Λ_0), association constant (K_A), cosphere 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.

Temp./K	$\Lambda_0\cdot10^4$/ $S\cdot m^2\cdot mol^{-1}$	$K_A/dm^3.\ mol^{-1}$	R/Å	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

Table 4: Thermodynamic parameters for [bmim][Cl] in ACN.

ΔG_a^0/ $kJ\cdot mol^{-1}$	ΔH_a^0/ $kJ\cdot mol^{-1}$	ΔS_a^0/ $JK^{-1}mol^{-1}$	$E_a/kJ\cdot mol^{-1}$
−16.33	−18.22	−6.35	8.55

ACN: Acetonitrile

Table 5: Walden product ($\Lambda_0\cdot\eta$) and Gibb's energy change (ΔG^0) of [bmim][Cl] in acetonitrile at 298.15 K, 303.15 K, and 308.15 K, respectively.

Temp./K	$\Lambda^0\cdot\eta\cdot10^4/S\cdot m^2\cdot mol^{-1}$ mPa	$\Delta G^0/kJ\cdot mol^{-1}$
298.15	64.24	–16.33
303.15	67.00	–16.29
308.15	67.85	–16.26

Table 6: Limiting ionic conductance ($\lambda_0^{\pm}$), 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.

Temp./K	Ion	$\lambda_0^{\pm}$/S·m^2·mol^{-1}	$\lambda_0^{\pm}\eta$/S·m^2·mol^{-1} mPa	r_s/Å	r_c/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

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 $\lambda_0^{\pm}$ 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 5.

3.1.2. Thermodynamic parameters

The Gibbs free energy change ΔG^0 is given by the following relationship [35] and is given in Table 5.

$$\Delta G^0 = -RT \ln K_A \tag{9}$$

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]:

$$\Lambda_0 = A.e^{Ea/RT} \tag{10}$$

$$\log \Lambda_0 = \log A - \frac{E_a}{2.303RT} \tag{11}$$

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 4).

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:

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

From the slopes and intercepts of linear plots of $\ln K_a$ *vs.* $\frac{1}{T}$ (Figure 2), the values of enthalpy (ΔH_a^0) and entropy (ΔS_a^0) of ion association process were determined and the results are also included in Table 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^0. The value of ΔG_a^0 was calculated using equation $\Delta G_a^0 = \Delta H_a^0 - T\Delta S_a^0$. The negative values of ΔG_a^0 (Table 4) suggest that the ion-pair formation process proceeds spontaneously.

3.1.3. Triple-ion formation

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

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]:

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

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

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

$$\beta^{/} = 1.8247 \times 10^6 / (\varepsilon T)^{1.5} \quad (15)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204\times10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \quad (16)$$

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}=[$(bmim^+)_2$][Cl]/{[$bmim^+$][bmim][Cl]} and K_{T2}=[bmim][$(Cl^-)_2$]/{[Cl^-][bmim][Cl]} equal to each other has been adopted, i.e., $K_{T1}=K_{T2}=K_T$ [36] and Λ_0 values for the studied electrolyte have been calculated following the scheme as suggested by Krumgalz [37]. Λ_o^T has been calculated by setting the triple-ion conductance equal to 2/3 Λ_0 [38].

Thus, the ratio Λ_0^T / Λ_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 molar conductance of simple ion (Λ_0), limiting molar 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 7. We obtain K_P and K_T by applying the Fuoss–Kraus equation; the values are presented in Table 5. These values permit the calculation of other derived parameters such as K_P and K_T listed in Table 8. The values of K_P and K_T predict 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

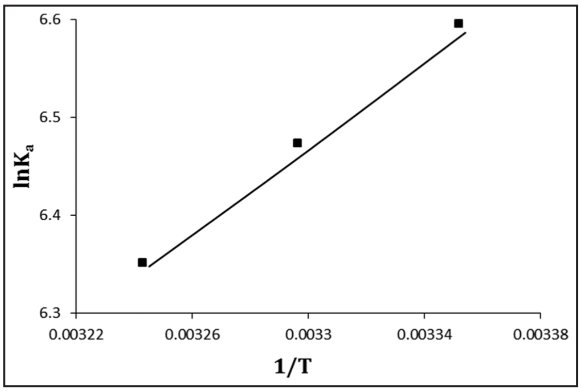


Figure 2: The linear relationships of lnKa versus 1/T for the ion-pair formation in acetonitrile.

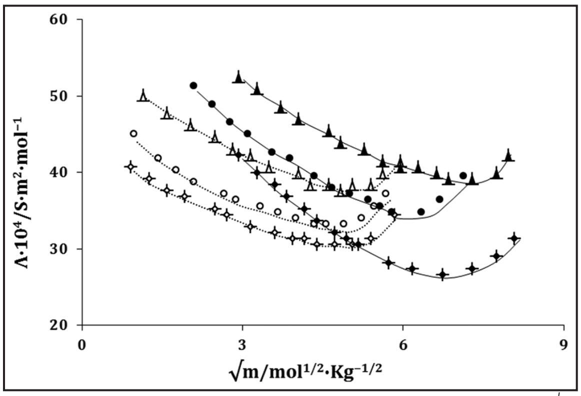


Figure 3: Plot of molar conductance (Λ) versus $\sqrt{m}$ for [bmim][Cl] in dichloromethane at 298.15 K (♦), 303.15 K (●) and 308.15 K (▲) and in tetrahydrofuran at 298.15 K (◊), 303.15 K (○) and 308.15 K (Δ).

Table 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·m²·mol⁻¹	$\Lambda_0^T \times 10^4$/S·m²·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

THF: Tetrahydrofuran, DCN: Dichloromethane solvent, i.e., ε<10, electrostatic ionic interactions are very large. Hence, 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.,

$$M^{+}+A^{-}\leftrightarrow M^{+}A^{-}\leftrightarrow MA \text{ (ion-pair)} \quad (17)$$

$$MA+A^{-}\leftrightarrow MAA^{-} \text{ (triple-ion I)} \quad (18)$$

$$MA+M^{+}\leftrightarrow MAM^{+} \text{ (triple-ion II)} \quad (19)$$

where M^+ is [bmim$^+$] and A^- is [Cl$^-$]. The effect of ternary association [40] thus removes some nonconducting 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 3). The pictorial representation of triple-ion formation for the selected IL ([bmim$^+$][Cl$^-$]) in DCM and THF solvents is depicted in Scheme 2.

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]:

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

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

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

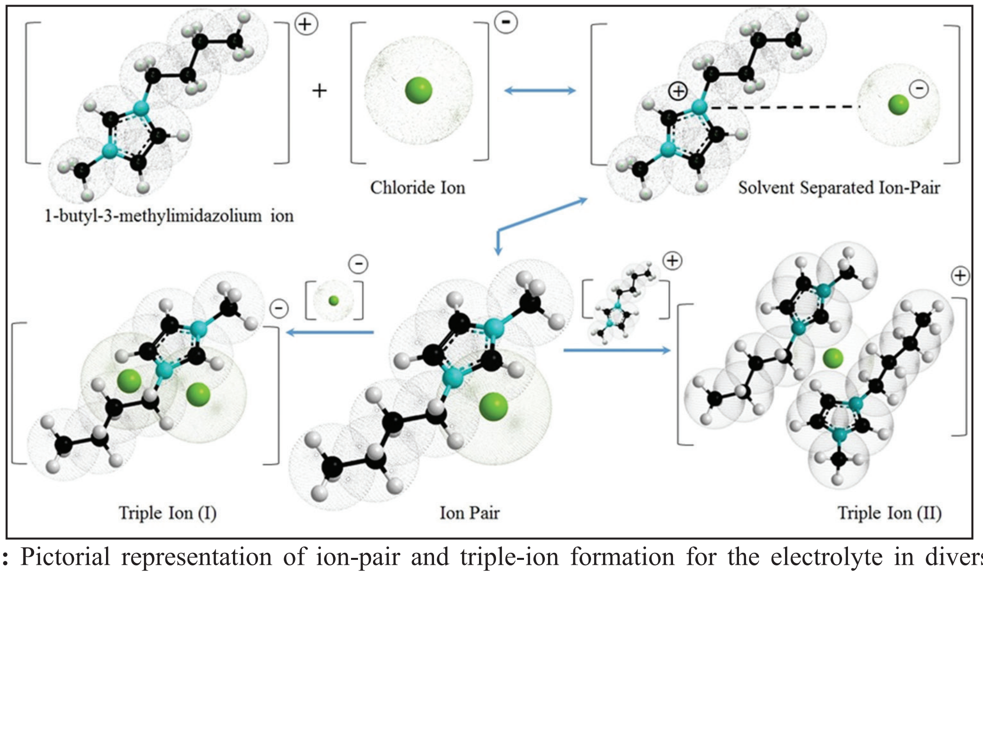
$$C_T = \left(K_T / K_P^{1/2}\right)C^{3/2} \quad (23)$$

The fraction of ion-pairs (α) and triple-ions (α_T) present in the salt solutions are given in Table 8. The

Table 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	$c_{min}\cdot 10^4$/mol·dm^{-3}	log c_{min}	K_P. 10^2/(mol·dm^{-3})$^{-1}$	K_T. 10^3/(mol·dm^{-3})$^{-1}$	K_T/K_P. 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

THF: Tetrahydrofuran, DCN: Dichloromethane



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

calculated values of C_P and C_T are also presented in Table 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 exists 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 9); after that, the fraction of triple-ions in the solution increases with the increasing concentration in the studied solution medium.

3.2. Volumetric Properties

The apparent molal 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 10) at different concentrations were calculated using density data (Table 11) through the following equation:

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

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. The values of the apparent molar volume at infinite dilution (ϕ_V^0) and the experimental slopes (S_V*) were determined using least squares 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 12. The plot of ϕ_V^0 values for the studied IL in different solvent systems at different temperatures has shown in Figure 4. The values of ϕ_V^0 are positive for all the systems and is highest in THF, suggesting the presence of strong solute-solvent interactions in case of THF than in DCM than in ACN shown in Scheme 3. The values of ϕ_V^0 increases with an increase in temperature which indicates that stronger interaction occurs 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. 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 indicate 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.

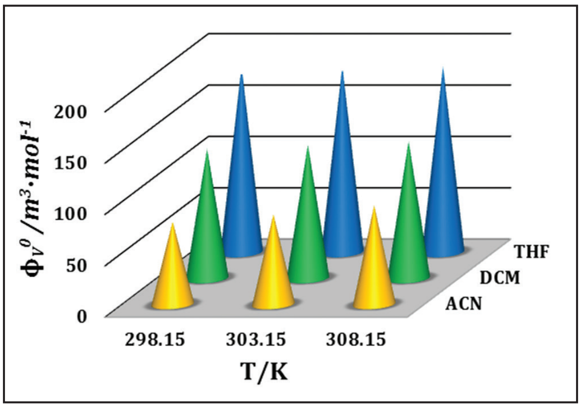


Figure 4: Plot of limiting apparent molal volume (ϕ_V^0) versus temperature for [bmim][Cl] in acetonitrile (yellow), dichloromethane (green) and tetrahydrofuran (blue).

Table 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.

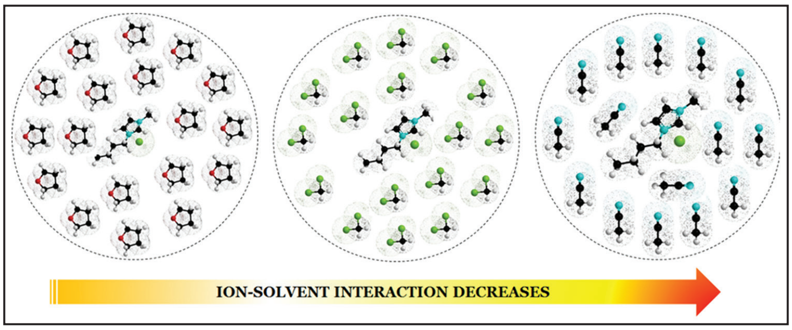
Solvents	$c_{min} \cdot 10^4$/mol·dm^{-3}	α 10^{-2}	$\alpha T \cdot 10^2$	c_P 10^{-3}/mol·dm^{-3}	$c_T \cdot 10^{-2}$/mol·dm^{-3}
298.15 K					
DCM	6.89	14.98	57.34	0.96	3.43
THF	5.19	17.67	59.23	0.94	3.12
303.15 K					
DCM	6.86	15.21	65.24	1.56	5.45
THF	5.11	16.14	67.81	1.04	3.46
308.15 K					
DCM	6.84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

THF: Tetrahydrofuran, DCN: Dichloromethane

Table 10: 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 ACN, DCM and THF at different temperatures.

Molality/ mol·kg^{-1}	ϕ_V·10^6/m^3·mol^{-1}	$\frac{(\eta_r - 1)}{\sqrt{m}}$	Molality/ mol·kg^{-1}	ϕ_V·10^6/m^3·mol^{-1}	$\frac{(\eta_r - 1)}{\sqrt{m}}$	Molality/ mol·kg^{-1}	ϕ_V·10^6/m^3·mol^{-1}	$\frac{(\eta_r - 1)}{\sqrt{m}}$
ACN	298.15 K		303.15 K			308.15 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			308.15 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			308.15 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

ACN: Acetonitrile, THF: Tetrahydrofuran, DCN: Dichloromethane



Scheme 3: Extent of ion-solvent interaction of ionic liquid in various solvent systems.

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:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (26)$$

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 13).

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

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T\right)_P = a_1 + 2a_2 T \quad (27)$$

Differentiation of Equation 26 with respect to temperature gives the values of the limiting apparent

Table 11: Density (ρ) and viscosity (η) of1-butyl-3-methylimidazolium chloride in different mass fraction of ACN, DCM, and THF at different temperatures.

Molality/mol·kg^{-1}	ρ 10^{-3}/kg m^{-3}	η/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

(Contd...)

Table 11: (*Continud*).

ACN: Acetonitrile, THF: Tetrahydrofuran,
DCN: Dichloromethane

molar expansibilities (ϕ_E^0) (Table 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].

Hepler [48] developed a technique of examining the sign of $\left(\delta\varphi_E^0/\delta T\right)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the solution using the general thermodynamic expression:

$$\left(\delta\phi_E^0/\delta T\right)_P = \left(\delta^2 \phi_V^0/\delta T^2\right)_P = 2a_2 \tag{28}$$

If the sign of the second derivatives of the limiting apparent molal volume with respect to the temperature $\left(\delta\varphi_E^0/\delta T\right)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a

Table 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=(298.15-308.15) K respectively.

Solvents	$\phi_V^0 \cdot 10^6$/m^3·mol^{-1}	$S_V^* \cdot 10^6$/m^3·mol$^{-3/2}$ ·kg$^{1/2}$	B/kg$^{1/2}$·mol$^{-1/2}$	A/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

ACN: Acetonitrile, THF: Tetrahydrofuran, DCN: Dichloromethane

Table 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	$a_0 \cdot 10^6$/m^3·mol^{-1}	$a_1 \cdot 10^6$/m^3·mol^{-1}·K^{-1}	$a_2 \cdot 10^6$/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

ACN: Acetonitrile, THF: Tetrahydrofuran, DCN: Dichloromethane

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

T/K[a]	$\varphi_E^0 \cdot 10^6$/ 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	

[a]Standard uncertainties in temperature (T)=±0.01 K. ACN: Acetonitrile, THF: Tetrahydrofuran, DCN: Dichloromethane

structure breaker [49]. It is evident from Table 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.

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 11. The relative viscosity (η_r) has been analyzed applying the Jones-Dole equation [50]:

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

Where relative viscosity $\eta_r=\eta/\eta_o$, η_o 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 $\sqrt{m}$ by least-squares method and reported in Table 10.

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 indicate 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 with 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 5). These observations are in excellent agreement with the conclusions drawn from the analysis of apparent molal volume, ϕ_V^0 discussed earlier.

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.

3.5. Infrared Spectroscopy

Solvation is caused by specific interactions of functional groups. The FT-IR spectroscopy provides 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 15. The ν(C≡N) stretching vibrations of ACN are 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 occur due to the disruption of the dipole–dipole interaction of ACN [52] leading to the formation of ion–dipole interaction between the $[bmim]^+$ ions and C≡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].

Table 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	C≡N	2253.66	2290.64
DCM	C-Cl	746.54	736.00
THF	C-O	1069.30	1086.00

ACN: Acetonitrile, THF: Tetrahydrofuran, DCN: Dichloromethane

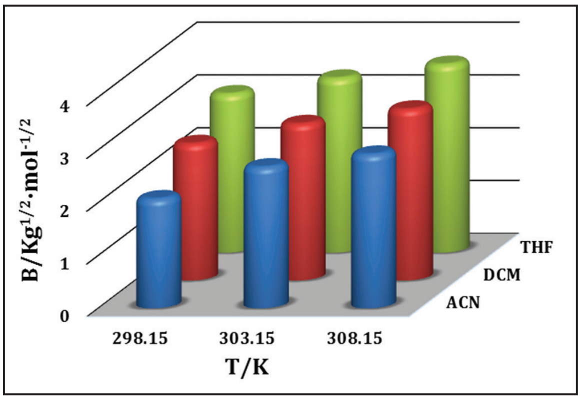


Figure 5: Plot of viscosity B-coefficient versus temperature for [bmim][Cl] in acetonitrile (blue), dichloromethane (red), and tetrahydrofuran (green).

4. CONCLUSIONS

An extensive study was done on the ion-solvation behavioral aspect of the IL 1-butyl-3-methylimidazolium chloride in industrially-important nonaqueous polar solvents ACN (CH_3CN), DCM (CH_2Cl_2) and THF (C_4H_8O) with the help of conductometric, FT-IR, density and viscosity measurements. From the conductometric measurements, it becomes clear that the IL exists as ion-pairs in ACN and as triple ions in THF, DCM solvents. The tendency of the ion-pair and triple-ion formation of [bmim][Cl] depends on the dielectric constant of the medium. This study revealed that this type of experimental study is being accompanied for a better understanding of the interionic interactions of ILs. The evaluated values of thermodynamic functions of association suggest the spontaneity of the association process.

5. ACKNOWLEDGMENTS

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