Study of Solvation Consequences of 1-Butyl-1-Methylpyrrolidinium Bromide and Chloride Prevailing in Protic Solvent System

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ABSTRACT

Electrolytic conductivities, densities, viscosities, and Fourier transform infrared (FTIR) studies of 1-buty-1-methyl pyrrolidiniumbromide ([BMPyrr][Br]) and 1-butyl-1-methylpyrrolidiniumchloride ([BMPyrr][Cl]) have been studied in methanol at different temperatures. The limiting molar conductivities, association constants, and the distance of closest approach of the ions have been analyzed using the Fuoss conductance equation (1978) for ion-pair formation. Ion-solvent interactions have been interpreted in terms of apparent molar volumes and viscosity B-coefficients which are obtained from the results of density and viscosity measurements. The limiting apparent molar volumes, experimental slopes derived from the Masson equation and viscosity A and B coefficients using the Jones–Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions respectively. The FTIR spectra for the methanol, as well as the ionic liquids in methanol have also been recorded. The experimental results have been discussed in terms of ion-dipole interactions, hydrogen bonds formation, structural aspect, and configurational theory.

Key words: Solvation consequence, Ion-pair formation, Viscosity, Density, Conductance, Fourier transform infrared spectra.

1. INTRODUCTION

In many academic and industrial research areas, ionic liquids (ILs) have been considered as attractive compounds for extensive studies due to their unique properties, such as ability to dissolve variety of chemicals, wide liquids range, negligible vapor pressure, high thermal stability, large electrochemical window and their potential as "designer solvents" and "green" replacements of volatile organic solvents used in reaction involving inorganic, organic and bio-catalysis, etc., [1-3]. They are also used in solar cells and battery industries as a heat transfer fluids and current conducting liquids respectively [4-6]. These types of application are better understood by the solvation phenomena and ionic association behavior of salts in diverse solvent systems.

On the other hand, to examine the nature, mode and magnitude of ion-ion, ion-solvent interactions in non-aqueous solution systems are of great importance to industrialists, technologists and theoreticians as many chemical reactions occurs in these solvent systems [7].

The physical properties such as melting point, density, viscosity, and hydrophobicity or hydrophilicity can be

customized by replacing the cations and anions [8] of the studied ILs. Polar anionic functional groups (here, Br$^-$ and Cl$^-$) are able to interact with polar solvents. Owing to their diversity of structural and chemical properties they are capable to participate in most types of interactions, i.e. H-bonding, ion-dipole, dipole-dipole, van der Waals forces [9,10].

Our present work is mainly focused on the comparative study of solvation consequences of ILs 1-butyl-1-methylpyrrolidiniumbromide ([BMPyrr] [Br]) and 1-butyl-1-methylpyrrolidiniumchloride ([BMPyrr][Cl]) in methanol at different temperatures. To ascertain this interaction phenomena Fourier transform infrared (FTIR) spectroscopic technique is also used in this study.

2. EXPERIMENTAL

2.1. Source and Purity of Samples

The ILs selected for this work puriss grade were procured from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of the ILs were ≥0.99.

Spectroscopic grade methanol was procured from Sigma-Aldrich, Germany and used as purchased. The

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mass fraction of purity of the methanol was 0.995. The purity of the solvent was checked by measuring the density, viscosity and conductivity values, which was in good agreement with the literature values as shown in Table 1.

2.2. Apparatus and Procedure

All the stock solutions of the electrolytes (ILs) in studied solvent were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003 g). The working solutions were obtained by mass dilution of the stock solutions.

The specific conductance of ILs were measured by a systronics-308 conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell, CD-10, with a cell constant of approximately (0.1 ± 0.001) cm^{-1}. Measurements were carried out in a thermostat water bath maintaining a deviation of ±0.01 K from the experimental temperatures. The cell was calibrated by the method proposed by Lind et al. [11] and cell constant was measured based on 0.01 M aqueous KCl solution. During all the measurements, cell constant was maintained within the range of 1.10-1.12 cm^{-1}. The conductance data were reported at a frequency of 1 kHz and the accuracy was ±0.3%.

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

The viscosities were measured using a Brookfield DV-III ultra-programmable rheometer with spindle size-42 fitted to a Brookfield digital bath TC-500. The viscosities were obtained using the following equation.

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

Where, RPM, TK (0.09373) and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant respectively. It was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous CaCl$_2$ solutions [12]. Temperature of the experimental solution was maintained ±0.01°C using Brookfield Digital TC-500 thermostat bath. Viscosities were measured with an accuracy of ±1%. Each measurement

Table 1: Density (ρ), viscosity (η) and relative permittivity (ε) of the solvents at different temperatures.

Solvent	Temp (K)	ρ 10^{-3}/kg m^{-3}	η/mPas	ε
Methanol	293.15	0.79159	0.594	32.70
	303.15	0.78180	0.507	-
	313.15	0.77232	0.449	-

reported herein is an average of triplicate reading with a precision of 0.3%.

Infrared spectra of ILs in methanol were recorded in 8300 FTIR spectrometer (Shimadzu, Japan). The details of the instrument have already been described [5].

3. RESULTS AND DISCUSSION

The solvent properties are given in Table 1. The concentrations and molar conductance (Λ) of ILs in Methanol at different temperatures are given in Table 2. Conversions of specific conductance (κ) to molar conductance (Λ) have been done by using the following equation.

$$\Lambda = (10^3 \, \kappa)/c \tag{1}$$

Linear curve (Λ vs. $\sqrt{c}$) was obtained and extrapolation of $\sqrt{c}$=0 evaluated the initial limiting molar conductance for the electrolyte at infinite dilution shows in Figure 1.

3.1. Ion-pair Formation

The ion-pair formation in case of conductometric study of [BMPyrr] [Br] and [BMPyrr][Cl] in Methanol are analyzed using the Fuoss conductance (6) equation. The equation was used for analyzing the linear variation conductance data in higher or moderate relative permittivity solvents. For a given set of conductivity values (c_j, Λ_j; j=1…….n), three variable parameters, i.e. Λ_0, K_A, and R have been derived from the said equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance, i.e. the maximum center to center distance between the ions in the solvent separated ion-pairs. There is no precise method [8] for determining the R value but in order to treat the data in our system,
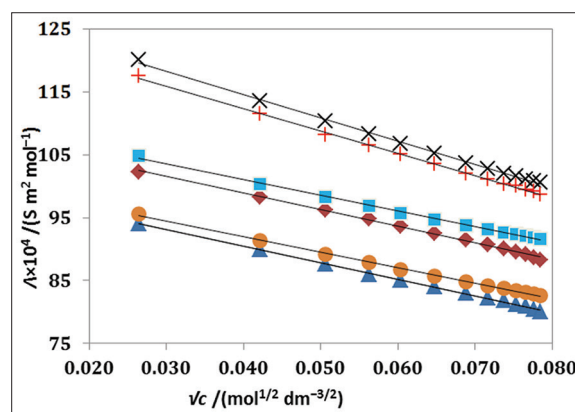

Figure 1: Plot of molar conductance ($\wedge$) versus $\sqrt{C}$ of 1-butyl-1-methylpyrrolidiniumbromide in methanol at 293.15K (▲), 303.15K (◆), 313.15K (+) and 1-butyl-1-methylpyrrolidiniumchloride in methanol at 293.15K (●), 303.15K(■), 313.15K (×).

Table 2: The concentration (c) and molar conductance (Λ) of [BMPyrr][Br] and [BMPyrr][Cl] in methanol at 293.15, 303.15, 313.15 K respectively.

[BMPyrr][Br]		[BMPyrr][Cl]	
$c \cdot 10^4$ mol^{-1}·dm^{-3}	$\Lambda \cdot 10^4$ S^{-1}·m^2·mol^{-1}	$c \cdot 10^4$ mol^{-1}·dm^{-3}	$\Lambda \cdot 10^4$ S^{-1}·m^2·mol^{-1}
293.13 K			
6.99	94.09	6.99	95.59
17.75	90.00	17.75	91.42
25.64	87.58	25.64	89.22
31.68	86.00	31.68	87.85
36.44	85.06	36.44	86.77
41.96	84.00	41.96	85.75
47.34	83.00	47.34	84.83
51.28	82.25	51.28	84.18
54.30	81.85	54.30	83.74
56.68	81.25	56.68	83.40
58.61	80.95	58.61	83.09
60.20	80.45	60.20	82.86
61.54	80.12	61.54	82.61
303.15 K			
6.99	102.26	6.99	104.83
17.75	98.25	17.75	100.35
25.64	96.25	25.64	98.28
31.68	94.78	31.68	96.87
36.44	93.69	36.44	95.77
41.96	92.56	41.96	94.72
47.34	91.46	47.34	93.77
51.28	90.78	51.28	93.16
54.30	90.12	54.30	92.64
56.68	89.56	56.68	92.44
58.61	89.12	58.61	92.13
60.20	88.68	60.20	91.89
61.54	88.25	61.54	91.61
313.15 K			
6.99	117.5	6.99	120.15
17.75	111.52	17.75	113.52
25.64	108.21	25.64	110.32
31.68	106.56	31.68	108.25
36.44	105.12	36.44	106.80
41.96	103.56	41.96	105.25
47.34	102.01	47.34	103.72
51.28	101.12	51.28	102.74
54.30	100.35	54.30	102.08
56.68	100.12	56.68	101.57
58.61	99.45	58.61	101.18
60.20	99.15	60.20	100.83
61.54	98.65	61.54	100.58

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide,
[BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride

R value is assumed to be, R = a + d, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given in Equation 2 [9]

$$d = 1.183 \, (M/\rho)^{1/3} \tag{2}$$

Where, M is the molecular mass and ρ is the density of the solvent.

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

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \tag{3}$$

$$P = 1-\alpha(1-\gamma) \tag{4}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{5}$$

$$-\ln f = \beta\kappa / 2(1+\kappa R) \tag{6}$$

$$\beta = e^2 / (\varepsilon_r k_B T) \tag{7}$$

$$K_A = K_R / (1-\alpha) = K_R / (1+K_S) \tag{8}$$

Where, Λ_0 is the limiting molar conductance, K_A is the observed association constant, R is the association distance, R_X is the relaxation field effect, E_L is the electrophoretic counter current, k is the radius of the ion atmosphere, ε is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations were executed using the program proposed by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [13]. By putting the number of data, n, followed by ε, η (viscosity of the solvent), initial Λ_0 value, T, ρ (density of the solvent), mole fraction of the first component, molar masses, M_1 and M_2 along with c_j, Λ_j values where j=1, 2 ……. n and an instruction to cover preselected range of R values.

The best value of a parameter is the one when equations are best fitted to the experimental data corresponding to minimum standard deviation, δ, for a sequence of predetermined R values. The standard deviation, δ, was calculated by the following equation:

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n-m) \tag{9}$$

Where, n is the number of experimental points and m is the number of fitting parameters. The conductance data were evaluated by fixing the distance of closest approach R with two fitting parameters (i.e. m=2). No significant minima were observed in the curve of δ versus R for studied ILs in methanol and R values were arbitrarily preset at the center to center distance of the solvent separated ion pair. Thus, R values is assumed to be R = a + d, with terms having usual significance. The limiting ionic conductances have been calculated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate as the "reference electrolyte" method along with a numerical evaluation of ion-pair formation constants ($K_P \approx K_A$).

Finally, the corresponding 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 for both ILs at 293.15 K, 303.15 K, and 313.15 K, respectively are given in Table 3. Table 3 shows that K_A values increases with the increasing temperature for both ILs. With increasing temperature the number of free ions per unit volume decreases and hence the tendency of ion pair formation increases. The data in Table 3 reveals that the anion species dependence of the association constant of the ILs follows the order: $Br^- > Cl^-$. Considering the fact that Cl^- anion has a much smaller size, higher surface charge density and thus stronger electrostatic interaction with the cation relative to the Br^-. This suggest that the high solvation of the Cl^- anion significantly reduces its association with the cation [BMPyrr$^+$] in methanol, which shapes the order observed experimentally. The plausible solvation consequences of the ILs in methanol are depicted in Schemes 1 and 2.

The standard Gibbs free energy change of solvation, ΔG^o, for ILs in methanol is given by the following equation [14].

$$\Delta G^o = -RT \ln K_A \qquad (10)$$

The negative values of standard Gibbs free energy obtained from Table 4 reflect the consideration of participation of specific covalent interaction in the ion-association process.

Table 5 shows the value of ionic conductance ($\lambda_0^\pm$) and ionic Walden product $(\lambda_0^\pm \eta)$ (product of ionic conductance and viscosity of the solvent) along with Stokes' radii (r_s) and crystallographic radii (r_c) of ILs in methanol at different temperatures.

3.2. Apparent Molar Volume
The measured values of densities of [PMB][Br] and [PMB][Cl] in methanol at 293.15, 303.15, and 313.15 K are reported in Table 1. The densities of

Table 3: Limiting molar conductance (Λ_0), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for [BMPyrr][Br] and [BMPyrr][Cl] in methanol at 293.15 K, 303.15 K, and 313.15 K respectively.

ILs	$\Lambda_o \cdot 10^4$ $S^{-1} \cdot m^2 \cdot mol^{-1}$	$K_A/dm^3\ mol^{-1}$	R/Å	Δ
293.15 K				
[BMPyrr][Br]	99.08	54.52	9.94	0.15
[BMPyrr][Cl]	100.07	53.86	9.80	0.12
303.15 K				
[BMPyrr][Br]	107.42	56.23	9.92	0.11
[BMPyrr][Cl]	108.09	55.48	9.83	0.15
313.15 K				
[BMPyrr][Br]	123.64	60.35	9.99	0.13
[BMPyrr][Cl]	126.56	58.55	9.84	0.17

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride, ILs=Ionic liquids

Table 4: Walden product ($\Lambda_o\ \eta$) and standard Gibb's free energy change ($\Delta G°$) of [BMPyrr][Br] and [BMPyrr][Cl] in methanol at 293.15 K, 303.15 K, and 313.15 K respectively.

ILs	$\Lambda o \cdot \eta \cdot 10^4$ $S^{-1} \cdot m^2 \cdot mol^{-1}\ mPa$	$\Delta G°\ kJ^{-1} \cdot mol^{-1}$
293.15 K		
[BMPyrr][Br]	78.43	−33.24
[BMPyrr][Cl]	79.21	−33.14
303.15 K		
[BMPyrr][Br]	83.98	−33.50
[BMPyrr][Cl]	84.51	−33.39
313.15 K		
[BMPyrr][Br]	95.49	−34.08
[BMPyrr][Cl]	97.74	−33.84

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride, ILs=Ionic liquids

the electrolytes in methanol increase linearly with the concentration at the studied temperatures. For this purpose, the apparent molar volumes ϕ_v were determined from the solution densities using the following equation and the values are given in Table 6.

$$\phi_V = M/\rho - (\rho - \rho_0)/m\rho_0\rho \qquad (11)$$

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 apparent molar volumes ϕ_v were found to decrease with increasing molality (m) of ILs in solvents and increase

Table 5: Limiting ionic conductance ($\lambda_0^{\pm}$), ionic Walden product ($\lambda_0^{\pm}\eta$), stokes' radii (r_s), and crystallographic radii (r_c) of [BMPyrr][Br] and [BMPyrr][Cl] in methanol at 293.15 K, 303.15 K and 313.15 K respectively.

ILs	Ion	$\pm$ (S·m^2·mol^{-1})	$\lambda_0^{\pm}\eta$ (S·m^2·mol^{-1}mPa)	r_s (Å)	r_c (Å)
293.15 K					
[BMPyrr][Br]	BMPyrr$^+$	56.89	33.79	3.54	3.42
	Br$^-$	42.19	25.05	1.92	1.95
[BMPyrr][Cl]	BMPyrr$^+$	57.31	34.04	3.44	3.42
	Cl$^-$	42.76	25.39	1.83	1.81
303.15 K					
[BMPyrr][Br]	BMPyrr$^+$	58.17	29.49	3.54	3.42
	Br$^-$	49.23	24.95	1.86	1.95
[BMPyrr][Cl]	BMPyrr$^+$	58.27	29.54	3.44	3.42
	Cl$^-$	49.82	25.25	1.85	1.81
313.15 K					
[BMPyrr][Br]	BMPyrr$^+$	68.39	30.68	3.34	3.42
	Br$^-$	55.25	24.80	1.75	1.95
[BMPyrr][Cl]	BMPyrr$^+$	70.80	31.78	3.27	3.42
	Cl$^-$	55.75	25.03	1.90	1.81

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride, ILs=Ionic liquids
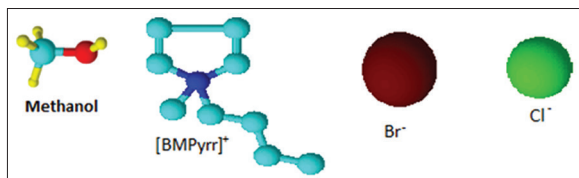
Scheme 1: "Ball and stick" representation of methanol and ions of ionic liquids.
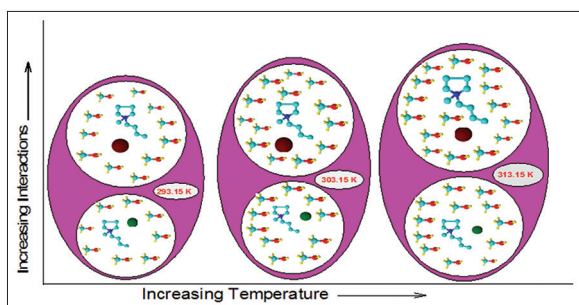
Scheme 2: Solvation consequences of ionic liquids at different temperatures.

with increasing temperature for the system under study. Which are shown in Figure 2a and b.

The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_v versus $\sqrt{c}$ using the following Masson equation [12].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \qquad (12)$$

Where, ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope.

The values of ϕ_V^0 and S_V^* are reported in Table 7. From Table 7, it is observed that ϕ_V^0 values are positive for both the ILs in solvent and is highest in case of [BMPyrr][Br] compared to [BMPyrr][Cl]. This indicate the presence of strong ion–solvent interactions and the extent of interactions increases from [BMPyrr][Cl] to [BMPyrr][Br].

On the contrary, the S_V^* indicates the extent of ion-ion interaction. The values of S_V^* show that the extent of ion-ion interaction is higher in case of [BMPyrr][Br] than [BMPyrr][Cl]. Owing to a quantitative comparison, the magnitude of ϕ_V^0 are much greater than S_V^*, in every solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that higher ion-solvent interaction in methanol leads to lower conductance of [BMPyrr][Br] than [BMPyrr][Cl], discussed earlier.

3.3. Temperature Dependent Limiting Apparent Molar Volume
The temperature dependent general polynomial equation for ϕ_V^0 are as follows:

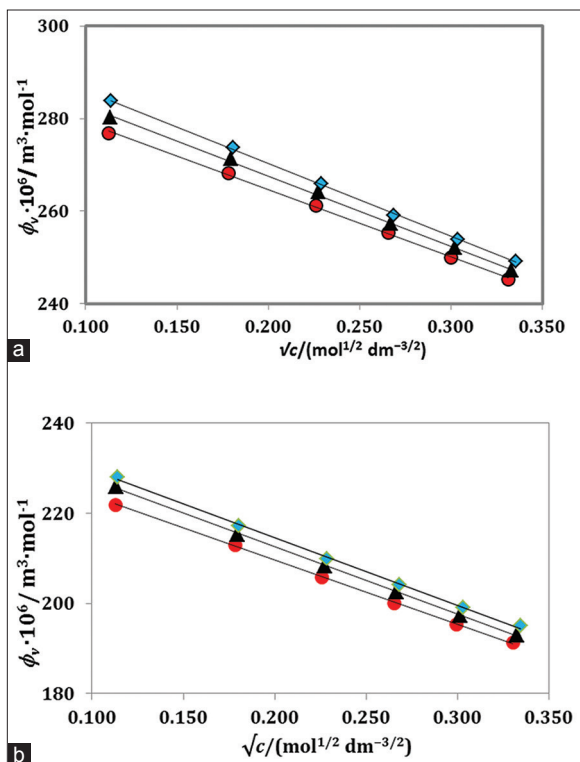$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \qquad (13)$$

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Figure 2: (a) Plot of apparent molar volume ϕ_V versus √C 1-butyl-1-methylpyrrolidiniumbromide at 293.15K (●), 303.15K (▲) and 313.15K(♦), (b) Plot of apparent molar volume (ϕ_V) versus √C at 1-butyl-1-methylpyrrolidiniumchloride at 293.15 K (●), 303.15 K (▲) and 313.15 K (♦).

Where, a_0, a_1, a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the co-solute ILs, and T is the Kelvin temperature. The values of these coefficients are presented in Table 8.

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

$$\phi_E^0 = \left(\delta\phi_V^0/\delta T\right)_P = a_1 + 2a_2 T \qquad (14)$$

Where, φ_E^0 is the change in magnitude with the change of temperature at constant pressure. The values of φ_E^0 for different solutions of the studied ILs at different Kelvin are reported in Table 9. The Table 9 reveals that φ_E^0 is positive for all the ILs in the studied solvent and studied temperatures. This fact can be ascribed to the absence of caging or packing effect for the ILs in solutions.

Helper [15] 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 mixed solvent systems using the general thermodynamic expression,
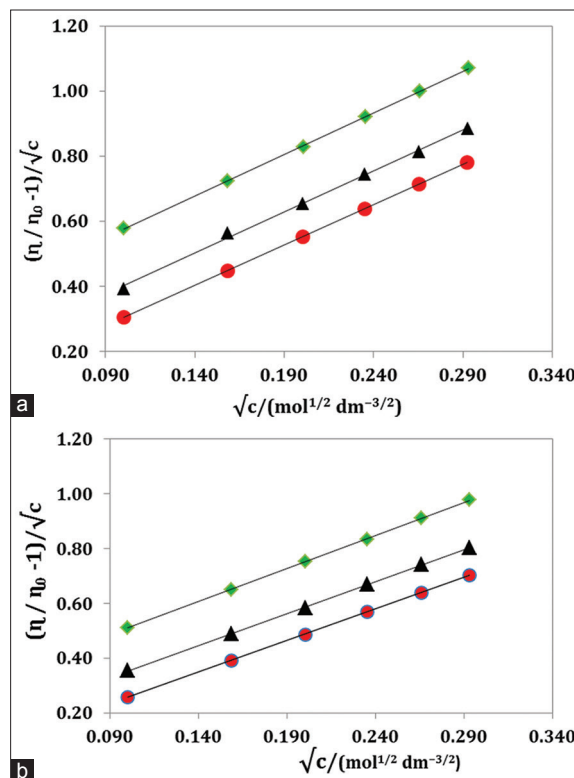

Figure 3: (a) Plot of $(\eta/\eta_0-1)/\sqrt{C}$ versus √C of 1-butyl-1-methylpyrrolidiniumbromide at 293.15 K (●), 303.15 K (▲) and 313.15 K (♦), (b) Plot of $(\eta/\eta_0-1)/\sqrt{C}$ versus √C of 1-butyl-1-methylpyrrolidiniumchloride at 293.15 K (●), 303.15 K (▲) and 313.15 K (♦).

$$\left(\delta\varphi_E^0/\delta T\right)_P = \left(\delta^2\phi_V^0/\delta T^2\right)_P = 2a_2 \qquad (14a)$$

If the sign of $\left(\delta\varphi_E^0/\delta T\right)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [16]. From Table 9 the $\left(\delta\varphi_E^0/\delta T\right)_P$ values for ILs in methanol are small negative implies predominantly that the molecules are structure makers in all of the experimental solutions.

3.4. Viscosity Calculation
The viscosity data have been analyzed using Jones–Dole equation [12].

$$\left(\eta/\eta_0 - 1\right)/\sqrt{c} = A + B\sqrt{c} \qquad (15)$$

Where, η and η_0 are the viscosities of the solution and solvent respectively. The values of A-coefficient and B-coefficient are obtained from the straight line by plotting $\left(\eta/\eta_0 - 1\right)/\sqrt{c}$ against √c which are reported in Table 6 and Figure 3. The positive value of B-coefficients indicates the ion-solvent interaction and small positive value of A-coefficients indicates the ion-ion interaction in solution.

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Table 6: Concentration, c, viscosity, η, $\dfrac{(\eta_r - 1)}{\sqrt{c}}$, viscosity A and B coefficients for [BMPyrr][Br] and [BMPyrr][Cl] in methanol at 293.15 K, 303.15 K, and 313.15 K respectively.

Salts	c mol^{-1}·dm^{-3}	η mP^{-1}·s	$\dfrac{(\eta_r - 1)}{\sqrt{c}}$	B /dm^3 · mol^{-1}	A /dm$^{3/2}$ · mol$^{-1/2}$
293.15 K					
[BMPyrr][Br]	0.010	0.61	0.306	2.473	0.057
	0.025	0.63	0.448		
	0.040	0.66	0.552		
	0.055	0.68	0.639		
	0.070	0.70	0.715		
	0.085	0.72	0.780		
[BMPyrr][Cl]	0.010	0.61	0.258	2.312	0.025
	0.025	0.63	0.391		
	0.040	0.65	0.486		
	0.055	0.67	0.571		
	0.070	0.69	0.639		
	0.085	0.71	0.704		
303.15 K					
[BMPyrr][Br]	0.010	0.52	0.394	2.509	0.152
	0.025	0.56	0.565		
	0.040	0.58	0.654		
	0.055	0.60	0.745		
	0.070	0.62	0.815		
	0.085	0.64	0.885		
[BMPyrr][Cl]	0.010	0.52	0.354	2.337	0.118
	0.025	0.54	0.489		
	0.040	0.56	0.584		
	0.055	0.58	0.669		
	0.070	0.60	0.741		
	0.085	0.62	0.804		
313.15 K					
[BMPyrr][Br]	0.010	0.47	0.577	2.551	0.320
	0.025	0.51	0.724		
	0.040	0.53	0.828		
	0.055	0.55	0.921		
	0.070	0.57	0.998		
	0.085	0.59	1.069		
[BMPyrr][Cl]	0.010	0.47	0.511	2.416	0.268
	0.025	0.50	0.652		
	0.040	0.52	0.752		
	0.055	0.54	0.835		
	0.070	0.56	0.911		
	0.085	0.58	0.978		

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride

Table 7: Concentration, c, density, ρ, apparent molar volume, ϕ_V, limiting apparent molar volume ϕ_V^0 and experimental slope for [BMPyrr][Br]and [BMPyrr][Cl]at methanol 293.15 K, 303.15 K and 313.15 K respectively.

ILs	c mol^{-1}·dm^{-3}	ρ·10^{-3} kg m^{-3}	ϕ_V ·10^6/m^3·mol^{-1}	ϕ_V^0 ·10^6/m^3·mol^{-1}	S$_V^*$ ·10^6/m^3·mol$^{-3/2}$·dm$^{3/2}$
293.15 K					
[BMPyrr][Br]	0.010	0.79162	276.87	293.60	−144.91
	0.025	0.79180	268.25		
	0.040	0.79209	261.25		
	0.055	0.79247	255.36		
	0.070	0.79295	250.06		
	0.085	0.79348	245.35		
[BMPyrr][Cl]	0.010	0.79161	221.97	238.02	−141.93
	0.025	0.79180	213.05		
	0.040	0.79216	205.89		
	0.055	0.79265	200.15		
	0.070	0.79320	195.44		
	0.085	0.79382	191.35		
303.15 K					
[BMPyrr][Br]	0.010	0.78229	280.17	297.93	−151.62
	0.025	0.78251	271.22		
	0.040	0.78288	264.19		
	0.055	0.78341	257.28		
	0.070	0.78401	252.05		
	0.085	0.78471	247.16		
[BMPyrr][Cl]	0.010	0.78227	225.89	242.5.5	−149.6
	0.025	0.78249	215.41		
	0.040	0.78285	208.31		
	0.055	0.78332	202.53		
	0.070	0.78389	197.40		
	0.085	0.78453	193.03		
313.15 K					
[BMPyrr][Br]	0.010	0.77237	283.77	301.2	−157.3
	0.025	0.77261	273.67		
	0.040	0.77301	265.97		
	0.055	0.77355	259.17		
	0.070	0.77421	253.95		
	0.085	0.77501	249.26		
[BMPyrr][Cl]	0.010	0.77235	228.09	244.6	−150.1
	0.025	0.77259	217.26		
	0.040	0.77299	209.86		
	0.055	0.77352	204.10		
	0.070	0.77419	199.10		
	0.085	0.77497	195.01		

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride, ILs=Ionic liquids

Table 8: Values of empirical coefficients (A_0, A_1, and A_2) of equation 4 for ionic liquids in methanol at 293.15-313.15 K respectively.

Solvent mixture	$a_0 \cdot 10^6$ m$^{-3} \cdot$mol^{-1}	$a_1 \cdot 10^6$ m$^{-3} \cdot$mol$^{-1} \cdot$K^{-1}	$a_2 \cdot 10^6$ m$^{-3} \cdot$mol$^{-1} \cdot$K^{-2}
MeOH+[BMPyrr][Br]			
293.15 K	−10.19	1.622	−0.002
303.15 K	−10.19	1.622	−0.002
313.15 K	−10.19	1.622	−0.002
MeOH+[BMPyrr][Cl]			
293.15 K	−960.3	7.605	−0.012
303.15 K	−960.3	7.605	−0.012
313.15 K	−960.3	7.605	−0.012

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride

Table 9: Limiting apparent molar expansibilities (ϕ_E^0) for ionic liquids in methanol at 293.15K to 313.15K respectively.

Solvent mixture	$\phi_E^0 \cdot 10^6$ m$^{-3} \cdot$mol$^{-1} \cdot$K^{-1}			$\left(\partial \phi_E^0 / \partial T\right)_P$ 10^6 m$^{-3} \cdot$mol$^{-1} \cdot$K^{-2}
MeOH+[BMPyrr][Br]				
T/K	293.15	303.15	313.15	−0.004
	0.4494	0.4094	0.3694	
MeOH+[BMPyrr][Cl]				
T/K	293.15	303.15	313.15	−0.024
	0.5694	0.3994	0.0894	

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride

From Table 6, it is clear that the values of the B-coefficient are positive and much higher than A-coefficient, thereby suggesting the solute-solvent interactions are dominant over the solute-solute interactions. The B-coefficient [17] value obtained from the viscosity measurements gives the important information regarding the extent of solvation of the solute molecules and the effects on the structure of the solvents in the local vicinity of the solute molecule in solution. The higher B-coefficient values for higher viscosity values are due to the solvated solutes molecule associated by the solvent molecules by solute-solvent interactions. These types of interactions are strengthened with rise in temperature and thus the values of B-coefficient increases with increase in temperature. These results are in good agreement with those obtained from ϕ_V^0 to S_V^* values, discussed earlier. Thus, the trend of ion-solvent interaction is [BMPyrr][Br] > [BMPyrr][Cl].

3.5. FTIR Spectroscopy

With the help of FTIR spectroscopy, the molecular interactions existing between the ILs and the methanol can be studied. At first the IR spectra of pure methanol was studied. The stretching frequencies of the key groups are given in Table 10 and Figure 4.
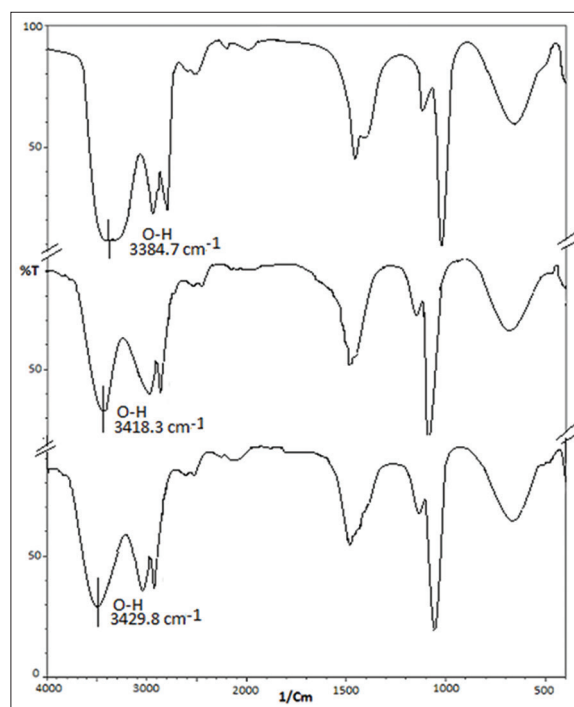
Figure 4: Infrared-spectra of, (a) Pure methanol, (b) CH$_3$OH+1-butyl-1-methylpyrrolidiniumchlorideand (c) CH$_3$OH + 1-butyl-1-methylpyrrolidiniumbromide.

Table 10: Stretching frequencies of the functional groups present in the pure methanol and change of frequency after addition of [BMPyrr][Br] and [BMPyrr][Cl] in methanol.

	Stretching frequencies (cm^{-1})		
Solvents	**Pure methanol**	**MeOH+ [BMPyrr][Br]**	**MeOH+ [BMPyrr][Cl]**
CH$_3$OH	O-H (3384.7)	O-H (3429.8)	O-H (3418.3)

[BMPyrr][Br]=1-butyl-1-methylpyrrolidiniumbromide, [BMPyrr][Cl]=1-butyl-1-methylpyrrolidiniumchloride
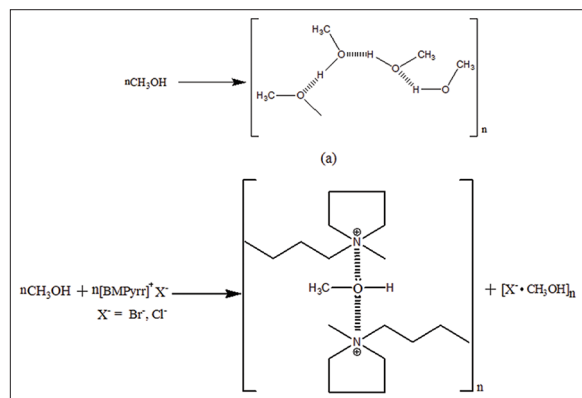
Scheme 3: Plausible polymeric association of methanol through H-bonding in path (a) and ion-dipole interaction of ionic liquids and methanol in path (b).

In case of pure methanol a broad peak is observed at 3384.7, attributed to the H-bonded O-H vibrational stretching. However, the broad peak is shifted toward the narrower peak with low intensity at 3429.8 and 3418.3 in the IR spectra of [BMPyrr][Br]+CH$_3$OH and [BMPyrr][Cl]+CH$_3$OH respectively. The shifting of frequency indicates that H-bonding between the molecules of the methanol is disrupted [18] by the addition of the ILs. This is due to the interaction of the ions of ILs (BMPyrr$^+$, Br-, Cl$^-$) with the −OH group of methanol. The plausible H-bonding interactions between methanol and ILs are shown in Scheme 3.

4. CONCLUSION

From the thorough study it is evident that the ion-solvent interaction increases for both the investigated ILs with increasing temperature. It is also pronounced that the ion-solvent interactions is greater for [BMPyrr][Br] compared to [BMPyrr][Cl] and it can be modulated by changing the anion for a particular cation in the same solvent.

5. ACKNOWLEDGMENT

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