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Effect of Additive (1-Butyl-1-methyl Pyrrolidinium Tetrafluoroborate) on Volumetric, Acoustic and Conductance Properties of Binary Aqueous Solutions of Benzylamine at T = (288.15, 298.15, 308.15, 318.15) K

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Effect of additive, 1-butyl-1-methyl pyrrolidinium tetrafluoroborate $[BmPyrr^+][BF_4^-]$ on the volumetric, acoustic and conductance properties of binary aqueous solution of benzylamine has been analyzed at equidistant temperature range using different techniques. Using density and speed of sound data, volumetric and acoustic parameters like apparent and partial molar volumes (V_ϕ and V_ϕ^0), apparent and partial molar isentropic compressions ($K_{\phi,S}$ and $K_{\phi,S}^0$), partial molar volume of transfer and partial molar isentropic compression of transfer (ΔV_ϕ^0 and $\Delta K_{\phi,S}^0$) have been calculated. Conductance parameters like molar conductance (Λ_m), limiting molar conductance (Λ_m°) and activation energy are also calculated using conductance data. All these parameters were used to analyze various types of interactions present in the system. Furthermore, density functional theory (DFT) calculations were conducted for comprehensive understanding of structural variations of ion pairs affecting their physical properties. The hydrogen bond formation in the mixture components was examined by using IR spectrum. Both DFT and Hartee-Fock (HF) methods were used to analyze the results. In addition, the DFT/B3LYP-D3 calculations were also carried out to gather data on the molecular geometry, interactions and other molecular characteristics of the ionic liquid under study.

Keywords: 1-Butyl-1-methylpyrrolidinium tetrafluoroborate, Benzylamine, Partial molar volume, Solute-solvent interaction, DFT.

INTRODUCTION

Today's scientific advances are the product of scientists' attempts to find, synthesize or develop new materials that can be the result of the integration, fusion and penetration of several domains. It is a matter of fact that synthesis of new materials such as nanomaterials, gemini surfactants, ionic liquids, *etc.* are the resultant of such efforts of scientific community. These innovations lead to the investigation of new areas and development axes for the developed fields. Ionic liquids have emerged as a result of this backdrop, offering up new fields for chemical technological improvement. Ionic liquids are known as an emerging form of compounds which gained high surge of attention in 21st century [1]. The discovery of these liquids, which are typically referred as organic salts having characteristics like a wide voltage/electrochemical window, negligible vapour pressure, good solvation, low inflammability, high thermal stability, liquid state at a wide range of temperatures, high electrochemical stability, great solubility towards organic compounds and high conductivity. The aforesaid distinctiveness has been found to be the most fascinating areas of recent research in case of ionic liquids. Ionic liquids's are basically comprised of combinations of nitrogen containing organic cations like pyridinium, imidazolium, ammonium, pyrrolidinium, phosphonium derivatives, sulphonium, alkylammonium and bulky soft anions, such as bis[(trifluoromethyl)sulfonyl]imide, tetrafluoroborate $[BF_4^-]$, hexafluorophosphate $[PF_6^-]$ anion and $[(CFSO_2)_2N]$, halide ions and tetrachloroaluminate ($AlCl_4^-$) [2,3].

The physico-chemical characteristics of the ionic liquids can be easily modified by modifying the structure of the component ions in a variety of cationic and anionic forms. The right anion-cation combination in ionic liquids can control a variety of properties including density, hydrophobicity, viscosity, acid-base characteristics, polarity, *etc*. [4]. Moreover, modifying the selectivity of chemical reactions gives a range of new possibilities of utilizing ionic liquids in several industrial domains, including separation processes, catalytic activity and electrochemical gadgets [5]. They can be seen of as either materials or solvents, depending on the goal of their use. But due to ionic liquids distinction, the scientific and industrial communities are paying increasingly close attention to the use of ionic liquids (ILs) as possible green solvents [6,7]. Furthermore, besides these properties, the design-ability of ionic liquids makes them great alternatives to the already existing conventional organic elect-rolytes and other solvent systems and are also considered as a substitute to the volatile organic solvents. In addition to being environmentally benign because of their low vapour pressure, these may also demonstrate catalysis's potential as a solvent or auxiliary. Ionic liquids because of their specific set of charac-teristics have a very wide area of applications. They are also used in energy storage devices [8-11], fuel cells, solar cells, as separation solvents, reaction media and also in pharmaceuticals due to their antimicrobial and antifungal properties [12-14].

On the other hand, benzylamine has a great role in purification, production of amino acids, drug industries and also considered as an important solvent in energy storage applications [15]. Pyrrolidinium-based ionic liquids (PILs) have been chosen for the investigation in the present study because they have more charge localized aliphatic cation which has a much larger electrochemical aperture compared to other delocalized aromatic cations like imidazolium. In contrast to other ILs, particularly imidazolium-based ILs, PILs exhibits perceptual characteristics such as better flexibility, higher aliphaticity and positively charged localization.

Keeping the aforementioned factors in mind, densities, speed of sound and conductance measurements for a ternary system of pyrrolidinium-based ILs with aqueous benzylamine at various temperatures were performed in present study. The findings of these observations have been interpreted in the context of a variety of possible interactions, including proton-solvent and ion-solvent/solute-solvent interactions, proton-anion that may survive in the system and changes in the solvent structure. The studies reported also focus on the analysis of solvation behaviour by determining different volumetric and acoustic parameters using density, speed of sound and conductance data at different concentrations and temperatures. With the help of volumetric, acoustic and conductance studies, efforts were made to analyze the different interactions present in the ternary systems exploring the possibility of such systems for potential applications in a variety of fields, such as energy storage devices, green surface-active agents, actuators and corrosion inhibitors.

This work aims to systematically study of densities (ρ), speeds of sound (u) and thermophysical and conductance properties as well as look into the interactions in the considered ternary mixtures. This work also emphasizes DFT calculations based on the quantum mechanics to comprehend the impact of anions on the types of interactions and bonding intensities in ionic liquids [16]. Using an infrared spectrum, we were able determine the interactions and structural alterations in the systems by obtaining the ideal structures of the cation and anion, the charge distribution, interaction energy and hydrogen bonds [17,18].

EXPERIMENTAL

1-Butyl-1-methyl pyrrolidinium tetrafluoroborate $[BmPyrr^+][BF_4^-]$ (molar mass = 229.07 g mol^{-1}) purchased from Sigma-Aldrich whereas benzylamine (107.15 g mol^{-1}) was purchased from Hi-Media Laboratories. Before using, all the compounds were suction dried and stored over P_2O_5 in a vacuum for 2 days. For the preparation of the solutions, double distilled and degassed water with specific conductance $< 2 \times 10^{-6}$ S cm^{-1} was used taken from Millipore, Milli-Q water purification system.

Methods: The instrument, Anton Paar DSA 5000 M was employed for the measurement of density and speed of sound of various ternary solutions (ionic liquid + water + benzylamine). At 293.15 K, the density and speed of sound were determined in dried air and triple-distilled, deionized water in order to calibrate the instrument. Due to the fact that density and speed of sound measurements are temperature sensitive, a built-in peltier module was used. For the estimation of speed of sound, measurement propagation time technique was utilized. The accuracy of measurements of speed of sound and density were found to be 1×10^{-3} kg m^{-3} and 1×10^{-2} m s^{-1}, respectively. For the purpose of ensuring the consistency of the results, the density and speed of sound measurements were performed two times. The average uncertainties of the measurements were found to be (δρ) = 0.1 kg m^{-3} for density and ± 0.05 m s^{-1} for speed of sound. Standard uncertainties in the measurement of molality, temperature and pressure were found to be ± 0.01 mol kg^{-1}, ± 0.01 K and ± 0.01 Mpa, respectively. The digital conductivity meter of Labtronics Pvt. Ltd. (India) was used to measure the conductivity of the solutions. For the calibration of conductivity cell having cell constant equal to 1 cm^{-1}, 0.01 M KCl solution was used. The measurement of conductance was done after stirring the solution gently with magnetic stirrer.

RESULTS AND DISCUSSION

Density and speed of sound data: The densities as well as speed of sound of different solutions of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in 0.01, 0.03 and 0.05 mol kg^{-1} of binary aqueous benzylamine at four equidistant temperatures have been measured. The data for density and speed of sound is tabulated in Table-1. It is clear that values of the density increase with increase in concentration of ionic liquid as well as benzylamine whereas these values decrease as temperature increases.

On the other hand, the speed of sound values increases with the increase in concentration of the ionic liquid as well as content of benzylamine in water. Also, these values were found escalated with increase in temperature. An increase in density with concentration reveals the fact that there are strong interactions between the solute (ionic liquid) and solvent (aqueous benzylamine), which decrease further with increase in the temperature. The effect of temperature may also be explained

TABLE-1
VALUES OF DENSITIES (ρ) AND SPEED OF SOUND (u) OF TERNARY MIXTURES OF VARIOUS MOLALITIES OF 1-BUTYL-1-METHYL PYRROLIDINIUM TETRAFLUOROBORATE IN BINARY AQUEOUS SOLUTIONS OF BENZYLAMINE AT DIFFERENT TEMPERATURES

[a]m_A (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})				u (m s^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.01 mol kg^{-1} benzylamine in water								
0	0.999221	0.998052	0.996584	0.995016	1469.32	1478.95	1488.98	1496.95
0.009826	0.999473	0.998289	0.996809	0.995227	1470.23	1479.78	1489.68	1497.54
0.029940	0.999992	0.998776	0.997269	0.99565	1472.08	1481.47	1491.11	1498.74
0.049965	1.000509	0.999261	0.997728	0.996090	1473.92	1483.16	1492.53	1499.93
0.069714	1.001019	0.999739	0.998180	0.996514	1475.74	1484.83	1493.93	1501.11
0.089688	1.001533	1.000222	0.998637	0.996944	1477.58	1486.51	1495.35	1502.30
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.03 mol kg^{-1} benzylamine in water								
0	0.999298	0.997425	0.995622	0.993602	1480.55	1496.06	1511.26	1527.26
0.009829	0.999515	0.997628	0.995812	0.993777	1481.92	1497.41	1512.59	1528.56
0.029489	0.999949	0.998035	0.996194	0.994129	1484.65	1500.10	1515.25	1531.15
0.049115	1.000383	0.998441	0.996574	0.994481	1487.38	1502.80	1517.90	1533.74
0.068800	1.000818	0.998849	0.996956	0.994833	1490.12	1505.50	1520.56	1536.33
0.088511	1.001254	0.999257	0.997339	0.995186	1492.86	1508.20	1523.22	1538.93
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.05 mol kg^{-1} benzylamine in water								
0	0.999408	0.997451	0.995568	0.993372	1503.42	1507.64	1511.78	1516.21
0.009813	0.999608	0.997639	0.995745	0.993537	1503.65	1507.83	1512.02	1516.47
0.029470	1.000009	0.998016	0.996101	0.993870	1504.11	1508.20	1512.49	1516.98
0.049163	1.000410	0.998394	0.996457	0.994202	1504.57	1508.57	1512.97	1517.50
0.068823	1.000811	0.998772	0.996813	0.994535	1505.04	1508.94	1513.45	1518.01
0.088453	1.001212	0.999149	0.997169	0.994866	1505.50	1509.31	1513.92	1518.53

[a] m_A is the molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in aqueous benzylamine solutions. Standard uncertainties in molality of benzylamine u (m_{BA}) and ionic liquid u (m_{IL}) are 0.0022 mol kg^{-1} and 0.0039 mol kg^{-1} respectively. The respective values of standard uncertainty in density, temperature and pressure are u (δρ) = 0.1 kg m^{-3}, u (T) = 0.01 K and u (P) = 0.01 MPa

in terms of enhanced thermal energy of molecules that results in increased kinetic energy and hence decreased density.

Apparent molar volume (V_ϕ) and apparent molar isentropic compression ($K_{\phi,S}$): Apparent molar volume (AMV) and isentropic compression were determined by using the measured data for density and speed of sound with the help of the following equations:

$$V_\phi = \left[\left(\frac{M}{\rho}\right) - \frac{(\rho - \rho_o)}{m_A \rho \rho_o}\right] \quad (1)$$

$$K_{\phi,s} = \left[\frac{M\kappa_s}{\rho} - \left(\frac{k_s \rho_o - \kappa_{s,o}\rho}{m_A \rho \rho_o}\right)\right] \quad (2)$$

where M and m_A represents the molecular mass and molality of ionic liquid respectively; ρ is the density of solution and ρ_o denotes density of pure solvent. The isentropic compressibility of the pure solvent is $\kappa_{s,o}$ while that of the solution is κ_S.

The uncertainty in V_ϕ was estimated using eqn. 3 [19]:

$$\delta V_\phi = -\left(\frac{M+1}{m_A}\right)\frac{\delta\rho}{\rho^2} \quad (3)$$

where δρ represents density uncertainty (taking concentration uncertainty as negligible).

Laplace Newton's equation has been employed for the calculation of the isentropic compressibility, κ_S using the measured density and speed of sound data:

$$\kappa_S = \frac{1}{u^2 \rho} \quad (4)$$

In this equation, ρ represents the density of ternary mixture and u is the speed of sound [20].

The magnitude of apparent molar volume values along with sign are the indicator of ion-solvent interactions present in the specific system. It has been suggested that the positive magnitude of apparent molar volume indicates occurrence of ionic interactions among species present in the system, while the negative magnitude reflects non-ionic interactions. In the present ternary system ($[BmPyrr^+][BF_4^-]$ + benzylamine + water), values of V_ϕ come out to be positive (Table-2) demonstrating that the system under study has significant solute-solvent interactions. Apparent molar volume (AMV) values decrease with increase in concentration of ionic liquid in aqueous solutions of benzylamine, whereas these values further increase with the addition of benzylamine content in water.

These observations can reveal that the solute-solvent interactions are strengthened with the addition of benzylamine in water and decline with increase in amount of ionic liquid. Fig. 1 represents the values of AMV as a function of molality for (0.01 mol kg^{-1} and 0.05 mol kg^{-1}) at four equidistant temperatures. As the temperature increased, values of V_ϕ also increase, explaining the stronger interactions among solute and solvent molecules at higher temperature range.

The values obtained for $K_{\phi,s}$ reported in Table-2 are negative at all concentrations and temperatures under consideration and these values become less negative, when both the temperature and concentration of the ionic liquid increased. For this system, the negative values of $K_{\phi,s}$ specifies the solvation of solute and solvent molecules, which results in the stronger affinity among

TABLE-2
APPARENT MOLAR VOLUME (V_ϕ) AND APPARENT MOLAR ISENTROPIC COMPRESSION ($K_{\phi,s}$) VALUES OF TERNARY MIXTURES OF VARIOUS MOLALITIES (m) OF IONIC LIQUID IN AQUEOUS BENZYLAMINE AT DIFFERENT TEMPERATURES

$^a m_A$ (mol kg^{-1})	$V_\phi \times 10^6$ (m^3 mol^{-1})				$K_{\phi,s} \times 10^6$ (m^3 mol^{-1} GPa^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.01 mol kg^{-1} benzylamine in water								
0.009826	23.36	25.18	26.76	28.46	-18.49	-15.60	-13.26	-10.82
0.029940	23.26	25.08	26.66	28.37	-18.00	-15.08	-12.74	-10.24
0.049965	23.15	24.98	26.57	28.28	-17.51	-14.56	-12.22	-9.67
0.069714	23.05	24.88	26.47	28.19	-17.03	-14.05	-11.71	-9.11
0.089688	22.95	24.78	26.38	28.11	-16.55	-13.53	-11.19	-8.54
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.03 mol kg^{-1} benzylamine in water								
0.009829	25.05	26.81	27.47	29.38	-21.20	-20.29	19.65	-16.41
0.029489	24.96	26.73	27.39	29.31	-21.03	-19.93	-18.82	-15.58
0.049115	24.87	26.64	27.31	29.23	-20.86	-19.58	-18.00	-14.77
0.068800	24.78	26.56	27.23	29.16	-20.67	-19.14	-17.16	-13.94
0.088511	24.69	26.47	27.15	29.08	-20.00	-18.84	-16.33	-13.12
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.05 mol kg^{-1} benzylamine in water								
0.009813	26.74	27.32	28.79	30.44	-22.86	-20.12	-17.28	-14.71
0.029470	26.66	27.24	28.71	30.37	-22.07	-19.29	-16.57	-14.11
0.049163	26.57	27.17	28.64	30.29	-21.29	-18.45	-15.85	-13.51
0.068823	26.49	27.09	28.56	30.22	-20.50	-17.62	-15.13	-12.90
0.088453	26.41	27.01	28.49	30.15	-19.72	-16.78	-14.41	-12.30

$^a m_A$ is the molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in aqueous benzylamine solutions. Standard uncertainties in molality of benzylamine u (m_{BA}) and ionic liquid u (m_{IL}) are 0.0022 mol kg^{-1} and 0.0039 mol kg^{-1} respectively. The respective values of standard uncertainty in apparent molar volume, temperature and pressure are u (δV_ϕ) = ± (0.01-0.10) × 10^{-3} m^3 mol^{-1}, u (T) = 0.01 K and u (P) = 0.01 MPa

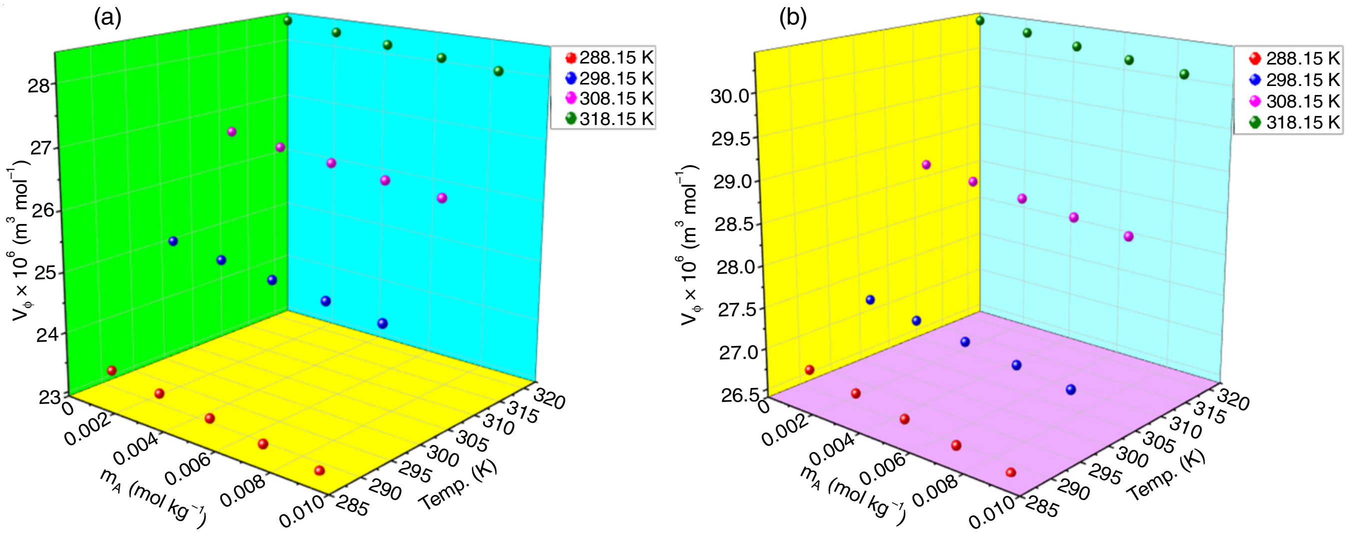

Fig. 1. Plot of apparent molar volume (V_ϕ) *versus* molality (m) for 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in (a) 0.01 mol kg^{-1} and (b) 0.05 mol kg^{-1} aqueous solution of benzylamine at different temperatures

solute and solvent molecules. The decrease of compressibility of the surrounding solvent molecules due to significant electrostrictive pressures causes electrostrictive solvation. In comparison to the water molecules in the bulk solution, the water molecules close to the ionic charged centers of the ionic liquid are less compressible, which improves the ordering of the water molecules and hence less compressibility of the solution resulting in escalation in the values of $K_{\phi,s}$ as depicted in Table-2.

Partial molar volume (V_ϕ°) and partial molar isentropic compression ($K_{\phi,s}^\circ$): The apparent molar volume and isentropic compression at infinite dilution are the partial molar properties that can be used for the determination of the presence of solute-solvent interactions. Since the solute is entirely encircled by the solvent molecules at infinite dilution, the interactions between the solute and the solvent are minimal. The value of V_ϕ° and $K_{\phi,s}^\circ$ were determined by using the least square fitting method using below mentioned equations:

$$V_\phi = V_\phi^o + S_V^* m_A \quad (5)$$

$$K_{\phi,s} = K_{\phi,s}^o + S_K^* m_A \quad (6)$$

where V_ϕ° denotes partial molar volume (PMV) and $K_{\phi,s}^\circ$ represents the partial molar isentropic compression, m_A is the molal concentration of the ionic liquid in aqueous benzylamine [21].

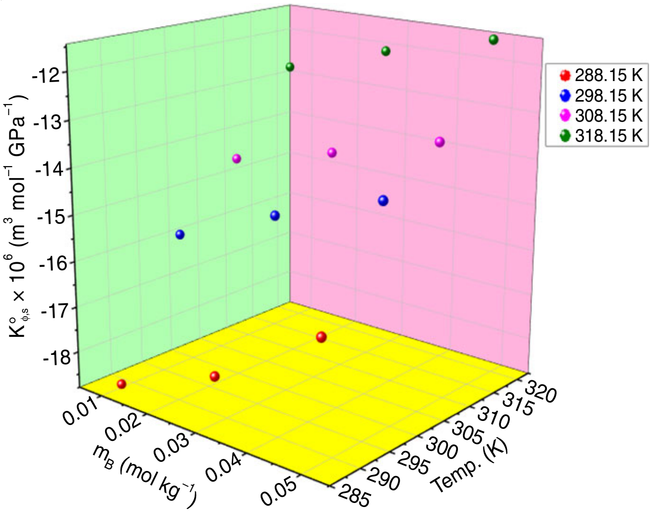

Fig. 2. Plot of variation of apparent molar isentropic compression against against ($K^\circ_{\phi,s}$) molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in 0.01 and 0.05 mol kg^{-1} of aqueous benzylamine at four equidistant temperatures

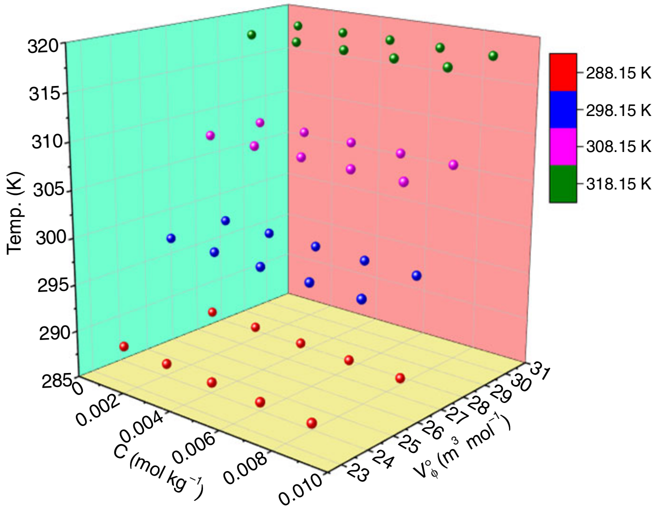

Fig. 3. Plot of variation of partial molar volume (V_ϕ) against molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in 0.01 and 0.05 mol kg^{-1} of aqueous benzylamine at four equidistant temperatures

On the other hand, S^*_V and S^*_K are the inclines of the graphs, volumetric and sound velocity coefficients which help in the prediction of solute-solute interactions while V_ϕ and $K_{\phi,s}$ helps in predicting solute-solvent interactions. The values of V°_ϕ and S^*_V are tabulated in Table-3 along with standard errors. The positive value of V°_ϕ at all concentrations and temperatures confirms the dominance of ion-aquaphillic synergies over the ion-aquaphobic and aquaphobic-aquaphobic synergies which corroborate the results obtained from AMV and apparent molar isentropic compression studies. Fig. 3 illustrates the relationship between V°_ϕ and the concentration of the ionic liquid, which demonstrates that these values increase with both temperature and concentration.

The observed trend reveals that ion-hydrophilic interactions become stronger with concentration of benzylamine as well as temperature. Strengthening of these interactions with temperature and content of benzylamine has also been confirmed from AMV and molar isentropic compression. The $K^\circ_{\phi,s}$ and S^*_K values are represented in Table-4 with the standard errors. The negative values of $K^\circ_{\phi,s}$ calculated using the AMV values again confirmed the solute-solvent interactions in this system. As the temperature and concentration increases, these values become less negative signifying the decrease of electrostriction force because of enhanced kinetic energy and hence decreased force the water molecules enter the bulk solution. Plot of variation of apparent molar isentropic compression against against molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in 0.01 and 0.05 mol kg^{-1} of aqueous benzyl amine at four equidistant temperatures is shown in Fig. 2. Therefore, the water molecules are more compressible at the lower concentrations [21,22].

TABLE-3

VALUES OF PARTIAL MOLAR VOLUMES (V°_ϕ) AND EXPERIMENTAL SLOPE (S^*_V) OF TERNARY MIXTURES OF IONIC LIQUID IN VARIOUS MOLALITIES OF AQUEOUS BENZYLAMINE AT DIFFERENT TEMPERATURES

$^a m_B$ (mol kg^{-1})	$V^\circ_\phi \times 10^6$ (m^3 mol^{-1})				$S^*_V \times 10^6$ (m^3 kg mol^{-2})			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate+ aqueous benzylamine								
0.01	23.41±0.0001	25.22±0.0009	26.80±0.0008	28.50±0.0007	-5.23±0.0018	-4.96±0.0016	-4.74±0.0014	-4.49±0.0013
0.03	25.09±0.0007	27.85±0.0006	28.51±0.0006	30.42±0.0005	-4.57±0.0013	-4.32±0.0012	-4.09±0.0011	-3.82±0.0001
0.05	28.78±0.0006	29.36±0.0006	31.82±0.0005	32.42±0.0005	-4.25±0.0011	-4.04±0.0001	-3.84±0.0009	-3.62±0.0008

$^a m_B$ is molality of aqueous solution of benzylamine.

TABLE-4

VALUES OF LIMITING APPARENT MOLAR ISENTROPIC COMPRESSION ($K^\circ_{\phi,s}$) AND EXPERIMENTAL SLOPES (S^*_K) OF TERNARY MIXTURES OF IONIC LIQUID IN VARIOUS MOLALITIES, m OF AQUEOUS BENZYLAMINE AT DIFFERENT TEMPERATURES

$^a m_B$ (mol kg^{-1})	$K^\circ_{\phi,s} \times 10^6$ (m^3 mol^{-1} GPa^{-1})				$S^*_K \times 10^6$ (kg m^3 mol^{-2} GPa^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate+ aqueous benzylamine								
0.01	-18.73±0.01	-15.85±0.01	-14.52±0.01	-12.70±0.01	2.75±0.06	1.55±0.17	1.12±0.06	0.83±0.08
0.03	-17.79±0.01	-14.88±0.01	-13.92±0.01	-12.01±0.01	1.62±0.17	1.32±0.05	1.07±0.07	0.74±0.11
0.05	-16.25±0.05	-14.04±0.01	-13.24±0.01	-11.44±0.01	1.07±0.19	0.98±0.37	0.86±0.04	0.49±0.03

$^a m_B$ is the molality of aqua solution of benzylamine

The negative S_V^* values do not follow any specific trend; however, their negative values support the weak solute-solute interactions of the system. The values of $K_{\phi,s}^o$ as compared to the values of S_V^* also support the almost nonexistent nature of solute-solute interactions.

Partial molar volume of transfer (ΔV_ϕ^o) and partial molar isentropic compression of transfer ($\Delta K_{\phi,s}^o$): The values of ΔV_ϕ^o and $\Delta K_{\phi,s}^o$ are calculated from water to aqueous benzylamine for 1-butyl-1-methyl pyrrolidinium tetrafluoroborate using following eqns. 7 and 8:

$$\Delta V_\phi^o = V_\phi^o(\text{in aqueous benzylamine solution}) - V_\phi^o(\text{in water}) \quad (7)$$

$$\Delta K_{\phi,s}^o = K_{\phi,s}^o(\text{in aqueous benzylamine solution}) - K_{\phi,s}^o(\text{in water}) \quad (8)$$

The values of ΔV_ϕ^o and $\Delta K_{\phi,s}^o$ in water are used in the above equations for the calculation of ΔV_ϕ^o and $\Delta K_{\phi,s}^o$ and their calculated data is represented in Table-5. At all the temperatures and concentrations, values of ΔV_ϕ^o found to be be positive, confirming the ion-ion interactions among ionic liquid and benzylamine molecules.

Furthermore, the values of ΔV_ϕ^o increase with concentration of benzylamine, while decrease with the increase in the temperature. This confirms the strengthening of ion-ion interactions with increase in concentration of benzylamine. On the other hand, with temperature there is release of water molecule from the loose hydration layer of ionic liquid, which results in expansion of volume and hence small values of ΔV_ϕ^o. The values of $\Delta K_{\phi,s}^o$ are positive, which becomes higher in magnitude with increasing concentration of benzylamine and temperature. The positive values of $\Delta K_{\phi,s}^o$ indicates the structure making tendency of the solute which further intensifies with increasing concentration because of the decreased electrostriction. However, with rise in temperature the expansion of volume due to release of structured water molecules from the loose hydration layer of ionic liquid make solution compressible and hence higher $\Delta K_{\phi,s}^o$ values.

In the investigated ternary mixture, four types of interactions do exist and these different types of interactions are (a) hydrophilic-hydrophilic interactions (b) ion-hydrophilic interactions (c) ion- hydrophobic interactions and (d) hydrophobic-hydrophobic interactions. According to the co-sphere model, hydrophilic-hydrophilic and ion-hydrophilic interaction are dominant over the other two type of interactions in the investigated system. The positive values of ΔV_ϕ^o confirms the (a) type of interactions [23,24].

Dependence of partial molar volume on temperature: Partial molar volume shows dependency on temperature, can be demonstrated by following polynomial equation:

$$V_\phi^o = a + b\,(T - T_{ref}) + c\,(T - T_{ref})^2 \quad (9)$$

where a, b and c are the empirical constants which are tabulated in Table-6. T is the temperature (in Kelvin) and T_{ref} is 298.15 K.

The values of constants a and b are positive and slightly negative for 'c' at 0.01 mol kg^{-1}. In order to calculate the partial molar expansibilities ϕ_E^o, which further help us to determine the different interactions present in the current system following equation is employed.

$$\phi_E^o = \left(\frac{\partial V_\phi^o}{\partial T}\right)_p = b + 2c\,(T - T_{ref}) \quad (10)$$

For all the concentration, ϕ_E^o values are positive and are tabulated in Table-7. Positive ϕ_E^o values signify the existence of solute-solvent interactions in the specific system.

The structure making or destroying ability of the solute is determined using the following equation given by Hepler [25]:

$$\left(\frac{\partial \phi_E^o}{\partial T}\right)_p = \left(\frac{\partial^2 V_\phi^o}{\partial T^2}\right)_p = 2c \quad (11)$$

$(\partial\phi_E^o/\partial T)_p$ determines the ability of ionic liquid to behave as structure maker or destroyer. In the system under consideration

TABLE-5
VALUES OF PMV OF TRANSFER (ΔV°_ϕ) AND LIMITING MOLAR ISENTROPIC COMPRESSION OF TRANSFER ($\Delta K^\circ_{\phi,s}$) OF TERNARY MIXTURES OF IONIC LIQUID IN VARIOUS CONCENTRATION (MOLALITY, m = 0.01, 0.03 AND 0.05) mol kg^{-1} OF AQUEOUS BENZYL AMINE

$^a m_B$ (mol kg^{-1})	$\Delta V^\circ_\phi \times 10^6$ (m^3 mol^{-1})				$\Delta K^\circ_{\phi,s} \times 10^6$ (m^3 mol^{-1} GPa^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate+ aqueous benzylamine								
0.01	2.49	2.11	1.81	1.57	6.39	7.27	7.94	8.48
0.03	3.46	3.18	2.78	2.42	7.33	7.74	8.04	8.87
0.05	4.51	4.22	3.85	3.49	8.17	8.58	8.82	9.47

$^a m_B$ is the molality of aqua solution of benzyl amine

TABLE-6
VALUES OF EMPIRICAL PARAMETERS (a, b AND c) OF TERNARY MIXTURE OF IONIC LIQUID IN VARIOUS MOLALITIES (m) OF AQUEOUS BENZYL AMINE AT VARIOUS TEMPERATURES

$^a m_B$ (mol kg^{-1})	a × 10^6 (mol kg^{-1})	b × 10^6 (m^3 mol^{-1} K)	c × 10^6 (m^3 mol^{-1} K^{-2})	R^2	ARD (σ)
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate+ aqueous Benzylamine					
0.01	25.17	0.1723	-0.0002	0.9989	0.00071
0.03	28.80	0.1635	0.0003	0.9999	0.00066
0.05	31.32	0.1538	0.0011	0.9977	0.00057

$^a m_B$ is the molality of aqua solution of benzyl amine

TABLE-7
VALUES OF MOLAR EXPANSIBILITIES, ϕ°_{E} OF TERNARY MIXTURE OF IONIC LIQUID IN DIFFERENT CONCENTRATIONS OF AQUEOUS BENZYLAMINE AT DIFFERENT TEMPERATURES

$^{a}m_{B}$ (mol kg^{-1})	$\phi^{\circ}_{E} \times 10^{6}$ (m^{3} mol^{-1} K^{-1})				$(\partial\phi^{\circ}_{E}/\partial T)$
	288.15 K	298.15 K	308.15 K	318.15 K	
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate+ aqueous benzylamine					
0.01	0.177	0.171	0.166	0.160	-0.00055
0.03	0.165	0.172	0.180	0.188	0.00036
0.05	0.151	0.154	0.157	0.160	0.00071

$^{a}m_{B}$ is the molality of aqua solution of benzyl amine

$(\partial\phi^{\circ}_{E}/\partial T)_{p}$ values wer found to be positive confirming the structure making tendency which authenticate the resultant data derived from partial molar volume and isentropic compressibility.

Pair and triplet interaction coefficients: Friedman & Krishnan modified the theory, which was earlier given by McMillan and Mayer to understand the concept of the solute-solvent interactions in the solvation sphere [26,27]. By fitting the values of ΔV°_{ϕ} and $\Delta K^{\circ}_{\phi,s}$ in eqns. 12 and 13, respectively, the pair interaction coefficients and triplet interaction coefficients were calculated:

$$\Delta V^{\circ}_{\phi}(\text{water to aqueous benzylamine solution}) = 2V_{AB}m_{B} + 3V_{ABB}m_{B}^{2} \tag{12}$$

$$\Delta K^{\circ}_{\phi,s}(\text{water to aqueous benzylamine solution}) = 2K_{AB}m_{B} + 3K_{ABB}m_{B}^{2} \tag{13}$$

where A is the solute and B is the solvent; m_B represents the molal concentration of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate; V_{AB} and V_{ABB} denotes molar volume and K_{AB}, K_{ABB} denotes the adiabatic compressibility.

The values of pair and triplet coefficients are given in Table-8. For this system values of coefficients V_{AB}, K_{AB} are positive whereas values of V_{ABB}, K_{ABB} are negative.

The positive values of V_{AB} show the pairwise interaction between the benzylamine and ionic liquid are significant. Because of the overlap, water molecules leave the hydration co-sphere when non-bonding favourable interactions are present and move into the bulk. The values of V_{AB} are significantly greater than the triplet interaction coefficients V_{ABB}, which explains the dominance of pair-wise interactions in the mixture of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate and benzylamine.

Conductance studies: Conductance of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in aqueous benzylamine at different concentrations (0.01, 0.03 and 0.05) mol kg^{-1} and various temperatures were measured. The conductance of electrolytic solutions determines the character of interactions between solute-solute, solvent-solvent and solute-solvent. These studies provide the kinetic information in the form of ionic conductivities and thermodynamic information in the form of association constants.

Eqn. 14 was used for the calculation of molar conductivity (Λ_m) of the ternary solution:

$$\Lambda_{m} = \frac{1000.\kappa}{C} \tag{14}$$

The efficiency of an electrolyte carrying electricity in solution is measured by the conductivity of all the ions produced by dissolving one mole of an electrolyte in solutions, where C is the concentration of solution, κ is its conductivity and Λ_m is its molar conductivity [28].

Specific conductivity (κ) and molar conductivity (Λ_m) were measured at four equidistant temperatures (288.15 K to 318.15 K) and data for specific conductivity and molar conductivity is tabulated in supplementary Tables 9 and 10, respectively.

From the obtained data, it is concluded that values of molar conductivity increase with increase in concentration of ionic liquid and benzylamine. Also, these values increase further as the temperature increases. Higher the temperature, higher the frequency resulting in the breakage of bond due to increase in the vibrational and translational degrees of freedom resulting in increases mobilities of the ions and hence higher the magnitude of conductivity [22,29].

Plots of Λ_m against $\sqrt{c}$ over the entire composition (Fig. 4) range within investigated concentration range were found to be straight lines at all the studied temperatures, which demonstrates the complete dissociation of ionic liquid in the solvent system.

The values of molar conductivity obtained were used for the calculation of limiting molar conductivity using the Onsager relation (eqn. 15):

TABLE-8
VALUES OF PAIR (V_{AB} AND K_{AB}) AND TRIPLET INTERACTION COEFFICIENTS (V_{ABB} AND K_{ABB}) OF TERNARY MIXTURES OF IONIC LIQUID IN AQUEOUS BENZYLAMINE AT DIFFERENT TEMPERATURES

T (K)	$V_{AB} \times 10^{6}$ (m^{3} mol^{-2} kg)	$K_{AB} \times 10^{6}$ (m^{3} mol^{-2}kgGPa^{-1})	$V_{ABB} \times 10^{6}$ (m^{3} mol^{-3} kg^{2})	$K_{ABB} \times 10^{6}$ (m^{3} mol^{-3} kg^{2} GPa^{-1})
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + aqueous benzylamine				
288.15	36.61	232.80	-783.86	-924.28
298.15	32.51	240.83	-715.84	-2956.18
308.15	28.28	277.46	-658.15	-3280.17
318.15	22.03	317.57	-400.21	-3711.36

TABLE-9
SPECIFIC CONDUCTIVITY 1-BUTYL-1-METHYL PYRROLIDINIUM TETRAFLUOROBORATE IN AQUEOUS SOLUTION OF BENZYLAMINE

$^a m_A$ (mol kg^{-1})	K (μS cm^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.01 aqueous benzylamine				
0.009826	859.80	773.56	705.00	642.65
0.029940	1327.30	1233.63	1156.55	1086.94
0.049965	1792.73	1691.66	1606.09	1529.25
0.069714	2251.74	2143.36	2049.43	1965.46
0.089688	2715.98	2600.22	2497.82	2406.64
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.03 aqueous benzylamine				
0.009829	1173.65	1059.84	928.17	805.49
0.029489	1773.74	1659.11	1518.91	1386.07
0.049115	2372.80	2257.34	2108.62	1965.65
0.068800	2973.68	2857.39	2700.13	2546.99
0.088511	3575.35	3458.24	3292.42	3129.10
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.05 aqueous benzylamine				
0.009813	1340.55	1212.84	1129.17	998.59
0.029470	2051.51	1920.35	1809.30	1669.56
0.049163	2763.79	2629.19	2490.71	2341.79
0.068823	3474.87	3336.82	3170.95	3012.87
0.088453	4184.89	4043.41	3850.19	3682.95

TABLE-10
MOLAR CONDUCTIVITY (Λ_m) 1-BUTYL-1-METHYL PYRROLIDINIUM TETRAFLUOROBORATE IN AQUEOUS SOLUTION OF BENZYLAMINE

$^a m_A$ (mol kg^{-1})	Λ_m (S cm^2 mol^{-1})			
	288.15 K	298.15 K	308.15 K	318.15 K
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.01 aqueous benzylamine				
0.009826	49.51	51.30	53.68	49.51
0.029940	51.77	53.60	55.95	51.77
0.049965	54.04	55.91	58.22	54.04
0.069714	56.30	58.21	60.50	56.30
0.089688	58.56	60.51	62.77	58.56
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.03 aqueous benzylamine				
0.009829	53.8	56.08	58.02	60.10
0.029489	56.12	58.34	60.48	62.54
0.049115	58.44	60.59	62.94	64.98
0.068800	60.76	62.85	65.41	67.42
0.088511	63.08	65.11	67.86	69.86
1-Butyl-1-methyl pyrrolidinium tetrafluoroborate + 0.05 aqueous benzylamine				
0.009813	57.33	59.46	61.53	63.48
0.029470	59.59	61.70	63.77	65.71
0.049163	61.84	63.95	66.02	67.92
0.068823	64.09	66.19	68.26	70.14
0.088453	66.35	68.43	70.50	72.36

$^a m_A$ is the molality of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in aqueous benzylamine solutions. Standard uncertainties in molality of benzylamine u_r (m_{BA}) and ionic liquid u_r (m_{IL}) are 0.0022 mol kg^{-1} and 0.0039 mol kg^{-1}, respectively

$$\Lambda_m = \Lambda^o - S\sqrt{c} \qquad (15)$$

In the plots of Λ_m against √c, straight lines give the intercept, which is equal to the limiting molar conductivity and slope is equal to Onsager constant (denoted by S). Table-11 tabulates the resultant values of the limiting molar conductivity.

From the calculated values, it is observed that the values of limiting molar conductivity increase as the temperature increases at all concentrations, which is due to the mobility of ions. An increase in temperature causes bond breakage and higher frequencies, which increase the degrees of freedom for translation and vibration, thus the mobility of ions increases [30-32]. These values obtained helps in interpreting the ion-solvent interactions. Higher the values of limiting molar conductance, greater the ion-solvent interactions [33-35]. Among all the concentrations, in these ternary mixtures 0.005 mol kg^{-1} have the greatest ion-solvent interactions. It is worth to mention here that the results obtained from volumetric, acoustic and conductance studies substantiate each other's observations and confirms the presence of ion-ion interactions in the system which get strengthened with the concentration. The influence of temperature on conductivity is given by eqn. 16, where E_A is the activation energy and R stands for the gas constant.

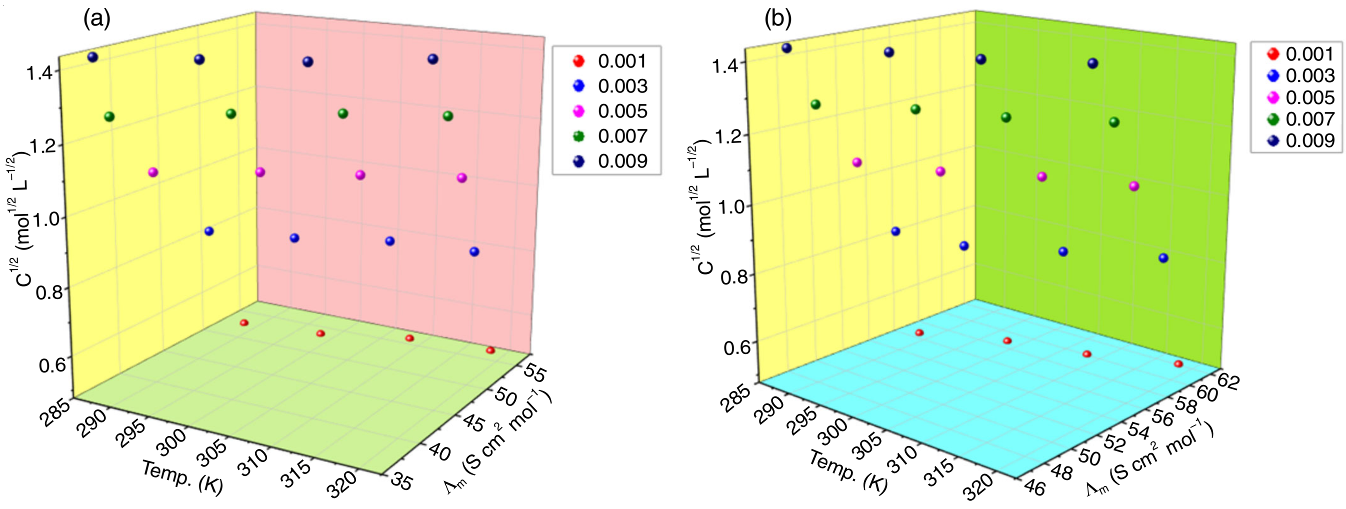

Fig. 4. Plots showing the variation of Λ_m with √C for 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in 0.01 mol kg^{-1} aqueous benzyl amine at T = (288.15, 298.15, 308.15, 318.15) K

TABLE-11
LIMITING MOLAR CONDUCTIVITY (Λ°) OF 1-BUTYL-1-METHYL PYRROLIDINIUM TETRAFLUOROBORATE IN AQUEOUS SOLUTION OF BENZYLAMINE

$^a m_B$ (mol kg^{-1})	Λ° (S cm^2 mol^{-1})				$E_A \times 10^{-3}$ (kJ mol^{-1})
	288.15 K	298.15 K	308.15 K	318.15 K	
0.001	23.55	24.33	24.76	25.52	0.00778
0.003	24.40	25.24	25.77	26.61	0.00605
0.005	25.26	26.15	26.78	27.70	0.00465

$^a m_B$ is the molality of aqua solution of benzyl amine

$$\Lambda_m = \Lambda_o e^{E_A/RT} \tag{16}$$

The slope of the straight line produced by the plot of the log Λ_m *vs.* 1/T can be used to compute activation energy (E_A) and Table-11 lists the values of activation energy. The fact that all activation energy values are positive, which leads to the conclusion that solubilization is beneficial [30].

Computational studies: In order to obtain the most stable structure, the ionic liquid was optimized by employing density functional theory (DFT) and Hartee-Fock (HF) methodologies. To obtain the optimized geometry and infrared bands, DFT computations were executed at the Lee-Yang-Parr correlation functional (B3LYP) level of theory 6-31++ G(d,p) basis set for Becke's three-parameter hybrid model utilizing the Gaussian 09 program. At the same theoretical level, frequency calculations were also carried out to ascertain the thermochemical information and verify that the optimized structures were minima on the potential energy hypersurface.

Geometry optimization of [BmPyrr$^+$][BF$_4^-$] using (B3LYP)6-31++G(d,p) in DFT and HF approach: Statistics for the ionic liquid's architectural optimization was obtained using the Gaussian 09 package software. Their electronic properties were studied using DFT and HF methodologies. The gaseous phase molecular geometry optimization of [BmPyrr$^+$]-[BF$_4^-$] was performed at the B3LYP/6-31++ G(d,p) level as illustrated in Fig. 5.

The dotted line represents the hydrogen bonds that exist within these moieties. The HF H-bonding energies in [BmPyrr$^+$]-[BF$_4^-$] were determined using DFT as well as HF approaches. The optimized structure of [BmPyrr$^+$][BF$_4^-$] elucidates three H-bonding interactions between an anion and cation, with bond lengths of 2.19, 2.18 and 2.05 Å in DFT and 2.27, 2.26, 2.16 Å in HF basis set. H-bonding, which is prevalent in pyrrolidinium ions or salts, exerts a significant influence on the physical characteristics of the moieties. Table-12 shows the bond lengths calculated by DFT and HF methods. However, the bond lengths computed at the B3LYP level of theory are considerably greater in magnitude than those determined at other level.

Insights on the molecular interactions of [BmPyrr$^+$]-[BF$_4^-$]: The calculated orbital energy gaps ($\Delta E = E_{LUMO} - E_{HOMO}$) of the ionic liquid, which are a crucial stability measurement, are illustrated in Fig. 6.

These gaps provide the kinetic stability of the molecule. Table-13 presents the polarity of the ionic liquid through the representation of its bond dipole moment as a Gaussian function and some other minimal self-consistent field molecular energies as well as a number of significant molecular properties, including the dipole moment, polarizability, hyperpolarizability, thermodynamic parameters, contact energy, HOMO-LUMO energy gap and electronic energy.

Electrostatic potential maps: Electrostatic potential maps provide three-dimensional representations of a molecule's

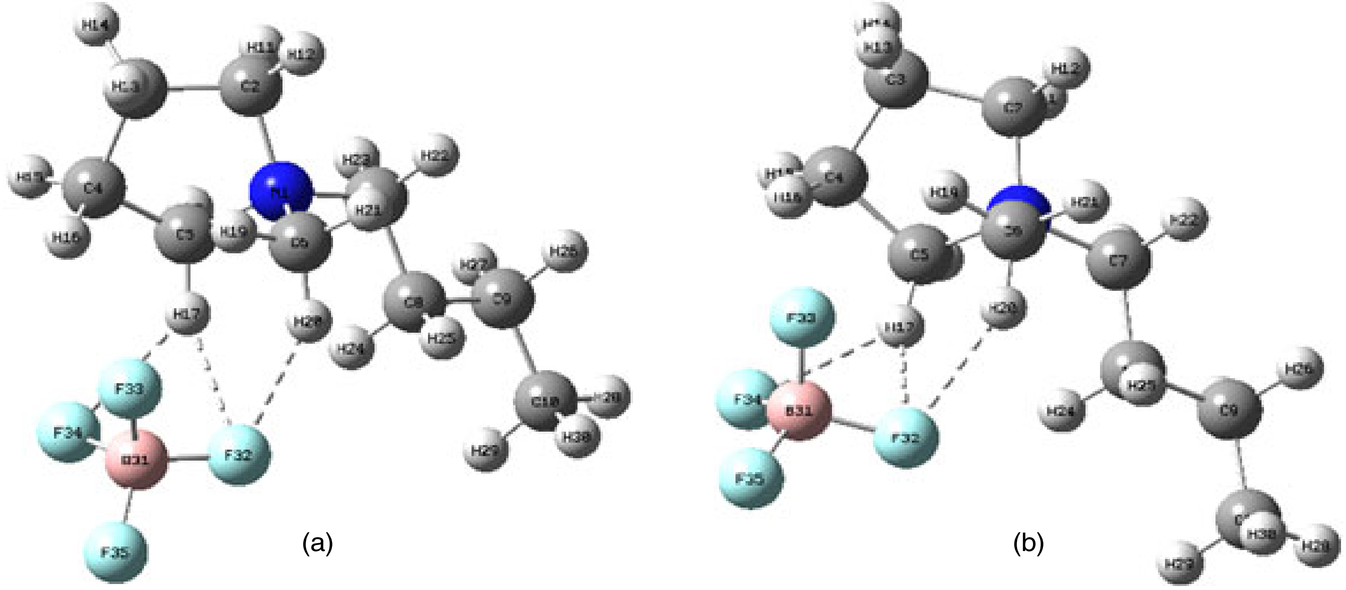

Fig. 5. The optimized energy structure of [BmPyrr$^+$][BF$_4^-$] determined using the utilization of (a) density-functional theory (DFT) and (b) Hartree-Fock (HF) with a hybrid density functional B3LYP/6-31++ G(d,p) level

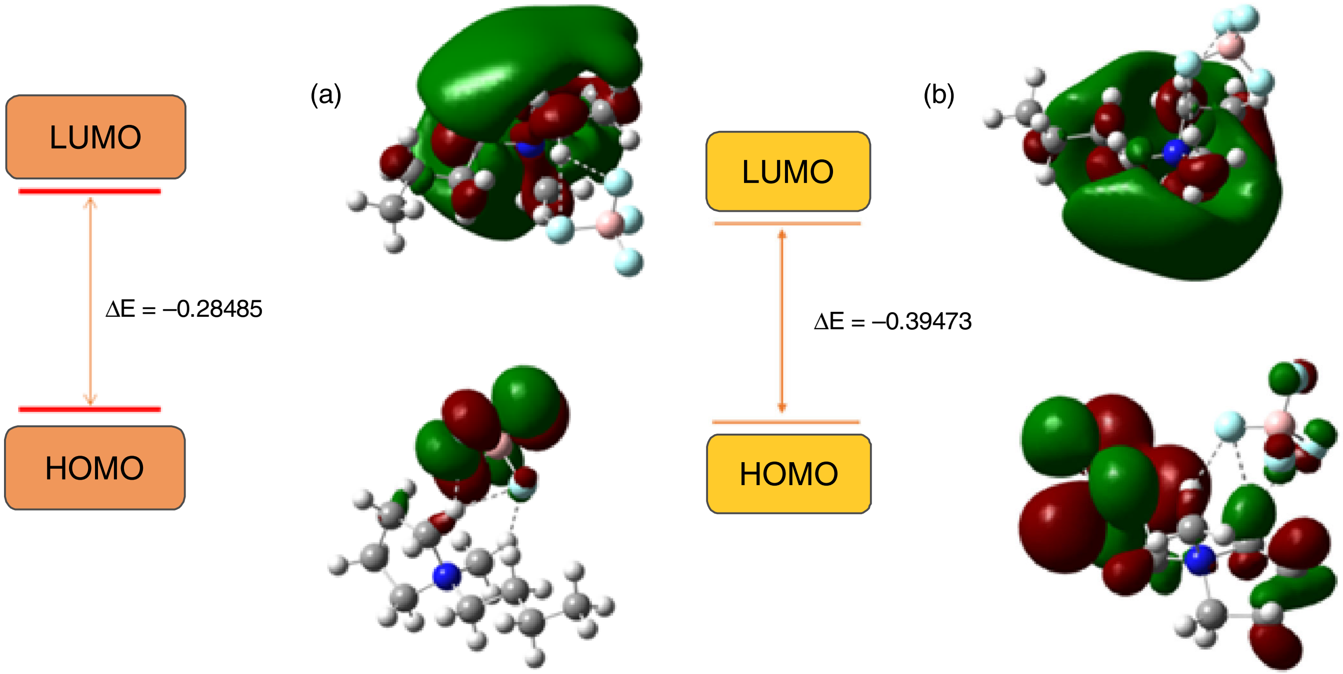

Fig. 6. Pictorial representation of the molecular orbitals for [BmPyrr$^+$][BF$_4^-$] with HOMO–LUMO plot of density and calculated ΔE of LUMO–HOMO computed at B3LYP/6-31++ G(d,p) level in gaseous phase (a) DFT approach (b) HF approach

TABLE-12
SELECTED BOND LENGTHS FOR OPTIMIZED STRUCTURE OF [BmPyrr$^+$][BF$_4^-$] USING DFT APPROACH AS WELL AS HF APPROACH

Parameters	Bond length (Å) using DFT	Bond length (Å) using HF
C-H	1.089	1.078
C_4-C_5	1.528	1.526
C_5-N_1	1.528	1.511
N_1-C_2	1.517	1.498
C_2-C_3	1.536	1.532
C_3-C_4	1.554	1.547
N_1-C_7	1.513	1.498
C_7-C_8	1.527	1.526
N_1-C_6	1.509	1.498
C_7-H_{17}	1.084	1.073
C_6-F_{34}	1.085	1.074
H_{17}-F_{34}	2.191	2.275
H_{17}-F_{32}	2.189	2.267
H_{20}-F_{32}	2.058	2.166
B_{31}-F_{33}	1.473	1.404
B_{31}-F_{35}	1.373	1.359
B_{31}-F_{34}	1.427	1.392
B_{31}-F_{32}	1.448	1.417

charge distributions. The blue region has the lowest electron density, while the red area has the highest. Fig. 7 shows molecular electrostatic potential (MEP) contour of ionic liquid and Fig. 8 shows ESP surface using DFT and HF approach. The red, blue and green colours represent negative, positive and zero electrostatic potential, respectively [36-38]. Green-coloured areas indicate neutral sites, while red and blue-coloured surfaces can indicate electrophilic and nucleophilic reactions.

Comparison between the observed and predicted infrared spectra: Fig. 9 displays the experimental infrared (IR) spectrum for [BmPyrr$^+$][BF$_4^-$]. The main, highly intense peaks have been observed at 554, 930, 1107, 1292, 1381, 1497, 1524, 2953 and 3010 cm^{-1}. These peaks are also analyzed utilizing DFT and HF methods for frequency computation. A thorough theoretical investigation was carried out to ascertain which method best replicates the experimental result. Using the DFT/B3LYP and HF techniques, the vibrational frequency of the [BmPyrr$^+$][BF$_4^-$] ion pair in gaseous phase were calculated. Plotting combined experimental *versus* theoretical vibrational frequencies using B3LYP and HF techniques is shown in Fig. 10.

TABLE-13
THE BOND DIPOLE MOMENT OF THE [BmPyrr$^+$][BF$_4^-$] AND THE VECTORS (USED TO CALCULATE TOTAL NET CHARGE) COMPUTED USING THE DFT AND HF APPROACHES

Parameters	DFT/B3LYP/ 6-31++ G(d,p)	HF/B3LYP/ 6-31++ G(d,p)
Dipole moment	14.101 Debye	15.334 Debye
X	9.648	11.603
Y	10.272	10.505
Z	0.444	0.492
HOMO	-0.29582	-0.49846
LUMO	-0.01097	-0.10373
ΔE	-0.28485	-0.39473
Electronic energy	-834.428 Hartree	-829.776 Hartree
Mode of vibrations	99	99
Polarizability	–	110.117 a.u.

In comparison to the HF approach, the DFT/B3LYP method correlates better with the experimental results. To generate the experimental vibrational frequencies, a scale factor of 0.916 (DFT) is needed for [BmPyrr$^+$][BF$_4^-$] ion pair in the upper wavenumber area (above 1500 cm^{-1}). In order to duplicate the experimental frequencies, the HF approach needs a scale factor of 0.915 and overestimates the vibrational frequencies more than the B3LYP method does. The computed vibrational frequencies at the B3LYP level show a reasonably good overall agreement

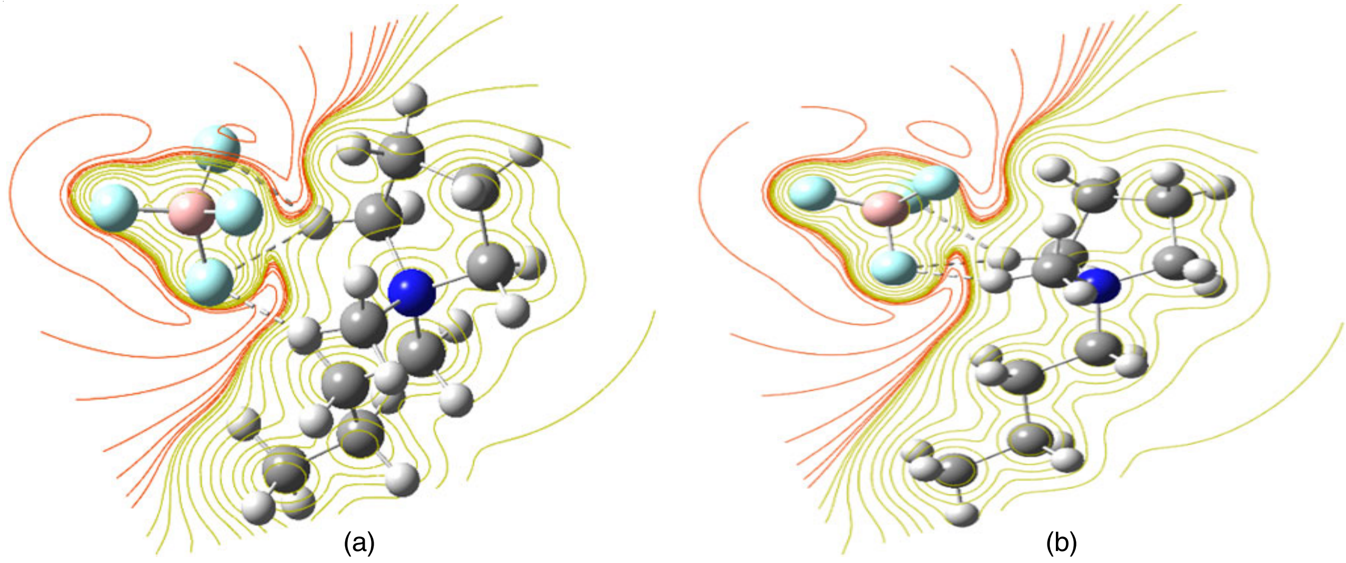

Fig. 7. The electrostatic potential maps of [BmPyrr$^+$][BF$_4^-$]

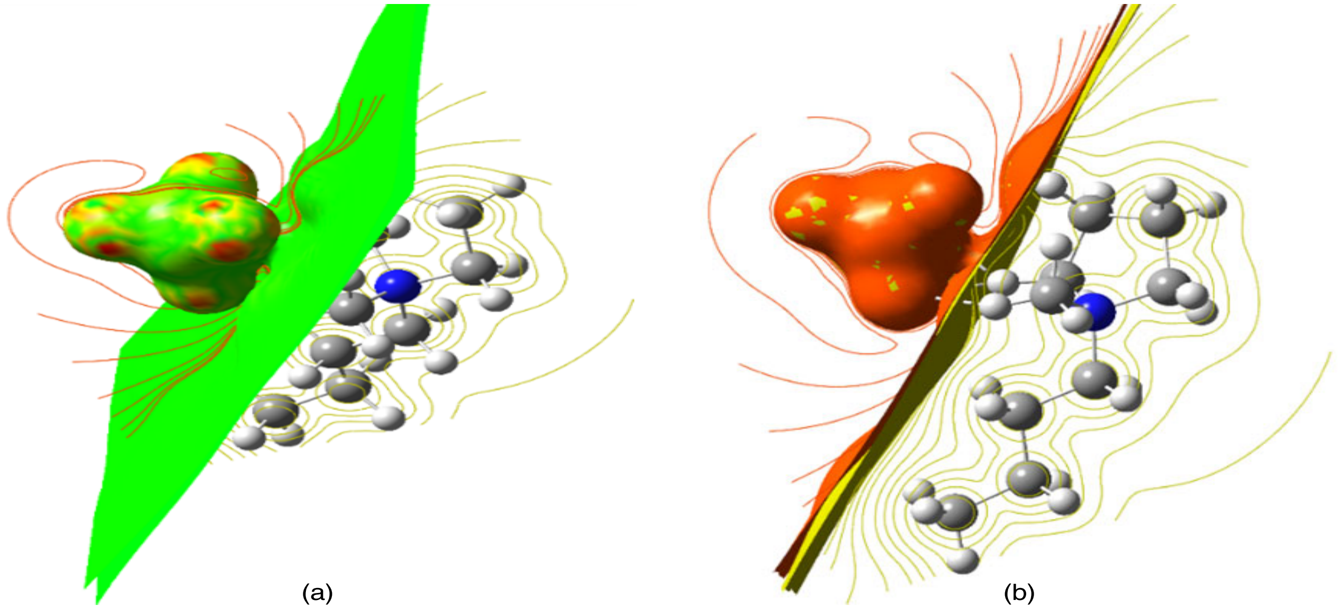

Fig. 8. The electrostatic potential maps of BmPyrr$^+$][BF$_4^-$] using DFT and HF approach

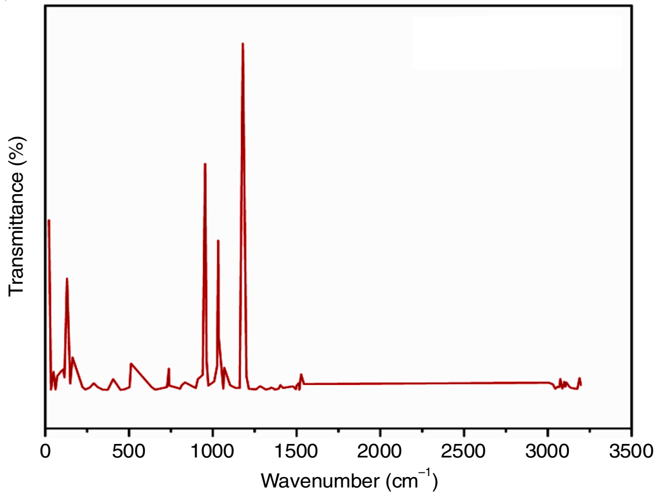

Fig. 9. Experimental infrared (IR) spectrum for [BmPyrr$^+$][BF$_4^-$]

of band locations with the obtained experimental frequencies. Table-14 displays the experimental peaks that have been assigned based on the DFT and HF computation.

Conclusion

At four equidistant temperatures (288.15 K to 318.15 K), the density and speed of sound values of 1-butyl-1-methyl pyrrolidinium tetrafluoroborate [BmPyrr$^+$][BF$_4^-$] were measured in various molal concentrations of benzylamine ranging from 0.01 mol kg^{-1} to 0.05 mol kg^{-1} in binary aqueous solution of benzylamine. Several types of interactions was predicted in the present ternary systems based on the multiple volumetric and acoustic parameters by utilizing the calculated density and speed of sound data. The positive values of V_ϕ and the negative values of $K_{\phi,s}$ indicate the existence of significant solute-solvent interactions of ionic nature. The transfer volumes, as well as the V_ϕ° and $K_{\phi,s}^\circ$ values show that the system under investigation

TABLE-14
EXPERIMENTAL AND THEORETICAL WAVENUMBERS (cm^{-1}), TENTATIVE ASSIGNMENTS AND INTENSITY VALUES FOR [BmPyrr$^+$][BF$_4^-$] USING THE DFT AND HF (B3LYP/6-31++ G (d,p) METHOD) IN GAS PHASE

Experimental ATR (cm^{-1})	DFT (B3LYP/6-31++ G(d,p) method)		HF (B3LYP/6-31++ G(d,p) method)		Tentative assignments
	Calculated (cm^{-1})	Intensity (%)	Calculated (cm^{-1})	Intensity (%)	
3497	3189	49.13	3382	33.06	O-H stretching
3010	3030	22.74	3165	27.06	N-H stretching
2953	3005	28.65	3149	39.23	C-H stretching *sp*^{2}
1524	1527	31.22	1536	11.28	C-H stretching *sp*^{3}
1497	1511	13.28	1489	6.86	C=C stretching
1381	1403	8.85	1415	4.92	C-H stretching
1334	1347	4.11	1398	10.33	C-N stretching
1292	1283	6.23	1248	640.55	-C-O stretching
1186	1179	532.78	1146	45.73	CH$_2$ bending
1107	1068	31.01	1115	273.16	-C-O stretching
1076	1032	201.20	1053	297.72	-C-O stretching
930	954	281.66	999	14.37	CH=CH bending
840	737	20.48	786	12.01	=CH$_2$ wagging

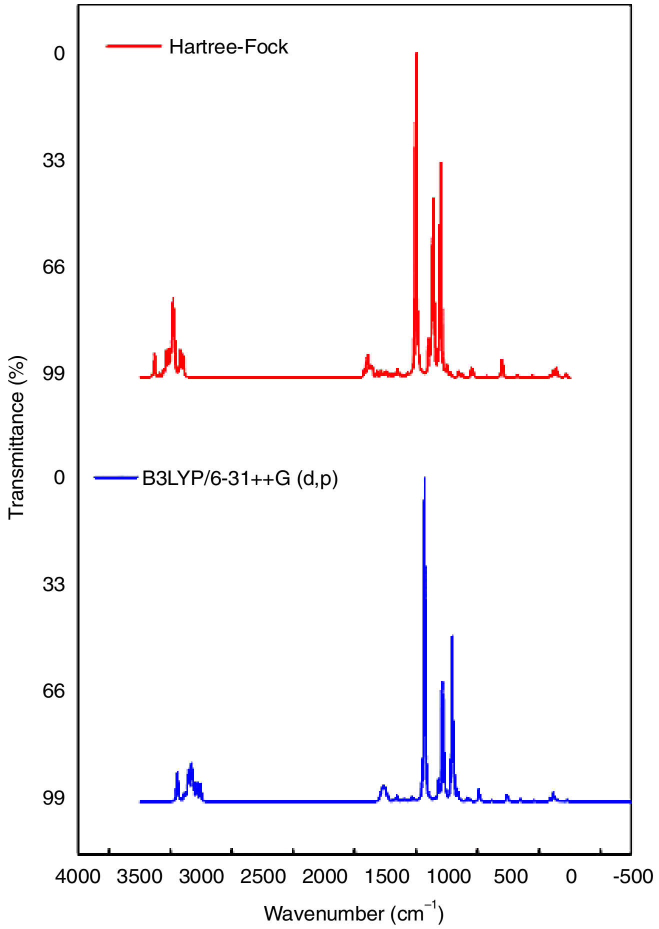

Fig. 10. Infrared (IR) spectra of [BmPyrr$^+$][BF$_4^-$] computed at B3LYP/6-31++ G(d,p) level in gaseous phase using DFT approach and HF approach

has ion-ion, hydrophilic-hydrophilic and ion-hydrophilic interactions. Also, the conductance studies for 1-butyl-1-methyl pyrrolidinium tetrafluoroborate in aqueous solution of benzylamine at various temperatures were investigated and the data obtained was further optimized for the calculation of different parameters like molar conductivity, limiting molar conductivity and activation energy. The results show that the conductivity of the solution is directly dependent on temperature and concentration. The nature of interactions determined using limiting molar conductance shows the presence of ion-solvent interactions in the present system. Higher the values of limiting molar conductance, greater the ion-solvent interactions. Also, the activation energy values confirm the great solubilization of ionic liquid in the solvent system. Based on the results of the volumetric, acoustic, and conductivity experiments, it can be concluded that the system exhibits the ion-ion, hydrophilic-hydrophilic and ion-hydrophilic interactions. In addition, DFT/B3LYP-D3 calculations were also carried out to gather data on the molecular geometry, interactions and other molecular characteristics of the ionic liquid under study. Changes in the structural parameters have been observed as a result of interactions among the molecules under study.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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