CHAPTER-IX

PHYSICOCHEMICAL STUDY OF AN IONIC LIQUID IN DIVERSE SEQUENTIAL ALKANOLS WITH THE MANIFESTATION OF SOLVATION CONSEQUENCE

9.1. Introduction:

Ionic liquids (ILs) are molten salts made of an anion an organic cation and were discovered the first IL, the ethylammonium nitrate in 1914 by Paul Walden, but their systematic study begun with the present century[1]. One or both the ions are large and the cation is usually organic and has low degree of symmetry. For this reason, anion-cation interactions are weak and hence their melting points are below 100˚C and usually below room temperature; however, if the size of the cation is too large, the van der Waals' forces will increase the fusion temperature [1]. Due to their ionic nature, all ILs have peculiar properties such as good solvents for organic and inorganic compound including some metal salts lack of vapour pressure, electrical conductivity and high thermal and electrochemical stability. All these characteristics make ionic liquids promising compounds for being used for batteries[2-4], organic synthesis, extraction and alloy electrodeposition[5], as well as potential "green solvent" replacements for volatile organic compounds (VOCs)[1].

Among the numerous proposed industrial applications of ionic liquids (ILs), their use to improve electrochemical process is one of the most interesting. To do that, it is necessary to know the physicochemical properties (mainly density, viscosity, electrical conductivity, refractive index) of binary mixture of IL and molecular solvent.

To the best of our knowledge, the studies of the present binary solution systems have not been reported earlier. Therefore, in present study, volumetric, viscometric, conductometric and refractometric studies have been carried for an IL, [BTMA]Cl in 1-Hexanol, 1-Heptanol and 1-Octanol. These solvents have useful applications in cosmetic, medicinal industry.

9.2. Experimental Section:

9.2.1 Source and purity of Materials:

The studied IL, [BTMA]Cl puriss grade was procured from Sigma-Aldrich, Germany and used as purchased as the purity assay of the salt was ≥97.0%. All the solvents of analytical grade were procured from sd. Fine Chemicals. The purities of solvents were ≥99.5%. The solvents were dried using standard methods.

9.2.2 Apparatus and Procedure:

A stock solutions of IL and 1-Alkanol were prepared by mass (Mettler Toledo AG-285 with uncertainty ±0.0003 g) and then working solutions were obtained by mass dilution. The conversions of molarity into molality[6] had been done using density values of respective solutions and adequate precautions were taken to reduce evaporation losses during mixing and throughout the experiment. The uncertainty molality of the solutions is evaluated to ±0.0001 mol.kg^{-1}.

The conductance measurements were carried out in a Systronic-308 conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately 0.1± 0.001 cm^{-1}. Measurements were made in a water bath maintained within T= (298.15 ± 0.01) K and the cell was calibrated by the method proposed by Lind et al. [7]. The conductance data were reported at a frequency of 1 kHz and the accuracy was ±0.3%.

The densities of the solvents and experimental solutions (°) were measured by means of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with a precision of ±0.00005g cm^{-3} maintained at ±0.01K of the desired temperature. It was calibrated by triply-distilled water and passing dry air [8].

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

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

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 [9]. Temperature of the experimental solution was maintained ± 0.01K using Brookfield

Digital TC-500 thermostat bath. Viscosities were measured with an accuracy of ±1 %. Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.

Refractive index was measured by means of Mettler Toledo digital refractometer. The light source was LED, λ= 589.3 nm. The calibration of refractometer was done twice using triply distilled water and being checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units [10].

9.3. Result and Discussion:

The solvent- properties are given in Table 1. The concentrations and molar conductances (Λ) of IL in 1-Hexanol, 1-Heptanol and 1-Octanol at298.15 K temperature are given in Table 2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation.

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

Linear conductance curve (Λ versus $\sqrt{c}$) were obtained for the electrolyte, [BTMA]Cl in 1-Hexanol extrapolation of $\sqrt{c}$ = 0 evaluated the starting limiting molar conductance for the electrolyte.

9.3.1 Ion-pair Formation

The ion-pair formation in case of conductometric study of [BTMA]Cl in 1-Hexanol is analysed by using the Fuoss conductance equation[11]. With a given set of conductivity values (c_j, Λ_j; j = 1…….n), three adjustable parameters, i.e., Λ_0, K_A and R have been derived from the Fuoss 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 centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [12] for determining the R value but in order to treat the data in our system, 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 by [13],

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

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

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

$$i = P\, i_o[(1+R_X)+E_L] \quad (3)$$

$$P = 1-\sim(1-¥) \quad (4)$$

$$¥ = 1-K_A c¥^2 f^2 \quad (5)$$

$$-\ln f = \quad © / 2(1+©R) \quad (6)$$

$$= e^2 / \left(£_r k_B T\right) \quad (7)$$

$$K_A = K_R / (1-\sim) = K_R / (1+K_S) \quad (8)$$

where, i_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, ¥ is the fraction of solute present as unpaired ion, ~ 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 performed using the program suggested by Fuoss. The initial i_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [14]. Input for the program is the no. of data, n, followed by ε, η (viscosity of the solvent mixture), initial i_0 value, T, ρ (density of the solvent mixture), mole fraction of the first component, molar masses, M_1 and M_2 along with c_j, i_j values where j = 1, 2…….n and an instruction to cover preselected range of R values.

In practice, calculations are performed by finding the values of i_0 and α which minimize the standard deviation, δ, whereby

$$¢^2 = \sum[\, i_j(cal) - i_j(obs)]^2 / (n-m) \quad (9)$$

for a sequence of R values and then plotting δ against R, the best- fit R corresponds to the minimum of the δ–R versus R curve. So, an approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minima is found in the δ - R curves, thus R values is assumed to be $R = a + d$, with terms having usual significance. 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 [BTMA]Cl in 1-Hexanol at 298.15 K is given in Table 3.

The standard Gibbs free energy change of solvation, ΔG^o, for [BTMA]Cl in 1-Hexanol is given by the following equation[15],

$$\mathrm{a}G^{o} = -RTlnK_{A} \tag{10}$$

It is observed from the Table 4 that the value of the Gibbs free energy is entirely negative for 1-Hexanol and it can be explained by considering the participation of specific covalent interaction in the ion-association process. The variation of equivalent conductance with square root of concentrations for 1-Hexanol has been shown in Figure 1.

The ionic conductances $\lambda_0^{\pm}$ (for $[BTMA]^{+}$ cation and $[Cl]^{-}$ anion) in solvent 1-Hexanol was calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a "reference electrolyte" . Table 5 shows the value of ionic conductances $\lambda_0^{\pm}$ and ionic Walden product $(\lambda_0^{\pm}\text{¦})$ (product of ionic conductance and viscosity of the solvent) along with Stokes' radii (r_S) and Crystallographic Radii (r_c) of [BTMA]Cl in 1-Hexanol at 298.15 K temperature.

9.3.2 Triple-ion Formation

But for the electrolyte in 1-Heptanol and 1-Octanol, a deviation in the conductance curves were obtained and show a decrease in conductance values up to a certain concentrations reach a minimum and then increase, indicating triple-ion formation.

The conductance data for the electrolyte in 1-Heptanol and 1-Octanol have been analysed using the classical Fuoss-Kraus equation [16] for triple-ion formation,

$$\text{i}\; g(c)\sqrt{c} = \frac{\text{i}_0}{\sqrt{K_p}} + \frac{\text{i}_0^{T} K_T}{\sqrt{K_p}}\left(1 - \frac{\text{i}}{\text{i}_0}\right)c \tag{11}$$

$$g(c) = \frac{\exp\{-2.303\quad {}^{/}(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \tag{12}$$

$${}^{/} = 1.8247\times10^{6}/(\text{£}T)^{1.5} \tag{13}$$

$$S = \sim\Lambda_0 + \quad = \frac{0.8204\times10^{6}}{(\text{£}T)^{1.5}}\Lambda_0 + \frac{82.501}{\text{¦}(\text{£}T)^{0.5}} \tag{14}$$

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 conductances of the two triple ions $[BTMA]_2^{+}Cl^{-}$ and $BTMA^{+}(Cl)_2^{-}$. $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make equation (11) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted [17] and Λ_0 values for the studied electrolytes have been calculated. Λ_0^T is calculated by setting the triple ion conductance equal to $2/3\Lambda_0$ [18].

The ratio Λ_0^T/Λ_0 was thus set equal to 0.667 during linear regression analysis of equation (11). Limiting molar conductance of triple-ions (Λ_0^T), slope and intercept of Eq. (11) for [BTMA]Cl in 1-Heptanol and 1-Octanol at 298.15 K are given in Table 6. A perusal of Table 6 and Figures 2 and 3 shows that the limiting molar conductance (Λ^0) of [BTMA]Cl is higher in 1-Heptanol than in 1-Octanol.

Linear regression analysis of equation (11) for the electrolytes with an average regression constant, $R^2 = 0.9653$, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_P and K_T listed in Table 7. It is observed that Λ passes through a minimum as c increases. The K_P and K_T values predict that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadrupoles). Here, the value of log (K_T/K_P) is found to be higher in 1-Octanol than in 1-Heptanol. This shows that 1-Octanol has higher tendency to form triple ion than 1-Heptanol.

At very low permittivity of the solvent ($\varepsilon<10$) electrostatic ionic interactions are very large. So the ion-pairs attract the free $_+$ve and -ve ions present in the solution medium as the distance of the closest approach of the ions become minimum as a result the possibility of higher aggregation through hydrogen bonding increases in low permittivity media[19,20]. This results in the formation of triple-ion, which acquire the charge of the respective ions in the solution [21] i.e.,

$$M^+ + A^- \leftrightarrow M^+\cdots\cdots\cdots A^- \leftrightarrow MA \qquad \text{(ion-pair)} \qquad (15)$$

$$MA + M^+ \leftrightarrow MAM^+ \qquad \text{(triple-ion)} \qquad (16)$$

$$MA + A^- \leftrightarrow MAA^- \qquad \text{(triple-ion)} \qquad (17)$$

where M^+ and A^- are respectively $[BTMA]^+$ and Cl^-. The effect of ternary association thus removes some non-conducting species, MA, from solution, and replaces them with triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolyte in 1-Heptanol and 1-Octanol.

Furthermore, the ion-pair and triple-ion concentrations, c_P and c_T respectively of the electrolyte have also been calculated at the minimum conductance concentration of [BTMA]Cl in 1-Heptanol and 1-Octanol using the following relations [22]:

$$\alpha = 1 / (K_P^{1/2} \cdot c^{1/2}) \qquad (18)$$

$$\alpha_T = (K_T / K_P^{1/2}) c^{1/2} \qquad (19)$$

$$c_P = c(1- \alpha - 3\alpha_T) \qquad (20)$$

$$c_T = (K_T / K_P^{1/2}) c^{3/2} \qquad (21)$$

Here α and α_T are the fractions of ion-pairs and triple-ions present in the salt-solutions respectively and are given in Table 8. Thus, the values of C_P and C_T given in Table 8 indicate that the ions are mainly present as ion-pairs even at high concentration and a small fraction existing as triple-ions.

9.3.3 Apparent molar volume:

Volumetric properties, like, apparent molar volume (φ_V) and limiting apparent molar volume (φ_V^0) consider important parameter for understanding of interactions taking place in solution systems. The apparent molar volume can be considered to be the sum of the geometric volume of the central solute molecule and changes in the solvent volume due to its interaction with the solute around the peripheral or co-sphere. Therefore, the apparent molar volumes (φ_V) have been calculated from the solutions densities using the suitable equation [23] and the values are given in Table 10.

$$\varphi_V = M/\rho - 1000 (\rho - \rho_0)/m\rho\rho_0 \qquad (22)$$

where M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_0 are the density of the solution and pure solvent respectively.

The values of (φ_V) are positive and large for all the systems, indicating strong solute-solvent interactions. The apparent molar volumes (φ_V) are found to decrease with increasing concentration (molality, m) of IL in same solvent at a particular temperature. It is also found that apparent molar volumes (φ_V) increase with increasing temperature and varied linearly with $\sqrt{m}$ and could be least-squares fitted to the Masson equation [24] from where limiting molar volume, φ_V^0 (infinite dilution partial molar volume) have been estimated and the values have been represented in Table 11.

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{m} \qquad (23)$$

where φ_V^0 is the apparent molar volume at infinite dilution, S_V^* is the experimental slope. At infinite dilution each solute molecule is bounded only by the solvent molecules and remains infinite distant from each other. As a result, that φ_V^0 is unaffected by solute-solute interaction and it is a measure only of the solute-solvent interaction.

An inspection of Table 11 and fig 4 shows that φ_V^0 are large and positive for IL, [BTMA]Cl at all the studied temperatures and highest in case of 1-Octanol. This indicates the presence of strongest solute–solvent interactions in 1-Octanol and the extent of interactions increases from 1-Hexanol to 1-Octanol. Comparing φ_V^0 and S_V^* values show that the magnitude of φ_V^0 is greater than S_V^*, suggesting that solute-solvent interactions dominates over the solute-solute interactions in all solutions at all studied temperature. Moreover, S_V^* values are negative at all temperatures and the values decreases with increasing temperature which indicates deteriorating force of solute-solute interaction.

The variation of φ_V^0 with temperature are fitted to a polynomial of the following

$$\varphi_V^0 = a_0 + a_1 T + a_2 T^2 \qquad (24)$$

where T is the temperature in Kelvin scale and a_0, a_1 and a_2 are the empirical coefficients depending on the solute, solvent. Values of coefficients of the above equation for the [BTMA]Cl in different solvent systems are reported in Table 12.

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

$$\varphi_E^0 = (\delta\varphi_V^0/\delta T)_P = a_1 + 2a_2T \qquad (25)$$

The limting apparent molar expansibilities, φ_E^0, change in magnitude with the change of temperature. The values of φ_E^0 for different solutions of studied IL at (T=298.15, 303.15 and 308.15 K) are reported in Table 13.

All the values of φ_E^0 shown in the Table 13 are positive for [BTMA]Cl in all the solvents and studied temperature. This fact helps to explain the absence of caging or packing effect for the [BTMA]Cl in solution [25].

The long-range structure-making and breaking capacity of the solute in mixed system can be determined by examining the sign of $(\delta\varphi_E^0/\delta T)_P$ developed by Hepler [26].

$$(\delta\varphi_E^0/\delta T)_P = (\delta^2\varphi_V^0/\delta T^2)_P = 2a_2 \qquad (26)$$

The positive sign or small negative of $(\delta\varphi_E^0/\delta T)_P$ signifies the molecule is a structure-maker; otherwise, it is a structure-breaker [27]. The perusal of Table 13 shows that, $(\delta\varphi_E^0/\delta T)_P$ values of [BTMA]Cl are all positive under examination. This signifies the IL, [BTMA]Cl is definitely structure–makers in all of the solutions.

9.3.4 Viscosity:

The experimental viscosity data for studied systems are listed in table 9. The relative viscosity (η_r) has been calculated using Jones-Dole equation [28].

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \qquad (27)$$

Where $\eta_r = \eta/\eta_0$ is the relative viscosity, η and η_0 are the viscosities of binary solutions (IL +1-alkanol) and solvent (1-alkanol) respectively and m is the molality of [BTMA]Cl in binary solutions. Where A is known as Falkenhagen coefficient [29] as it is determined by the ionic attraction theory of Falkenhagen-Vernon and B is empirical constants known as viscosity B- coefficients, which are specific to solute-solute and solute-solvent interactions respectively. The values of A- and B- coefficients are evaluated by least-square method by plotting $(\eta_r - 1)/\sqrt{m}$ against $\sqrt{m}$ and reported in Table 10. It is observed from Table 10 the values of the A-coefficient are found to decrease with rise in temperature. This fact indicates the presence of very weak solute-solute interaction and also in excellent agreement with those obtained from S_V^* values.

The valuable information about the solvation of the solute and its effect on the structure of the solvent in the local vicinity of the solute molecules in solutions has been obtained from viscosity B-coefficient [30]. It is found from Table 11 and Fig 5; the values of B-coefficient are positive and much higher than A-coefficient which signifies solute-solvent interaction is leading over solute-solute interaction. It is also observed that the value of viscosity B-coefficient increases with increasing temperature and also increases from 1-Hexanol to 1-Octanol. These results are in good agreement with those obtained from φ_V^0 values.

It is observed from Table 11 that the values of the B-coefficient of [BTMA]Cl increases with temperature, i.e. the dB/dT values are positive. From Table 15, the small positive dB/dT values for the [BTMA]Cl behaves almost as structure-maker.

The free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0\neq}$ as proposed by Eyring and co-workers [31] could be calculated from the following equation:

$$\eta_0 = (hN_A/ V_1^0) \exp(\Delta\mu_1^{0\neq}/RT) \qquad (28)$$

Where h, N_A and V_1^0 are the Planck's constant, Avogadro's number and partial molar volume of the solvent respectively. The equation (28) can be rearranged as follows we get

$$\Delta\mu_1^{0\neq} = RT \ln (\eta_0 V_1^0/ hN_A) \qquad (29)$$

Feakins et al. [32-34] suggested that if equations (27) and (28) are obeyed, then

$$B = (V_1^0 - V_2^0) + V_1^0 [(\Delta\mu_1^{0\neq} - \Delta\mu_2^{0\neq})/RT] \qquad (30)$$

where V_2^0 is the limiting partial molar volume (φ_V^0) of the solute and $\Delta\mu_2^{0\neq}$ is the ionic activation energy per mole of solute at infinite dilution . Rearranging the equation (30) we get

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/ V_1^0)[B - (V_1^0 - V_2^0)] \qquad (31)$$

From Table 7, it is evident that $\Delta\mu_2^{0\neq}$ values are all positive and much larger than $\Delta\mu_1^{0\neq}$, suggesting that interaction between solute (IL) and solvent (1-Alkanol) molecules in the ground state is stronger than in the transition state. According to free energy terms the solvation of solute in the transition state is unfavourable.

The entropy of activation ($\Delta S_2^{0\neq}$) [33] for the solution has been calculated using relation:

$$\Delta S_2^{0\neq} = - d(\Delta\mu_2^{0\neq})/dT \qquad (32)$$

where $\Delta S_2^{0\neq}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against T by using a least-squares treatment.

The enthalpy of activation ($\Delta H_2^{0\neq}$) [33] has been obtained from the relation:

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \qquad (33)$$

The values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are also reported in Table 14.

It is evident from Table 14, that $\Delta\mu_1^{0\neq}$ is practically constant at all the solvents suggesting that $\Delta\mu_2^{0\neq}$ is mainly dependent on the viscosity coefficients and $(V_1^0 - V_2^0)$ terms. Positive $\Delta\mu_2^{0\neq}$ values at all studied temperature and all solvent suggests that the process of viscous flow becomes difficult as we move from 1-Hexanol to 1-Octanol and with rise in the temperature. Therefore, the formation of transition state becomes less favourable. Feakins et al. [33] proposed that, $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes having positive *B*-coefficients and indicates a stronger solute –solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure [33, 35]. The negative values of both $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ suggest that the formation of transition state is associated with bond-making and an increase in order. Although a detailed mechanism for this is not easily advanced, it may be suggested that the slip-plane is in the disordered state [33, 36]. According to Feakins et al. model, as $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$, the solute [BTMA]Cl behaves as structure makers. This again supports the behaviour of *dB/dT* for the solute in the solvent systems.

Furthermore, it is attractive to observe that there is linear correlation between viscosity *B*-coefficients of the studied IL, [BTMA]Cl with the limiting apparent molar volumes (φ_V^0) in different solvent systems. From the above fact it means

$$B = A_1 + A_2\,\varphi_V^0 \qquad (34)$$

The coefficients A_1 and A_2 are listed in Table 15. As both viscosity *B*-coefficient and limiting apparent molar volume define the solute-solvent interaction in solution. The linear variation of viscosity *B*-coefficient and limiting apparent molar volume (φ_V^0) reflects the positive slope (or A_2).

9.3.5 Refractive Index:

The measurement of refractive index is also a suitable method for investigating the molecular interaction existing in solution. The molar refraction (R_M) can be calculated from the Lorentz-Lorenz relation [37]. The refractive index of a substance is defined as the ratio c_0/c, where c and c_0 is the velocity of light in the medium and in vacuum respectively. Stated more simply that the refractive index of a compound describes its ability to refract light as it passes from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [38]. As stated by Deetlefs et al.[39] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser.

The Limiting molar refraction (R_M^0) estimated from the following equation (35) and presented in Table 16.

$$R_M = R_M^0 + R_S \sqrt{m} \qquad (35)$$

Hence, a perusal of Table 16 we found that the refractive index and the molar refraction are higher for the studied [BTMA]Cl in all the solvent systems, indicating to the fact that the molecules are more tightly packed in the solution. It is also revealed that the [BTMA]Cl in 1-Octanol is more tightly packed and more solvated than 1-Heptanol and 1-Hexanol. This is also in good agreement with the results obtained from apparent molar volume and viscosity *B*-coefficient and discussed above.

9.4. Conclusion

The extensive study of IL, [BTMA]Cl in 1-Hexanol, 1-Heptanol and 1-Octanol leads to the conclude that, the IL is more associated in 1-Octanol than the other two solvents (scheme 2). It can also be found that in the conductometric studies in 1-Heptanol and 1-Octanol the [BTMA]Cl mostly remains as triple-ions than ion-pairs but in 1-Hexanol the [BTMA]Cl remains as ion-pairs (scheme 3). There is more ion-solvent interaction in 1-Octanol than 1-Heptanol than 1-Hexanol. The experimental values obtained from the volumetric, viscometric and refractometric studies also suggest that in solution the ion–solvent interaction is more than the ion–ion interaction due to the greater covalent interaction (van der Waals' interaction) between the hydrocarbon part of [BTMA]Cl and the hydrocarbon chain of 1-Alkanols (scheme 1). As the length of the alkyl-chain decreases the extent of van der Waals' force of attraction decreases hence the extent of ion–solvent interaction of [BTMA]Cl is enhanced by the following order (scheme 2):

1-Octanol > 1-Heptanol > 1-Hexanol.

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Tables:

Table 1: Experimental values of density (ρ), viscosity (η) at three different temperatures (298.15 K, 303.15 K and 308.15 K); refractive index (n_D) and relative permittivity (ε) at 298.15 K of different solvent systems*

Solvent	Temperature (K)	$\rho \times 10^{-3}$ /kg·m^{-3}	η /mP·s	n_D	ε
1-Hexanol	298.15	0.81648	4.61	1.4161	13.3
	303.15	0.81340	4.05		
	308.15	0.80976	3.95		
1-Heptanol	298.15	0.81942	5.95	1.4221	6.1
	303.15	0.81572	5.12		
	308.15	0.81217	4.29		
1-Octanol	298.15	0.82237	7.62	1.4274	5.1
	303.15	0.81898	6.68		
	308.15	0.81547	5.65		

*Standard uncertainties *u* are: *u* (ρ) =2×10^{-5} kg·m^{-3}, *u* (η) =0.003 mP·s, *u* (n_D) =0.0002 and *u* (*T*) =0.01K

Table 2. The concentration (*c*) and molar conductance (Λ) of [BTMA]Cl in 1-Hexanol, 1-Heptanol and 1-Octanol at 298.15 K.

$c \cdot 10^4$/ mol·dm^{-3}	$\Lambda \cdot 10^4$/ S·m^2·mol^{-1}	$c \cdot 10^4$/ mol·dm^{-3}	$\Lambda \cdot 10^4$/ S·m^2·mol^{-1}	$c \cdot 10^4$/ mol·dm^{-3}	$\Lambda \cdot 10^4$/ S·m^2·mol^{-1}
1-Hexanol		1-Heptanol		1-Octanol	
1.0153	31.22	0.8906	18.06	0.8934	14.94
1.4234	29.82	1.2048	16.78	3.3664	13.66
1.8547	27.57	1.6082	15.61	4.9587	12.48
2.2115	26.4	2.0023	14.72	5.9398	11.65

2.7127	25.21	2.4885	13.87	7.5234	10.75
2.9235	24.12	2.7678	13.31	8.3302	10.19
3.3214	22.62	3.1851	12.64	9.1667	9.52
3.8456	21.15	3.5089	12.21	10.3584	9.09
4.1252	20.21	3.8682	11.57	11.4448	8.45
4.4451	19.64	4.1787	11.08	12.4613	7.96
4.6652	18.96	4.5847	10.4	13.3139	7.28
4.8424	18.14	4.83	10.02	14.4328	6.47
5.2436	17.35	5.2378	9.09	15.3593	5.97
5.4363	16.54	5.6238	8.98	16.3615	5.86
5.7211	15.87	5.8905	9.91	17.4811	6.79

Table 3. Limiting molar conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss-conductance equation for [BTMA]Cl in 1-Hexanol at 298.15 K.

Solvent	**$\Lambda_o\cdot10^4/S\cdot m^2\cdot mol^{-1}$**	**K_A/ dm^3ĕmol^{-1}**	**R/Å**	**δ**
1-Hexanol	33.65	513.61	11. 21	2.11

Table 4. Walden product ($\Lambda_o\cdot$¦) and Gibbs energy change (ΔG°) of Benzyltrimethylammonium chloride in 1-Hexanol at 298.15 K.

Solvent	**$\Lambda_o\cdot$¦$\cdot10^4$/ $S\cdot m^2\cdot mol^{-1}mPa$**	**$\Delta G^{\circ}\cdot10^{-4}$/ $kJ\cdot mol^{-1}$**
1-Hexanol	155.13	-15.4221

Table 5. Limiting Ionic Conductance ($\lambda_0^{\pm}$), Ionic Walden Product ($\lambda_0^{\pm}$¦) , Stokes' Radii (r_s), and Crystallographic Radii (r_c) of [BTMA]Cl in 1-Hexanol at 298.15 K.

Solvent	ion	$\lambda_0^{\pm}$ ($S{\cdot}m^2{\cdot}mol^{-1}$)	$\lambda_0^{\pm}$¦ ($S{\cdot}m^2{\cdot}mol^{-1}mPa$)	r_s (Å)	r_c(Å)
1-Hexanol	$BTMA^+$	56.18	258.98	4.21	3.53
	Cl^-	112.41	518.21	2.05	1.77

Table 6. 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 [BTMA]Cl in 1-Heptanol and 1-Octanol at 298.15 K.

Solvent	$\Lambda_0{\cdot}10^4$ $/S{\cdot}m^2{\cdot}mol^{-1}$	$\Lambda_0^T{\times}10^4$ $/S{\cdot}m^2{\cdot}mol^{-1}$	Slope×10^3	Intercept ×10^{-2}
1-Heptanol	42.39	28.28	3.74	-6.66
1-Octanol	54.65	36.45	8.81	-12.29

Table 7. Salt concentration at the minimum conductivity (C_{min}) along with the ion-pair formation constant (K_P), triple ion formation constant (K_T) for [BTMA]Cl in 1-Heptanol and 1-Octanol at 298.15 K.

Solvent	$c_{min}{\cdot}10^4$/ $mol{\cdot}dm^{-3}$	log c_{min}	K_P. 10^2/ $(mol{\cdot}dm^{-3})^{-1}$	K_T. 10^3/ $(mol{\cdot}dm^{-3})^{-1}$	K_T / K_P	log K_T / K_P
1-Heptanol	5.34	0.7102	13.29	25.44	19.1	1.28
1-Octanol	5.56	0.7256	3.18	6.21	19.5	1.29

Table 8. 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 [BTMA]Cl in 1-Heptanol and 1-Octanol at 298.15 K.

Solvents	$c_{min}{\cdot}10^4$/ $mol{\cdot}dm^{-3}$	$\alpha \cdot 10^{-3}$	$\alpha_T \cdot 10^2$	$c_P \cdot 10^{-3}$/ $mol{\cdot}dm^{-3}$	$c_T{\cdot}10^{-2}$/ $mol \cdot dm^{-3}$
1-Heptanol	5.15	11.18	16.56	11.28	12.54
1-Octanol	5.68	18.35	7.24	22.34	5.38

Table 9: Experimental values of density (ρ) and viscosity (η) of [BTMA]Cl in different solvent systems at three different temperatures*

molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s
				1-Hexanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0123	0.81691	4.77	0.0123	0.81377	4.17	0.0124	0.81006	3.58
0.0308	0.81760	4.91	0.0309	0.81439	4.29	0.0310	0.81059	3.68
0.0493	0.81833	5.04	0.0495	0.81508	4.41	0.0498	0.81117	3.78
0.0680	0.81908	5.16	0.0683	0.81580	4.52	0.0686	0.81181	3.87
0.0868	0.81987	5.28	0.0871	0.81659	4.62	0.0876	0.81249	3.97
0.1056	0.82068	5.39	0.1060	0.81738	4.73	0.1066	0.81321	4.07
				1-Heptanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0122	0.81979	6.16	0.0123	0.81602	5.27	0.0123	0.81241	4.40
0.0306	0.82041	6.35	0.0308	0.81656	5.43	0.0309	0.81287	4.53
0.0492	0.82108	6.53	0.0494	0.81716	5.58	0.0496	0.81341	4.66
0.0678	0.82179	6.70	0.0681	0.81781	5.73	0.0684	0.81402	4.78
0.0865	0.82253	6.86	0.0869	0.81848	5.87	0.0873	0.81471	4.91
0.1053	0.82329	7.01	0.1058	0.81920	6.03	0.1063	0.81541	5.05
				1-Octanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0122	0.82268	7.89	0.0122	0.81922	6.89	0.0123	0.81564	5.80
0.0305	0.82321	8.14	0.0307	0.81969	7.10	0.0308	0.81605	5.98
0.0490	0.82381	8.38	0.0492	0.82023	7.31	0.0494	0.81654	6.15
0.0675	0.82444	8.61	0.0678	0.82083	7.51	0.0682	0.81711	6.33
0.0862	0.82511	8.82	0.0866	0.82146	7.71	0.0870	0.81773	6.51
0.1049	0.82581	9.04	0.1054	0.82211	7.93	0.1059	0.81834	6.70

* Standard uncertainties u are: $u(\rho) = 2\times10^{-5}$ kg·m^{-3}, $u(\eta) = 0.003$ mP·s and $u(T) = 0.01$K

Table 10: Apparent molar volume (φ_V) and $(\eta_r\text{-}1)/\sqrt{m}$ of [BTMA]Cl in different solvent systems at three different temperatures*

molality /mol·kg^{-1}	φ_V ×10^6 / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	molality /mol·kg^{-1}	φ_V ×10^6 / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	molality /mol·kg^{-1}	φ_V ×10^6 / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$
				1-Hexanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0123	174.76	0.3133	0.0123	182.68	0.2670	0.0124	192.88	0.2189
0.0308	172.46	0.3711	0.0309	179.41	0.3372	0.0310	188.32	0.3026
0.0493	170.78	0.4200	0.0495	176.65	0.3994	0.0498	185.78	0.3725
0.0680	169.44	0.4575	0.0683	174.55	0.4441	0.0686	183.29	0.4157
0.0868	168.11	0.4934	0.0871	172.26	0.4768	0.0876	181.15	0.4648
0.1056	166.91	0.5207	0.1060	170.72	0.5156	0.1066	179.19	0.5090
				1-Heptanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0122	181.34	0.3192	0.0123	190.74	0.2714	0.0123	199.08	0.2267
0.0306	178.19	0.3840	0.0308	186.40	0.3451	0.0309	194.16	0.3181
0.0492	175.97	0.4397	0.0494	183.51	0.4042	0.0496	190.47	0.3871
0.0678	174.02	0.4842	0.0681	181.05	0.4565	0.0684	187.22	0.4366
0.0865	172.39	0.5201	0.0869	179.30	0.4989	0.0873	183.96	0.4891
0.1053	171.05	0.5491	0.1058	177.45	0.5464	0.1063	181.70	0.5434
				1-Octanol				
	T = 298.15 K			T = 303.15 K			T = 308.15 K	
0.0122	188.10	0.3211	0.0122	197.43	0.2802	0.0123	206.86	0.2411
0.0305	184.84	0.3906	0.0307	192.20	0.3591	0.0308	199.06	0.3328
0.0490	182.02	0.4507	0.0492	188.58	0.4252	0.0494	194.91	0.3980
0.0675	180.03	0.5001	0.0678	185.66	0.4771	0.0682	191.14	0.4610
0.0862	178.20	0.5367	0.0866	183.47	0.5242	0.0870	188.12	0.5161
0.1049	176.59	0.5773	0.1054	181.77	0.5766	0.1059	186.30	0.5733

* Standard uncertainties *u* are: *u* (*T*) =0.01K

Table 11: Limiting apparent molar volume (φ_V^0), experimental slope (S_V^*), viscosity A- and B-coefficient of [BTMA]Cl in different solvent systemss at three different temperatures*

Solvent	Temperature (K)	$\varphi_V^0 \times 10^6$ / $m^3\ mol^{-1}$	$S_V^* \times 10^6$ / $m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$	B / $kg \cdot mol^{-1}$	A / $kg^{1/2} \cdot mol^{-1/2}$
1-Hexanol	298.15	178.8	-36.46	0.980	0.202
	303.15	189.1	-56.43	1.161	0.137
	308.15	199.7	-62.81	1.341	0.068
1-Heptanol	298.15	186.6	-48.34	1.093	0.196
	303.15	197.3	-61.70	1.278	0.124
	308.15	208.3	-81.69	1.452	0.064
1-Octanol	298.15	194.1	-54.32	1.207	0.184
	303.15	205.2	-73.82	1.376	0.122
	308.15	216.6	-96.03	1.536	0.063

* Standard uncertainties values of u are: u (T) =0.01K

Table 12: Values of various coefficients of equation-24 for [BTMA]Cl in different solvent systems*

Solvent	$a_0 \times 10^6$ / $m^3\ mol^{-1}$	$a_1 \times 10^6$ / $m^3\ mol^{-1} K^{-1}$	$a_2 \times 10^6$ / $m^3\ mol^{-1} K^{-2}$
1-Hexanol	162.9654	-1.9146	0.0066
1-Heptanol	128.2303	-1.7123	0.0064
1-Octanol	93.1952	-1.5101	0.0062

* Standard uncertainties values of u are: u (T) =0.01K

Table 13: Limiting apparent molar expansibilities (φ_E^0) for [BTMA]Cl in different solvent systems at 298.15, 303.15 and 308.15 K*

Solvent	$\varphi_E^0\times10^6$/ m^3 mol^{-1} K^{-1}			$(\delta\varphi_E^0/\delta T)_P\times10^6$ / m^3 mol^{-1} K^{-2}
	T=298.15 K	T=303.15 K	T=308.15 K	
1-Hexanol	2.02098	2.08698	2.15298	0.0132
1-Heptanol	2.10402	2.16802	2.23202	0.0128
1-Octanol	2.18696	2.24896	2.31096	0.0124

* Standard uncertainties values of *u* are: *u* (*T*) =0.01K

Table 14: Values of V_1^0, (V_1^0–V_2^0), $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ for [BTMA]Cl in different solvent systems at different temperatures*

Parameters	1-Hexanol			1-Heptanol			1-Octanol		
	T=298.15K	303.15K	308.15K	T=298.15K	303.15K	308.15K	T=298.15K	303.15K	308.15K
$V_1^0.10^6$ /$m^3\cdot mol^{-1}$	124.93	125.40	125.96	141.56	142.21	142.83	158.08	158.73	159.42
$(V_1^0–V_2^0).10^6$ /$m^3\cdot mol^{-1}$	-53.87	-63.70	-73.74	-45.04	-55.49	-65.47	-36.02	-46.47	-57.18
$\Delta\mu_1^{0\neq}$ /KJ.mol^{-1}	18.03	18.02	17.95	18.97	18.93	18.80	19.86	19.87	19.78
$\Delta\mu_2^{0\neq}$ /KJ.mol^{-1}	38.55	42.63	46.72	38.90	42.56	46.02	39.35	42.46	45.39
$T\Delta S_2^{0\neq}$ / KJ.mol^{-1}	-243.59	-247.67	-251.76	-211.98	-215.54	-219.09	-179.78	-182.80	-185.81
$\Delta H_2^{0\neq}$ /KJ.mol^{-1}	-205.04	-205.04	-205.04	-173.08	-172.98	-173.08	-140.43	-140.34	-140.43

* Standard uncertainties values of *u* are: *u* (*T*) =0.01K

Table 15: Values of *dB/dT*, A_1 and A_2 coefficients for the [BTMA]Cl in different solvent systems at different temperatures at 298.15 K, 303.15 K and 308.15 K*

Solvent	*dB/dT*	A_1	A_2
1-Hexanol	0.0361	-2.107	0.017
1-Heptanol	0.0359	-1.993	0.016
1-Octanol	0.0329	-1.628	0.014

* Standard uncertainties values of *u* are: *u* (*T*) =0.01K

Table16: Refractive Index (n_D), Molar Refraction (R_M) and Limiting Molar Refraction (R_M^0) [BTMA]Cl in different solvent systems at 298.15 K*

molality /mol·kg^{-1}	n_D	$R_M \times 10^6$ / m^3 mol^{-1}	$R_M^0 \times 10^6$ / m^3 mol^{-1}
1-Hexanol			
0.0123	1.4163	57.072	
0.0307	1.4168	57.085	
0.0493	1.4173	57.099	57.03
0.0679	1.4178	57.112	
0.0867	1.4184	57.123	
0.1055	1.4190	57.134	
1-Heptanol			
0.0122	1.4223	57.592	
0.0306	1.4227	57.600	
0.0492	1.4232	57.607	57.57
0.0678	1.4236	57.613	
0.0865	1.4241	57.618	
0.1053	1.4246	57.624	
1-Octanol			
0.0122	1.4277	58.035	
0.0305	1.4281	58.043	
0.0490	1.4285	58.050	58.01
0.0675	1.4289	58.058	
0.0861	1.4294	58.063	
0.1048	1.4299	58.071	

*Standard uncertainties *u* are: *u* (n_D) =0.0002 and *u* (*T*) =0.01K

Figures:

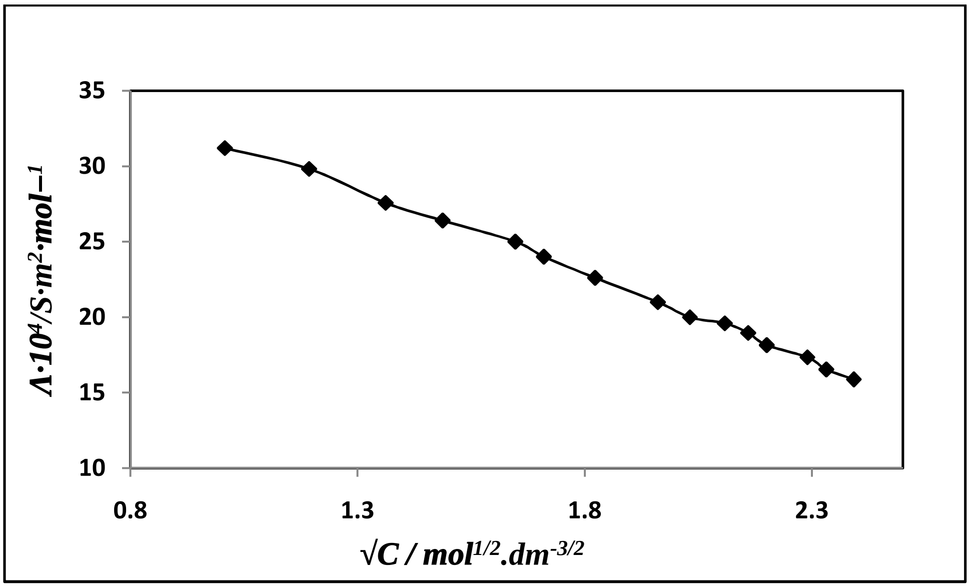


Figure 1. Plot of molar conductance (Λ) versus √C for [BTMA]Cl in 1-Hexanol at 298.15 K.

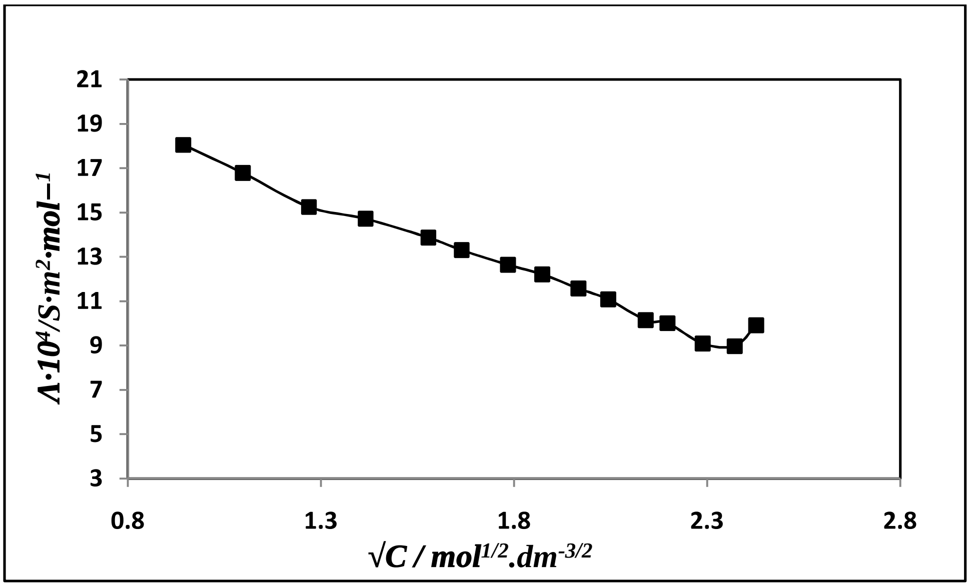


Figure 2. Plot of molar conductance (Λ) versus √C for [BTMA]Cl in 1-Heptanol at 298.15 K.

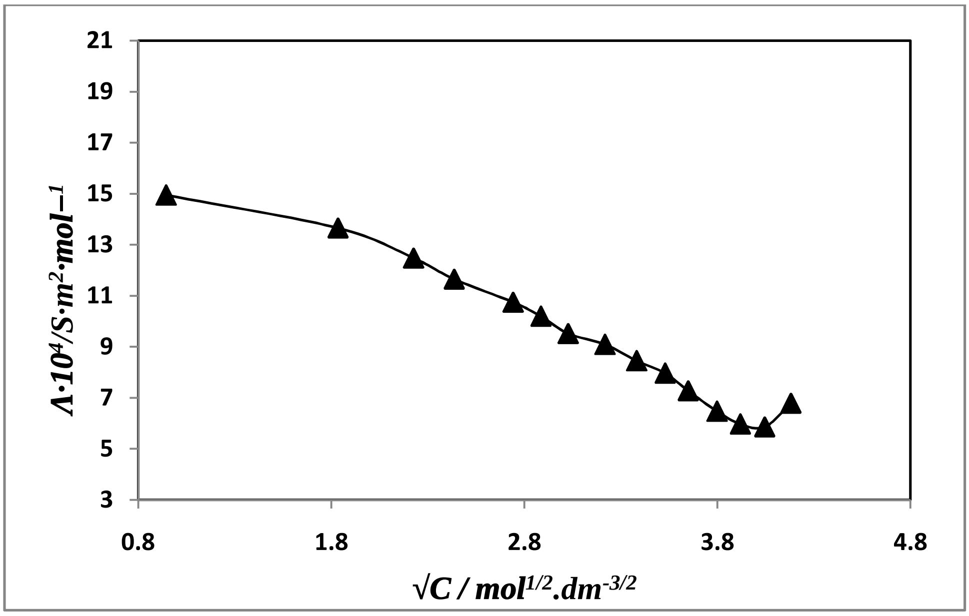


Figure 3. Plot of molar conductance (Λ) versus √C for [BTMA]Cl in 1-Octanol at 298.15K.

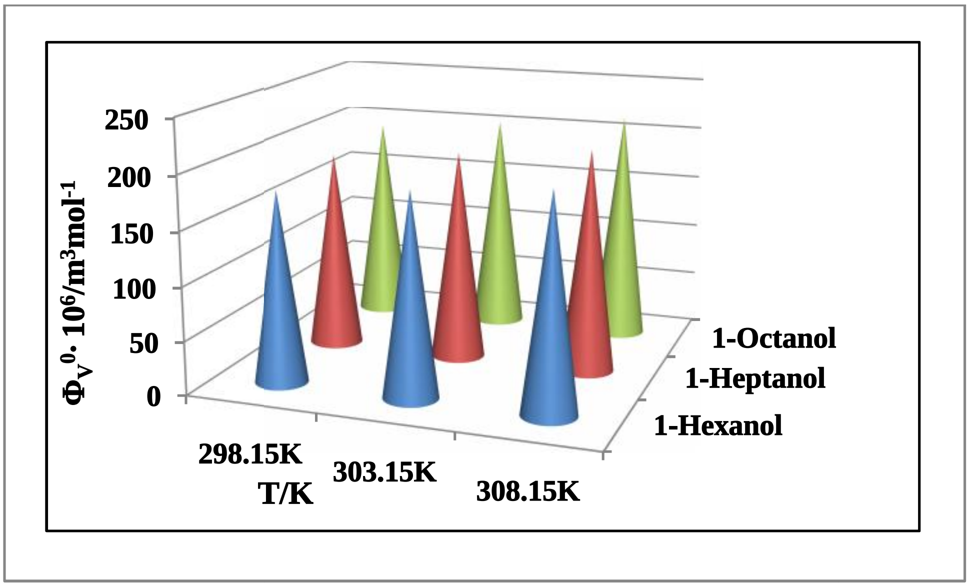


Figure 4: Plot of *φv⁰* as a function of temperature (*T/K*) in different solvent systems

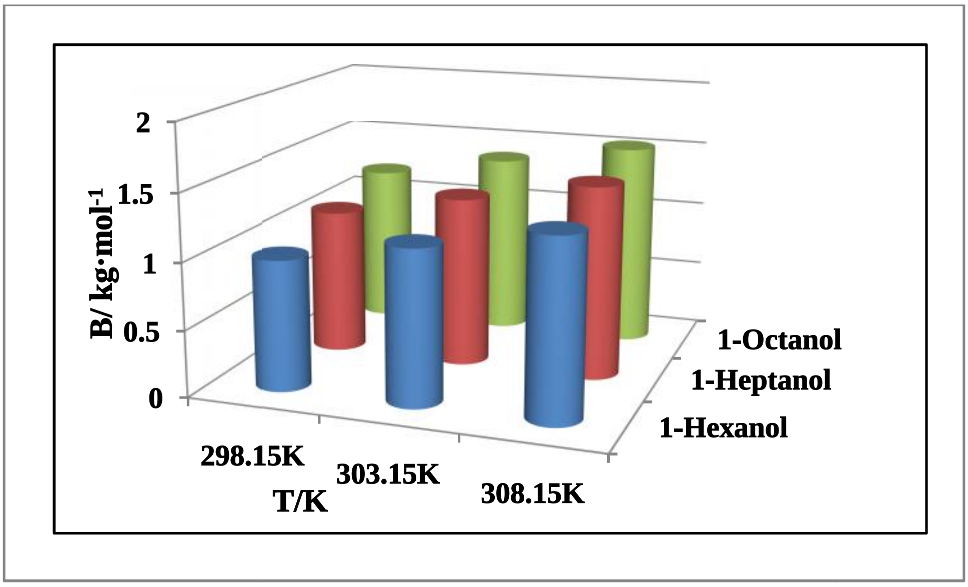


Figure 5: Plot of *B* as a function of temperature (*T/K*) in different solvent systems

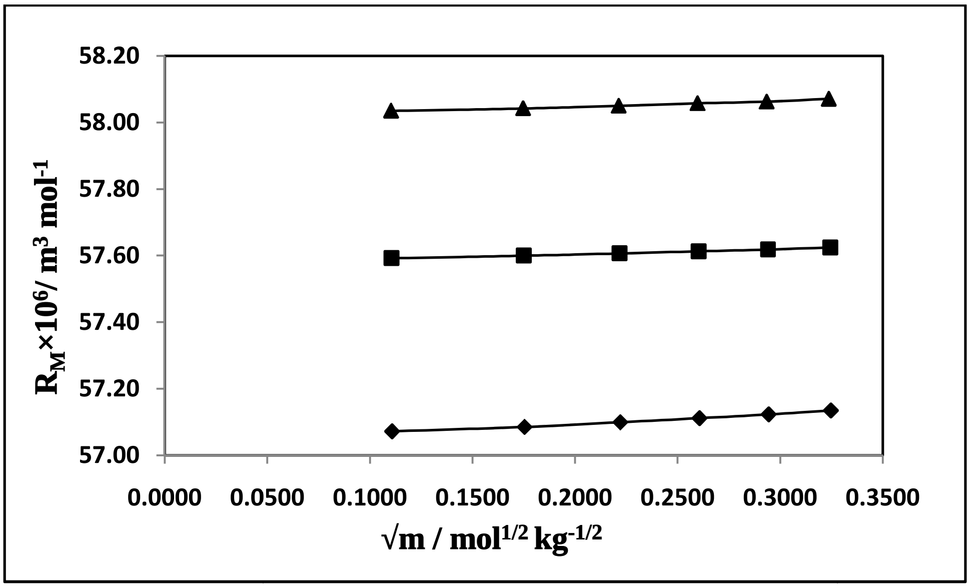
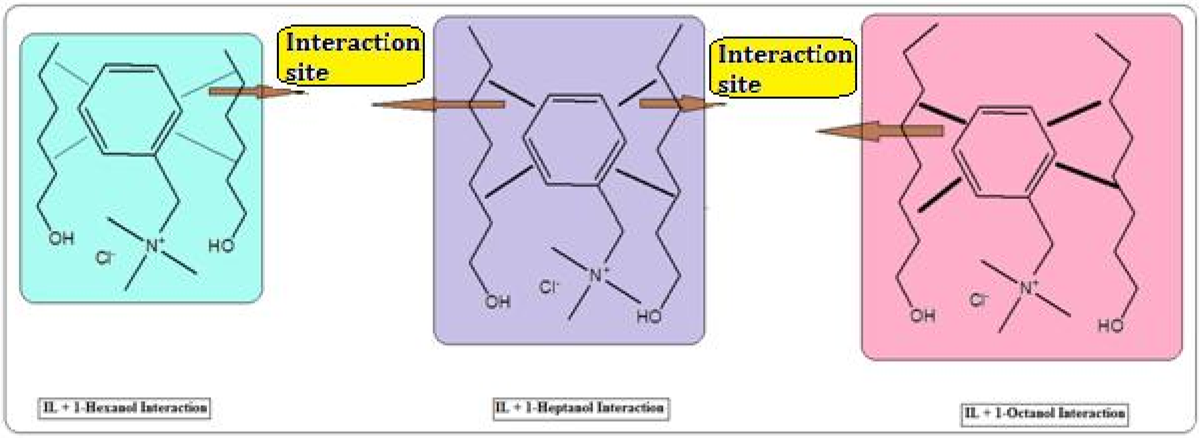
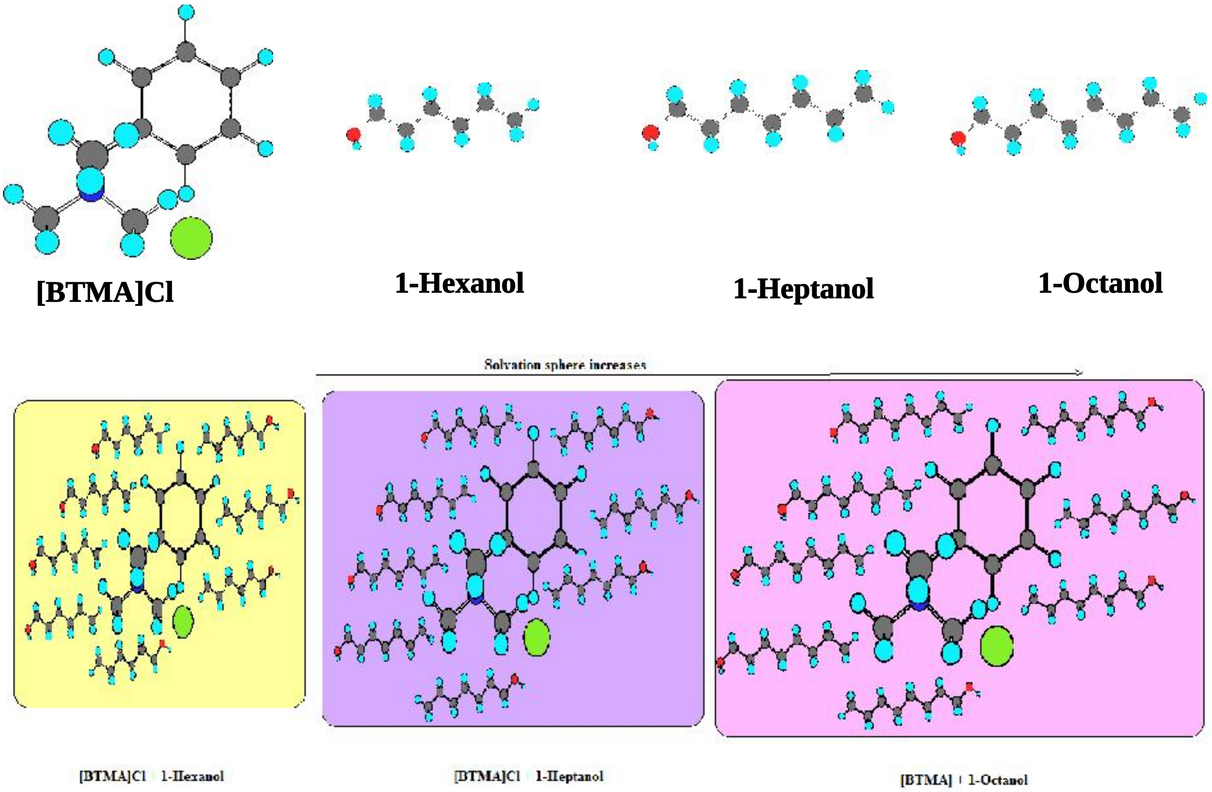


Figure 6: Plot of molar refractive index (R_M) against square root of concentration ($\sqrt{m}$) for [BTMA]Cl in different solvent systems, (♦) *1-Hexanol*; (■) *1-Heptanol* and (▲) 1-*Octanol*.

Schemes:



Scheme 1. Plausible sites of interactions between solute-solvent ([BTMA]Cl-1-Alkanol)

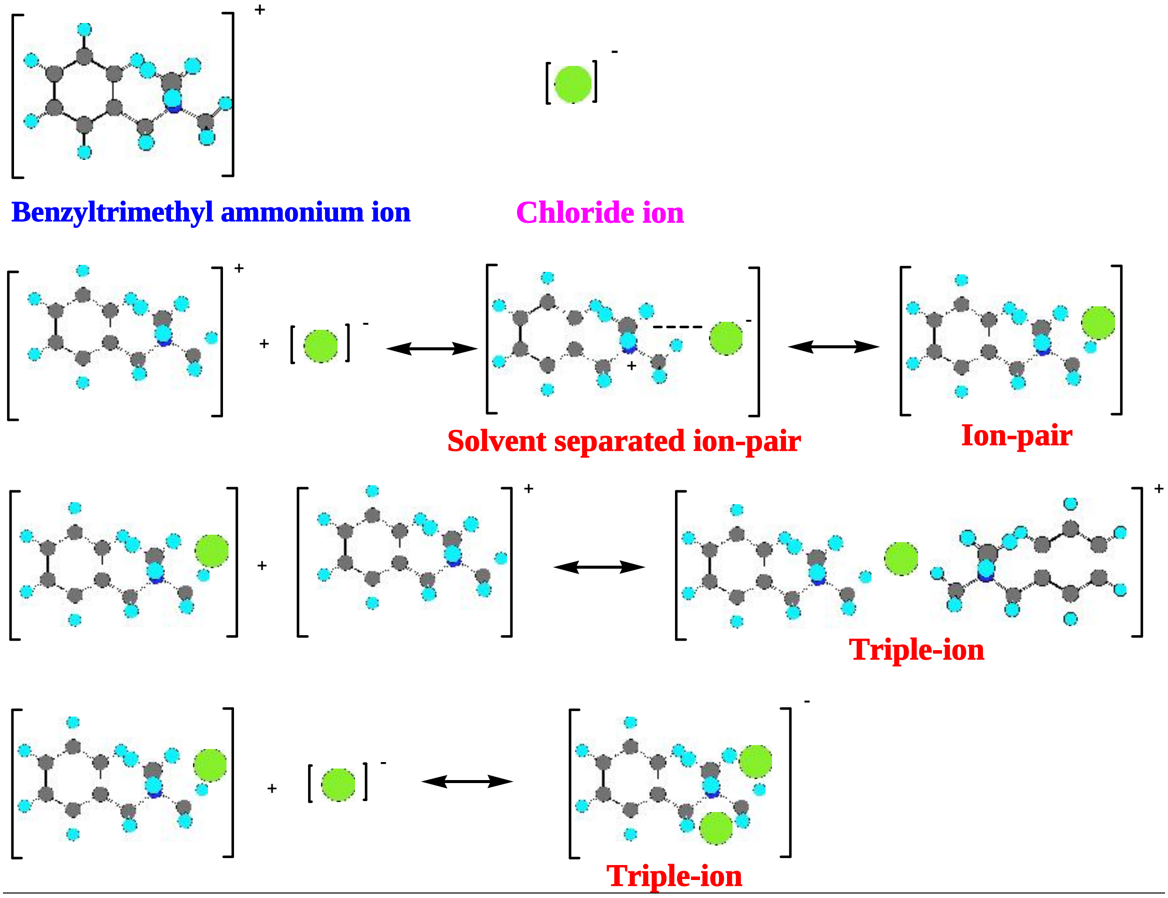

[BTMA]Cl

1-Hexanol

1-Heptanol

1-Octanol

Scheme 2: Molecular structure of IL and solvents and Plausible Association of ionic liquid in different solvents



Scheme 3: Formation of Ion-pair (IL + 1-Hexanol) and triple-ion (IL + 1-Heptanol; IL + 1-Octanol).