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Article

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Influence of Cation Size on the Ionicity, Fluidity and Physiochemical Properties of 1,2,4-Triazolium Based Ionic Liquids

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Abstract

Interpreting the physiochemical properties and structure-property correlations of ionic liquids (ILs) is a key to the enlargement of their optimized structures for specific applications. In this work, a series of ILs based on 1- alkyl- 1,2,4- triazolium cation with trifluromethane sulfonate anion were synthesized and studied the effect of cation and temperature on physiochemical properties such as density, viscosity, speed of sound, conductivity and rheology. Temperature dependence densities were correlated with the densities estimated by Gardas and Coutinho model whereas viscosity and molar conductivity has been found to satisfy Vogel-Tammann-Fulcher (VTF) equation over studied temperature range (293.15-343.15) K. Further, to explore the wide range of applications, ionicity has been tested by correlating the fluidity with molar conductivity and found that synthesized ILs can be referred as "good ILs". Furthermore, the fluidity behavior describing the interactions between cation and anion of ILs were investigated through their rheological properties; and the Newtonian behavior of ILs has been examined by varying the effect of shear rate on viscosity. Finally, the impact of structure variant in terms of N-1 functionalized 1,2,4-triazole ring has been analyzed over studied properties.

Introduction

Ionic liquids (ILs) are novel solvents of greater interest as an alternative for conventional organic solvents which have aimed at facilitating sustainable chemistry through their tunable properties.[1-3] Among various class of ILs, the potential utilization and applications of nitrogen- rich ILs have been rapidly increased over conventional energetic materials, mainly due to low carbon and hydrogen content and thus resulting in good oxygen balance.[4-5] Generally, nitrogen- rich ILs exhibits high heat of formation, high density, with dinitrogen as decomposition product, because of these properties such class of ILs are considered as highly accomplished energetic materials for industrial and military applications.[6] Shreeve and coworkers[7] explored the application of nitrogen- rich ILs consisting of various families, e.g. imidazolium, picrate, urotropinium, triazolium, tetrazolium, tetrazine etc. as '*energetic salts*'. A combination of theoretical and empirical calculations conveyed that 5-aminotetrazolatate based salts have desirable properties to be consigned as energetic materials.[8] Energetic behavior of tetrazolium based ILs were investigated by Dong and coworker[9] and found that on increasing the alkyl chain length, density decreases and consequently energetic behavior of ILs was found to be reduced.

Triazolium based ILs have gained increased interest due to their potential use in energy-rich applications. Salts consisting of the triazolium moiety have been found to exhibit large heat of formation (ΔH_f = 109 kJ/mol), compared to similar salts having imidazolium moiety (ΔH_f = 58.5 kJ/mol), and they also possess the combination of unique properties, such as higher densities, enhanced thermal stabilities, and reduced vapor pressure thus making them to more advantageous as compared to conventional energetic materials.[6,10-12] 1,2,4- triazolium salts can be used as energetic materials and efficient CO_2 absorbents with low reaction enthalpy.[13,14] Strassner et al.[15] explored the mesomeric effect to modify the alkylated or arylated 1,2,4-triazolium ILs for desired properties. 1-alkyl- 1,2,4-triazolium methane sulfonate based Brønsted acidic ILs can exhibit good catalytic activity for Mannich base reaction with appreciable efficiency.[16] Additionally, –SO_3H functionalized ILs have been reported offering a new possibility for developing environmentally-friendly acidic catalysts because they are flexible, nonvolatile, non-corrosive and immiscible with many organic solvents and could be used as dual solvents and catalysts.[17]

In spite of wide range of applications, very few reports are available[18,19] on systematic study of structure variants and the effect of temperature on physiochemical properties of 1,2,4- triazolium based ILs. Study on physiochemical properties is essential (i) to understand the geometrical configurations and intermolecular interactions of these ILs; (ii) to develop the structure-property correlations and predictive models; and (iii) for the design of processes and products involving these compounds.[20,21] By considering these factors, Narita et al had shown that how alkyl chain length can improve the performance of zwitterions as ion conductive matrices.[23] In the present work, we have synthesized 1,2,4- triazolium based ILs by the N-1 alkylation of 1,2,4- triazole followed by N-4 quaternization with trifluromethane sulfonic acid and studied their thermophysical properties, viz. density, viscosity, conductivity and speed of sound, as a function of temperature. The experimental density data were correlated with the estimated density obtained by Gardas and Coutinho model,[24] whereas experimental viscosity and conductivity data were fitted with Vogel- Tammann- Fulcher (VTF) equation. Fluidity behavior and ionicity behavior of studied ILs have been investigated through rheological profiling methods and Walden’s rule, respectively. Furthermore, experimentally measured and derived properties were analyzed to understand the influence of the temperature and structure variants in cation molecular architecture of triazolium-based ILs.

▪ Experimental Section

General Experimental Methods. All commercial reagents were reagent or HPLC grade and used without further purification. Synthesized ILs was purified by using high vacuum at 60°C. Water content has been measured by Metrohm 870 KF Titrino plus which is KF titrator for volumetric water content determination. ^{1}H, ^{13}C and DEPT NMR were recorded by Bruker avance 500 MHz NMR instrument and chemical shift reported in parts per million using as standard solvent signal ($CDCl_3$: ^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm). High resolution mass spectra (HRMS) have been measured by Q- Tof- Mass spectrometer.

Measurement of Physiochemical Properties. Thermal stability of ILs have been measured for NETZSH STA449 F3 Jupiter TGA instrument, which can operate in a temperature range from 25 to 1400 ˚C. The instrument is equipped with a dual furnace made up of SiC to enhance the sample throughput. The Sensor is made up of Pt-Rh wire and measurement can be carried out at inert, oxidizing and vacuum conditions with heating rate 10°C. min^{-1}. Temperature dependent density and speed of sound were measured with an Anton Paar (DSA 5000 M) instrument which is based on oscillating U- tube principle. It can measure density very precisely in the range of (0-3000) kg.m^{-3} and speed of sound from 1000 to 2000 m.s^{-1} simultaneously in temperature range of (273.15- 343.15) K. Dynamic Viscosity of ILs were measured by Anton Paar micro viscometer (Lovis 2000ME) attached with the master instrument (DSA 5000M) over studied temperature range (293.15 to 343.15) K at atmospheric pressure. This instrument is based on rolling ball technique and can measure viscosity in the range (0.3 to 10,000) mPa.s. The temperature is controlled by a built- in precise Peltier thermostat with an accuracy of ±0.01 K. The standard uncertainties over measurements were estimated to be less than 0.05 kg.m^{-3} for density, 0.05 m.s^{-1} for speed of sound and 0.05 mPa.s for viscosity. For better precision the density meter was calibrated with dry air and Millipore water at regular interval whereas, lovis was calibrated with the reference liquid (S3, N26, N100 liquid for 1.59 mm, 1.8 mm and 2.5 mm capillary respectively) provided by Anton Paar. The samples were filled in density, speed of sound cell as well as lovis capillary in single cycle and measurements were carried out by slow equilibration mode instantaneously.

Measurement of electrical conductivity was accomplished through Eutech (PC 700) instrument that includes an electrode with a cell constant of K=1 and built in temperature sensor. The conductance cell was calibrated with an aqueous solution of 0.01 N KCl and the cell can measure conductivity from 0.0 μS to 200 mS. Nitrogen atmosphere was sustained throughout the measurement by using an in-house fabricated double layered glass jacket setup. The inlet and outlet of the setup were connected to the water bath for temperature maintenance. As we are dealing with high density and high viscosity samples, the instrument used in this work were also calibrated with reference ionic liquid namely, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6Mim][Tf_2N]$.[25]

Measurement of Rheological Properties. Rheological studies were performed on an Anton Paar's MCR (Modular Compact Rheometer) 102, with a CP 40 Cone and Plate measuring system. All ILs were kept under high vacuum before starting the experiments. A small portion of IL was placed on the smooth plate of rheometer and cone- plate geometry was lowered to its truncation gap, and IL was allowed to equilibrate for 10 minutes for allowing the experiment. The experimental temperature was controlled by P-PTD 200/AIR Plate– Peltier temperature device. Measurements were performed in frequency sweep (1-100 rad.s^{-1}) with 50 % strain and strain sweep (100 - 1000 s^{-1}) modes at a constant frequency of 1 Hz.

Preparation of 1-Alkyl- 1,2,4-triazoles (1a-c).

1-butyl and 1-hexyl-1,2,4-triazoles have been previously reported.[26] Here, we have synthesized 1-isopentyl-1,2,4-triazole by modified Shreeve's Procedure[24] as briefly described below.

Preparation of 1-Isopentyl-1,2,4-triazole (1c)

To the solution of 1,2,4-triazole (16.4 mmol) in dry methanol (15 ml), dry methanolic solution of sodium methoxide (16.5 mmol) was added. The mixture was left to stir for 30 min at room temperature, and then (16.56 mmol) of 1- bromo- 3- methyl butane was added dropwise and left to stir for 4 h followed by refluxed through overnight at 70°C. Reaction was monitored through TLC. After completion, the methanol was removed by using rotary evaporator and halide impurity was removed by washing with water and ethyl acetate mixture. Moreover, using rotavapor removed the ethyl acetate and compound was dried through $MgSO_4$. The crude product was purified through column chromatography in neutral alumina. The resulting solution was then placed into high vacuum, affording a colorless liquid. (89% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1 H), 7.92 (s, 1 H), 4.17 (t, J = 7.5 Hz, 2H), 1.77 (m, 2H), 1.56 (m, 1 H), 0.94 (d, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.7,48.1, 38.6, 25.5, 22.3.HRMS (ESI+) m/z for $[M]^+$ calcd140.1188, found 140.1184.

*1-butyl-1,2,4-triazole (1a).*1-butyl-1,2,4-triazole (1a) was obtained as colorless liquid following a method described above.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1 H), 7.93 (s, 1 H), 4.16 (t, J = 7.25 Hz, 2H), 1.86 (m, 2H), 1.34 (m, 2 H), 0.94 (t, 7.5 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.8,49.5, 31.8, 19.7, 13.5.HRMS (ESI+) m/z for $[M]^+$ calcd126.1031, found 126.1026.

*1-Hexyl-1,2,4-triazole (1b).*1-Hexyl-1,2,4-triazole (1b) was obtained as light yellow viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1 H), 7.92 (s, 1 H), 4.12 (t, J = 7.5 Hz, 2H), 1.86 (m, 2H), 1.28 (m, 6 H), 0.85(t, 6.5 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 142.7, 49.7, 31.1, 29.7, 26.0, 22.4, 13.9. HRMS (ESI+) m/z for $[M]^+$ calcd154.1344, found 154.1349.

Preparation of Ionic Liquids (2a-c). 1-Alkyl-4-methyl-1,2,4- triazolium based ILs (2a-c) were synthesized by a modified Shreeve's procedure. In a double necked round bottom flask 1-4-butane sultone (14.4 mmol) was added dropwise to the 1- alkyl- 1,2,4- triazole (14.4 mmol) (1a-c) at 0˚C. The resulting solution was allowed to stir at room temperature until a solid was obtained. In order to remove unreacted starting materials reaction mixture was washed with toluene followed by diethyl ether. The crude product was dried under reduced pressure to get the zwitterionic compound. This zwitterionic compound was further allowed to react with trifluromethane sulfonic acid (14.5 mmol) at 0˚C. Resulting solution was stirred at 60˚C until a thick liquid formed. Obtained thick liquid was washed with diethyl ether to remove the excess trifluromethane sulfonic acid and placing under high vacuum as light yellow color liquid obtained as ILs (85% yield) (2a-c).

1-isopentyl-4-(4-sulfobutyl)-1H-1,2, 4-triazol- 4 -ium trifluoromethanesulfonate (2c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1 H), δ 8.55 (s, 1 H), 4.55 (t, J = 5.0 Hz, 2H), 4.43 (t, 7.5 HZ, 2H), 3.16 (t, 6.25 Hz, 2H), 2.25 (m, 2H), 1.87 (m, 4 H), 1.64 (m, 1 H), 0.98 (d, 6 H).^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 140.8, 124.0, 121.5, 118.9, 116.4, 74.0, 51.3, 48.4, 37.6, 25.6, 23.7, 23.0, 22.0, 19.6. HRMS (ESI+) m/z for $[M]^+$ calcd 276.1382, found 276.1373.

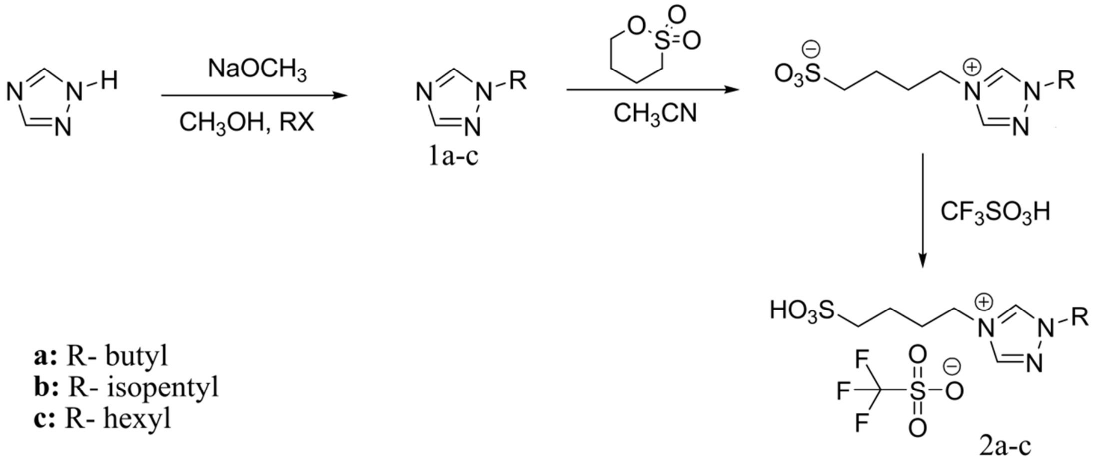
1-butyl-4-(4-sulfobutyl)-1H-1,2,4-triazol-4-ium trifluoromethanesulfonate (2a).^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1 H), δ 8.56 (s, 1 H), 4.54 (t, J = 5.0 Hz, 2H), 4.42(t, 7.25 Hz, 2H), 3.15 (t, 6.25 HZ, 2H), 2.24 (m, 2H), 1.96 (m, 2 H), 1.84 (m, 2 H), 1.38 (m, 2 H), 0.97 (t, 7.5 HZ, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 140.9,124.0, 121.5, 119.0, 116.4, 74.1, 52.5, 48.4, 30.8, 23.7, 23.0, 19.4, 13.2. HRMS (ESI+) m/z for $[M]^+$calcd 262.1225, found 262.1223.

1-hexyl-4-(4-sulfobutyl)-1H-1,2,4-triazol-4-ium trifluoromethanesulfonate (2b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1 H), δ 8.56 (s, 1 H), 4.55 (t, J = 5.0 Hz, 2H), 4.40 (t, 7.5 Hz, 2H), 3.16 (t, 6.0 Hz, 2H), 2.25 (m, 2H), 1.96 (m, 2 H), 1.84 (m, 2 H), 1.31 (m, 6 H), 0.87 (t, 7.25 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 140.9,124.0, 121.5, 118.9, 116.4, 74.1, 52.7, 48.4, 31.0, 28.8, 25.8, 23.7, 23.0, 22.3, 13.8.HRMS (ESI+) m/z for $[M]^+$calcd 290.1538, found 290.1525.

▪ Results and Discussion

Synthesis. A number of methods for the alkylation of 1,2,4-triazole are documented in the literature, Among all of them Shreeve's methods are well-known. Here, In this work we have reported alkylation of 1,2,4- triazole at the N-1 position followed by modified Shreeve procedure. [18,24] In brief, commercially available 1,2,4-triazole were alkylated with appropriate 1-bromoalkane in the methanolic solution of sodium methoxide. These substituted triazole (1a-c) were quaternized with 1,4- butane sultone at N-4 position, which gave zwitter ionic salts. Moreover these salts have been further reacted with trifluromethane sulfonic acid which leads to proton transfer, providing the desired triazolium based ionic liquids (2a-c) as clear and light yellow oils. Synthesized ILs have been characterized through ^{1}H, ^{13}C, DEPT NMR and HRMS spectral techniques (see in supporting information Figure S1 to S6). The proton shifting from CF_3SO_3H to RSO_3H has been studied through ^{1}H NMR. As illustrates in figure S10, the chemical shift of triazole ring proton (H_a and H_b) in zwitterion intermediate is appeared at 8.2 and 7.9 ppm respectively. When this intermediate is further reacted with equimolar trifluromethane sulfonic acid the NMR peaks of triazole ring (H_a' and H_b') is shifted towards down-field as 9.7 and 8.5 ppm respectively. The proton transport mechanism between zwitterion blends and Brønsted acid was studied by Ohno and coworkers[27] through their physiochemical properties.[27] The water content is less than 1000 ppm in all studied ILs which have measured with Karl-Fischer volumetric titrator.

Scheme1. Synthesis of 1- Alkyl-4- (4-sulfobutyl) - 1H-1,2,4-triazol-4-iumtrifluoromethanesulfonate Ionic Liquids 2a-c



Physiochemical Properties. To minimize the water content, ILs were dried under high vacuum for 24 h. Thermal stability of synthesised triazolium based ILs were investigated by Thermogravimetry analysis. As mentioned in Figure S7, TGA curves of ILs has two- step degradation. Although the mechanism of degradation was not studied but it might be said that composition of the ions controlled the degradation pathway as reported in the literature.[28] On varying the linear alkyl substituent the thermal stability decreases in order [BtTzm][CF_3SO_3] > [HxTzm][CF_3SO_3] > [IpTzm][CF_3SO_3] following the usual trend.

The experimental densities were measured over temperature range (298.15 to 343.15) K at atmospheric pressure. It is widely known that density is one of the major indices to reflect the energy performance of energetic materials because the higher density usually means the higher mole number of an energetic ILs that can be packed into a limited volume, indicating higher energy contribution to the explosive composition.[9] The ILs developed in this work exhibited higher density which lies in the range of (1.317- 1.373) g.cm^{-3} at 298.15 K, which is higher than the density reported for some energetic ILs[7], thus showing good agreement for energetic ILs. Moreover, the effect of temperature and variation in alkyl chain length has also agreed with the trend reported earlier.[28,29] In general, an increase in density occurs when a better arrangement of the ions in the liquid takes place thus allowing a greater number of ions to be located in a unit volume.[30] As reported in Table S1 the density of the studied ILs decreased with increasing in the chain length and increased with the branching following the trend [HxTzm][CF_3SO_3] < [BtTzm][CF_3SO_3] < [IpTzm][CF_3SO_3]. With the increase in linear chain length in ILs from [BtTzm][CF_3SO_3] to [HxTzm][CF_3SO_3] density decreases (1.371-1.317) g.cm^{-3} up to 5 % because longer alkyl chain substituent entail more stearic hindrance and consequently leading to poor packing arrangement which also results in less interionic interactions.[31,32] whereas, branching in alkyl chain decreases steric hindrance in the [IpTzm][CF_3SO_3] than in case of lesser alkyl chain length analogue [BtTzm][CF_3SO_3], that might account for its very slightly increased density (1.373 g.cm^{-3}) at 298.15 K which leads to comparatively more interionic interactions. As illustrated in Figure 1, density of ILs decrease linearly with temperature. This decrease in density can be attributed to difficulty for the formation of interionic interactions such as H-bonding and packing which arises due to asymmetry of ions. Moreover, experimental density data have been correlated through estimated density obtained from Gardas and Coutinho model[33] using equation (1)

$$\rho_{cal} = \frac{M}{N_A V_m (a + bT + cP)} \qquad (1)$$

Where, ρ_{cal} is the calculated density (kg.m^{-3}), M is the molar mass (kg.mol^{-1}), N is the Avogadro's number, V_m is molecular volume (Å^3), T is temperature (K) and P is the pressure (MPa). The coefficient a, b, and c were estimated by fitting equation (1) to about 800 experimental density data points[34,35] covering the large density range (987-1547 kg.m^{-3}), temperature range (293.15-393.15) K and pressure range (0.1-30) MPa and found as 0.8005, $6.6520\times10^{-4}(K^{-1})$ and $-5.919\times10^{-6}(MPa^{-1})$ respectively at 95% confidence level.[36] The molecular volume of anion (V_a*), for $[CF_3SO_3]^-$ has been taken from literature[21,24,37] as 129 $Å^3$ whereas cation molecular volumes (Vc*) are estimated in this work and presented in Table-1 along with maximum absolute deviation (MAD) and absolute relative deviation (ARD) obtained using Gardas and Coutinho model[33]. As presented in figure 3, the calculated density, ρ_{cal} for triazolium based ILs using Gardas and Coutinho model[33] shows very good agreement with the experimental density, ρ_{exp} and were related as $\rho_{cal} = (1.0003\pm0.0001)\ \rho_{exp}$ with a confidence level of 95% and $R^2=0.9999$.

Information obtained from the temperature dependency and the effect of cation and/or anion of ILs on speed of sound can be useful to understand the extent of intermolecular interactions involved.[38,39] For studied 1,2,4- triazole based ILs, the effect of temperature and alkyl chain length on speed of sound are tabulated in Table S1. The speed of sound decreases linearly with the addition of methyl group at N-1 position as illustrated in Figure 2. This decrease in speed of sound from $[BtTzm][CF_3SO_3]$ (1387.43 $m.s^{-1}$) to $[IpTzm][CF_3SO_3]$ (1344.92 $m.s^{-1}$) to $[HxTzm][CF_3SO_3]$ (1320.79 $m.s^{-1}$) at 298.15 K could be attributed to the increased spatial distance between the molecules. With the addition of one more methyl group the steric hindrance increases leading to more intermolecular free space thereby, decreasing the speed of sound.

For the better understanding of the extent of molecular interactions, industrially relevant thermodynamic parameters have been derived, such as thermal expansion coefficient (α_p) and isentropic compressibility (κ_s), from experimental density and speed of sound data using equations (2) and (3).

$$\alpha_p = \left(\frac{\partial\rho}{\partial T}\right)_P \tag{2}$$

$$\kappa_s = \frac{1}{\rho \mathrm{u}^2} \tag{3}$$

As shown in table S1, among the studied ILs, [HxTzm][CF_3SO_3] shows the higher value of compressibility which suggests that with increase in asymmetry of ILs, the packing density and the extent of degree of hydrogen bonding is decreasing.[40] The effect of temperature on expansivity (α_p) and compressibility (κ_s) of studied ILs were shown in figures S8 and S9, respectively.

Viscosity is an imperative intensive property which helps to describe the potential applications of any ILs and is significantly influenced by intermolecular interactions such as H-bonding, dispersive forces and columbic interactions.[41] The viscosity for the developed ILs has been measured in the temperature range (293.15-343.15) K. At a particular temperature the viscosity of the linear ILs increases monotonically with an increase in the cation chain length for example viscosity increased from 99.14 to 123.83 mPa.s at 298.15 K, when chain length increased from butyl to hexyl i.e., [BtTzm][CF_3SO_3] to [HxTzm][CF_3SO_3], which could be mainly due to the augmentation in molecular size, packing and orientation into a bulk fluid.[42] M. Watanbe and coworkers[43] also suggested that with increasing number of carbon atoms in the alkyl chain, the inductive forces in the ILs increase, which causes enhancement of the viscosity owing to frictional forces among ions, aggregates, and clusters.[43] Furthermore, when linear chain is replaced by branched chain, the viscosity is observed to be higher than their linear longer chain analogue. The increase in viscosity of branched isopentyl substituted IL, [IpTzm][CF_3SO_3] is similar to an increase with number of branched isopropyl group in 1,2,3- triazolium based ILs[32] and is elucidated mechanistically as branched chain has more stabilized packing causing an increase in the shear resistance to intermolecular motion, which subsequently results in higher viscosity of [IpTzm][CF_3SO_3].[44] whereas, the viscosities of synthesized ILs decreases asymptotically over studied temperature range (293.15-343.15) K as shown in Figure 4(A). This effect is recognized due to the increase in Brownian motion of the constituent ions of ILs.[45] The viscosity values of studied ILs with respect to temperature is shown in table S1. The experimental temperature-dependent viscosity data were correlated with empirical equation proposed by Vogel-Tammann- Fulcher (VTF) (equation 4) and VTF parameters are presented in Table 2.

$$\eta = \eta_0 \exp\left[\frac{B}{(T-T_0)}\right] \tag{4}$$

Where η_0(mPa.s) is the viscosity at the temperature limit, B (K) is the quantity related to the activation barrier and T_0 is the absolute or "ideal glass transition" temperature.

The measured molar conductivity of synthesized 1,2,4-triazolium based ILs in the temperature range 293.15K to 343.15K is presented in Figure 4(B) and the values are given in table S1. In general, the 1,2,4-triazolium based ILs are shown to have lower conductivity than imidazolium based ILs having similar anions, because of larger cation size and stronger intermolecular interactions.[18] The measured experimental molar conductivity of studied ILs followed the trend [HxTzm][CF_3SO_3] < [IpTzm][CF_3SO_3]] < [BtTzm][CF_3SO_3]] at 298.15 K, which further emphasized the fact that the smaller ions have higher mobility than bigger ions.[46] In general, with increase in substituent chain length the viscosity of IL increases and molar conductivity decreases.[47] The effects that lead to an increase in viscosity and decrease in conductivity of the ionic liquids were studied by testing two hypotheses: (1) ion association, and (2) differences in the potential energy surface profile.[48] The experimentally obtained data for studied ILs suggests that when branching in the substituent is increased, the viscosity of the corresponding IL (isopentyl substituted) is increased to a greater extent that its value exceeds that of linear long chain analogue (hexyl substituted) and shows the trend as ([BtTzm][CF_3SO_3] (99.14 mPa.s) < [HxTzm][CF_3SO_3] (123.83 mPa.s) < [IpTzm][CF_3SO_3] (136.47 mPa.s), whereas in case of molar conductivity the ILs followed the regular trend of decrease in conductivity with increase in substituent alkyl chain length i.e., [HxTzm][CF_3SO_3] (0.564 $mS.cm^{-1}$) < [IpTzm][CF_3SO_3] (0.881$mS.cm^{-1}$) < [BtTzm][CF_3SO_3]

(1.459mS.cm^{-1}). The difference in the trend of molar conductivity and viscosity is due to different factors responsible, for example molar conductivity is mainly governed by the molecular size of the cation whereas viscosity is influenced by their size as well as their packing and intermolecular interactions. Although, there is branching in the IL having intermediate chain length (isopentyl substituted), due to continuous increase in the substituted chain length (butyl to hexyl) of cation the molar conductivity followed regular decreasing trend. In case of viscosity, branching in the chain greatly influences the packing arrangements and increases intermolecular interactions which in turn lead to higher viscosity of isopentyl substituted IL. With increase in temperature the molar conductivity of studied ILs is observed to increase due to increase in the rate of mobility of ions. The experimental molar conductivity data were correlated with VTF equation (equation 5) and results are presented in Table 3.

$$\Lambda_m = \Lambda_0 \exp\left[\frac{-\mathrm{B}}{(\mathrm{T}-\mathrm{T}_0)}\right] \qquad (5)$$

Where Λ_0 (mS.cm^2.mol^{-1}) is the molar conductivity at the temperature limit and B (K) and T_0 (K) are the variable parameters.[49] Temperature dependent molar conductivity (Λ_m) data are presented in Figure 4(B) where symbols represents the experimental data points while solid lines signifies the VTF fitted curves.

For assessing the ionicity, Walden plot as an approximate and readily accessible approach. Ionicity does not necessarily describe the chemical availability of individual ions, which may depend more strongly on the associated nature of the IL.[50] The Fractional Walden's rule (equation 6) describes the relationship between fluidity and molar conductivity, where $\wedge_m$ is the molar conductivity, η is the viscosity, C is the constant that accounts for cation and anion radius and shifts plots vertically in the Walden plot, and α is an exponent allowing for deviations from slopes of unity in the Walden plot, which has been verified to explore the completeness of dissociation and the ionicity of synthesized ILs.[51] In Walden plot, the reference or "ideal line" is commonly symbolized by a 0.01 M dilute KCl solution, which is an indicator of the ideal interionic interaction between cation and anion of the ILs.[52] ILs lie within 20% of KCl reference line of Walden plot are considered as highly dissociated and termed as "good ILs" whereas those are far from this line can be classified as "Poor ILs".[53]

$$\log\Lambda_m = \log C + \alpha \log\eta^{-1} \tag{6}$$

As shown in figure 5, for the logarithmic plot of Walden rule, the synthesized triazolium based ILs behave as that of less ionic in nature and fall below the ideal line due to strong ion pairing and the ionicity follows the order [BtTzm][CF_3SO_3] > [IpTzm][CF_3SO_3] > [HxTzm][CF_3SO_3]. Moreover, plot showed very good linear relation with regression coefficient R^2≈0.999 and studied ILs can be referred as "good" ILs.[54] The slope (α) and intercept (log C) values for linear equation 6 are shown in Table S3.

Rheological Study. The effect of chain length and branching of synthesized triazolium based ILs have been investigated by the steady rheological measurements at room temperature. In Newtonian flow, shear stress (resistance to flow) is proportional to shear rate (rate of motion of fluid with respect to nearby fluid elements). Therefore, viscosity should be constant regardless of shear rate unless a sample is non-Newtonian fluid.[55] Figure 6(A) shows the variation of steady shear viscosity as a function of shear rate for studied ILs and exhibits a constant viscosity, which is indication to the Newtonian flow of behavior.[56] The viscosity (η) values over the studied range of shear rate has been estimated and it follow the same trend as [IpTzm][CF_3SO_3] > [HxTzm][CF_3SO_3] > [BtTzm][CF_3SO_3]. Additionally, steady shear rheology (see figure 6(B)) also depicts that the relation between shear stress and shear rate is linear over studied range (0-1000) s^{-1}, which is also appropriate for the Newtonian fluid behavior of ILs.[56,57]

The flow behavior of the ILs was then studied by frequency-sweep dynamic rheology. The G' (Storage modulus) normally tell us about solid like nature while G" (Loss modulus) tell us about liquid like nature. Usually for gels (G' > G'') which states that storage modulus is greater than loss modulus.[58] Figure 7, represents the frequency response of ILs where, the step in the storage modulus at ~ 80 rads/sec is not real as it is an instrument artifact. At high frequency range, due to inertia the equipment creeps in for low viscous samples (studied ILs). Although with increase in the angular frequency both G' and G" were changed while the G" (loss modulus) dominates the G' (storage modulus) over the frequency range. This response indicated more of liquid like behavior of ILs.

▪ Conclusions

A series of 1- alkyl-1,2,4- triazolium [CF_3SO_3] ionic liquids were synthesized by the N-alkylation followed by quaternization at N-4 position of triazole. Temperature dependence of physiochemical properties such as density, speed of sound, viscosity and conductivity were determined and Walden plot was constructed in order to determine the ionicity of ILs. ILs having branched substituent at N-1 position are found to be more denser and viscous than linear alkyl substituent analogues. The density and speed of sound are found to decrease linearly with temperature. Densities of studied ILs were also predicted through Gardas and Coutinho model, and are found to be in good accordance with the experimental values. Furthermore, molecular volume of the triazolium cation has been predicted for the first time with a deviation less than 0.04%. With increase in temperature, viscosity of studied ILs decreases whereas conductivity increases asymptotically, and the measured data have been correlated well using the VTF equation. Walden plot shows that the values of studied ILs fall close to the magnitude of ideal KCl line and thus can be considered as good (high ionicity) ILs”. Among the studied ILs, the ionicity is found to be highest for the IL having smaller cation size, [BtTzm][CF_3SO_3] and this indicates that constituted ions could move more independently of one another. Additionally, Newtonian flow behavior of ILs inspected by shear rate experiment shows that the viscosity of studied ILs is not affected over the studied range of shear rate. The higher value of storage modulus (G’) than the loss modulus (G”) found through frequency sweep method indicates the typical liquid-like behavior of all the studied ILs.

▪ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. ^{1}H, ^{13}C and DEPT NMR spectra of synthesized ILs, TGA curve, plot of temperature dependent expansivity (α_p) and compressibility(κ_s) of ILs, plot of proton transfer from CF_3SO_3H to RSO_3H of [IpTzm][CF_3SO_3]. Table of temperature dependent expansivity (α_p) and compressibility (κ_s), experimental data of density, viscosity, speed of sound, molar conductivity, expansivity and compressibility over studied range of temperature (293.15-343.15) K, coefficient of linear fitted density and absolute relative deviation and liner fitted parameters of Walden plot are provided in supporting information.

▪ Acknowledgements

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▪ Figure Captions

Figure 1. Temperature dependent Density curve for an ionic liquid over studied range (298.15- 343.15)K. The symbol represents experimental values and the solid line symbolizes the values calculated from equation 1.

Figure 2. Temperature dependent Speed of Sound curve for an ionic liquid over studied range (298.15- 343.15)K.

Figure 3. Correlation between experimental density and estimated density of ionic liquids at temperature range from 298.15 to 343.15 K.

Figure 4. Temperature dependent viscosity (A) and molar conductivity (B) curves for an ionic liquid over studied temperature range (298.15- 343.15) K. where the symbols represents experimental values and solid lines represents the values calculated from equation 4 and 5 respectively.

Figure 5. Molar conductivity against the fluidity (Walden Plot) for the studied ILs.

Figure 6. **(A)** Curve for Steady Shear Viscosity as a function of Shear rate and
(B) Plot of Shear stress versus shear rate of studied ILs.

Figure 7. Frequency sweep dynamic rheology of ILs: Open symbol represents the Storage modulus (G’) and closed symbols symbolized the loss modulus (G”).

Table 1. Effective molecular Volume of anion (V^*_a) and cation (V^*_c) and estimated molecular volumes (V_m) of the studied ILs at 298.15K along with absolute relative deviation (ARD) and maximum absolute deviation (MAD) obtained from Gardas and Coutinho model.

IL	M (g.mol^{-1})	V^*_c (Å^3)$^{\#}$	V^*_a (Å^3)$^{\$}$	V_m (estd) (Å^3)	V_m (expt)$^{\perp}$ (Å^3)	ARD	MAD
[BtTzm][CF_3SO_3]	411.42	369.5	129.0	498.5	498.0	0.04	0.06
[IpTzm][CF_3SO_3]	425.44	386.0	129.0	515.0	514.0	0.02	0.06
[HxTzm][CF_3SO_3]	439.47	425.5	129.0	554.5	554.0	0.04	0.09

estimated in this work;

$ from reference [21], [27] and [30].

⊥ calculated from experimental density at 298.15 K

Table 2. VTF equation (4) parameters for viscosity data

ILs	η_0 (mPa.s)	B (K)	T_0 (K)
[BtTzm][CF_3SO_3]	0.074	1059	151
[IpTzm][CF_3SO_3]	0.094	987	162
[HxTzm][CF_3SO_3]	0.098	995	158

Table 3. VTF equation (5) parameters for molar conductivity data

ILs	Λ_o (S.cm^2.mol^{-1})	B (K)	T_0 (K)
[BtTzm][CF_3SO_3]	370.6	859	171
[IpTzm][CF_3SO_3]	666.5	1006	169
[HxTzm][CF_3SO_3]	945.1	970	185

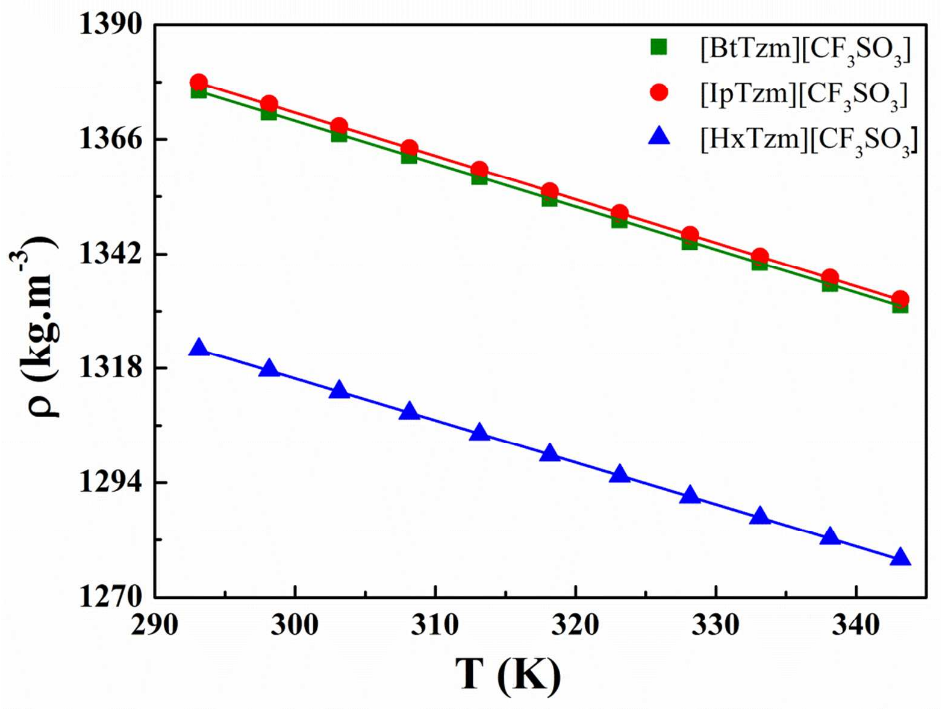


Figure 1

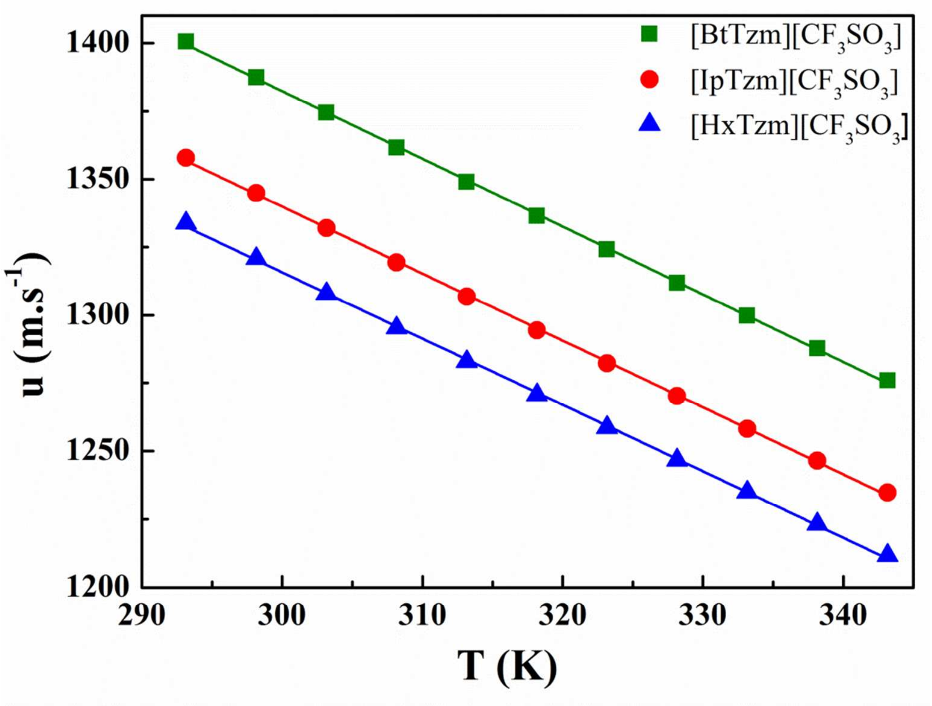
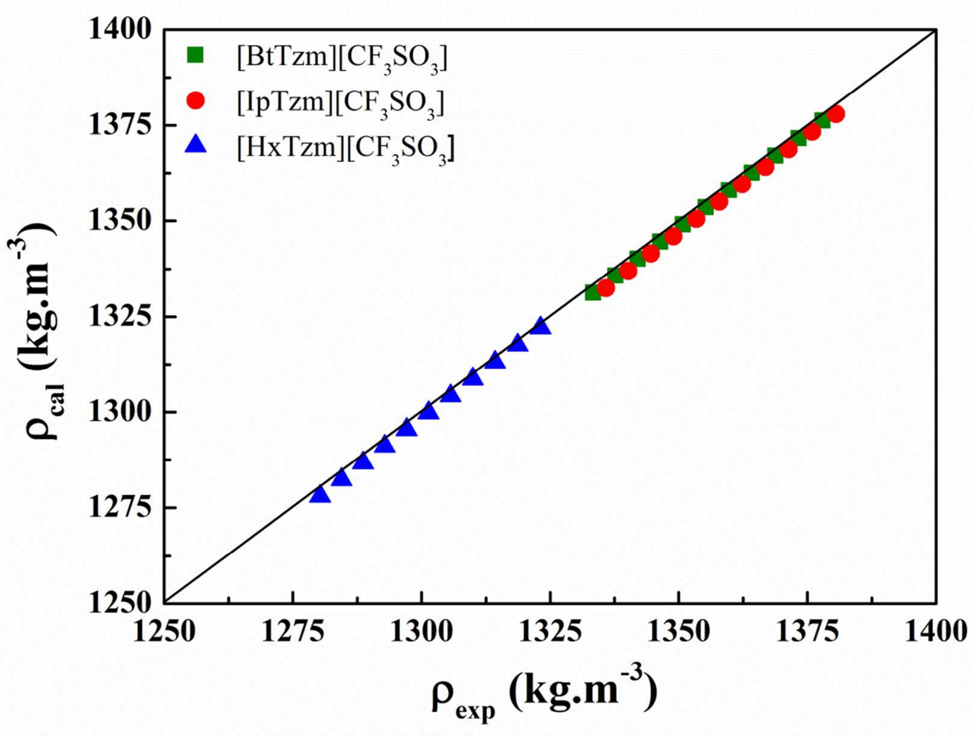


Figure 2



1400
1375
1350
1325
1300
1275
1250
1250
1275
1300
1325
1350
1375
1400
■ [BtTzm][CF$_3$SO$_3$]
● [IpTzm][CF$_3$SO$_3$]
▲ [HxTzm][CF$_3$SO$_3$]
ρ_{cal} (kg.m^{-3})
ρ_{exp} (kg.m^{-3})

Figure 3

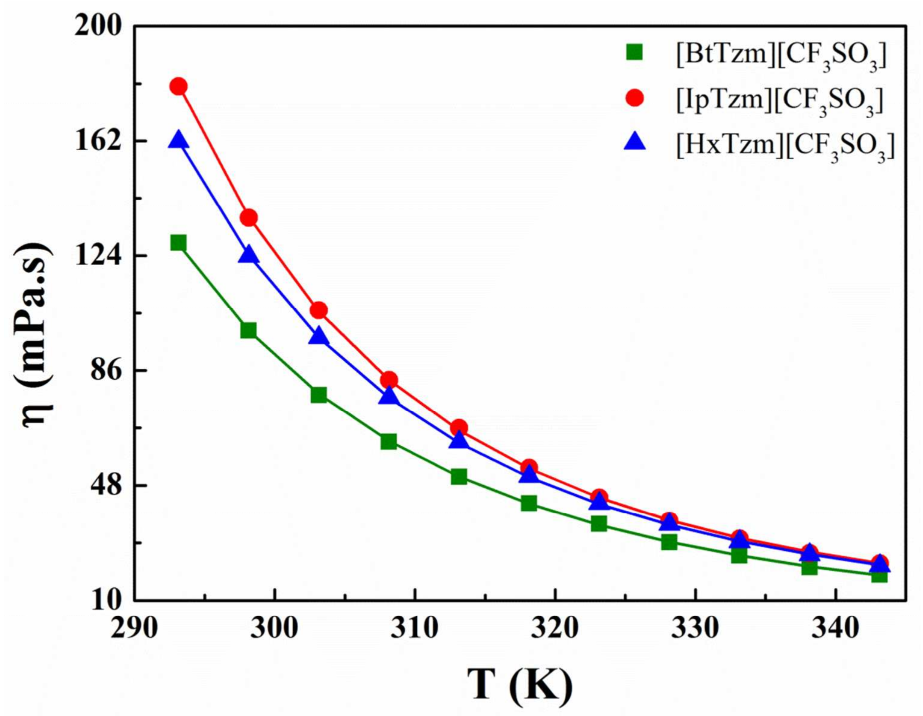


Figure 4(A)

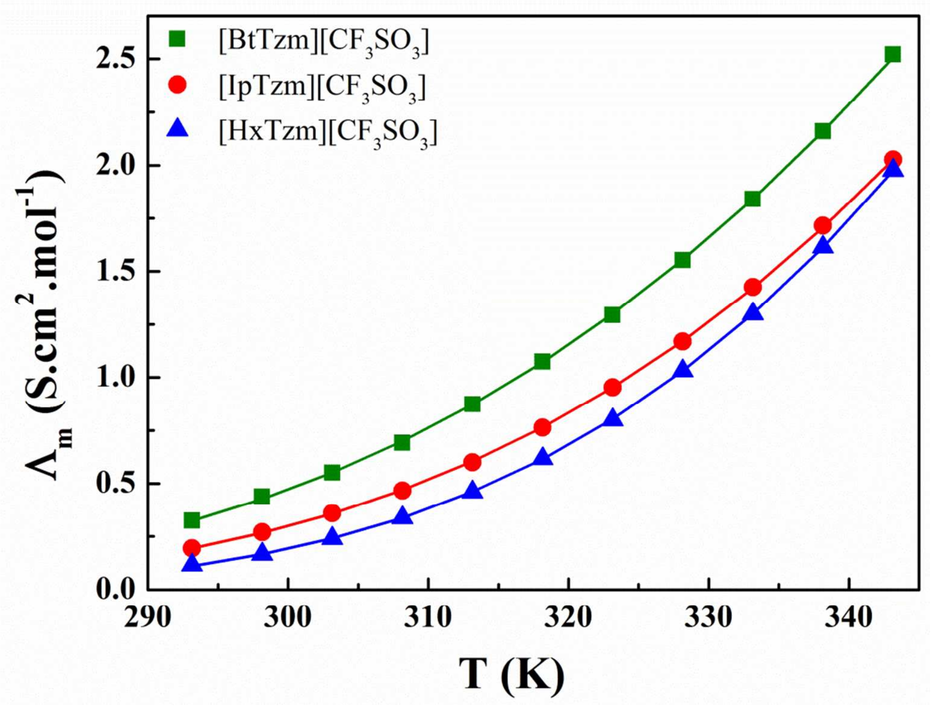


Figure 4(B)

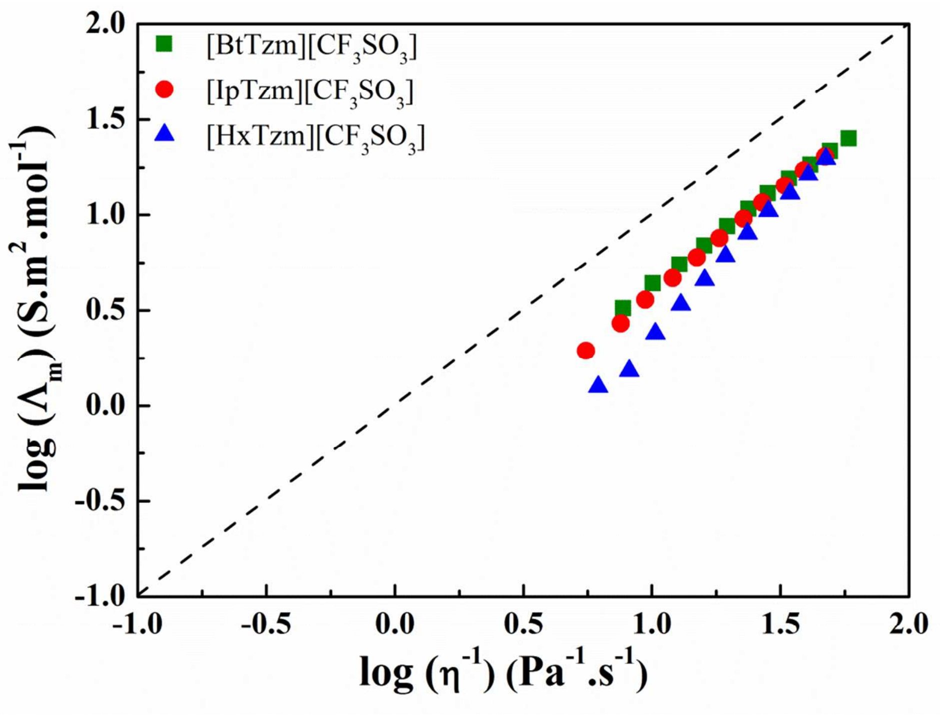

■ [BtTzm][CF$_3$SO$_3$]
● [IpTzm][CF$_3$SO$_3$]
▲ [HxTzm][CF$_3$SO$_3$]
log (Λ_m) (S.m^2.mol^{-1})
log (η^{-1}) (Pa^{-1}.s^{-1})
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Figure 5

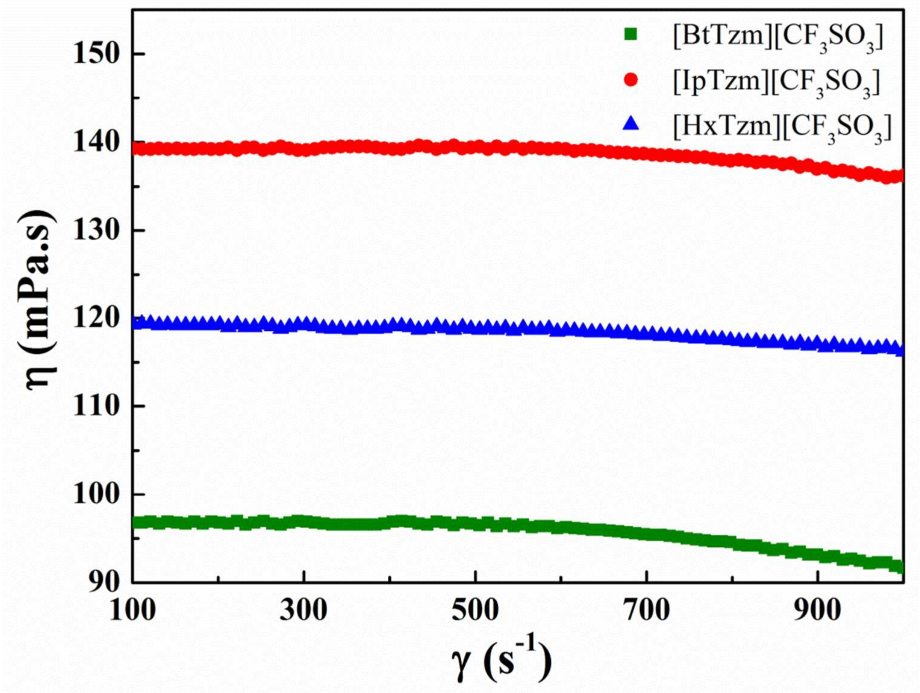


Figure 6(A)

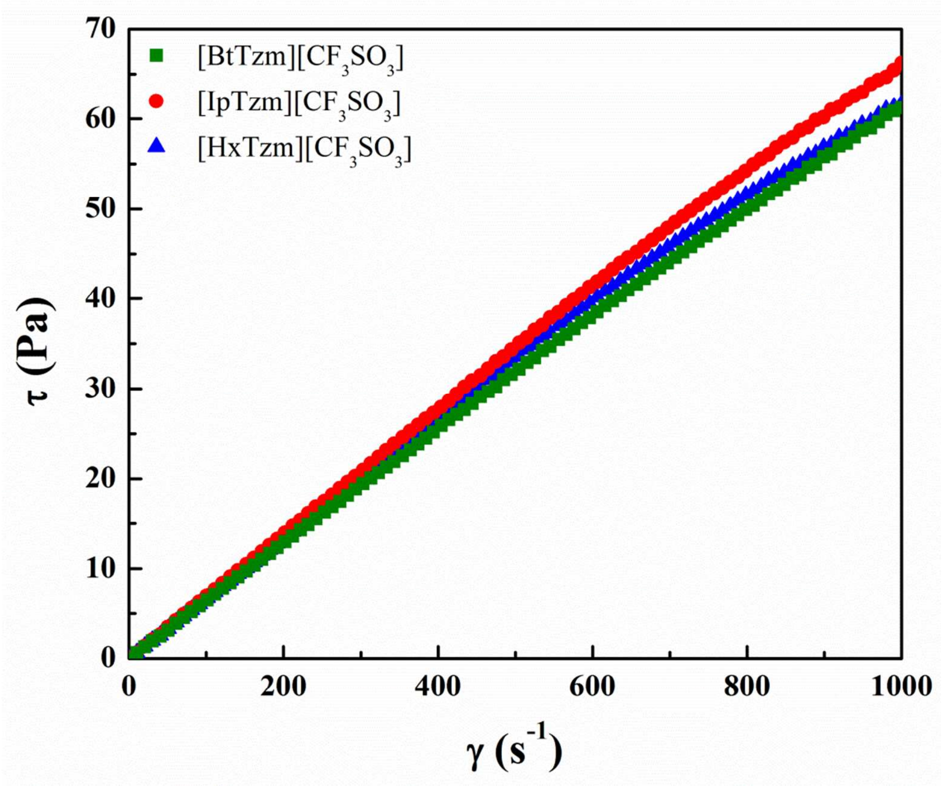


Figure 6(B)

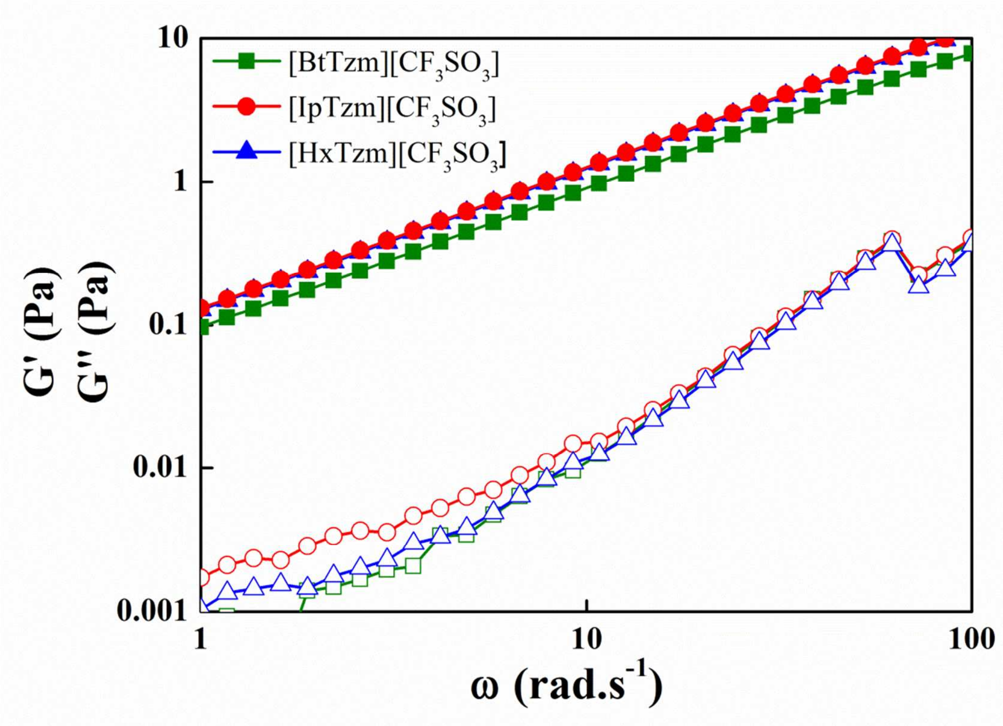
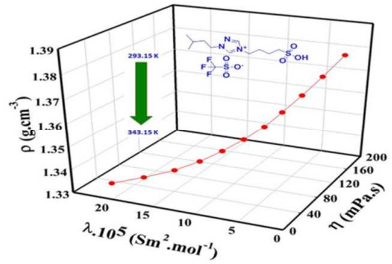
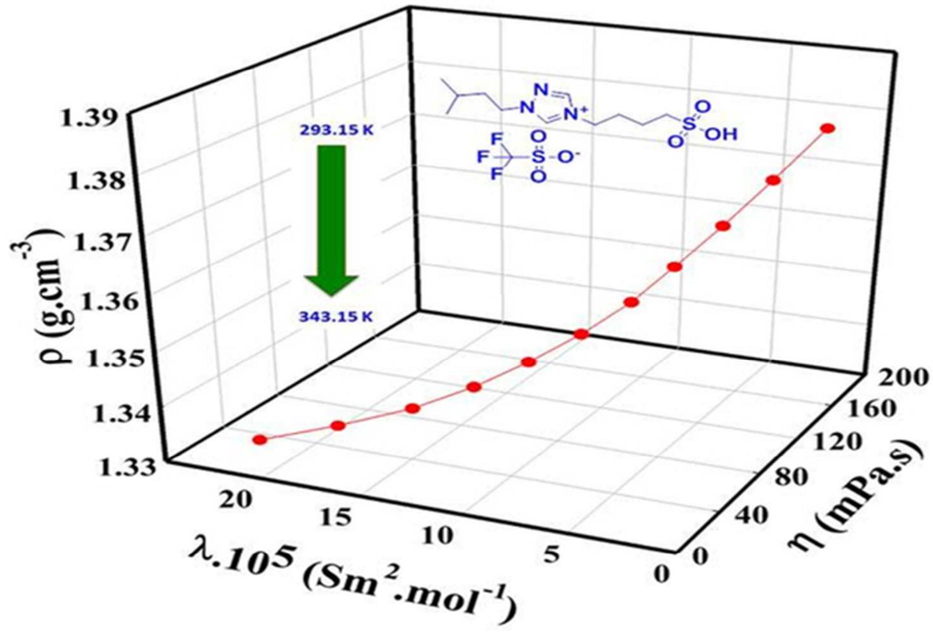

10
1
0.1
0.01
0.001
G' (Pa)
G'' (Pa)
1
10
100
ω (rad.s^{-1})
[BtTzm][CF$_3$SO$_3$]
[IpTzm][CF$_3$SO$_3$]
[HxTzm][CF$_3$SO$_3$]

Figure 7

Table of Contents Graphic





Temperature effect on density, viscosity and molar conductivity of [IpTzm][CF3SO3]
57x39mm (300 x 300 DPI)