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Synthesis, Characterization and Effect of Temperature on Different Physicochemical Properties of Protic Ionic Liquids

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Abstract

In this work, eleven protic ionic liquids (PILs) containing different cations and anions were prepared and their physicochemical properties were measured. All PILs's structures were confirmed by NMR and elemental analysis (CHNS) were carried out. The physicochemical properties such as density, surface tension, viscosity and thermal degradation behaviour were measured, and the effect of cation/anion was investigated. The density and viscosity were measured within the temperature range of 293.15-373.15 K at atmospheric pressure. The thermal expansion coefficient values were calculated from the density data. Surface tensions were measured in the temperature range of 293.15 to 353.15 K and further the values were used to estimate the surface entropy and enthalpy of the ionic liquids at 303.15 K. The boiling and critical temperature were also estimated according to the Eötvos and Rebelo methods. The refractive indices were measured within the temperature range of 293.15 to 323.15 K. The thermal gravimetric analysis was performed in the temperature range of 373.15-773.15 K.

Key Words: *Protic ionic liquid, Standard entropy, Critical temperature, Surface tension, Enthalpy of vaporization.*

Introduction

Ionic liquids are organic salts with low melting points (<100°C), or even at room temperature and sometimes measured as low as -96°C, therefore under traditional organic liquid phase reaction conditions it can be used as a solvents [1]. As reaction media, the application of ILs for a wide variety of synthetic processes is an area of intensive research. Ionic liquids provide a vapour less, good thermal stability, designable structures and recyclable green-solvent for many chemical reactions [2, 3]. ILs are also being used in variety of applications viz. in food industry [4], extraction processes[5], nuclear science [6], biotechnology [7], material engineering [8], as electrolytes in batteries [9], fuel cells [10], solar cells [11], biosensors [12], light emitting electrochemical cells [13] etc. Apart from these important applications, recently, ILs in confined geometry [14, 15] attracted attention along with synthesis [16], as reaction media [17] and effect of salts on IL [18]. There have been research papers and reviews of almost all parts of aprotic ILs (AILs), including their role in the synthesis of nano-materials structure, electro-chemistry, catalysis and reaction media[19-21]. Currently protic ionic liquids (PILs) have got popularity due to their extensive liquid temperature range, ionic conductivity and high thermal stability, which is ample for practical applications [22]. PILs, usually synthesized by the neutralization reaction of Bronsted acid and base, establish one of the most vital sub-classes of ILs. Although the 1st IL (ethylammonium nitrate) ever reported (ca. 100 years ago) is a protic ionic liquid, these materials structure-property organized study relationship have newly been initiated and remains in the developmental stage [23]. The important characteristic that differentiates PILs from another ILs is the transfer of a proton from the acid to base, to make proton donor and proton acceptor sites [24]. Nowadays proton conducting electrolyte are developing as beneficial material owing to various possible applications such as fuel cells, an electrolyte in aqueous batteries, double layer capacitors, actuators or dye-sensitized solar cell. These potential many new fields of application for PILs [25]. To date based on ILs studies a limited literature available on PILs. However, this family of ILs have several suitable properties and potential application, its due to their protic nature [26]. For industrial processes design and ILs based new products are only possible when their physicochemical properties such as density, surface tension and viscosity are acceptably known. Unfortunately, a limited literature available on the physicochemical properties and characterization of ILs, but it is required to accumulate large data bank on these important properties, it's not only for product design and process but for their properties adequate correlations development [27]. The diversity of possible ILs is the reason, that the experimental determination of

physicochemical properties complete set is almost impossible, since it would cause vast investment in time and resources [28]. ILs depending on the cations and anions, show a broad range of physicochemical properties. Many studies have investigated their different physicochemical properties [29]. The PILs physicochemical properties are determined and according to the nature of cation and anion are discussed. The PILs physicochemical properties analysis depends on temperature have been measured and examined in details. This study of PILs physicochemical properties initiated to present reliable data, which include viscosity, density, diffusion coefficient, surface tension, refractive index and thermal behaviour, over a wide range of temperature.

Experimental Section

All the chemicals such as 1-methyl piperidine, 4-methyl pyridine, ethyl amine, 1-methyl imidazole, 1, 4 sultone, Pyridine, Trifluoromethanesulfonic acid (Merck), Pyrazole, sulphuric acid (Sigma-Aldrich), piperazine, methyl pyrrolidine, (Acros) were purchased and were used as received.

Synthetic procedure of protic ionic liquids (General procedure)

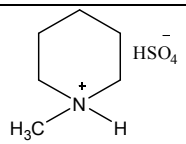
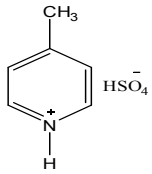
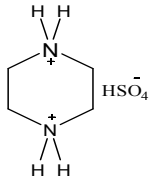
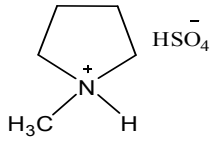
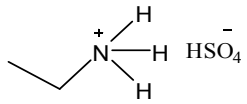
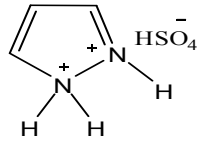
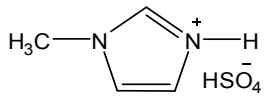
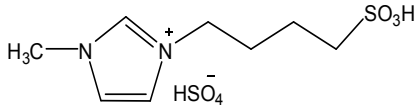
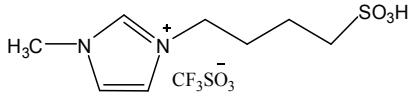
The proposed cationic moiety (*1-methyl piperidinium, 4-methyl pyridinium, Piperazinium, Methyl pyrrolidinium, Ethyl ammonium, Pyrazolium and 1-methyl imidazolium,* (0.1 mol) for each ionic liquid was dissolve in 5 mL of acetonitrile and then concentrated H_2SO_4 (0.1 mol) was added drop wise under cooling condition. The reaction mixture was stir for 24 h and refluxes it in the presence of nitrogen gas flow. The resultant obtained *1-methyl piperidinium hydrogensulfate* [MPip][HSO_4], *4-methyl pyridinium hydrogensulfate* [MPy][HSO_4], *Piperazinium hydrogensulfate* [Pi][HSO_4], *Methyl pyrrolidinium hydrogensulfate* [MPyr][HSO_4], *Ethyl ammonium hydrogensulfate* [EAm][HSO_4], *Pyrazolium hydrogensulfate* [P][HSO_4], *1-methyl imidazolium hydrogensulfate* [MIM][HSO_4], ionic liquid was washed with diethyl ether three times and dried in vacuum oven for overnight.

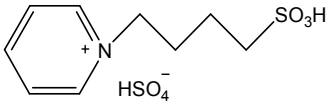
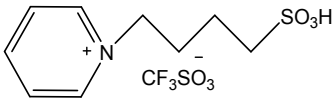
Synthesis of protic ionic liquids with SO_3H-functionalized side chain

To obtain the SO_3H-functionalized PILs, the 1-methylimidazole/pyridine and 1, 4 sultone was mixed in equal molar concentration and stirred it for 36 h at 40^oC without using any reaction solvent. A white solid product (zwitterion) was obtained which has been washed three times with toluene to remove any unreacted reactants and further dried in vacuum oven. After drying a stoichiometric amount of concentrated sulfuric acid or triflouromethanesulfonic acid, was added drop wise to the prepared zwitterion using continue stirring at room temperature for 30 minutes. The reaction temperature was then increased to

50°C and continues the stirring for another 10 h which results in the formation of desired PILs i.e. *1, 4 sultone-methyl imidazolium hydrogensulfate* [BSMIM][HSO_4], *1, 4 sultone-methyl imidazolium triflouromethanesulfonate* [BSMIM][CF_3SO_3], *1, 4 sultone-pyridinium hydrogensulfate* [BSPy][HSO_4], *1, 4 sultone-pyridinium triflouromethanesulfonate* [BSPy][CF_3SO_3]. The synthesized PILs were washed with toluene and diethyl ether repeatedly to remove the unreacted materials and further subjected to drying under vacuum.

Table 1. Name, abbreviation and chemical structure of the synthesized ILs.

Description	Abbreviation	Chemical Structure
1-Methylpiperidinium Hydrogensulfate	[MPip][HSO_4]	
4-Methylpyridinium Hydrogensulfate	[MPy][HSO_4]	
Piperazinium Hydrogensulfate	[Pi][HSO_4]$_2$	
Methylpyrrolidinium Hydrogensulfate	[MPyr][HSO_4]	
Ethylammonium Hydrogensulfate	[EAm][HSO_4]	
Pyrazolium Hydrogensulfate	[P][HSO_4]$_2$	
1-Methylimidazolium Hydrogensulfate	[MIM][HSO_4]	
1,4-Sultone-Methylimidazolium Hydrogensulfate	[BSMIM][HSO_4]	
1,4-Sultone-Methylimidazolium	[BSMIM][CF_3SO_3]	

Triflouromethanesulfonate		
1,4-Sultone-Pyridinium Hydrogensulfate	[BSPy][HSO_4]	
1,4-Sultone-Pyridinium Triflouromethanesulfonate	[BSPy][CF_3SO_3]	

Characterization

^{1}H and ^{13}C NMR spectra were taken in (DMSO and D_2O) solvent and recorded on a Bruker Avance 500 spectrometer. Carbon, hydrogen, nitrogen, and sulphur content were analyzed using elemental analyzer (CE Instruments EA-1110). Additionally their structure was also characterized by FTIR (Shimadzu) and their spectra's were recorded from 500-4000 cm^{-1}. A coulometric Karl Fisher titrator, DL 39 (Mettler Toledo) was used for the synthesized PILs water determination. using the Hydranal coulomat AG reagent (Riedel-de Haen), the method adopted our research group [30]. The measurement was made in triplicate for each IL, and reported the average values.

Density and Viscosity. An Anton Paar viscometer (model SVM3000) was used to measure the viscosity of PILs. Density measurement was carried out using an Anton Paar densitometer (DMA 5000). Standard uncertainties are $u(\rho)$ = ± 0.00001 g·cm−3, $u(\eta)$ = ± 0.32 % mPa·s, and u(T) = ± 0.01 K.

Surface tension. Surface tension was measured by a pendant drop method, and a syringe was used to generate a drop. To make a photograph used a camera (OCA 20). To evaluate the shape of the drop used software (SCA22). The measurement was recorded in the temperature range of 293.15-353.15 K. The measurements were performed with an accuracy of ±0.04 K and uncertainties of ± 1.2%. All measurements were performed in triplicate and average values are reported.

Refractive index. Refractive index was measured for all ionic liquids by ATAGO digital refractometer (RX-5000α). The samples were measured within the temperature range of 293.15 to 323.15 K with an accuracy of ± 0.05 K and uncertainties of 3.5×10^{-5}. Likewise, triplicate measurements were noted and the values were reported as an average.

Thermal decomposition. The thermal decomposition temperature of the PILs was measured using a thermogravimetric analyzer (PerkinElmer, Pyris V-3.81). Samples were heated from 50 to 500 °C in a crucible under a nitrogen atmosphere. The heating rate was 10 K min^{-1}. The accuracy of the measurement is better than ± 1 K.

Melting point and glass transition determination. The melting point and glass transition temperature was determined by DSC (differential scanning calorimetry; PerkinElmer, model pyris 1). The samples was weighted in aluminium pans and heated this sealed pans in a nitrogen atmosphere from 0 to 130°C and then cooled to -150°C and then heated again to 130°C. The heating and cooling rate is 10°C·min^{-1}.

Results and Discussion

The prepared PILs were obtained in good yield with high purity more than 98%. The purity of ionic liquid was assessed from the mole fraction of water (A coulometric Karl Fischer titrator) and mole fraction of unreacted impurities using NMR and elemental analysis. The NMR, elemental analysis and water content for each ionic liquid is given below.

1-methyl piperidinium hydrgensulfate [MPip][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.479 (s, 1H), 1.695-1.741 (m, 4H), 2.636 (s, 3H), 2.977 (s, 4H).

^{13}C NMR (500 MHz, DMSO): 21.692, 23.253, 43.801, 54.392.

CHNS elemental analysis for $C_6H_{15}NSO_4$, Found (%): C: 36.58, H: 8.01, N: 7.20, S: 17.08.

Calculated (%): C: 36.53, H: 7.66, N: 7.10, S: 16.26.

FT-IR (cm^{-1}): 3456.07, 2947.29, 2712.00, 2541.65, 1648.61, 1453.04, 1193.30, 1037.46, 852.59, 595.14.

4-methyl pyridinium hydrogensulfate [MPy][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.898 (s, 3H), 7.789-7.801 (d, 2H), 8.703-8.710 (d, 2H).

^{13}C NMR (500 MHz, DMSO): 21.957, 127.602, 143.086, 157.762

CHNS elemental analysis for $C_6H_9NSO_4$, Found (%): C: 38.22, H: 4.51, N: 7.09, S: 15.26. Calculated (%): C: 37.69, H: 4.74, N: 7.33, S: 16.77.

FT-IR (cm^{-1}): 3439.27, 2941.18, 2712.00, 2541.65, 1644.02, 1453.80, 1194.83, 1022.95, 857.17, 589.03.

Piperazinium hydrogensulfate [Pi][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.510 (s, 4H), 2.712 (s, 4H).

^{13}C NMR (500 MHz, DMSO): 47.29.

CHNS elemental analysis for $C_4H_{13}N_2SO_4$, Found (%): C: 26.04, H: 7.45, N: 16.72, S: 18.18. Calculated (%): C: 25.94, H: 7.07, N: 15.12, S: 17.31.

FT-IR (cm^{-1}): 3447.67, 2937.36, 2686.03, 2541.65, 1631.04, 1469.85, 1231.50, 1112.33, 1031.35, 793.77, 618.82.

Methyl pyrrolidinium hydrogensulfate [MPyr][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.840-1.897 (m, 2H), 1.969-2.040 (m, 2H), 2.819 (s, 3H), 2.942-3.012 (m, 2H), 3.472-3.526 (m, 2H), 7.078 (s, 1H).

^{13}C NMR (500 MHz, DMSO): 33.173, 120.913, 128.867, 138.

CHNS elemental analysis for $C_5H_{13}NSO_4$, Found (%): C: 13.10, H: 7.12, N: 7.92, S: 16.69.

Calculated (%): C: 32.87; H, 7.15, N, 7.64; S, 17.50.

FT-IR (cm^{-1}): 3443.09, 2937.36, 2702.84, 2545.47, 1632.56, 1461.44, 1197.12, 1035.93, 848.77, 587.43.

Ethyl ammonium hydrogen sulfate [EAm][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.161-1.190 (t, 3H), 3.042-3.086 (q, 2H), 3.860 (s, $N^{+}H_3$).

^{13}C NMR (500 MHz, DMSO): 8.987, 46.265.

CHNS elemental analysis for $C_2H_9NSO_4$, Found (%): C: 16.86, H: 7.03, N: 8.51, S: 19.20.

Calculated (%): C: 16.78, H: 6.34, N: 9.78, S: 22.40.

FT-IR (cm^{-1}): 3451.49, 2942.71, 2715.82, 2541.65, 1631.04, 1456.86, 1180.32, 1035.93, 857.17, 593.61.

Pyrazolium hydrogensulfate [P][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 3.381 (s, 2H), 6.260-6.267 (t, 1H), 7.505 and 7.712 (d, 2 N-H).

^{13}C NMR (500 MHz, DMSO): 107.441, 134.528.

CHNS elemental analysis for $C_3H_7N_2SO_4$, Found (%): C: 21.30, H: 4.48, N: 17.14, S: 18.98.

Calculated (%): C: 21.56, H: 4.22; N: 16.76, S: 19.18.

FT-IR (cm^{-1}): 3434.66, 2937.36, 2699.09, 2541.65, 1631.04, 1462.97, 1188.72, 1041.28, 844.18, 602.02.

1-methyl imidazolium hydrogensulfate [MIM][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 3.86 (s, 3H), 5.72 (s, 1H), 7.59 (s, 1H), 7.66 (s, 1H), 8.98 (s, 1H).

^{13}C NMR (500 MHz, DMSO): 35.234, 119.270, 123.057, 135.809.

CHNS elemental analysis for $C_4H_8N_2SO_4$ Found (%): C: 26.68, H: 4.45, N: 15.56, 17.86.

Calculated (%): C: 26.66, H: 4.48, N: 15.55, S: 17.80.

FT-IR (cm^{-1}): 3434.68, 2941.18, 2705.89, 2541. 65, 1648.61, 1461.44, 1188.72, 1042.81, 850.30, 593.61.

1, 4 sultone-methyl imidazolium hydrogensulfate [BSMIM][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, D_2O): δ = 1.570-1.632 (m, 2H), 1.850-1.910 (m, 2H), 2.786-2.817 (t, 2H), 3.750 (s, 3H), 4.088-4.117 (t, 2H), 7.297 (s, 1H), 7.353 (s, 1H), 8.584 (s, 1H).

^{13}C NMR (500 MHz, D_2O): 20.949, 28.099, 35.695, 48.932, 50.092, 122.178, 123.680, 135.942.

CHNS elemental analysis for $C_8H_{16}N_2S_2O_7$, Found (%): C: 30.18, H: 5.25, N: 8.20, S: 19.11. Calculated (%): C: 30.37, H: 5.10, N: 8.86: S: 20.27.

FT-IR (cm^{-1}): 3451.08, 2945.73, 2716.49, 2541.31, 1640.91, 1452.04, 1192.52, 1048.34, 854.42, .

1, 4 sultone-pyridinium hydrogensulfate [BSPy][HSO_4]

Spectroscopic data: ^{1}H NMR (500 MHz, D_2O): δ = 1.376-1.461 (m, 2H), 1.731-1.807 (m, 2H), 2.542-2.573 (t, 2H), 2.894-2.919 (t, 2H), 4.230-4.260 (t, 2H), 7.662-7.690 (t, 1H), 8.132-8.163 (t, 2H), 8.435-8.447 (d, 2H).

^{13}C NMR (500 MHz, D_2O): 20.679, 22.564, 29.088, 49.806, 60.967, 128.142, 143.975, 145.530.

CHNS elemental analysis for $C_9H_{15}NS_2O_7$, Found (%): C: 33.70, H: 5.08, N: 4.21, S: 20.12. Calculated Found (%): C, 34.50; H, 4.83; N, 4.47; S, 20.47.

FT-IR (cm^{-1}): 3330.69, 2947.18, 2708.56, 2544.20, 1656.77, 1453.48, 1191.80, 1044.01, 858.02, 597.78.

1, 4 sultone-methyl imidazolium triflouromethanesulfonate [BSMIM][CF_3SO_3]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.539-1.600 (m, 2H), 1.858-1.917 (m, 2H), 2.580-2.610 (t, 2H), 3.853 (s, 3H), 4.173-4.201(t, 2H), 7.701(s, 1H), 7.763 (s, 1H), 9.130 (s, 1H).

^{13}C NMR (500 MHz, DMSO): 21.940, 28.939, 36.215, 48.950, 50.865, 119.859, 122.779, 124.085, 137.036.

CHNS elemental analysis for $C_9H_{15}N_2SO_6$, Found (%): C: 30.29, H: 5.10, N: 7.40, S: 18.90. Calculated (%): C: 29.35, H: 4.10, N: 7.61, S: 17.41.

FT-IR (cm^{-1}): 3439.55, 2945.73, 2720.81, 2547.80, 1637.31, 1454.92, 1195.40, 1044.01, 858.02, .38

1, 4 sultone-pyridinium triflouromethanesulfonate [BSPy][CF_3SO_3]

Spectroscopic data: ^{1}H NMR (500 MHz, DMSO): δ = 1.068-1.096 (t, 2H), 1.562-1.643 (m, 2H), 2.000-2.060 (m, 2H), 2.616-2.646 (t, 2H), 4.620-4.649 (t, 2H), 8.146-8.174 (t, 2H), 8.588-8.619 (t, 1H), 9.085-9.096 (d, 2H).

^{13}C NMR (500 MHz, DMSO): 21.825, 30.225, 50.778, 60.907, 119.851, 128.583, 145.216, 145.984.

CHNS elemental analysis for $C_{10}H_{14}NS_2O_6$, Found (%): C: 32.20, H: 4.44, N: 4.10, S: 18.25. Calculated (%): C: 32.87, H: 3.86, N: 3.83, S: 17.55.

FT-IR (cm^{-1}): 3322.76, 2947.18, 2700.63, 2539.87, 1673.35, 1451.32, 1199.73, 1051.22, 858.02, 589.13.

The viscosity, density, surface tension, refractive index and thermal study results of the synthesized PILs are discussed subsequently below. Those ILs which obtained as solid at room temperature were not evaluated for most of their properties due to the limitation of the tested instruments to measure their properties. The measured thermophysical properties were compared to the available literature. Generally for these ILs, a limited literature data were reported.

Viscosity

The dynamic viscosity data of the prepared ILs measured at the temperature range of (293.15-353.15) K and at atmospheric pressure are given in Table 2 and shown in Figure 1. It shows, with the increase in temperature the ILs viscosities are decreases. It has been observed that the viscosities of the present ILs increase as [BSMIM][HSO_4] > [BSMIM][CF_3SO_3] > [BSPy][HSO_4] > [MPy][HSO_4] > [MIM][HSO_4] > [BSPy][CF_3SO_3] > [MPyr][HSO_4]. Comparatively, the three SO_3H functionalized ILs ([BSMIM][HSO_4], [BSMIM][CF_3SO_3], [BSPy][HSO_4]) shows higher viscosities which might be due to interaction of SO_3H functionalized side chain to anion of the ionic liquid moiety. At 373.15 K the lowest viscosity was measured for SO_3H functionalized IL ([BSPy][CF_3SO_3]) which is 19.140 and contrary the IL ([MPy][HSO_4]) which do not contain the SO_3H functionalized group still has higher viscosity. The higher viscosity of IL ([MPy][HSO_4]) was assumed due to strong ion interaction, smaller size and low molecular weight as compared to SO_3H functionalized IL. The higher viscosity of IL ([MPy][HSO_4]) is also expected due to less steric hindrance of cation and anion structures and hence more interactions is observed in its ions as compare to SO_3H functionalized IL. These study shows that by small changes in ILs structure can produce considerable differences in viscosity. The protic IL ([MPy][HSO_4]) containing pyridinium cation with HSO_4^- anion shows higher viscosity values as compared to the imidazolium cation containing PIL and similar statement reported in literature [31]. As compared to conventional solvents, these ILs shows high viscosities. This may be due to the van der Waals interactions, chain tangling effects and hydrogen bonding interactions. Along

with the electrostatic and van der Waals interactions, a reason of ion size, the polarizability and flexibility of the anion and planarity of molecular structure are also possible. A similar agreement such as the room temperature ILs higher viscosities may be due to the additional H-bonding interactions relating the functional groups of the cation with other cation and anions is available in literature [32]. H. Ohno, [33] also reported that the only few ILs have low viscosity because it strongly depends on the structure of the ions components. The ion component structure relationship and the viscosity is not completely understood, probably due to various parameters, such as ions shape, charge density, influence of other interaction forces, and conformational change of alkyl chain etc, involved. So our study confirmed that by incorporation of functionalized group on the cation the ILs viscosities increases but the different parameters as mentioned above also strongly affect the viscosity of IL.

Table 2. Experimental dynamic viscosities for protic ionic liquids at temperature in the range of 293.15 to 373.15 K and at atmospheric pressure.

T/K	η/(mPa)						
	[MPy][HSO_4]	[MPyr][HSO_4]	[MIM][HSO_4]	[BSMIM][HSO_4]	[BSMIM][CF_3SO_3]	[BSPy][HSO_4]	[BSPy][CF_3SO_3]
293.15	1426.0	298.19	563.01	49850	2377.3	1567.1	537.78
303.15	683.57	185.44	312.04	16207	1054.1	775.72	285.63
313.15	364.16	123.83	191.76	6406.1	525.43	421.40	164.68
323.15	211.07	85.950	125.36	2903.7	296.11	247.17	102.07
333.15	130.92	61.741	86.005	1449.5	176.49	154.58	67.087
343.15	85.855	45.804	61.421	784.72	112.02	101.97	46.363
353.15	58.765	34.943	45.400	455.14	75.343	70.330	33.391
363.15	41.900	26.322	34.591	280.52	52.424	50.418	24.918
373.15	30.862	22.191	27.149	182.90	37.970	37.347	19.140

[a]Standard uncertainty μ is μ(T) = 0.01 K and the combined expanded uncertainty is $u_c(\eta)$ = 0.32 % mPa·s, (level of confidence = 0.95).

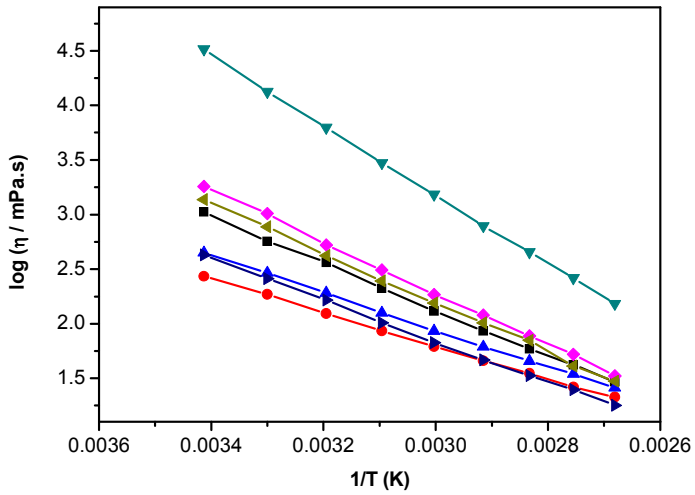


Figure 1: Viscosities as a function of temperature for Protic ionic liquids, [MPy][HSO_4]: ■, [MPyr][HSO_4]: ●, [MIM][HSO_4]: ▲, [BSMIM][HSO_4]: ▼, [BSMIM][CF_3SO_3]: ◄, [BSPy][HSO_4]: ►, [BSPy][CF_3SO_3]:

For each property, the Standard deviation *(SD)*[a] values were calculated using the equation

$$SD = \sqrt{\frac{(Z_{exp} - Z_{cal})^2}{n_{DAT}}}$$

Z_{exp} and Z_{cal} are experimental and calculated data values respectively. n_{DAT} is the number of experimental points.

The standard deviation *(SD)* and correlation coefficients calculated values for viscosity using equation (a) and (b) are shown in the below Table 3a.

[b]Equation for viscosity temperature dependence: $\log \eta / (mPa \cdot s) = A_0 + (A_1/T)$

Table 3a. Fitting parameter values with R^2 and standard deviation *(SD)*[a] for empirical correlation of viscosity [b], of the measured ionic liquids.

ILs	$SD\times10^{-02}$	R^2	A_0	A_1
[MPy][HSO_4]	1.470	0.9991	4.2351	2121.7
[MPyr][HSO_4]	9.033	0.9994	2.7886	1528.7
[MIM][HSO_4]	9.958	0.9994	3.1544	1699.7
[BSMIM][HSO_4]	1.357	0.9997	6.3256	3169.4
[BSMIM][CF_3SO_3]	1.420	0.9993	4.8005	2359.5
[BSPy][HSO_4]	1.688	0.999	4.6265	2273.2
[BSPy][CF_3SO_3]	1.292	0.9992	3.8132	1884.9

The correlation coefficients values calculated for viscosity using Vogel-Tamman-Fulcher equation are tabulated in Table 3b.

$$\eta = A_o e^{A1\ (T-Tg)}$$

Table 3b. Fitting parameter by Vogel-Tamman-Fulcher equation values of the measured ionic liquids.

ILs	R^2	A_0	A_1
[MPy][HSO_4]	0.9798	51894	-0.047
[MPyr][HSO_4]	0.9859	4554.9	-0.032
[MIM][HSO_4]	0.9808	14267	-0.037
[BSMIM][HSO_4]	0.9769	1000000	-0.069
[BSMIM][CF_3SO_3]	0.9777	69739	-0.051
[BSPy][HSO_4]	0.981	16477	-0.046
[BSPy][CF_3SO_3]	0.9797	8793.6	-0.041

Density

Figure 2 shows the temperature effect on the density values of the PILs. The density increasing order of the synthesized ILs are [BSPy][CF_3SO_3] > [BSPy][HSO_4] > [MIM][HSO_4] > [BSMIM][CF_3SO_3] > [BSMIM][HSO_4] > [MPy][HSO_4] > [MPyr][HSO_4].

In functionalised ILs, the $CF_3SO_3^-$ anion containing ILs shows higher density value as compare to the HSO_4^- anion. The reason may be due to the high molecular weight of $CF_3SO_3^-$ anion. Z. B. Zhou et al [34], reported different ILs with fluorinated anions and claim that the density gradually increased as the bulkiness of the fluoro anion increased. These obtained values are higher than those of water and traditional solvents such as ethanol, ethylacetate and methanol [35]. In order to know the effect of cation structure on the synthesized ILs density more directly especially when incorporate the functionalized group on the cation, except the simple imidazole cation with HSO_4^- anion had the high density value. In functionalized ILs, the anion $CF_3SO_3^-$ shows higher densities with the concern cations. These behaviours were in good agreement with many similar reported conclusions that the density increased by increasing the anion molecular weight [31]. Gardas et al, [27] reported for imidazolum cations, that when the liquid density increases it does not correspond directly to the anion high molecular weight. But it can be explained that thiocyanate anion had the strong localized charge than in the dicyanamide, which gives the possibility of a strong pairing with the imidazolium and pyridinium cation resulting in a higher density. The density of all these ILs showed a linear dependency with temperature.

Table 4. Experimental values of density (ρ) of the ionic liquids from (293.15 to 373.15) K at atmospheric pressure.

T/K	ρ/(g.cm^{-3})						
	[MPy] [HSO_4]	[MPyr] [HSO_4]	[MIM] [HSO_4]	[BSMIM] [HSO_4]	[BSMIM] [CF_3SO_3]	[BSPy] [HSO_4]	[BSPy] [CF_3SO_3]
293.15	1.3689	1.3633	1.4622	1.4386	1.4491	1.4775	1.4835
303.15	1.3623	1.3539	1.4555	1.4323	1.441	1.4704	1.4744
313.15	1.3556	1.3448	1.4491	1.4261	1.4327	1.4631	1.4658
323.15	1.3491	1.3372	1.4429	1.4199	1.4246	1.4562	1.4574
333.15	1.3427	1.3281	1.4367	1.4137	1.4168	1.4495	1.449
343.15	1.3363	1.3191	1.4306	1.4075	1.4091	1.4429	1.4405
353.15	1.3298	1.3101	1.4246	1.4011	1.4015	1.4363	1.4322
363.15	1.3233	1.2987	1.4187	1.395	1.394	1.4297	1.4239
373.15	1.3168	1.2894	1.4129	1.3891	1.3867	1.4234	1.4158

[a]Standard uncertainty μ is μ(T) = 0.01 K and the combined expanded uncertainty is $\mu c(\rho)$ = 0.00001 g·cm^{-3}, (level of confidence = 0.95).

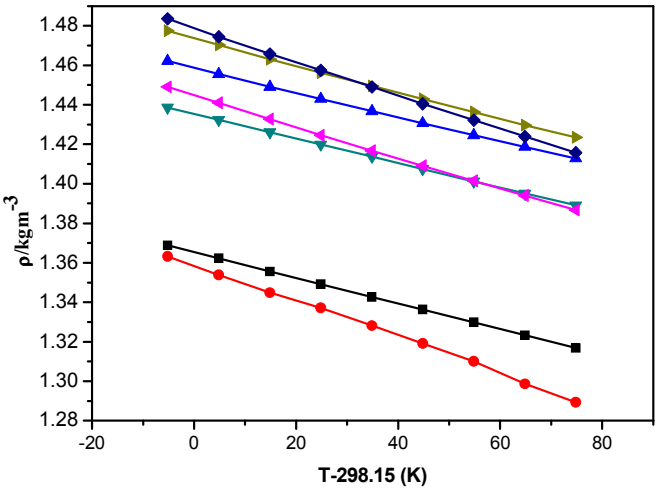


Figure 2: Densities (***ρ***) as a function of temperature (T) for the protic ionic liquids, [MPy][HSO_4]: ■, [MPyr][HSO_4]: ●, [MIM][HSO_4]: ▲, [BSMIM][HSO_4]: ▼, [BSMIM][CF_3SO_3]: ◄, [BSPy][HSO_4]: ►, [BSPy][CF_3SO_3]:

The standard deviation *(SD)* and correlation coefficients calculated values for density are shown in the below Table 5.

[c] Equation for density temperature dependence: ln ρ/ (kgm^{-3}) = A_2+A_3 (T-298.15), where

$$A_1 = \frac{\alpha}{K} = -\left(\frac{\partial ln\rho}{\partial(T-298.15)}\right)_p$$

Table 5**.** Fitting parameter values with R^2 and standard deviation $(SD)^a$ for empirical correlation of density [c], of the measured ionic liquids.

ILs	*SD*	R^2	A_2	A_3
[MPy][HSO_4]	6.738×10^{-04}	1.0	7.2193	-0.0005
[MPyr][HSO_4]	9.410×10^{-04}	0.998	7.2147	-0.0007
[MIM][HSO_4]	1.236×10^{-03}	0.999	7.2852	-0.0004
[BSMIM][HSO_4]	1.691×10^{-03}	1.0	7.2692	-0.0004
[BSMIM][CF_3SO_3]	2.133×10^{-03}	0.999	7.2756	-0.0006
[BSPy][HSO_4]	4.730×10^{-02}	0.999	7.2493	-0.0005
[BSPy][CF_3SO_3]	7.927×10^{-04}	1.0	7.2989	-0.0006

Estimation of volumetric properties

The apparent densities values for the present ionic liquids at 298.15 K were fitted by applying the following equation:[36]

$$ln\left[\frac{\rho}{g.cm^{-3}}\right] = A_O - A_1((T/K) - 298.15) \quad \textbf{(1)}$$

Where A_O is a constant and $A_1 = \frac{\alpha}{K} = -\left(\frac{\partial ln\rho}{\partial(T-298.15)}\right)_p$; where α is the thermal expansion coefficient.

The molecular volumes, V_m, the standard molar entropy (S^0) and the lattice energy of the synthesized ILs calculated using the equations 2, 3 and 4 respectively and the values were listed in Table 6.

$$V_m = \frac{M}{N_A \rho} \quad \textbf{(2)}$$

$$S^o(303.15)/J.K.mol^{-1} = 1246.5(V_m/nm^3) + 29.5 \quad \textbf{(3)}$$

$$U_{POT}/kJ/mol^{-1} = 1981.2\ (\rho/M)^{1/3} + 103.8 \quad \textbf{(4)}$$

where M is molecular weight and N_A is Avogadro's number.

From the Table 6 it can be found that the molar volume of ILs [BSMIM][CF_3SO_3] and [BSPy][CF_3SO_3] was larger than the rest of ILs because of the larger volume and high molecular weight of the triflouromethanesulfonate anion. The lattice energy values of [MPy][HSO_4], [MPyr][HSO_4], [MIM][HSO_4], [BSMIM][HSO_4], [BSMIM][CF_3SO_3], [BSPy][HSO_4], [BSPy][CF_3SO_3] are $3.916\times10^{+03}$, $3.963\times10^{+03}$, $4.079\times10^{+03}$, $3.381\times10^{+03}$, $3.226\times10^{+03}$, $3.421\times10^{+03}$, $3.258\times10^{+03}$ kJ·mol^{-1}, respectively, and adjacent to previously reported ionic liquids [37-39]. The studied ionic liquids have significantly lower lattice energy than alkali halides [40]. The lattice energy lower values for ionic liquids render them as liquid at room temperature [38, 41].

Table 6. Calculated values of Volume properties of ILs

Ionic liquid	ρ(kg·m^{-3})	V_m(nm^3)	S^o(J·K^{-1}·mol^{-1})	U_{POT}(kJ·mol^{-1})
[MPy][HSO_4]	1362.3	2.330×10^{-01}	$3.200\times10^{+02}$	$3.916\times10^{+03}$
[MPyr][HSO_4]	1353.9	2.247×10^{-01}	$3.096\times10^{+02}$	$3.963\times10^{+03}$
[MIM][HSO_4]	1455.5	2.055×10^{-01}	$2.857\times10^{+02}$	$4.079\times10^{+03}$
[BSMIM][HSO_4]	1432.3	3.667×10^{-01}	$4.866\times10^{+02}$	$3.381\times10^{+03}$
[BSMIM][CF_3SO_3]	1441	4.244×10^{-01}	$5.585\times10^{+02}$	$3.226\times10^{+03}$
[BSPy][HSO_4]	1470.4	3.538×10^{-01}	$4.705\times10^{+02}$	$3.421\times10^{+03}$
[BSPy][CF_3SO_3]	1474.4	4.114×10^{-01}	$5.423\times10^{+02}$	$3.258\times10^{+03}$

Surface Tension

The ILs are containing organic moieties, they are expected to exhibit the surface activities. The surface tension measured data is tabulated in Table 7 and shown in Figure 3. These selected ILs have higher surface tension values than most of the common organic solvents and lower than water. The surface tension values at 293.15 K of methanol, acetone and water are (22.6, 23.7 and 72.7 $mN{\cdot}m^{-1}$) [31, 42]. The reported ILs shows higher surface tension values even at a higher temperature while the lowest value is 19.62 for IL ([MPyr][HSO_4]) which is very close to the common organic solvents values. All these values are in an acceptable range which is very close to the reported values for ILs [43]. The lower surface tension values are attributed to a weakening of the Columbic interactions. The experimentally obtained data shows that both the cation and anion have an effect on the surface tensions. Since the surface tension is a measure of the surface cohesive energy and is related to the interaction strength of ILs cation and anion. For these high values of surface tension, the only explanation is the hydrogen bonding that exist between the cations, and the cations and anions, since that the interactions increases between the ions leading to enhanced the surface tension values.

Table 7. Experimental values of surface tension *(γ)* in the temperature range of 293.15-353 K at atmospheric pressure.

	Surface Tension-$10^2\gamma$ (Jm^{-2})						
T(K)	[MPy][HSO_4]	[MPyr][HSO_4]	[MIM][HSO_4]	[BSMIM][HSO_4]	[BSMIM][CF_3SO_3]	[BSPy][HSO_4]	[BSPy][CF_3SO_3]
293.15	5.111	3.260	5.394	4.465	4.529	4.362	4.421
303.15	4.973	3.042	5.320	4.318	4.424	4.242	4.298
313.15	4.840	2.81	5.227	4.172	4.324	4.124	4.181
323.15	4.658	2.586	5.127	4.029	4.227	3.997	4.062
333.15	4.480	2.352	5.032	3.889	4.117	3.869	3.957
343.15	4.329	2.180	4.903	3.749	4.020	3.738	3.823
353.15	4.210	1.962	4.790	3.618	3.912	3.612	3.702

[a]Standard uncertainty μ is μ(T) = 0.04 K and the combined expanded uncertainty is μc *(γ)* = 1.2% mN/m, (level of confidence = 0.95).

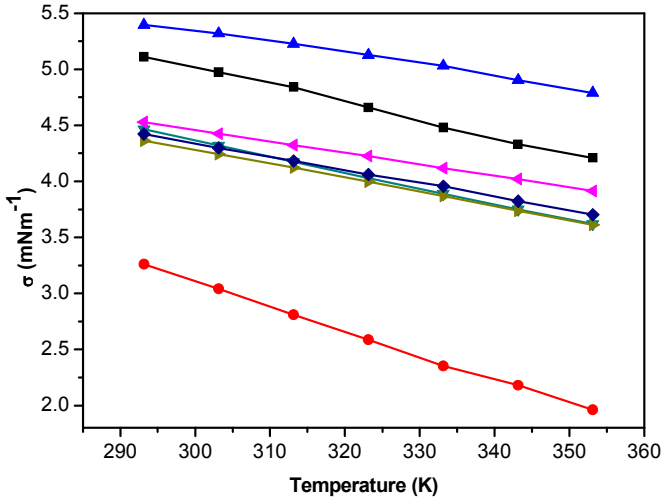


Figure 3: Surface tension *(γ)* as a function of temperature for the protic ionic liquids, ■ [MPy][HSO_4], ● [MPyr][HSO_4], ▲ [MIM][HSO_4], ▼ [BSMIM][HSO_4], ◄ [BSMIM][CF_3SO_3], ► [BSPy][HSO_4], ♦ [BSPy][CF_3SO_3].

The standard deviation *(SD)* and correlation coefficients calculated values for surface tension using equation (a) and (d) are shown in the below Table 8.

[d]Equation for surface tension temperature dependence: $\sigma\ /\ (mNm^{-1}) = A_4 + A_5T$.

Table 8. Fitting parameter values with R^2 and standard deviation *(SD)*[a] for empirical correlation of surface tension [d] , of the measured ILs.

ILs	*SD*	R^2	A_4	A_5
[MPy][HSO_4]	1.719×10^{-02}	0.9969	-0.01554	9.6788
[MPyr][HSO_4]	1.562×10^{-02}	0.9987	-0.0217	9.6112
[MIM][HSO_4]	1.577×10^{-02}	0.994	-0.0101	8.3921
[BSMIM][HSO_4]	4.905×10^{-03}	0.9997	-0.0142	8.6069
[BSMIM][CF_3SO_3]	3.147×10^{-03}	0.9998	-0.01025	7.5295
[BSPy][HSO_4]	4.582×10^{-03}	0.9997	-0.0125	8.0464
[BSPy][CF_3SO_3]	5.456×10^{-03}	0.9995	-0.0119	7.9078

The surface tension and the temperature are correlated using the following equation.

$$\sigma\ /\ (mNm^{-1}) = A_4 - A_5T \quad \textbf{(5)}$$

Where σ represents surface tension, A_2 and A_3 are fitting parameters, and T is the absolute temperature. Table 7 shows the estimated values of fitting coefficients along the standard deviation *(SD)*. The measured surface tension values were applied to calculate the entropy and enthalpy of surface formation. It was possible to determine the surface entropy from the slope, S_a, of equation (6). The estimated entropies are listed in Table 9, and the results show lower values compared with the other ionic liquids [37, 44] but close to the reported ionic liquids for example [C_{16}-mim][PF_6]-(109 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) and [($C_{16}$)2-Bim][Cl]-(255 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) [45]. The lower value of entropy leads to a greater ordering within the liquids.

$$S_a = A_3 = -(\frac{\partial\sigma}{\partial T})_P \quad \textbf{(6)}$$

The surface enthalpy *(E_s)* was calculated using equation (7) from the surface tension at 303.15 K and the results are tabulated in Table 9.

$$E_a = A_2 = \sigma - \left(\frac{\partial\sigma}{\partial T}\right)_P \quad \textbf{(7)}$$

The $NaNO_3$ has a surface enthalpy *(E_s)* value of 146 $mJ{\cdot}m^{-2}$, which is noticeably higher than ionic liquids [46]. It is a sign of the lower degree of interaction among the ions in ionic liquids. The surface enthalpy value of the ionic liquids is close to the common organic solvents such as octane (51.1 $mJ{\cdot}m^{-2}$) and benzene (67 $mJ{\cdot}m^{-2}$).

Table 9. Surface thermodynamic functions of pure ionic liquids at temperature 303.15 K: surface entropy, S_a, and surface enthalpy, E_s.

ILs	$10^3.S_a$($mJ{\cdot}K^{-1}.m^{-2}$)	E_s($mJ{\cdot}m^{-2}$)
[MPy][HSO_4]	155.4	54.44095
[MPyr][HSO_4]	217	36.99836
[MIM][HSO_4]	101	56.26182
[BSMIM][HSO_4]	142	47.48473
[BSMIM][CF_3SO_3]	102.5	47.34729
[BSPy][HSO_4]	125	45.52729
[BSPy][CF_3SO_3]	119	46.58749

Critical Temperature, Enthalpy of vaporization and Normal boiling point

Critical temperature (T_c), is an important parameter in correlating equilibrium and transport properties of liquids. Because of the intrinsic nature of the ionic liquids, it is difficult to get reliable data of their critical temperature [47]. To predict the critical temperature values for ILs, usually some estimated methods are used [48]. Hence in this work, Guggenheim [49] (equation 8) and Eötvos [50] (equation 9) empirical equations were used to predict the critical temperature of the ILs and the results are shown in Table 10. Enthalpy of vaporization of ionic liquids was estimated using (equation 10). The enthalpy of vaporization of ILs ([BSMIM][HSO_4], [BSMIM][CF_3SO_3], [BSPy][HSO_4], [BSPy][CF_3SO_3]) is higher as compared to the other ILs which is without sultone group, implying that these ILs shows lower volatility. Especially the triflouromethanesulfonate anion containing ILs. A similar agreement reported in literature [48].

$$\sigma = E^{\sigma}\left(1 - \frac{T}{T_c^G}\right)^{11/9} \quad \textbf{(8)}$$

$$\sigma\left(\frac{M}{\rho}\right)^{2/3} = K(T_c^E - T) \quad \textbf{(9)}$$

$$\Delta_1^g H_m^{\circ} = 0.01121(\sigma\, V^{2/3}\, NA^{1/3}) + 2.4 \quad \textbf{(10)}$$

where E^{σ} is total surface energy of ILs, which equals the surface enthalpy because of the tiny volume difference due to thermal expansion at the temperatures that are not similar to the critical temperature T_C^G, K is a constant, σ is surface tension, M is molecular weight, ρ is density and T is measured surface tension temperature and N_A is Avogadro number.

It is also possible to calculate boiling temperature, T_b, of ILs from the critical temperature T_c has been proposed by Rebelo *et al* [51] According to them, the relation between T_c and T_b is $T_b \approx 0.6T_c$ for an ILs. The calculated T_b values of ILs are given in Table 10.

Table 10.The critical temperature, T_c, Normal boiling temperature, T_b, and enthalpy of vaporization of ionic liquids at temperature 303.15 K:

ILs	Guggenheim		Eötvos		$\Delta_l^g H_m^{\circ}$
	T_c/K	T_b/K	T_c/K	T_b/K	kJ·mol^{-1}
[MPy][HSO_4]	4247.178	2548.307	942.7021	565.6213	129.5467
[MPyr][HSO_4]	2048.201	1228.921	684.9887	410.9932	78.31177
[MIM][HSO_4]	6774.106	4064.464	932.3981	559.4389	127.4982
[BSMIM][HSO_4]	4052.452	2431.471	1054.46	632.6761	151.7649
[BSMIM][CF_3SO_3]	5611.371	3366.823	1151.666	690.9999	171.0901
[BSPy][HSO_4]	5394.323	3236.594	1023.838	614.303	145.6771

[BSPy][CF_3SO_3]	4750.39	2850.234	1110.589	666.3533	162.9236

Interstice model for ionic liquids.

A new theoretical model called interstice model [52, 53] was developed for ILs by abstracting the essence of hole model for molten salts [54] The model is based on four assumptions which can be seen elsewhere [48, 55, 56]. In this model the interstice volume, *v*, for the ionic liquids was calculated using an equation from classical statistical mechanics.

$$V = 0.6791(k_bT/\sigma)^{3/2} \quad [48] \qquad \textbf{(11)}$$

The value of the average volume of the interstices of synthesized ILs was given in Table 11. The volume fractions of the interstice, $\sum v/V$, for all the measured ionic liquids are also given in Table 11. The values were in between 10.76 to 12.72 % and are in agreement with the substances which show a volume expansion of approximately less than 15% during the transformation from solids to liquids. The molar volume, *V*, is the summation of the inherent volume, V_i, and the sum of the volumes of all interstices, $\sum v = 2N_Av$, *i.e.*

$$V = V_i + 2N_Av \quad [48] \qquad \textbf{(12)}$$

The thermal expansion coefficient (α), was calculated by assuming that the ILs expansion results only by the expansion of the interstice during the temperature change. Hence, the equation of α derived from the interstice model is given below.

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P = \frac{3N_Av}{VT} \quad [48] \qquad \textbf{(13)}$$

The calculated and the experimental values of α for all the ionic liquids under study are shown in Table 10.

Table 11. Parameters of Interstice Model for the Protic ILs at 303.15 K:

ILs	$10^{-24}v$/cm^3	$\sum v$/cm^3	$\sum v/v$	$10^4\alpha$(calc)/K^{-1}	$10^4\alpha$(exp)/K^{-1}
[MPy][HSO_4]	16.58758	19.98139	14.23674	7.04	5
[MPyr][HSO_4]	34.67143	41.76521	30.86062	15.26	7
[MIM][HSO_4]	14.99143	18.05868	14.58786	7.22	4
[BSMIM][HSO_4]	20.50155	24.69616	11.18139	5.53	4

[BSMIM][CF_3SO_3]	19.76915	23.81391	9.316099	4.61	6
[BSPy][HSO_4]	21.05497	25.36282	11.90154	5.89	5
[BSPy][CF_3SO_3]	20.64481	24.86874	10.03599	4.96	6

Refractive Index

Table 12 presents the refractive index values for the investigated protic ILs, and the temperature effect on refractive indices is shown in Figure 4. The effects of temperature on refractive indices of the present ionic liquids were measured in the temperature range of 293.15-323.15 K. It is indicated that the refractive indices of these protic ILs makes an obvious reduction with increase in temperature. As presented in Table 12, among these studied PILs, ([MPy][HSO_4]) has the highest refractive index value while ([BSPy][CF_3SO_3]) has the lowest refractive index value. The increasing order of the refractive indices of the investigated ILs is [MPy][HSO_4] > [BSMIM][HSO_4] > [BSPy][HSO_4] > [MIM][HSO_4] > [MPyr][HSO_4] > [BSMIM][CF_3SO_3] >[BSPy][CF_3SO_3]. The present refractive indices values are very close to other reported ILs available in literature[57-61]. Due to the limited literature on protic ionic liquids the comparisons explain with aprotic ionic liquids. The Standard Deviations *(SDs)* and fitting parameters of refractive index for the present ionic liquids are given in Table 13.

Table 12. Experimental refractive indices n_D for the present ionic liquids in the temperature of 293.15-323K at atmospheric pressure.

	n_D						
T/K	[MPy][HSO_4]	[MPyr][HSO_4]	[MIM][HSO_4]	[BSMIM][HSO_4]	[BSMIM][CF_3SO_3]	[BSPy][HSO_4]	[BSPy][CF_3SO_3]
293.15	1.5335	1.46458	1.48955	1.5038	1.46042	1.49878	1.45608
298.15	1.53283	1.46359	1.48865	1.50287	1.45947	1.49827	1.45525
303.15	1.53168	1.46254	1.48761	1.502	1.45835	1.49739	1.45399
308.15	1.53051	1.46149	1.48655	1.50118	1.45718	1.49638	1.45254
313.15	1.52931	1.4604	1.48552	1.50033	1.45595	1.4953	1.45093
318.15	1.52812	1.45934	1.48432	1.49949	1.45473	1.49422	1.4493

323.15	1.52692	1.45827	1.48311	1.49864	1.45355	1.4931	1.44748

[a]Standard uncertainty μ is $\mu(T) = \pm 0.05$ K and the combined expanded uncertainty is $\mu c\ (nD) = 3.5 \cdot 10^{-5}$, (level of confidence = 0.95).

Table 13. Standard Deviations *(SDs)* and fitting parameters of Refractive Index: $n_D = A_6 + A_7$

ILs	*SD* ($\times 10^{-03}$)	R^2	A_6	A_7
[MPy][HSO_4]	6.849	0.9956	1.5998	-0.0002
[MPyr][HSO_4]	3.010	0.9999	1.5265	-0.0002
[MIM][HSO_4]	4.057	0.998	1.5527	-0.0002
[BSMIM][HSO_4]	7.957	0.9997	1.5538	-0.0002
[BSMIM][CF_3SO_3]	8.716	0.9987	1.5286	-0.0002
[BSPy][HSO_4]	1.541	0.9907	1.5561	-0.0002
[BSPy][CF_3SO_3]	2.458	0.9893	1.5419	-0.0003

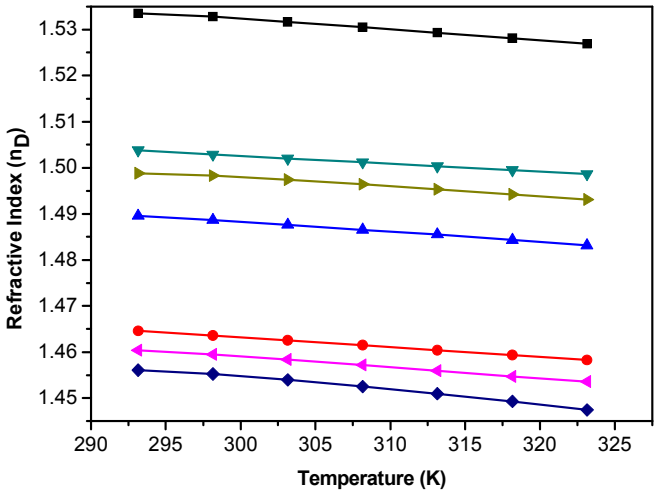


Figure 4: Refractive indices (n_D) as a function of temperature for the protic ionic liquids, ■ [MPy][HSO_4], ● [MPyr][HSO_4], ▲ [MIM][HSO_4], ▼ [BSMIM][HSO_4], ◄ [BSMIM][CF_3SO_3], ► [BSPy][HSO_4], ♦ [BSPy][CF_3SO_3].

Thermal Stability

The Thermogravimetric analysis (TGA) was used to evaluate the thermal degradation temperature of the Protic ionic liquids. It has been observed that ionic liquid based on imidazole cation have the higher stability as compare to other cations both with functionalized SO_3H group and without the functional group. In the functionalized four ILs the $CF_3SO_3^-$ anion containing ILs shows higher stability than HSO_4^- anion. The onset decomposition temperature of the present protic ILs are 252.36, 299.07, 263.97, 246.51, 253.98, 323.56, 333.92, 288.74, 243.22, 338.60, and 282.46 ^oC, for [MPip][HSO_4] , [MPy][HSO_4], [Pi][HSO_4], [MPyr][HSO_4], [EAm][HSO_4], [P][HSO_4], [MIM][HSO_4], [BSMIM][HSO_4], [BSPy][HSO_4], [BSMIM][CF_3SO_3], and [BSPy][CF_3SO_3] respectively. These data are in good agreement with the literature[62-64]. Miran et al, [65] reported that the DBU based protic ILs with different anions such as acetate, trifluoroacetate and methanesulfonate etc are in the temperature range from 171-451 ^oC. According to protic ionic liquids (PILs), it is generally believed that thermally unstable relative to aprotic ionic liquids (AILs). The protic ionic liquids (PILs) due to N—H bonding in its cations structure is thermally unstable as compare to aprotic ionic liquids (AILs), such as 1-methyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([C_2mim][NTf_2]) [23], Moreover the acetate base Protic liquids were observed more unstable as compared to other anion based Protic ionic liquids which might be due to degradation of acetate anion also. The thermal stability measured for these PILs were in reasonable range to be used in various applications. It has been assumed that the decomposition temperature of the ionic liquids depends upon the structure of cations and anions.

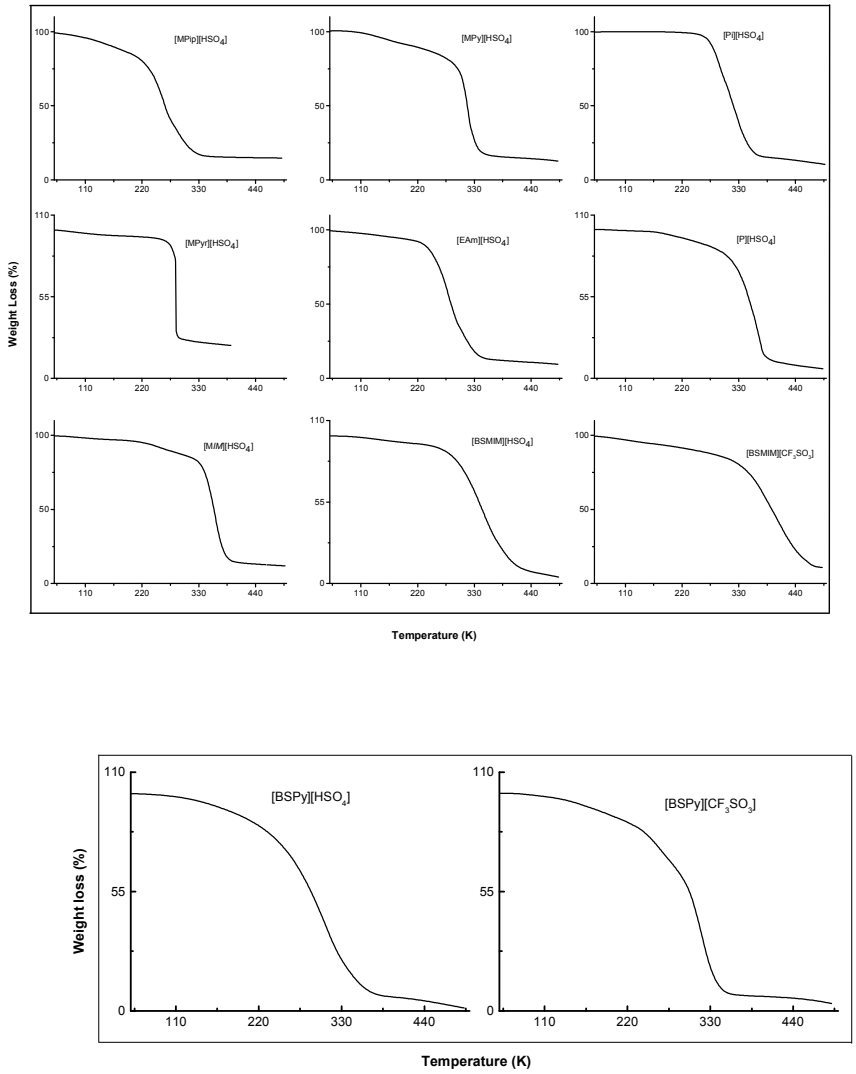


Figure 5: Thermogravimetric analysis (TG) of protic ionic liquids.

The melting point and glass transition was determined for the prepared ionic liquids, in which the exothermic peak onset temperature was assigned to the glass transition and endothermic peak onset temperature was assigned to the melting point. The obtained values are listed in Table 14.

Table 14. Glass transition and melting point of synthesized ionic liquids.

ILs	Tg	Tm
[MPip][HSO_4]	-62.79	------
[MPy][HSO_4]	-69.67	-18.95
[Pi][HSO_4]	------	60.33
[MPyr][HSO_4]	-96.24	------

[EAm][HSO_4]	-74.63	51.47
[P][HSO_4]	-73.73	45.20
[MIM][HSO_4]	-73.49	20.88
[BSMIM][HSO_4]	-34.72	------
[BSMIM][CF_3SO_3]	-54.75	------
[BSPy][HSO_4]	-40.90	------
[BSPy][CF_3SO_3]	-55.87	------

Conclusions

In the present work, a series of protic ILs were prepared and their various physicochemical properties were measured under the effect of temperature. The viscosity and density values are decrease with increase of temperature. Comparatively, the SO_3H functionalized ILs ([BSMIM][HSO_4], [BSMIM][CF_3SO_3], [BSPy][HSO_4]) shows higher viscosities. For Pyridinium cation ([MPy][HSO_4]) protic IL with HSO_4^- anion without any functional group shows higher viscosity values as compare to the imidazolium cation. In functionalised ILs, the $CF_3SO_3^-$ anion containing ILs shows higher density value as compare to the HSO_4^- anion because $CF_3SO_3^-$ anion had high molecular weight. From the experimental density values some thermodynamic properties like molecular volume, standard entropy, lattice energy and thermal expansion coefficient were calculated. The calculated values are in the range as reported for other ILs. The surface tension data was further used to calculate surface entropy and surface enthalpy. With the help of Guggenheim and Eötvos equations, critical temperature and normal boiling temperature was calculated for prepared PILs. The volume fractions of interstice, $\sum v/V$ were in between 10.76 to 12.72 % and are in good agreement with the substances which show a volume expansion of approximately less than 15% during the transformation from solids to liquids. The molar enthalpy of vaporization was also determined. It also suggested that the interstice model can be applied for ILs system, and the calculated values are in good agreement with the experimental ones. The present ionic liquids have lower lattice energy and higher standard entropy, while the thermal stabilities were measured higher as compared to most of the reported PILs.

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