Conductance of 1-Butyl-3-methylimidazolium nitrate [BMIm][NO$_3$] with N,N-dimethylformamide at T (293.15 – 323.15) K

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ABSTRACT

1 – Butyl – 3 – methylimidazolium nitrate [BMIm][NO3] was synthesized and characterized. Density and viscosity measurements were performed at room temperature. Density and viscosity measurements decreased with increasing temperature. Conductivity measurement of the ionic liquid at different temperatures showed increase in conductivity with increasing temperature. Conductivity measurement of the ionic liquid with N,N-dimethylformamide at different concentrations showed increase in conductivity with increase in concentration. The thermogravimetric analysis, (TGA) of the ionic liquid shows a high thermal stability of the ionic liquid with decomposition beginning at about 391.85 ^oC.

Keywords: Ionic liquid, 1-Butyl-3-methylimidazolium nitrate [BMIm][NO3], conductivity, density, viscosity.

1. INTRODUCTION

An ionic liquid is any salt that is liquid below 100 ^{o}C (Fung & Zhu, 2002). They also have unusual properties including non-volatility, conductivity, chemical and electrochemical stability (Bennett, *et al*., 2016).

While liquids like water are predominantly made of electrically neutral molecules, ionic liquids [ILs] are largely made of ions and short-lived ion pairs. These substances are called liquid electrolytes. Ionic liquids have many applications, such as powerful solvents and electrically conducting fluids (electrolytes) (Endres, *et al*., 2008).

ILs can have wide electrochemical potential and good electrical conductivity. Generally, it is expected that ILs possess very high conductivity, due to their entire ionic structure. Unfortunately, it is not the case. The conductivity of some classes of ionic liquids is similar with the best non-aqueous solvents-electrolyte solutions, being up to 10 mS/cm

(Wasserscheid & Welton (2002). However, they are less conductive than the concentrated aqueous electrolytes solutions. This fact can be attributed to the decreased availability of the charge carriers due to ion pairing or ions aggregation, having as result a large ion size and consequently a reduced mobility.

Ionic liquids can be used in various applications (Kokorin, 2011,Patachia, *et al*., 2009): controlled modification of hydrogels morphology, controlled release of ionic liquids, as antimicrobial agents (Patachia & Damain, 2014;Thanganathan & Nogami, 2015; Zhu, *et al*., 2010), replacing water as the electrolyte in metal-air batteries (Armand, *et al*., 2009, Hamilton, 2009), controlling solutions or polymeric matrix conductivity due to their association in water (Rilva & Santiago, 2011), or through their interaction with polymers in films and gels by obtaining conductive systems (Patachia, *et al*., 2011; Patachia & Damain, 2014).

Ionic liquids can be favorably combined to give mixtures with enhanced ionic transportation properties and electrochemical stability (Domańska, & Królikowska, 2012). Electrical conductivity of ionic liquid mixtures is of considerable interest both from practical as well as theoretical points of view. By means of conductivity data, conclusions on the structure and transport theories of ionic liquids may be tested. Furthermore, the current and energy efficiencies of electrolytic processes are closely related to the electrical conductivity of the electrolyte. Therefore, the studies allow the prediction of ionic liquids in various specific applications Agnieszka, *et al*., (2015).

Ngoyi, et al., (2011) carried out a conductivity study of 1-Butyl-3-Methylimidazolium Bromide with water, methanol, ethanol, acetonitrile and acetone over a wide range of temperature. They reported that the addition of water to the ionic liquid resulted in an increase in the conductivity of the mixture. The conductivity also increased with temperature and they attributed their observations to the presence of water-rich regions in the mixture. Agnieszka and Adams (2014) carried out conductometric studies on 1-ethyl-3-methylimidazolim tetrafluoroborate and 1-Butyl-3-methylimdazolium tetrafluoroborate in 1-propanol at the composition range of 283.15 – 318.15 K. They reported a tremendous increase in conductivity and this they attributed to the formation of strong ion – ion association between the components. Egashira, *et al.,*(2005) observed that when 10 wt% of cyano-substituted quaternary ammonium salt $[(NC)C_1C_n(C_1)_2N][NTf_2]$ (n = 1 or 2) was added to $[C_2C_1Im][NTf_2]$ there was a sharp increase in conductivity in spite of the fact that the conductivities of the simple ammonium salts were considerably lower than that of $[C_2C_1Im][NTf_2]$. Borun and Bald (2014) carried out conductance measurements of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3- methylimidazolium tetrafluoroborate solutions in N, N-Dimethylformamide. They confirmed that in this dipolar aprotic solvent, a slight ion association occurs for the ionic liquids over the whole investigated temperature range. They reported strong ionic association of 1-propanol, a protic solvent with the ionic liquids.

Tzi-Yi *et al.,* (2013) studied the ionic conductivity of 1-butyl-1-methylpyrrolidinium butyl sulphate and its binary mixtures with Poly (ethylene glycol) [PEG200 + [PyrMB][BuSO₄] as a function of temperature at atmospheric pressure, observed an increase in conductivity of the PEG200 in the ionic liquid.

Available literature shows that a limited number of research studies have been reported on the conductivity of [BMIm][NO₃] with DMF binary mixtures. N, N-dimethylformamide is an aprotic polar solvent that is not able to self-organize hydrogen bonding Abubaker, *et al*.,

(2013). It lacks hydrogen bonds, large dipole moment and high dielectric constant (Venkatesu, 2010) but a good donor-acceptor compound (Marcus, 1998). These properties allow DMF to dissolve both polar and non-polar liquids and it is used in electrolytic capacitors (Gopal, *et al*., 1976).

Following these observations, conductivity studies of $BMImNO_3$ in N, N-dimethylformamide were carried out in the present study. The ionic liquid, 1 – Butyl – 3 – methylimidazolium nitrate [BMIm][NO_3] was synthesized and its density, viscosity and conductivity in N, N-dimethylformamide were measured at different temperatures and concentrations.

2. EXPERIMENTAL
2.1. Materials
Reagent grade 1-bromobutane, methyl imidazole, N, N-Dimethylformamide were purchased from Acros Organics and used without further purification. Silver nitrate, dichloromethane, silica gel mesh 60 were purchased from Alfa Aesar and used without further purification.

2.2. Density Measurement
Density measurement of DMF and synthesized ionic liquid was carried out with an Anton Paar DMA-4500 M digital densitometer thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers were used for good precision in temperature control internally (T $\pm$ 0.01 K). The densitometer protocol includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1.0 x 10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than 1.0x10^{-4} g/cm^3. Calibration of the densitometer was performed at atmospheric pressure using doubly distilled and degassed water.

2.3. Viscosity Measurement
Viscosity measurements were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of 0.2 - 20 000 mPa.s, a kinematic viscosity ranges of 0.2 - 20 000 mm^2/s and a density range of 0.65 to 3 g/cm^3. The instrument is equipped with a maximum temperature range of 10°C and a minimum of 20°C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility 0.0005g/cm.

2.4. Infrared Measurement
Infra-red spectra of the synthesized ionic liquid were recorded using Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer in the range 400 – 4000 cm^{-1}.

2.5. NMR Measurement
Proton-NMR spectra of the ionic liquid in DMSO were measured using a Bruker Variance 400 NMR spectrometer operating at proton frequency of 300 MHz 75.48 MHz for ^{13}C protochemical shifts were recorded relative to an internal TMS standard.

2.6 Conductivity Measurement
Conductivity measurements were carried out using Thermo Fisher Scientific/Eutech Instrument PC700 pH/mV/Conductivity meter. Conductivity of the instrument ranges from

$0 – 2000$ μS and $0 – 200.0$ mS. The instrument has a full scale resolution of 0.5% and an accuracy of $\pm$1%. Before and after measurements, the instrument was calibrated with KCl solution. The temperature of the sample was kept at 20 ± 0.1 ^{o}C. Each measurement was repeated three times and the average values were calculated.

2.7 Preparation of 1-Butyl-3-methylimidazolium nitrate [BMIm][NO₃]

81.89 g (1.0 mol) of 1-butyl-3-methylimidazole and 128.95 g (1.0 mol) of 1-bromobutane were stirred with a magnetic stirrer in a three-necked round bottomed flask fitted with a reflux condenser at 80 ^{o}C for 12 hours. The reaction mixture was cooled and 2.0 g (0.012 mol) of silver nitrate was added and stirred at room temperature for 4 hours. The mixture was concentrated under reduced pressure at $40 – 50$ ^{o}C over rotavapor (Buchi). The mixture was diluted with 50 ml dichloromethane and passed through silica gel mesh (size 60). The volatile substance was evaporated in a vacuum oven at 120 ^{o}C. Yellow oil was obtained. (Yield 92%). The ionic liquid was characterized and by FTIR, ^{1}H and ^{13}C-NMR.
FTIR (Neat liquid); V/cm^{-1} 3096 NO_3, 2964 (s, aliphatic C-H stretch), 1573 (w, C=C), 1340 (s, sym ring stretch), 1171 (s, C−N vibration), 845 (s, C-H bend), 760 (s, C – H bend). ^{1}H NMR of the ionic liquid sample (300 MHz, DMSO) contains peaks at δ: 9.05 (singlet, 1H-imidazole), 7.86 (singlet, 1H-imidazole), 7.78 (singlet, 1H-imidazole), 4.19 (triplet, CH_2), 3.87 (triplet, CH_2), 1.74 (quintet, CH_2), 1.23 (sextet, CH_2), and 0.85 (triplet, CH_3). ^{13}C NMR (300 MHz, DMSO) contains peak δ: 13.27 (s, CH_3), 18.75 (s, CH_2), 31.39, (s, CH_2), 35.82 (t, CH3), 48.46 (t, CH_2),120.72 (q, imidazole CH), 123.51 (s, imidazole CH), 136.4 (t, imidazole CH).

3. RESULTS AND DISCUSSION

Density and viscosity measurements for the ionic liquid 1-Butyl-3-methylimidazolium nitrate are presented in figures 1 and 2. Figure 1 shows the density of the ionic liquid 1 – Butyl – 3 – methylimidazolium nitrate, measured at four temperatures. The density measurement curve obtained is linear indicating that the molar mass of the nitrate anion is what is responsible for the linearity obtained. This linear relationship of density of ionic liquids has been observed by Wei, *et al* (2006). As expected the density values decreased with increase in temperature.

Viscosity is an important property of ionic liquids because it strongly influences diffusion of species which are dissolved or dispersed in a media such as an ionic liquid (Jarosik, 2006). Ionic liquid viscosity is ordinarily influenced by the interaction of the cation, anion and other interactions such as hydrogen bonding and the symmetry of the ions (Kiki, *et al*., 2014; Virendra, *et al*.,2012). The viscosity of the ionic liquid measured at four temperatures from (293.15 – 323.15) K is presented in and Figure 2. The viscosity decreased with increase in temperature. It has been reported that temperature affects the viscosity of pure ionic liquid as well as ionic liquid saturated in water (Bejan, *et al*.,). The temperature dependent viscosity plot for 1 – Butyl – 3 – methylimidazolium nitrate is presented by the Arrhenius plot of viscosity against temperature, Figure 3. This is a nonlinear curve which is similar to that described for other ionic liquids (Bejan, *et al*.,). 1 – butyl – 3 – methylimidazolium nitrate [BMImNO₃], prepared showed conductivity of 6.12, 8.94, 10.41, 10.71 mScm^{-1} at 293.15 – 323.15 K as presented in Table 1 and Figure 4. The charge carriers in ionic liquids are ions. In solutions, the ionic liquids dissociation occurs, and ions dissociation degree, their concentration and mobility are influencing the system

conductivity. The charge carriers' mobility is influenced by the ions dimension. Increasing the charge carriers' concentration is increasing the conductivity (Hiroyuki, 2005). The conductivity of binaries of 1 – Butyl – 3 – methylimidazolium nitrate [BMIm][NO$_3$], with the cosolvent N,N-Dimethylformamide at different temperatures and different concentrations were also measured. The effect of the addition of a cosolvent is presented in Table 2 and Figures 5 – 8. The main aim of this measurement is to provide results of modification of transport coefficient upon addition of a cosolvent.

4. CONCLUSION

In this paper, we present measurements of density, viscosity and electrical conductivity of 1 – Butyl – 3 – methylimidazolium nitrate [BMIm][NO$_3$]. The density and viscosity decreased with increase in temperature. The electrical conductivity of the ionic liquid against temperature showed increase in conductivity with increasing temperature. Conductivity of binaries of the ionic liquid with N,N-dimethylformamide increased with increase in concentration. This could be due to the increasing number of the charge carriers (ions) in solution.

5. ACKNOWLEDGEMENTS

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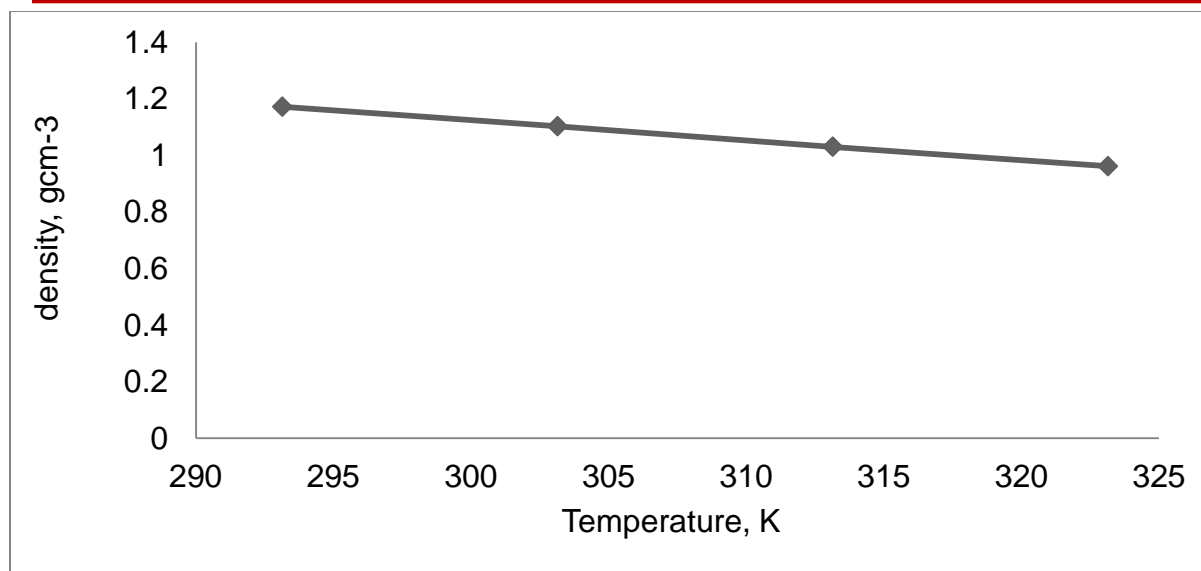
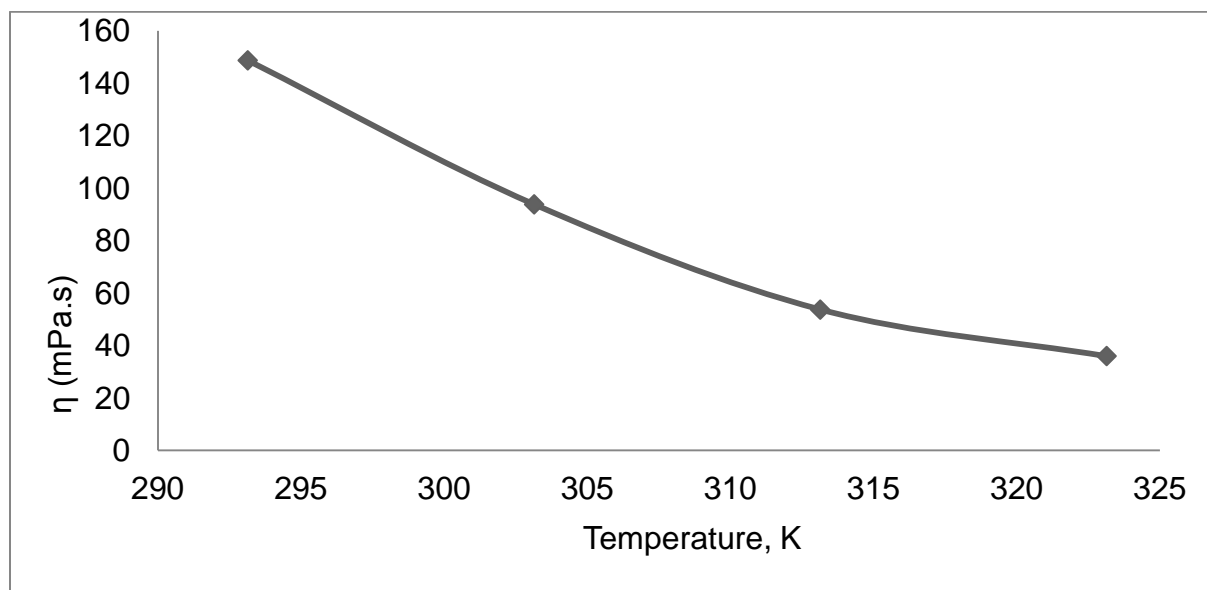Figure 1: Density measurement of 1 – Butyl – 3 – methylimidazolium nitrate (BMIm][NO$_3$]) as a function of temperature.

Figure 2: Viscosity measurement of pure 1-Butyl-3-methylimidazolium nitrate [BMIm][NO$_3$] as a function of temperature (K).
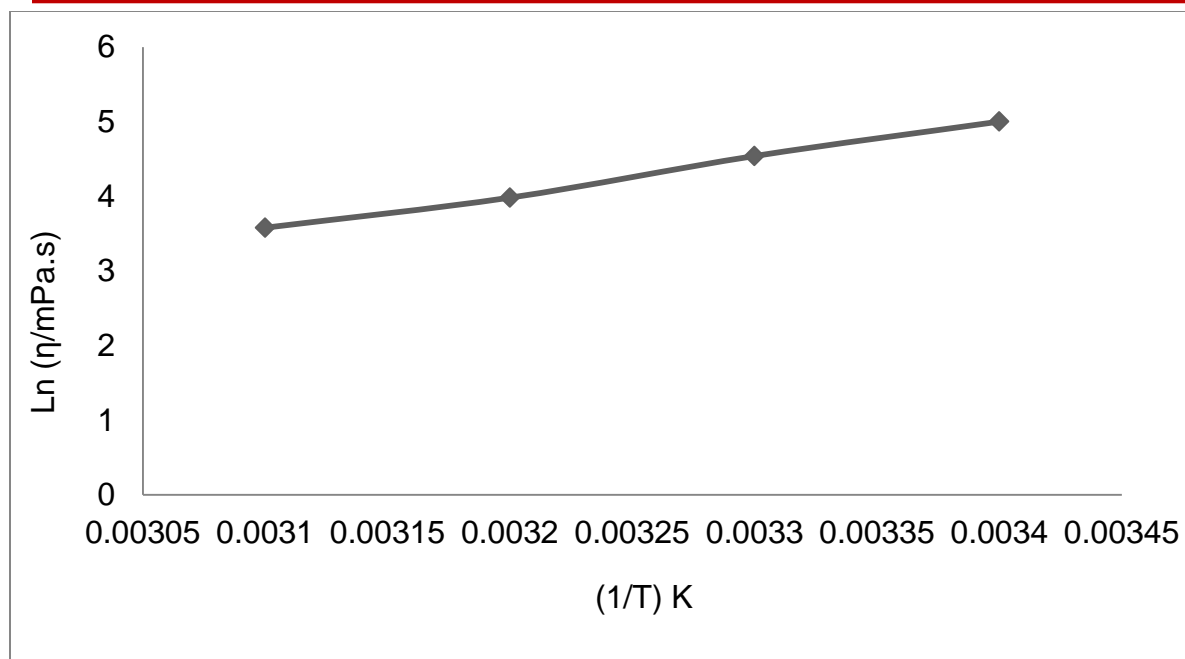
Figure 3: Arrhenius plot of viscosity of pure 1 – Butyl – 3 – methylimidazolium nitrate [BMImI][NO$_3$] as a function of inverse of temperature
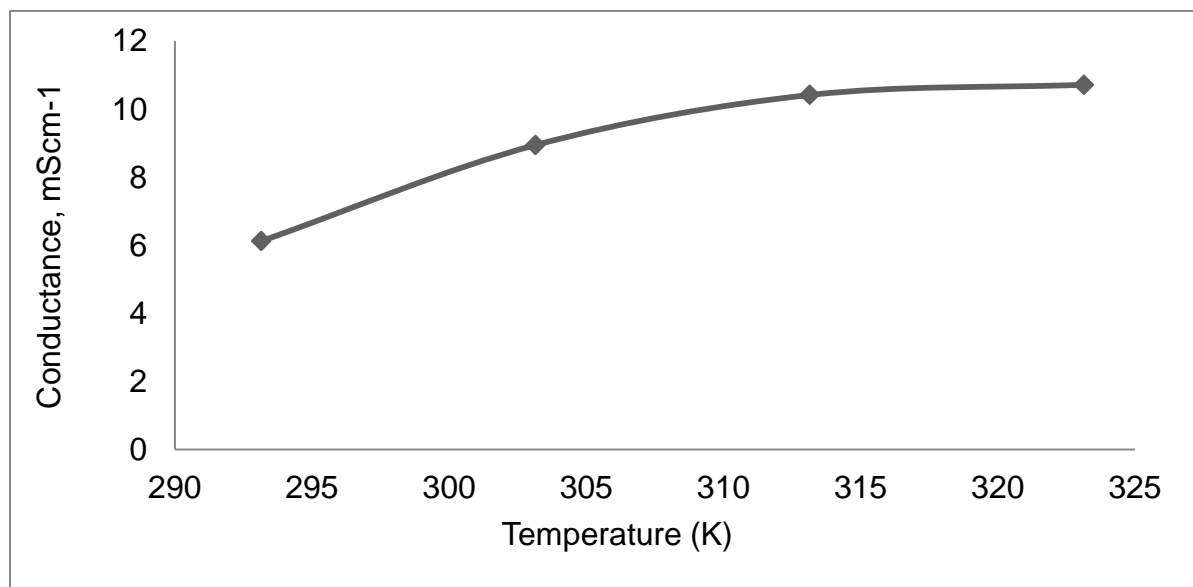

Figure 4: Plot of Conductivity of pure 1 – Butyl – 3 – methylimidazolium nitrate [BMIm][NO$_3$] as a function of temperature.
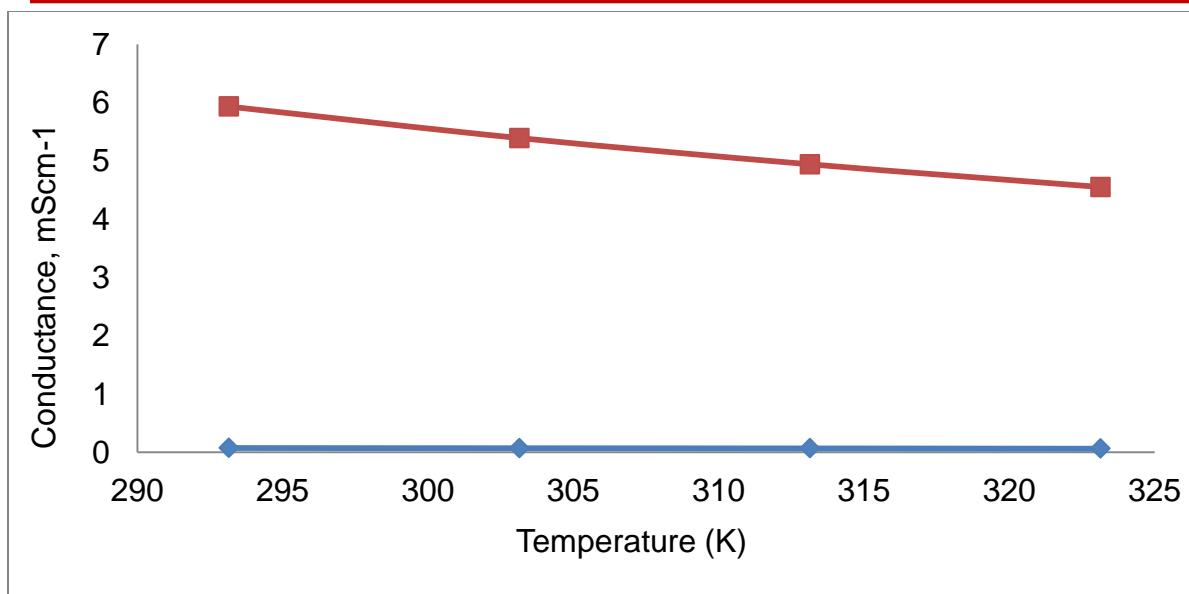
Figure 5: Plot of Conductivity of N,N-Dimethylformamide ( ) and 0.00125M 1 – Butyl – 3 – methylimidazolium nitrate in DMF ( ) as a function of temperature.
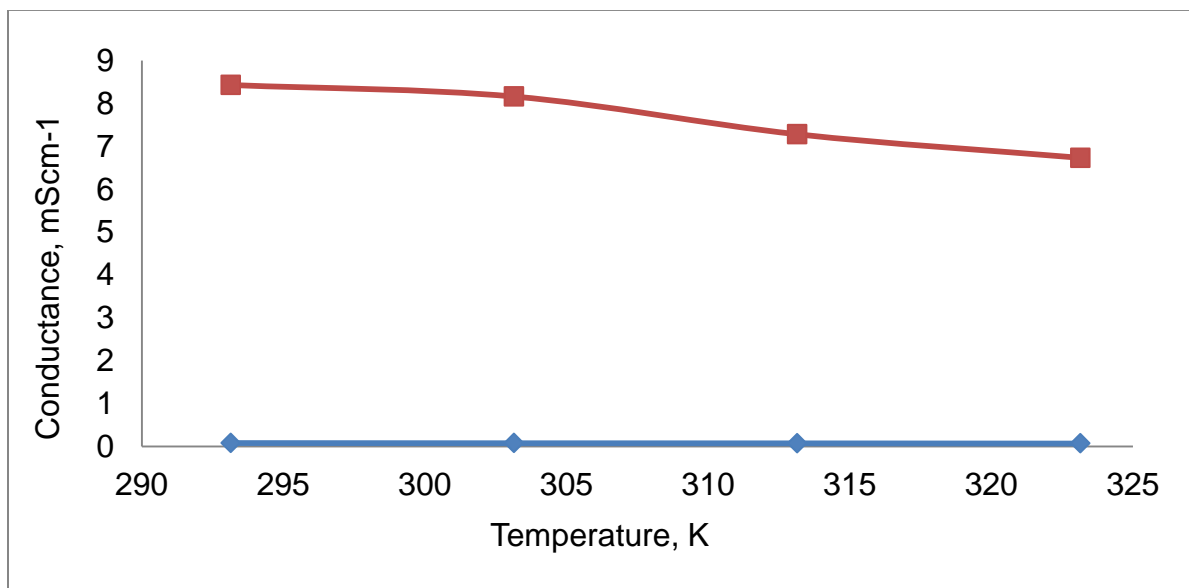

Figure 6: Plot of Conductivity of N,N-Dimethylformamide ( ) and 0.0025 M 1 – Butyl – 3 – methylimidazolium nitrate in DMF ( ) as a function of temperature.
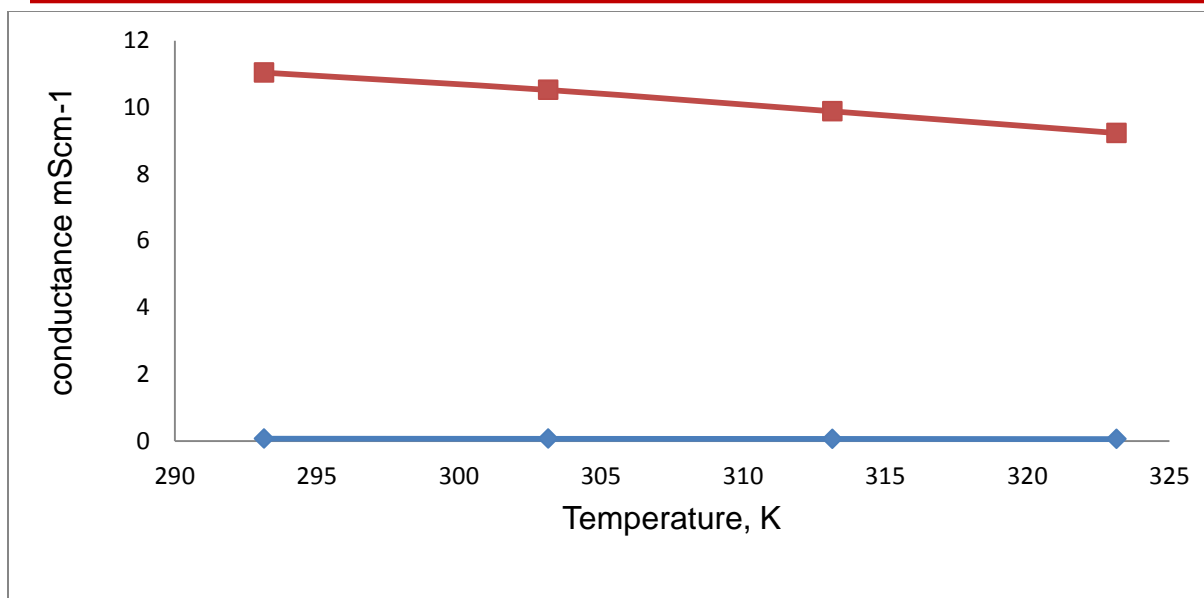
Figure 7: Plot of Conductivity of N,N-Dimethylformamide ( ) and 0.005M 1 – Butyl – 3 – methylimidazolium hexafluorophosphate in DMF ( ) as a function of temperature.
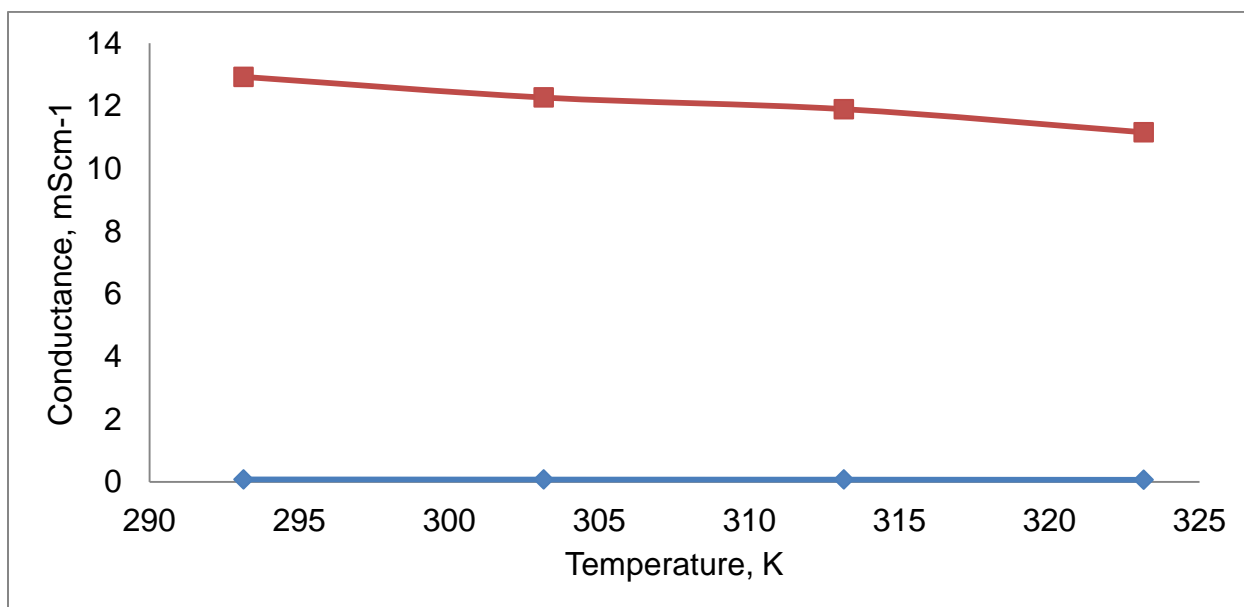

Figure 8: Plot of Conductivity of N,N-Dimethylformamide ( ) and 0.01M 1 – Butyl – 3 – methylimidazolium nitrate in DMF ( ) as a function of temperature.

Table 1: Conductivity data of [BMIm][NO$_3$] at 293.15 – 323.15 K

Temperature (K)	Conductivity, K, (mScm^{-1})
293.15	6.12
303.15	8.94
313.15	10.41
323.15	10.71

Table 2: Molar concentration (mol dm^{-3}), Temperature (K), Specific conductance (K) of 0.05 M DMF and Specific conductance (K) of [BMIm][NO$_3$] in 0.05 M DMF at 293.15 – 323.15 K

Molar Conc (mol dm^{-3})	Temp (K)	Specific Cond of DMF	Specific Cond of BMImNO$_3$ + DMF
0.00125	293.15	0.076	5.93
	303.15	0.072	5.39
	313.15	0.069	4.94
	323.15	0.064	4.55
0.0025	293.15	0.076	8.43
	303.15	0.072	8.16
	313.15	0.069	7.28
	323.15	0.064	6.73
0.005	293.15	0.076	11.04
	303.15	0.072	10.52
	313.15	0.069	9.88
	323.15	0.064	9.23
0.01	293.15	0.076	12.92
	303.15	0.072	12.26
	313.15	0.069	11.89
	323.15	0.064	11.15