

Effect of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆] on N,N-dimethylformamide: Conductivity Measurement at T (293.15 – 333.15) K

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Abstract

The ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆] was synthesized and characterized. Density and viscosity measurements of the synthesized compound were performed at room temperature. It was observed that density and viscosity measurements decreased with increasing temperature. FTIR and NMR spectra corroborate the successful synthesis of the ionic liquid. 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 temperatures and concentrations showed increase in conductivity with increase in concentration and temperature. The thermogravimetric analysis, (TGA) showed a high thermal stability of the ionic liquid with decomposition beginning at about 405.85 °C.

Keywords: Ionic liquid, FTIR, conductivity, density, viscosity, TGA.

1. Introduction

Ionic liquids (ILs) are salts that are liquid below 100 °C (Ngoyi et al, 2011, Dikio et al, 2013, Wikes, 2012, Bennett et al, 2016). Ionic Liquids have been attracted from many research fields (Egasira et al; 2006) due to their unique properties such as non-volatility, undetectable vapor pressure, wide liquid range, as well as ease to recovery and reuse (Dong, 2008; Earle and Seddon, 2000; Jie et al, 2005; Wikes, 2004). Depending on cation-anion combinations, the physico-chemical properties of ionic liquids could be transformed (Wassercheid et al, 2001). In addition, ILs have intrinsic conductivity at room temperature and a wide electrochemical window, exhibiting good electrochemical stability in the range of 4.0 – 5.7 V (Kuma et al, 2010; Ski et al, 2006). The conductivity of an ionic liquid is of vital importance for both theoretical research and industrial application. Ionic liquids have reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to 10 mScm⁻¹) (Bonhte et al, 1996). However, at room temperature, their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on the fact that ionic liquids are composed

solely of ions, it would be expected that ionic liquids have high conductivities. This is not the case since the conductivity of any solution not only depends on the number of charge carriers but also on their mobility. The large constituent ions of ionic liquids reduce the ion mobility which in turn, leads to lower conductivities. Furthermore, ion pair formation and/or ion aggregation lead to reduced conductivity. In fact the change in conductivity with composition in ionic liquids can be attributed almost directly to changes in viscosity (Trulove and Mantz, 2003). Hence, ionic liquids of higher viscosity exhibit lower conductivity, increasing the temperature results in increase in conductivity and decrease in viscosity.

Ionic liquids can be favorably combined to give mixtures with enhanced ionic transportation properties and electrochemical stability (Domanska and Krolikowska, 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 and others (2013) 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 the conductivity increase to the presence of water-rich regions in the mixture. Agnieszka and Adam (2014) carried out conductometric studies on 1-Ethyl-3-methylimidazolium tetrafluoroborate and 1-Butyl-3-methylimidazolium 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 components. Egashira and others, (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 protic solvent 1-PrOH with the ILs.

Tzi-Yiet *et al.*, (2013) studied the ionic conductivity of 1-Butyl-1-methylpyrrolidinium Butyl Sulfate and its binary mixtures with Poly (ethylene glycol) [PEG200 + [PyrMB][BuSO₄]] as a function of temperature at atmospheric pressure, and observed an increase in conductivity of the PEG200 in the ionic liquid. They suggested that the data obtained would be helpful for the application of the ionic liquid as electrolyte and also useful for the ionic liquids database.

1-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid [BMIm][PF₆] is one of the most important traditional ionic liquids and has been widely used in the fields of separation, catalysis, synthesis, etc (Zang et al, 2004; Charmicheal et al, 2000; Zhou et al, 2006). An extensive literature survey showed that a limited number of research studies have been reported on the conductivity of [BMIm][PF₆] with DMF binary mixtures. N,N-dimethylformamide (DMF) is an aprotic polar solvent that is not able to self-organize hydrogen bonding (Abubaker et al, 2013). It lacks hydrogen bond, large dipole moment and high dielectric constant

(Venkatesu, 2010). It is 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).

In this study, we have synthesized the ionic liquid, 1-Butyl-3-methylimidazoliumhexafluorophosphate [BMIm][PF₆] and measured the conductivity of N,N-dimethylformamide in the ionic liquid at different temperatures and at different concentrations.

2. Experimental

2.1. Materials

Reagent grade Iodobenzene, Methylimidazole, N,N-Dimethylformamide, were purchased from Acros Organics and used without further purification. Ethyl acetate, 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 1.0×10^{-5} g/cm³, and the uncertainty of the measurements was estimated to be better than 1.0×10^{-4} g/cm³. 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 range of 0.2 - 20 000 mm²/s and a density range of 0.65 to 3 g/cm³. The instrument is equipped with a maximum temperature range of 105 °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

IR spectra of 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

¹H-NMR spectra of the ionic liquid in DMSO were measured using a BrukerAvriqance 400 NMR spectrometer operating at proton frequency of 300 MHz 75.48 MHz for ¹³C protochemical shifts were recorded relative to an internal TMS standard.

2.6. Thermogravimetric Analysis

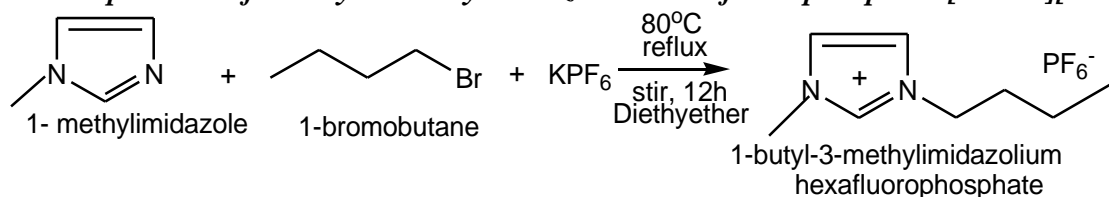
The thermal behavior of the ionic liquid was investigated using a Perkin Elmer Simultaneous Thermal Analyzer (STA 6000) under a nitrogen environment. The ionic liquid sample was heated in platinum crucibles with nitrogen gas flow rate of 19.7 mL/min and a gas pressure of 4.0 bars. The dynamic measurement was made from 30 °C and 950 °C with a ramp rate of 30 °C/min - 900 °C.

2.7 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 – 2000μS 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 °C. Each measurement was repeated three times and the average values were calculated.

2.8. Preparation of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆]



81.89g (1.0 mol) of 1-methylimidazole, 128.95g (1.0mol) of and 92.0g (1.0 mol) of potassium hexafluorophosphate in a 500 ml three necked round bottom flask with a reflux condenser at 80°C for 12hr. 1-bromobutane De-ionized water (100ml) was added and a bi-phase was formed. The immiscible ionic liquid layer was separated from the water phase with a separating funnel. The ionic liquid was washed with de-ionized water (2 x 50ml) until the water phase did not react with 0.001M aqueous silver nitrate (AgNO₃). Diethyl ether (2 x 30 ml) was added to the ionic liquid and separated in a separating funnel. The ionic liquid was dried in vacuum for 2hr. A colorless liquid was obtained Yield (96%).The ionic liquid was characterized by FTIR, TGA and ¹H and ¹³C-NMR

3. Results and Discussion

Density measurements for the ionic liquid 1-Butyl-3-methylimidazoliumhexafluorophosphate are presented in Figure 1. Figure 1 shows the density of the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate, measured at four temperatures. The density measurement curve obtained is linear, and it is attributed to the molar mass of the phosphate anion obtained. This linear relationship of density of ionic liquids has been observed by Wei, et al, (2008)

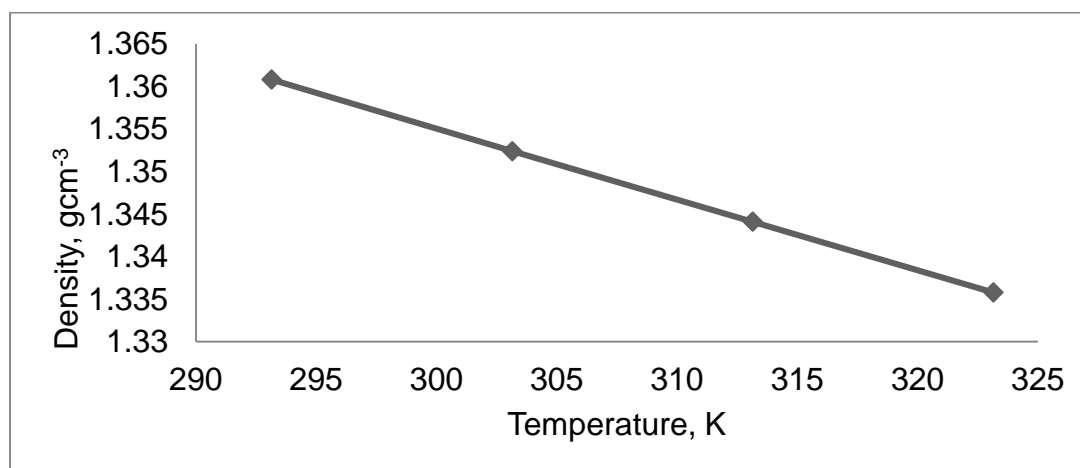


Figure 1: Density plot of pure [BMIm][PF₆] as a function of temperature.

Ionic liquids are highly viscous. The viscosity of ionic liquids is typically 10 to 100 times higher than that of water or organic solvents as a result of strong electrostatic and other interaction forces (Evans 1994). 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 at al, 2012). Temperature affects the viscosity of pure ionic liquids as well as ionic liquid saturated in water [Benja et al 2010]. The temperature dependent

viscosity plot for 1 – Butyl – 3 – methylimidazolium hexafluorophosphate is presented by the Arrhenius plot of viscosity against temperature in Figure 2. This is a non linear curve which is similar to that described for other ionic liquids (Benja et al, 2010). Viscosity decreased with increasing temperature. It has been reported that temperature affects the viscosity of pure ionic liquids as well as ionic liquids saturated in water (Benja et al, 2010).

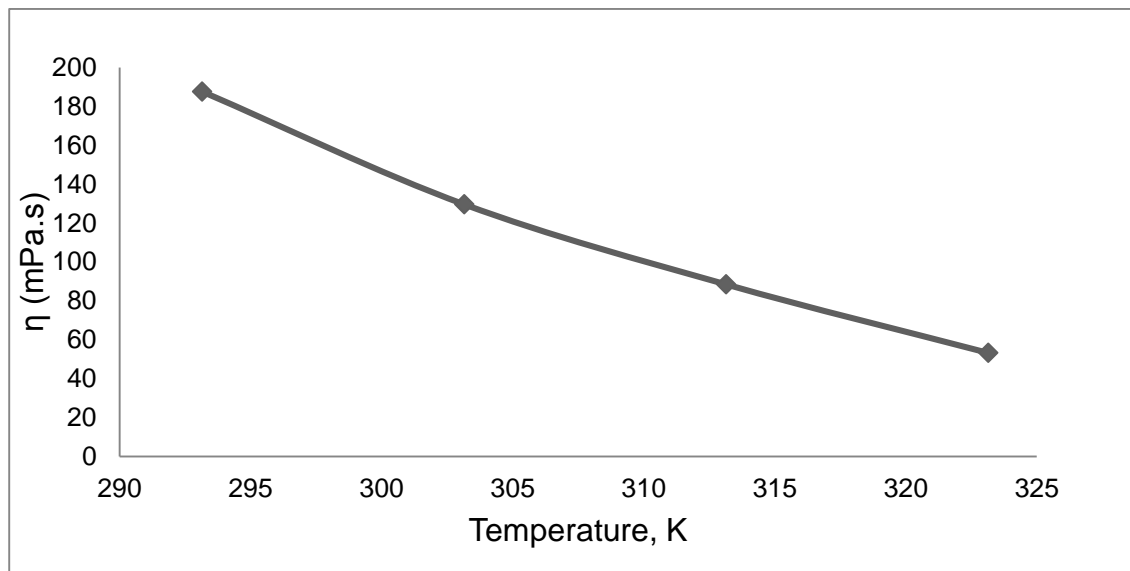


Figure 2; Viscosity plot of BMImPF₆ as a function of temperature

The FTIR spectrum of the synthesized ionic liquid is presented in Figure 3. The result obtained from this FTIR indicates the presence of key functional groups in the synthesized ionic liquid.

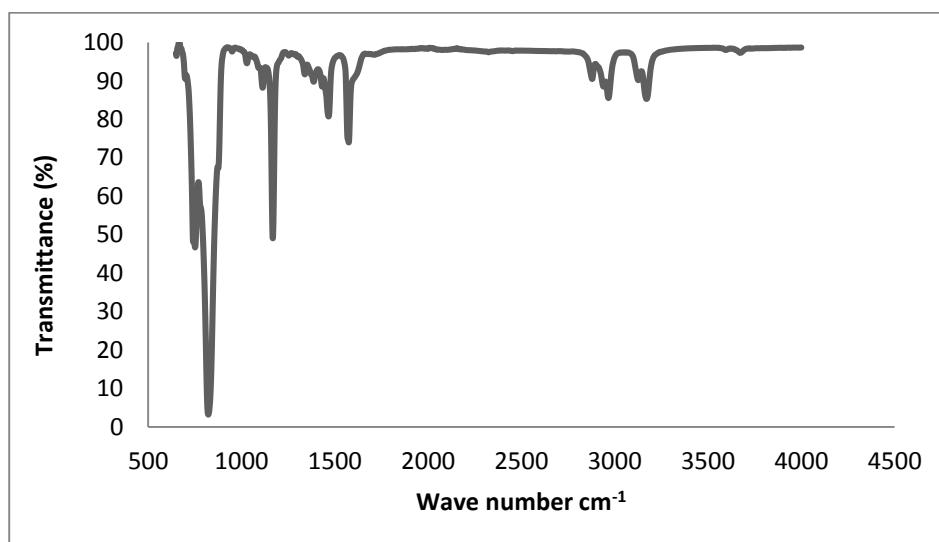


Figure 3: FTIR spectrum of [BMIm][PF₆]

FTIR (Neat liquid); V/cm⁻¹ 3160 PF₆, 2939 (s, aliphatic C-H stretch), 1568 (w, C=C), 1460 (s, sym ring stretch), 1167 (s, C-N vibration), 817 (s, C-H bend), 740 (s, C-H bend).

The FTIR shows important peaks. The peaks at 2939 cm⁻¹ corresponds to strong C – H bond originating from the butyl chain. The peak at 1568 cm⁻¹ corresponds to weak C = C bond originating from the aromatic ring. Peak at 1460 cm⁻¹ corresponds to strong symmetric ring stretch emanating from the aromatic ring. Peak 1167 corresponds to strong C – N vibration

from the Carbon - Nitrogen bond. Peaks at 817 cm^{-1} and 740 cm^{-1} correspond to strong C – H vibration from the aromatic ring.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra (obtained by a Bruker Avance 400) of the product dissolved in d^6 - dimethylsulfoxide (DMSO) are presented in Figures 4 and 5. On both spectra, only the peaks attributed to BMIm⁺ and impurity in solvent (proton-substituted DMSO) are observable and other indications are very small. The positions as indicated in Figures 4 and 5 are the relative intensity of each peak corresponding to the expected values for BMImPF₆. These spectra confirm the expected reaction quantitatively progressed to produce BMImPF₆ without significant side reaction.

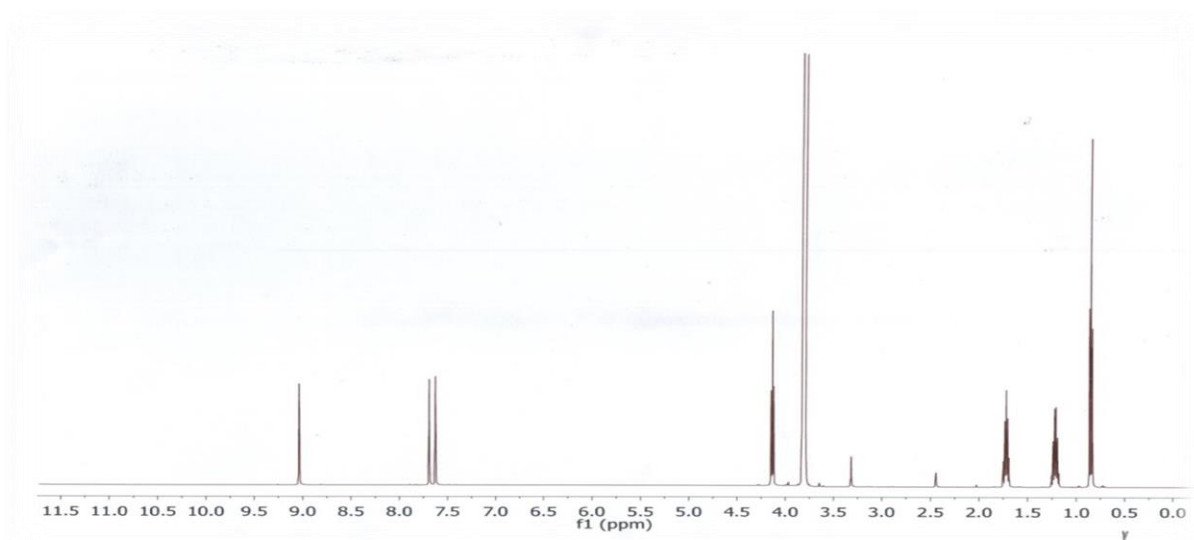


Figure 4. $^1\text{H-NMR}$ spectrum (300 MHz) of [BMIm][PF₆]

^1H NMR in Figure 4 (300 MHz, DMSO, 25 °C) contains peaks at δ (ppm) : 0.98 (3H, t, CH₃), 1.2 (6H, s, CH₂), 1.7 (5H, q, N-CH₂), 4.1 (3H, t, CH₃), 7.65 (3H,t, CH₃), 7.71 (2H, dd), 9.07(1H,s)

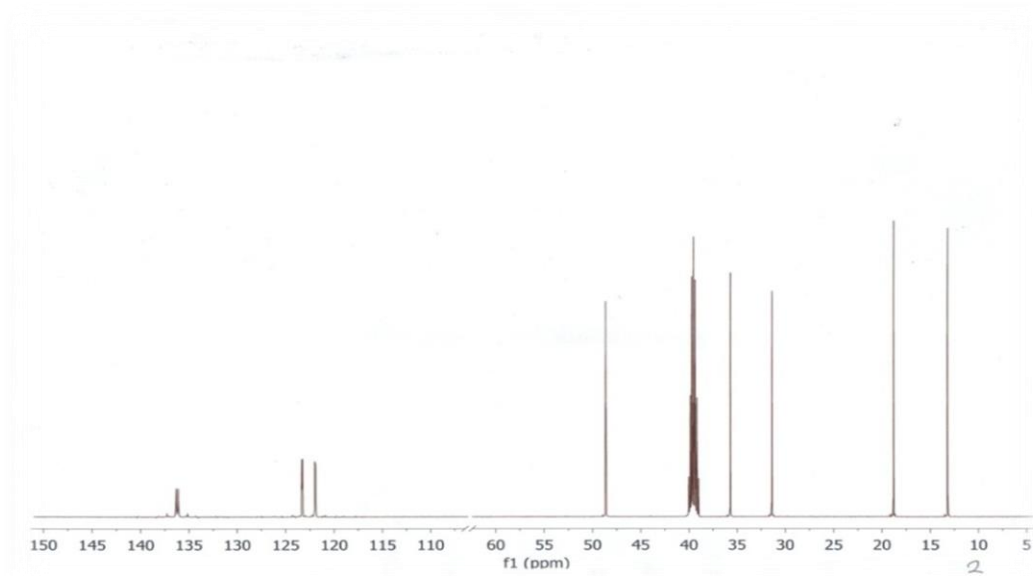


Figure 5: $^{13}\text{C-NMR}$ spectrum (300 MHz) of [BMIm][PF₆]

^{13}C NMR in Figure 4.8 (300 MHz, DMSO) δ : 13.40 (CH_3), 18.70 (CH_2), 31.39, (N-CH_2), 48.63 (N-methyl), 122.2 (imidazole CH), 123.5 (imidazole CH), 136.4 (imidazole CH).

The Thermogravimetric (TGA) analysis and Differential thermogravimetric (DTG) analysis profile of the ionic liquid are presented in Figures 6 – 7. The thermal stability was determined over a temperature range from of 30 – 600 °C. The onset of thermal decomposition started at 405.85 °C. No further decomposition or degradation was observed. This gives a high thermal stability for the ionic liquid under study.

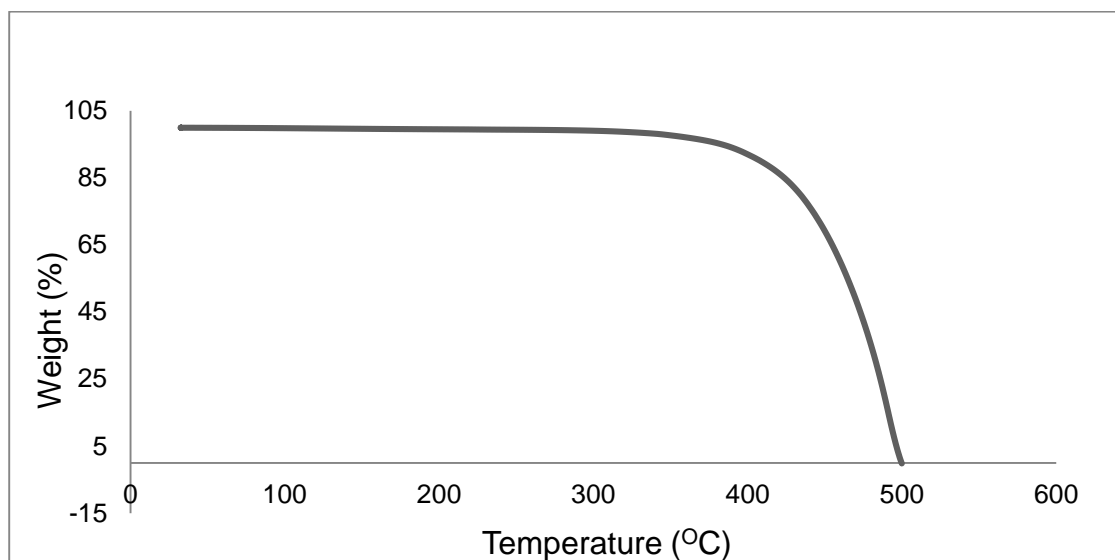


Figure 6: Thermogravimetric analysis of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆]

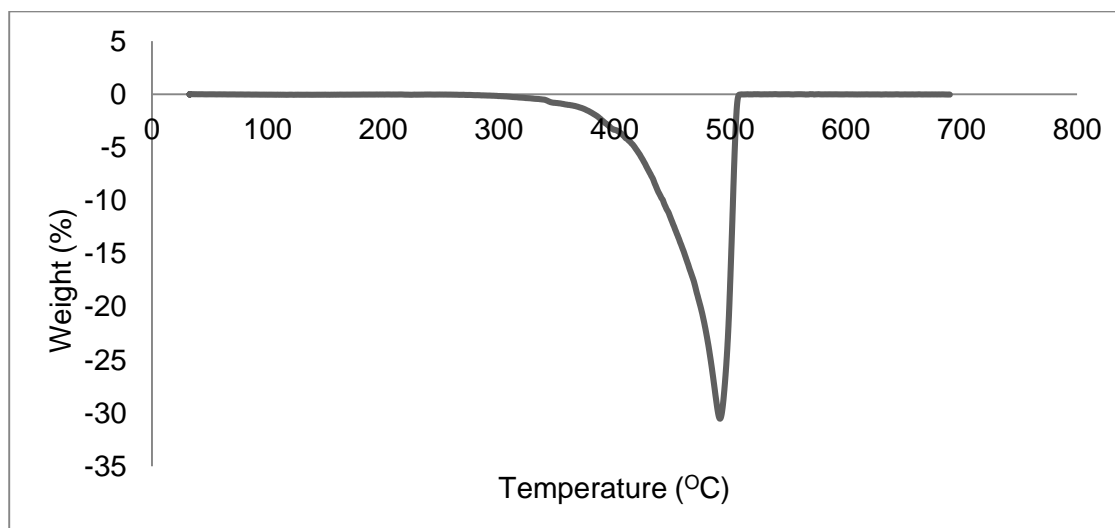


Figure 7: Differential Thermogravimetric analysis of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆]

Conductivity data of the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆] is presented in Figure 8.

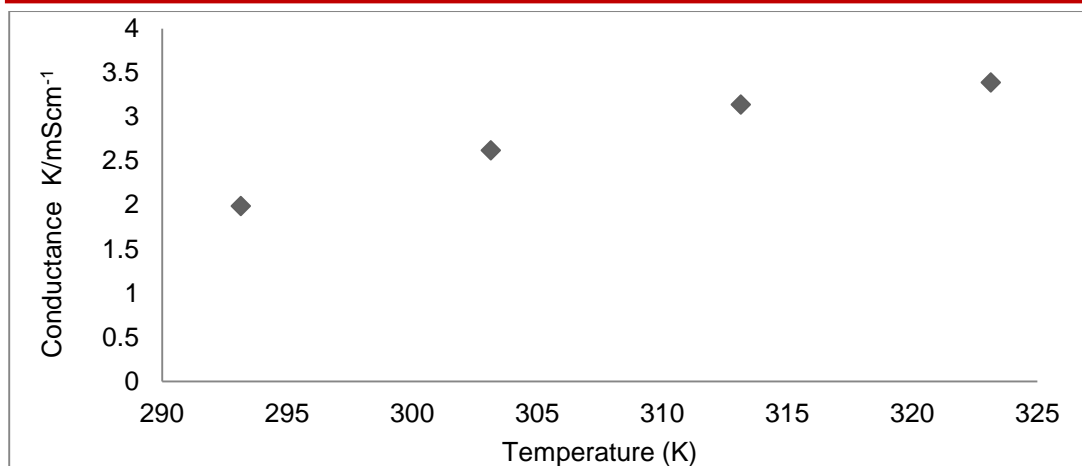


Figure 8: Conductivity measurement of 0.05 M 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆] as a function of temperature (K).

The plot shows an increase in conductivity with increasing temperature. The result indicates that the ionic liquid [BMIm][PF₆] consists of ions that are mobile in solution. Conductivity measurement of 0.05 M DMF is presented in graphically in Figure 9.

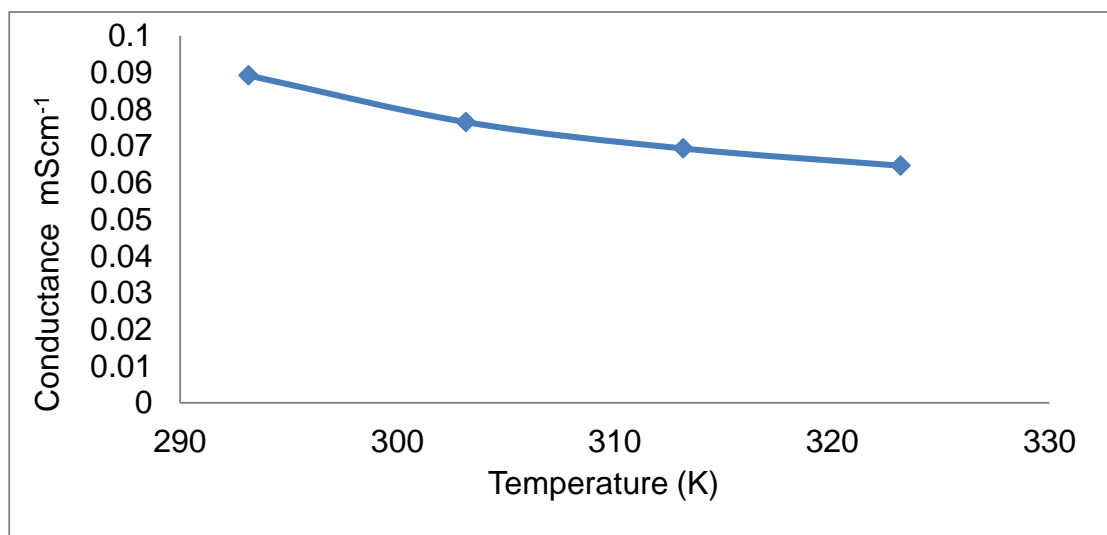


Figure 9: Plot of conductance of 0.05 M DMF against temperature (K)

The Figure shows a decrease in the conductivity of DMF with increasing temperature. To investigate the effect of the ionic liquid on DMF, binary mixtures of DMF and the ILs over the entire composition range at 293.15 - 323.15 K were prepared and their conductivities investigated. Molar conductivity data of the investigated ionic liquid was analyzed by means of the specific conductance formula

$$\Lambda = K_s \times \frac{1000}{C}$$

Where C is the molar concentration, K_s is the specific conductance, Λ is the molar conductance. The Conductivity data of 0.05 M N,N-Dimethylformamide in 0.00125, 0.0025, 0.005 and 0.01 M 1-Butyl-3-methylimidazolium hexafluorophosphate as a function of temperature is graphically represented in Figures 10 – 13.

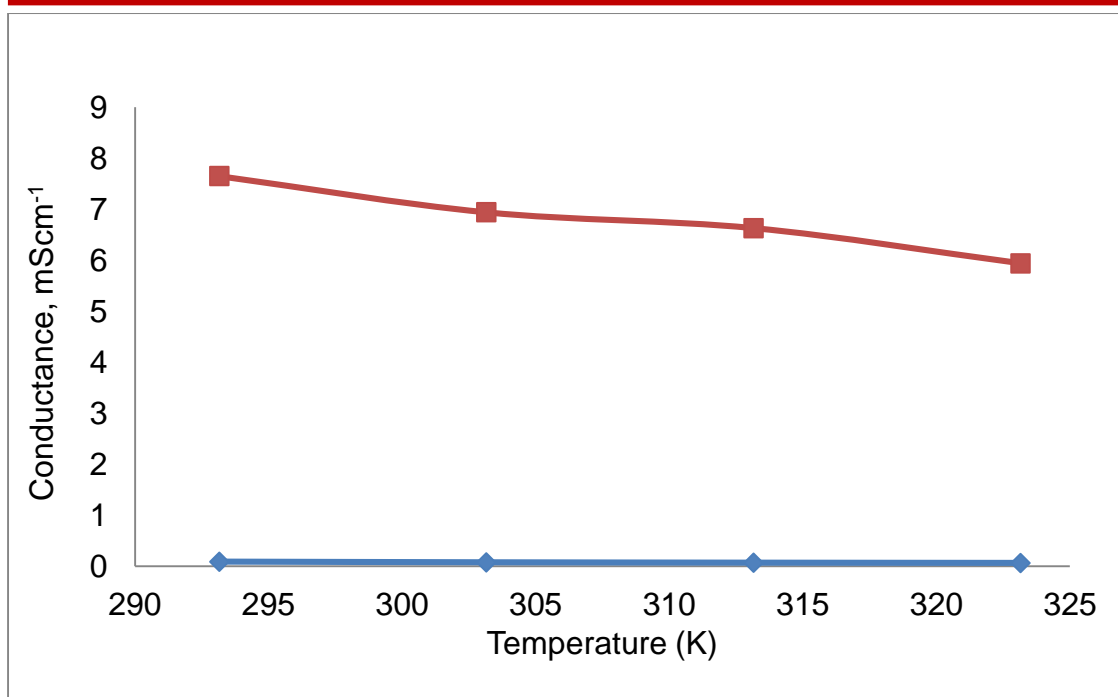


Figure 10: Plot of Conductivity of 0.05 M N,N-Dimethylformamide (▲) and 0.00125 M 1-Butyl-3-methylimidazolium hexafluorophosphate in 0.05 M DMF (■) as a function of temperature.

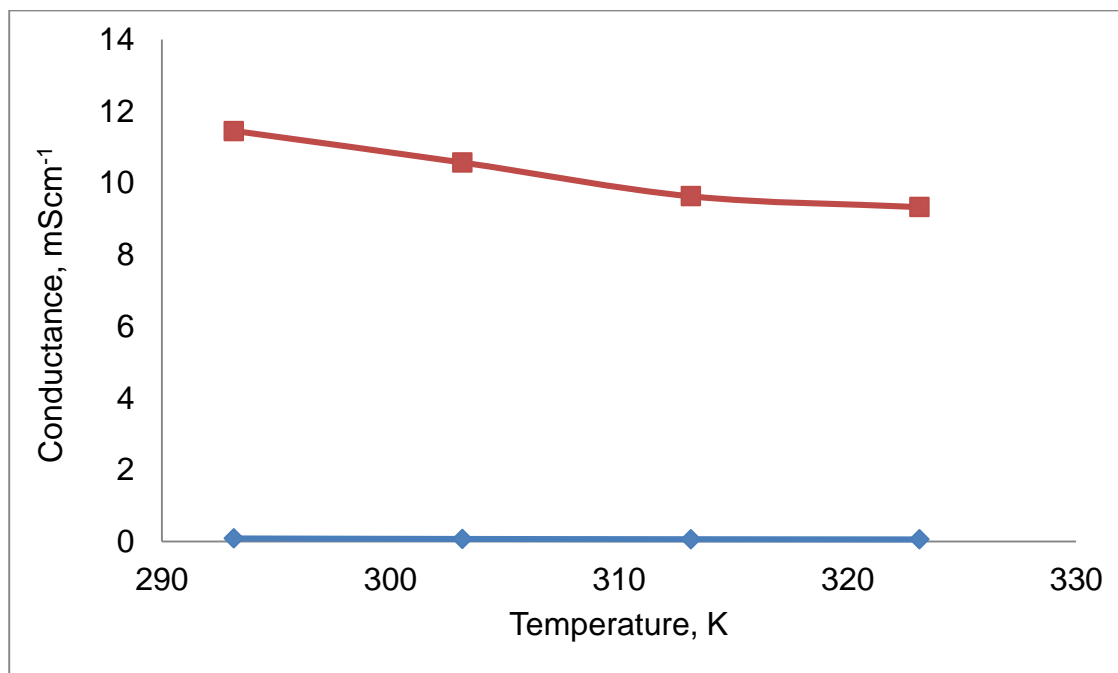


Figure 11: Plot of Conductivity of 0.05 M N,N-Dimethylformamide (▲) and 0.0025 M 1-Butyl-3-methylimidazolium hexafluorophosphate in 0.05 M DMF (■) as a function of temperature.

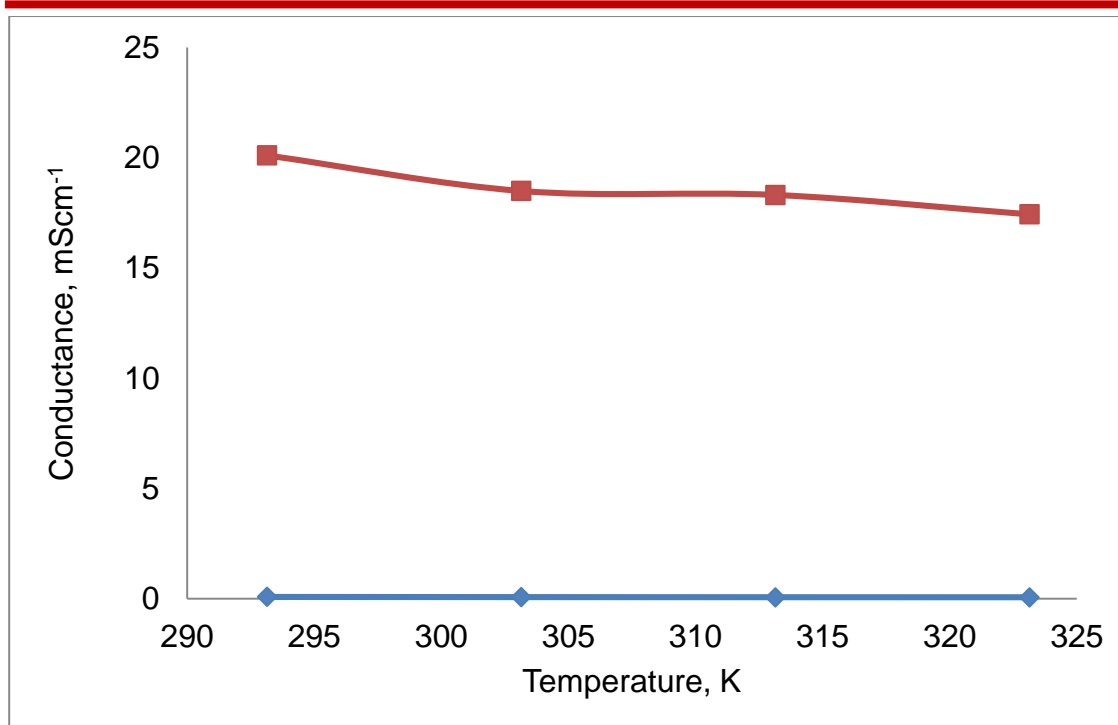


Figure 12: Plot of Conductivity of 0.05 M N,N-Dimethylformamide (▲) and 0.005 M 1-Butyl-3-methylimidazolium hexafluorophosphate in 0.05 M DMF (■) as a function of temperature.

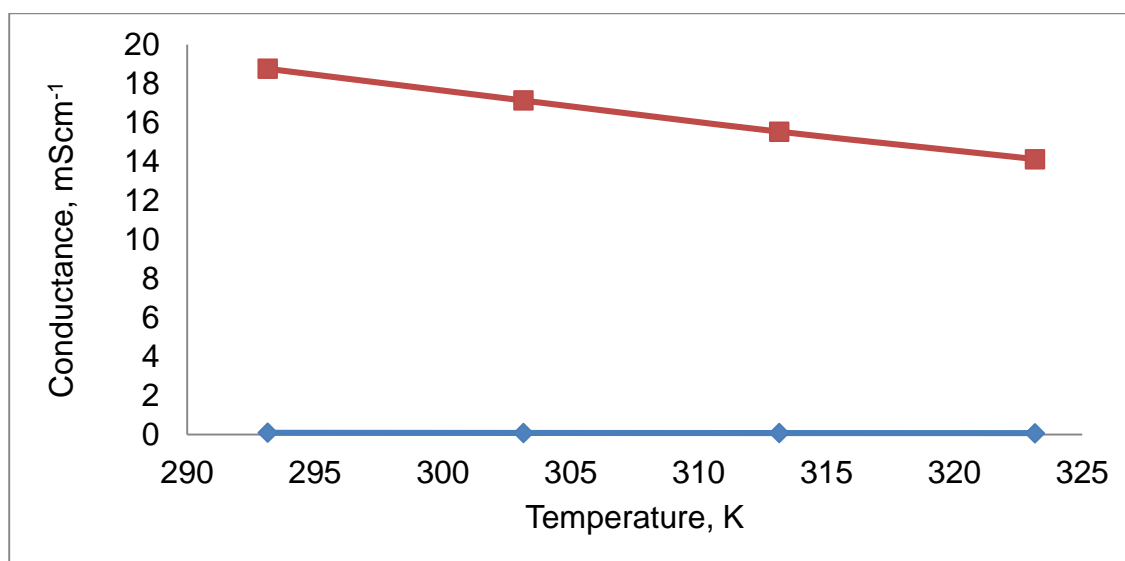


Figure 13: Plot of Conductivity of 0.05 M N,N-Dimethylformamide (■) and 0.01 M 1-Butyl-3-methylimidazolium hexafluorophosphate in 0.05 M DMF (▲) as a function of temperature.

A perusal of the Figures shows a significant increase in the conductivity of DMF with increasing temperature and increasing molar concentration of the IL, [BMIm][PF₆] in the mixtures. This suggests the formation of strong ion-ion interaction and ion-solvent interaction of the investigated binary mixtures. Patrick and others [1] observed a similar trend when they investigated the conductivity of 1-Butyl-3-methylimidazolium Bromide [BMIm][Br] in aqueous solutions. They attributed the increase in conductivity to an increase in the diffusion

constant and existence of smaller energies of interaction between water and the ions of the binary mixtures.

4. Conclusion

In this study, the conductivity of binaries of N,N-Dimethylformamide with the cosolvent 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆], at different temperatures and concentrations was measured. The main aim of this measurement is to provide results of modification of transport coefficient upon addition of a cosolvent. Conductivity of binaries of N,N-dimethylformamide with [BMIm][PF₆] increased with increase in temperature and concentration which was attributed to strong ion-ion interaction and ion-solvent interaction of the investigated binary mixtures.

Acknowledgements

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