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Synthesis, Characterization and Conductivity Study of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] at T (293.15 – 323.15) K.

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ABSTRACT

The study reposts the synthesis and characterization of1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]. Density and viscosity measurements of the synthesized compound in *N,N*-dimethylformamide (DMF) were performed at room temperature. It was observed that the density and viscosity measurements decreased with increasing temperature. FTIR and NMR spectra conforms the successful synthesis of the ionic compound. Conductivity measurement of the ionic liquid at different temperatures showed increase in conductivity with increasing temperature, likewise the ionic liquid in DMF at different concentrations showed increase in conductivity with increasing concentrations. The thermogravimetric analysis, (TGA) of the ionic liquid exhibited a high thermal stability with decomposition initiating at about 104 °C.

Keywords: Ionic Liquid; TGA; Density; Conductivity; Viscosity; FTIR; NMR spectra

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INTRODUCTION

Room Temperature Ionic Liquids (RTILs) have received attention from many researchers [1] due to their unique properties such as non-volatility, undetectable vapor pressure, wide liquid range, as well as ease to recovery and reuse [2-5]. In addition, RTILs have intrinsic conductivity at room temperature and a wide electrochemical window, exhibiting good electrochemical stability in the range of 4.0 – 5.7 V [6, 7].

In recent times, the use of proton-conducting ionic liquids (PCILs) have beenprojectedas a mean of ensuring high anhydrous proton conductivities, yet ensuring it maintains sufficient thermal stability. This fieldof study has aroused a countless deal of interest in view of its applications in Proton Exchange Membrane Fuel Cells (PEMFCs) [8, 9]. Also, bis(fluorosulphonyl) imide (FSI) as ionic liquid electrolytes for rechargeable lithium batteries have been reported [10]. Importantly, bis(fluorosulphonyl) imide (FSI)-based electrolytes comprising of Li-ion, have been reported to exhibit practical ionic conductivity, while the natural graphite/Li cell made up of FSI-based electrolytes and Lithium bis(trifluoromethanesulphonyl) imide (LITFSI) have showed brilliant cycle performance in the absence any solvent [10-12].

Some studies have reported on the safety and durability of high temperature electrochemical devices including: lithium rechargeable batteries [13]; electric double-layer capacitors [14, 15]; titanium oxide dye-sensitized solar cells [16]. The use of ionic liquids as electrolytes in conducting polymer-based electrochemical devices[17] in conducting polymer organic dispersions synthesis [18,19] and conducting polymer nanostructures [20] have gained attention.

Therefore, this study describe the synthesis of ionic liquid:1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I], and the study of its viscosity, density and conductivity measured in *N,N*-dimethylformamide (DMF) at different temperatures with varying concentrations.

EXPERIMENTAL

Materials and methods

Reagents of analar grade such as Iodobenzene, Methylimidazole, *N,N*-Dimethylformamide were purchased from Acros Organics, South Africa. Ethyl acetate, dichloromethane, silica gel mesh 60 were obtained from Alfa Aesar and used without further purification.

Density measurement

DMF and synthesized ionic liquid density measurement were performed using an Anton Paar DMA-4500 M digital densitometer thermostatted at various temperatures. In order to achieve good precision in temperature control internally(T ± 0.01 K), two integrated Pt 100 platinum thermometers were used. The instrument is precise to within 1.0 x 10^{-5} g/cm^3, and the uncertainty within the measurements were estimated to be higher than ±1.0x10^{-4}g/cm^3. The densitometer protocol comprisesof an automatic correction for the sample viscosity. Densitometer calibration was carried out at atmospheric pressure using doubly distilled and degassed water.

Viscosity measurement

Viscosity measurements were executed with Anton Paar SVM 3000 Stabinger Viscometer. The viscometer possesses a dynamic viscosity range of 0.2 - 20 000 mPa.s, a kinematic viscosity range of 0.2 - 20 000 mm^2/s and a density range of 0.65 to 3 g/cm^3. The instrument is furnished with a maximum temperature in the range of ±105°C and a minimum of 20 °C below ambient. Viscosity of the instrument reproducibility is 0.35% of measured value and density reproducibility 0.0005g/cm.

Infrared measurement

IR spectra of the synthesized ionic liquid were recorded on Perkin-Elmer Spectrum 400 FT-IR spectrometer in the range 4000 – 400 cm^{-1}.

NMR measurement

^{1}H and ^{13}C-NMR spectra of the ionic liquid in DMSO were measured using a Bruker Avariqance 400 NMR spectrometer operating at proton frequency of 300 MHz and 75.48 MHz for ^{13}C. Theproton chemical shifts were documented relative to an internal TMS standard.

Thermogravimetric Analysis

Investigation into the thermal stability of the synthesizedionic liquid was achieved using a Perkin Elmer Simultaneous Thermal Analyzer (STA 6000) under a nitrogen atmosphere. Heating of the sample was in crucibles (platinum) with nitrogen gas flow rate of 19.7 mL/min and a gas pressure of 4.0 bars. The measurement for the analysis ranged started from 30 °C to 950 °C with a ramp rate of 30 °C/min - 900 °C.

Conductivity Measurement

Thermo Fisher Scientific/Eutech Instrument PC700 pH/mV/Conductivity meter was employed for the conductivity measurements of the ionic liquid. Conductivity of the instrument ranged from 0 – 2000 μS and 0 – 200.0 mS. The instrument possesses afull-scale resolution of 0.5% and an accuracy of ±1%. The instrument was calibrated with KCl solution before and after every measurement. The temperature of the sample was kept at 20 ± 0.1 °C. Each measurement was repeated three times and the average values calculated.

Preparation of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]

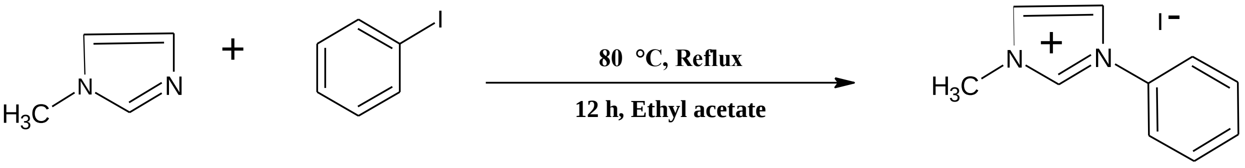
81.89 g (1.0 mol) of 1-methylimidazole and 204.01 g (1.0 mol) Iodobenzene were stirred in a 500 ml three-necked round bottom flask fitted with a reflux condenser for 12h at 80 °C. 100 ml Ultra-pure water was added and washed with ethyl acetate (2 x 50 ml). A bi-phase was formed and the compound material was separated. The reaction mixture was concentrated and dichloromethane (50 ml) was added and passed through silica gel mesh 60 and the liquid evaporated at 120 °C in vacuum. A yellow liquid was obtained. Yield (78%). The ionic liquid was characterized by FTIR, ^{1}H and ^{13}C-NMR.

FTIR (pure liquid); v/cm^{-1}: 3092 (b, CH_2/CH_3stretching), 1515 (b, C=C), 1229 (w, C=N stretching), 1075 (b, C-N-H stretch), 907 (s, C-C skeletal), 812 (s, C−N vibration), 732 (s, C−H bending), 662 (s, ring-in-plane and out-of-plane bending). ^{1}H NMR (*d*-DMSO; δ ppm): 1.09 (1H, s), 1.89 (1H, s), 2.12 (1H, s), 2.51 (1H, s), 3.81 (3H, m, N-CH_3), 6.8 (1H, s,), 7.21 (1H, s), 7.52-7.76 (H, m), 8.19 (1H, s) (Figure 1).^{13}C-NMR (*d*-DMSO; δ ppm): 32.50, 25.07, 21.50 (methyl carbon), 36.30 (methylene carbon), 62.20, 57.50, 120.61 (aromatic carbons), 128.35 (imidazole CH), 138.02 (phenyl- CH) (Figure 2) [21, 22].

RESULTS AND DISCUSSION

Synthesis and Characterization of the ionic liquid

Iodobenzene (C_6H_5I) is used as a solvent with low evaporation rate [23]. When this reagent is reacted with N-methylimidazole in a 1:1 mole ratio as shown in Scheme 1, the expected product is 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]. The synthesis of [MPhIm][I], gave a yield with reasonable value.



N-methylimidazole Iodobenzene 1-methyl-3-phenylimidazolium Iodide

Scheme 1: Synthesis route of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]

^{1}H and ^{13}C NMR spectral studies

The ^{1}H-NMR and ^{13}C-NMR spectra of the product dissolved in *d*-dimethylsulfoxide (d_6-DMSO, ppm) are presented in Figures 1 and 2. On both spectra, only the peaks attributed to MPhIm$^+$ and that of solvent (proton-substituted DMSO) were observable and other indications are small. The positions as indicated in Figures 1 and 2 are the relative intensity of each peak corresponding to the expected values for [MPhIm][I]. These spectra confirm the expected reaction quantitatively progressed to provide [MPhIm][I]without significant side reaction. Signals appearing as multiplets in the δ 7.52-7.76 ppm region are due to the aromatic protons, while signals at δ 62.20-120.61 ppm region are the aromatic carbons [21, 22].

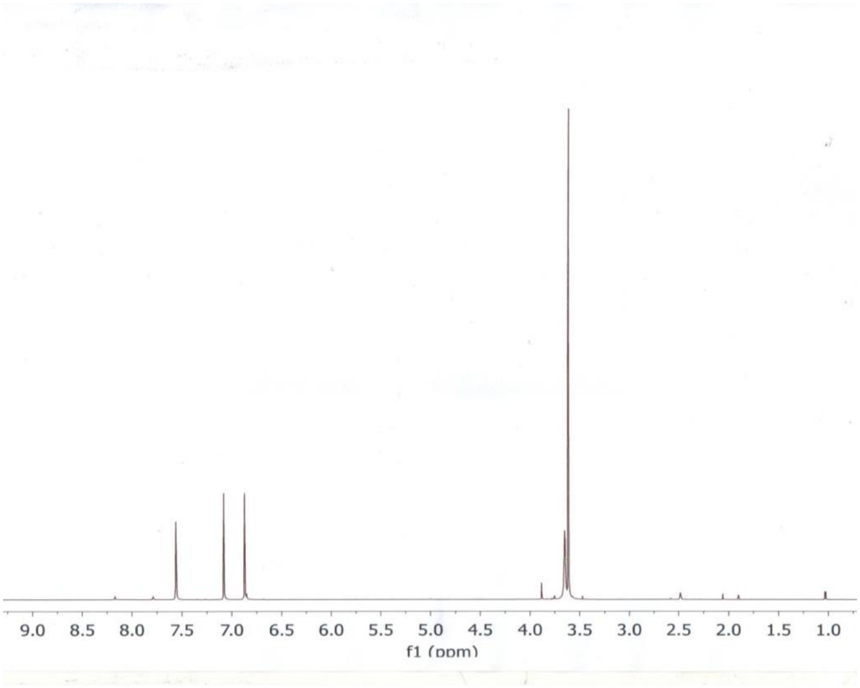


Figure 1: ^{1}H-NMR spectrum (300 MHz) of [MPhIm][I]

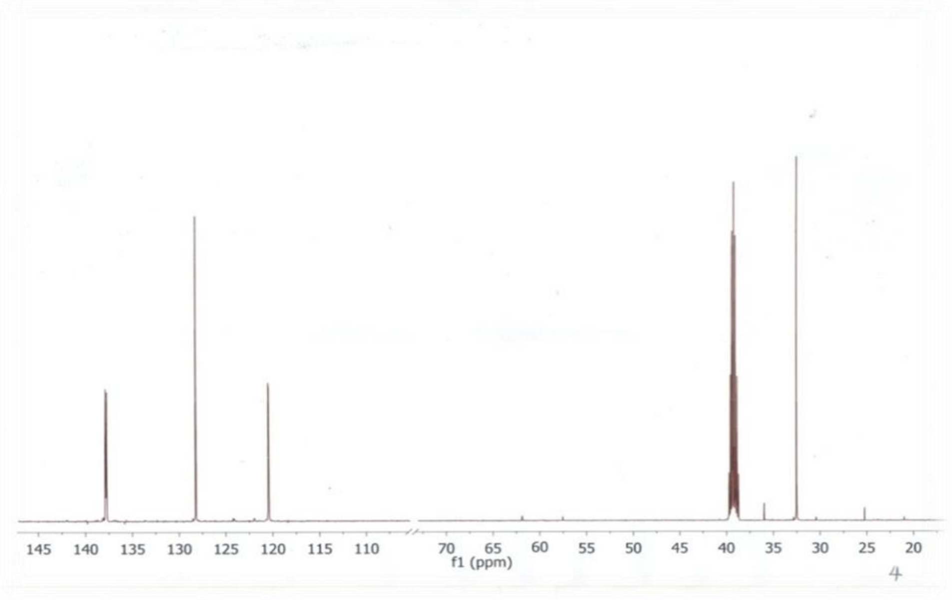


Figure 2: ^{13}C-NMR spectrum (300MHz) of [MPhIm][I]

Thermogravimetric Analysis (TGA)

The Thermogravimetric (TGA) analysis and Differential thermogravimetric (DTG) analysis profile of the ionic liquid measured under nitrogen atmosphere at heating rate of 5 °C min^{-1} from 0 °C to 800 °C presented in Figures 3 and 4. The thermal stability of the sample was determined over a temperature range of 30–600 °C. The onset of thermal decomposition started at 105.48 °C . No further decomposition or degradation was observed. This observation gives a thermal stability for the ionic liquid under study.

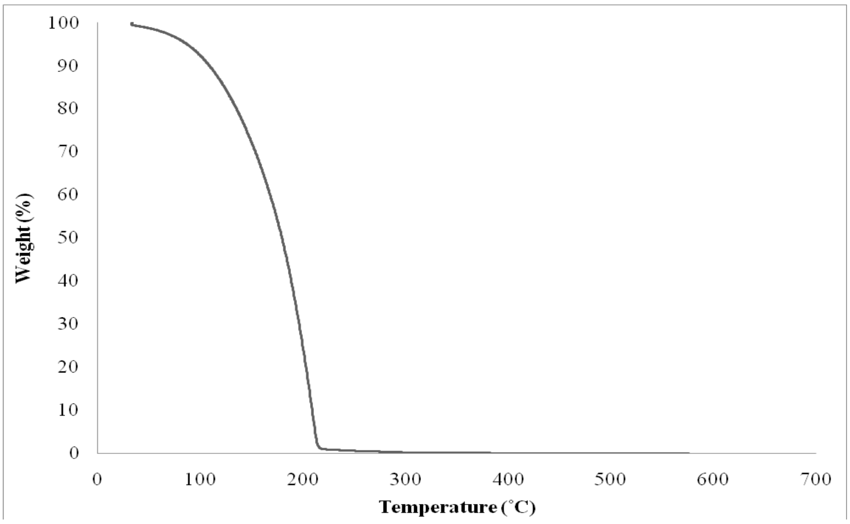


Figure 3: Thermogravimetric analysis curve of [MPhIm][I]

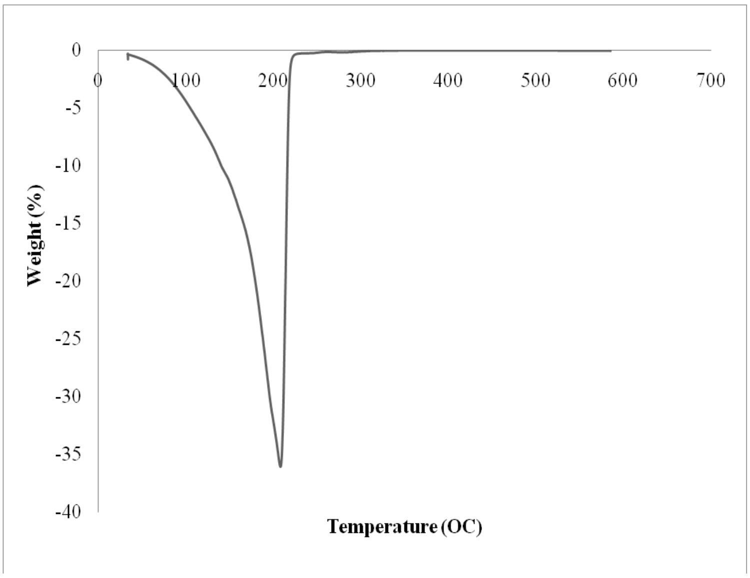


Figure 4: DTG pattern of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]

Density, Viscosity and Conductivity measurements

The ionic liquid: 1-Methyl-3-Phenylimidazolium Iodide density and viscosity measurements are presented in Figures 5 and 6. Figure 5 showsthedensityoftheionicliquid:1-Methyl-3-Phenylimidazolium Iodide measured at four different temperatures. The density measurement obtained gave a linear curve which indicate that the Iodide an ion molar mass could be responsible for the linearity observed. This density of ionic liquids linear relationship has been reported by Wei, *et al* [24].There was a decreased in density values with increase in temperature, and this was expected [24].

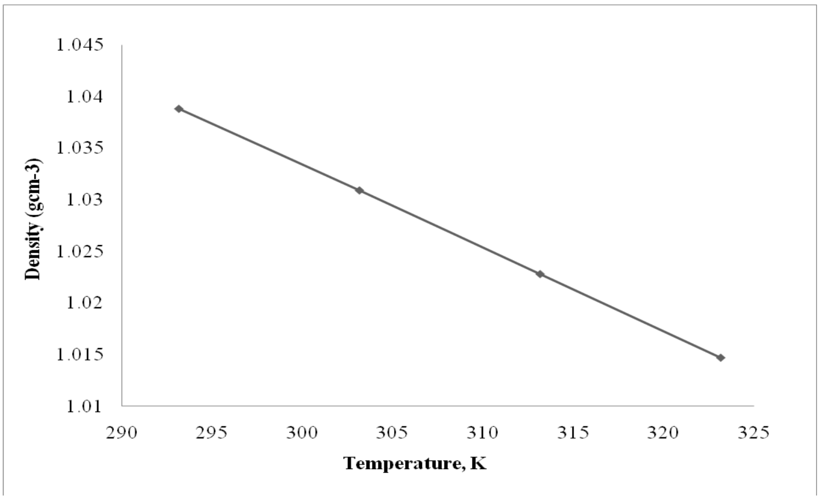


Figure 5: Density measurement of pure 1-Methyl-3-Phenylimidazolium Iodide MPhIm][I] as a function of temperature.

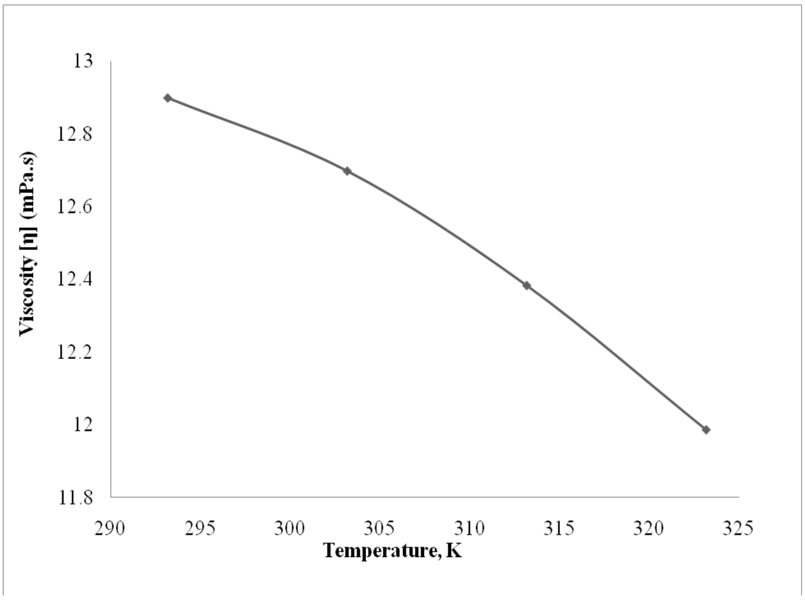


Figure 6: Viscosity measurement of pure 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] as a function of temperature.

An important property of ionic liquids is the viscosity measurement. This is because of the strong impact, it exhibits on the diffusion of species that are dissolved or dispersed in a media like ionic liquids [25]. The interaction of the cation, anion and other interactions like hydrogen bonding and ions symmetry are part of the factors influencing viscosity of ionic liquids[26,27].The measurement of the ionic liquid at different temperatures ranging from(293.15– 323.15 K) are presented in Figure 6. From this figure, it could be observed that viscosity decreased with increase in temperature and this is in accordance with previous reports, that temperature affects pure ionic liquid viscosity also the ionic liquid saturated in water[26]. Arrhenius plot of viscosity temperature dependent for the ionic liquid: 1-Methyl-3-PhenylimidazoliumIodide is presented in Figure 7. The type of curve obtain is a nonlinear curve which is similar to that described for other ionic liquids [26]. Pure MPhIm [I] prepared showed 2.21, 2.47, 2.61 and 2.65 mScm^{-}1 at298-323K as presented in Figure 8.

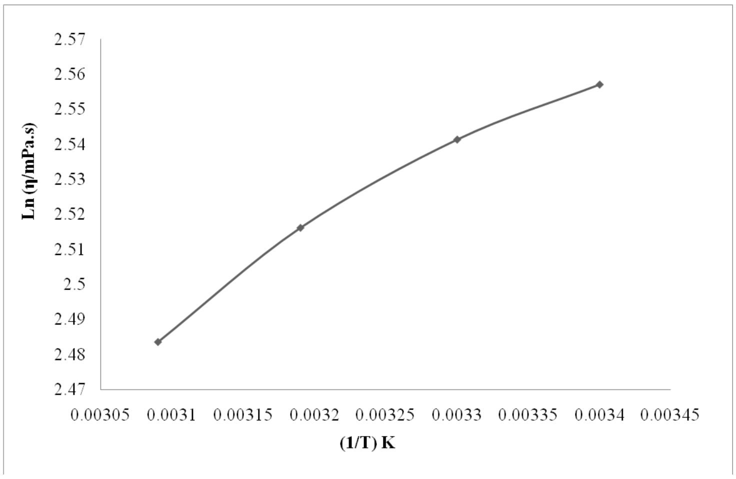


Figure 7: Arrhenius plot of viscosity of pure 1-Methyl-3-Phenylimidazolium Iodide MPhIm][I] as a function of inverse of temperature.

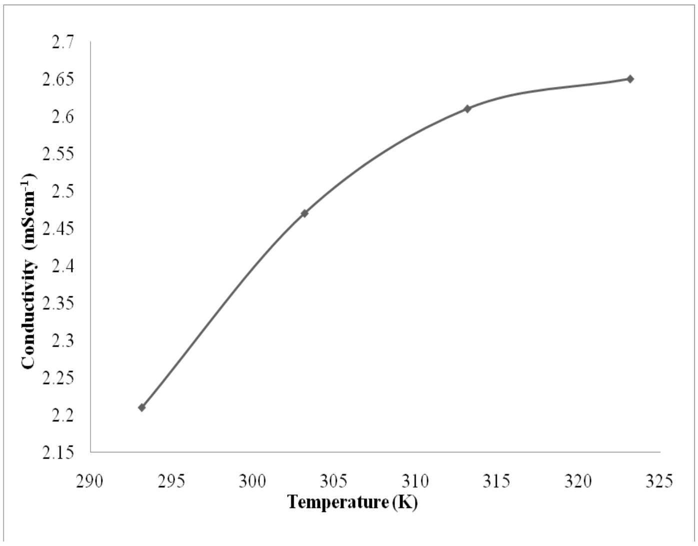


Figure 8: Plot of conductivity of pure 1-Methyl-3-Phenylimidazolium Iodide MPhIm][I] as a function of temperature.

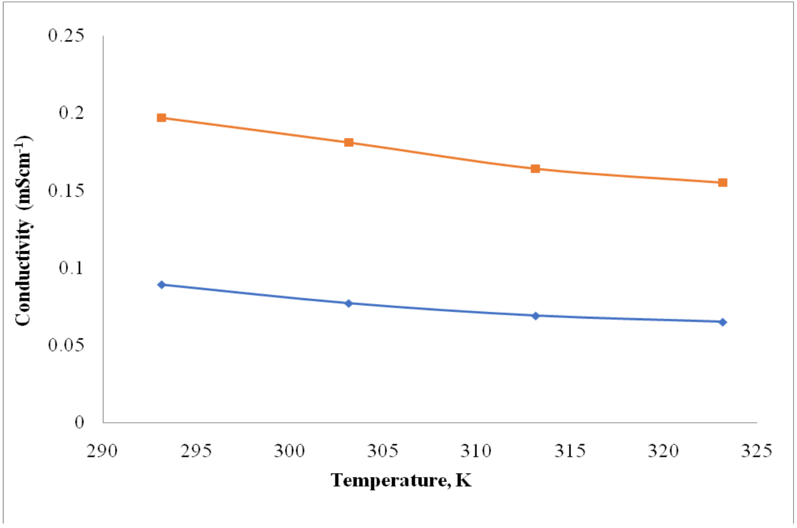


Figure 9: Plot of Conductivity of *N,N*-Dimethylformamide (◆) and 0.00125M 1-Methyl-3-Phenylimidazolium Iodide [MPhImI]in DMF (■) as a function of temperature.

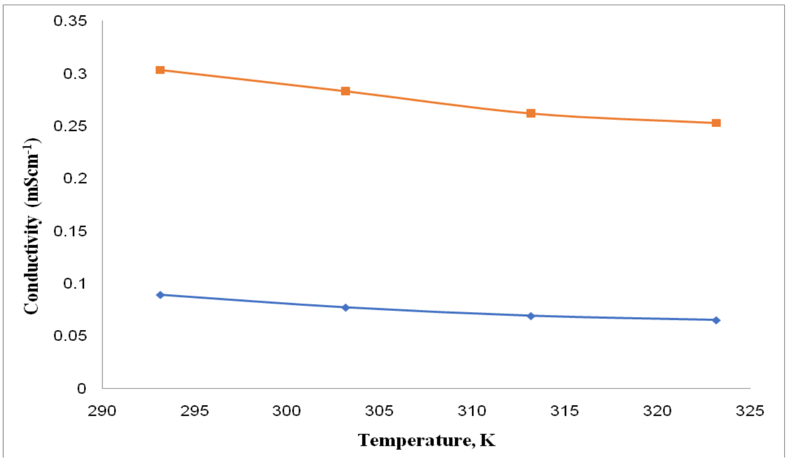


Figure 10: Plot of Conductivity of *N,N*-Dimethylformamide (▲) and 0.0025M 1-Methyl-3-Phenylimidazolium Iodide [MPhImI] in DMF (■) as a function of temperature.

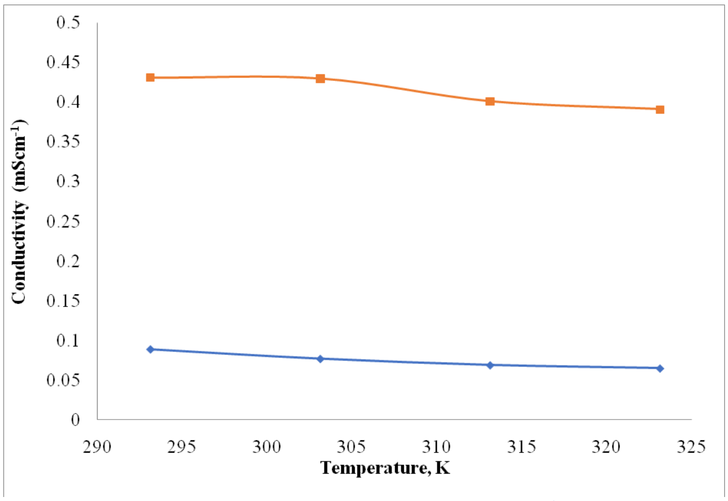


Figure 11: Plot of Conductivity of *N, N*-Dimethylformamide (▲) and 0.005M 1-Methyl-3-Phenylimidazolium Iodide [MPhImI]in DMF (■) as a function of temperature.

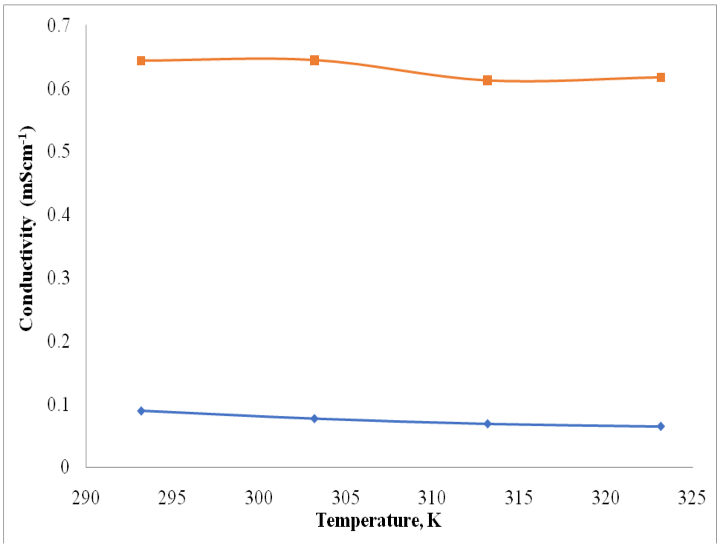


Figure 12: Plot of Conductivity of *N,N*-Dimethylformamide ▲) and 0.01M 1-Methyl-3-Phenylimidazolium Iodide [MPhImI]in DMF (■) as a function of temperature.

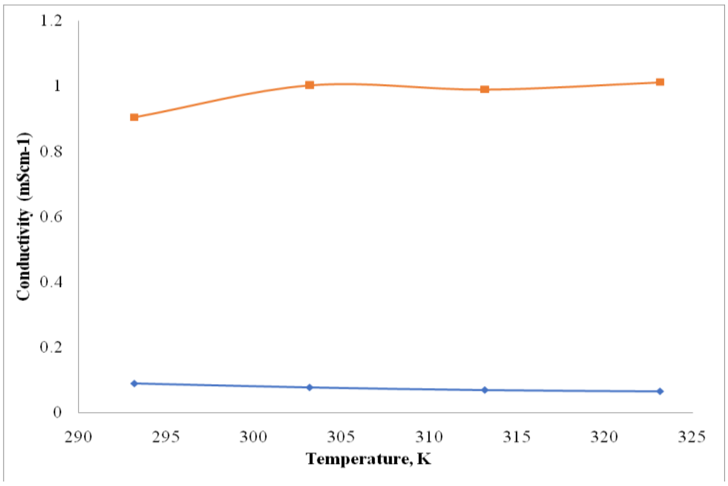


Figure 13: Plot of Conductivity of *N, N*-Dimethylformamide (▲) and 0.015M 1-Methyl-3-Phenylimidazolium Iodide [MPhImI]in DMF (■) as a function of temperature.

In this study, the conductivity of binaries of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I], with the co-solvent: *N,N*-Dimethyl formamide (DMF)at different temperatures and different concentrations were measured. Effect of the co-solvent addition is presented in figures 9 – 13. The main aim of this measurement is to give results of modification of transport coefficient upon addition of a co-solvent. The increase or decrease in conductivity depends on the concentration used and the degree of the resulting dissociation of ionic liquids into ions.

CONCLUSION

The study present measurements of viscosity, density and electrical conductivity of 1-Methyl-3-Phenylimidazolium Iodide MPhIm][I]. A decrease in density was observed to occur monotonically, while the viscosity decreased with increase in temperature. The electrical conductivity of the synthesized ionic liquid showed decrease in conductivity with concentrations ranging from 0.00125M -0.01M with increasing temperature and observable increase in conductivity with concentration of 0.0015M. Conductivity of binaries of the ionic liquid with *N,N*-dimethylformamide increased with increase in concentration.

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