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Density, Viscosity and Conductivity Study of 1-Butyl-3-Methylimidazolium Bromide

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1-Butyl-3-methylimidazolium bromide [BMIm][Br], was synthesized and characterized. Density and viscosity measurement were carried out at room temperature. Density measurement decreased monotonically while viscosity measurement decreased with increase in temperature. Conductivity measurement of the ionic liquid and mixtures of the ionic liquid with water, methanol, ethanol, acetonitrile and acetone at different temperature showed increase in conductivity due to the presence of the ionic liquid in water and ethanol, and decrease in other cosolvents. Conductivity measurement of the ionic liquid and mixture of the ionic liquid in various cosolvents at different concentrations shows increase in conductivity with increase in concentration. The thermogravimetric analysis, (TGA), of the ionic liquid shows high thermal stability of the ionic liquid with decomposition beginning at about 400^{o}C.

Keywords: Ionic liquid, 1-Butyl-3-methylimidazolium bromide [BMIm][Br], conductivity, density, viscosity, TGA,

1. INTRODUCTION

Ionic liquids (ILs) are compounds consisting of an organic cation with an organic or inorganic anion, with melting points below the boiling point of water [1]. ILs have unusual properties including non-volatility, non-flammability, high ionic density, conductivity, chemical and electrochemical stability, etc. Room-temperature ionic liquids (RTILs) are a class of organic salts that are comprised entirely of ions and are liquids at conditions around room temperature in their pure state. They are attracting growing interest as alternatives to conventional molecular liquids [2-8]. In addition, their chemical and physical properties can be readily adjusted by suitable selection of cation and anion species. Owing to these advantages, ionic liquids have currently been applied as novel solvents in organic synthesis [9-11], catalysis [8,12], electrochemistry [13], and chemical separation [14]. In addition, RTILs have intrinsic ionic conductivity at room temperature and a wide electrochemical window, exhibiting good electrochemical stability in the range of 4.0–5.7 V [15-16]. More recently, the use of proton-conducting ionic liquids (PCILs) was proposed in order to ensure high anhydrous proton conductivities while maintaining sufficient thermal stability. This domain has since aroused a great deal of interest with a view for application in Proton Exchange Membrane Fuel Cells (PEMFCs) [17-20].

Studies on ionic liquid electrolytes based on bis(fluorosulphonyl) imide (FSI) for rechargeable lithium batteries have been reported [21]. In particular, FSI-based electrolytes conta6ining Li-ion, exhibited practical ionic conductivity, and a natural graphite/Li cell with FSI-based electrolytes containing lithium bis(trifluoromethanesulphonyl) imide (LiTFSI) showed excellent cycle performance without any solvent [21-23]. Recently, some studies have been reported on the safety and durability of high temperature electrochemical devices such as lithium rechargeable batteries [24], electric double-layer capacitors (EDLCs) [25-29], and titanium oxide dye-sensitized solar cells [30-32].

ILs have been used as electrolytes in conducting polymer-based electrochemical devices, [33] in the electrochemical synthesis of conducting polymers, [34] and in the synthesis of conducting polymer organic dispersions [35-36] and conducting polymer nanostructures [37].

In this study, we have synthesized the ionic liquid, 1-Butyl-3-methylimidazolium bromide [BMIm][Br] and measured the density, viscosity and conductivity of the ionic liquid in different solvents at different temperatures and at different concentrations.

2. EXPERIMENTAL

2.1. Materials

Reagent grade bromobutane, 1-methylimidazole, ethyl acetate were purchased from Sigma-Aldrich South Africa and used without further purification. Acetone and methanol used were purchased from CJ lab in South Africa.

2.2. Density measurement

Density measurement of 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 provided for good precision in temperature control internally (T ± 0.01 K). The densimeter protocol includes an automatic correction for the viscosity of the sample. The calibration for temperature and pressure was made by the producer. The apparatus is precise to within 1.0×10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than $\pm 1.0 \times 10^{-4}$ g/cm^3. Calibration of the densimeter 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 to 20 000 mPa.s, a kinematic viscosity range of 0.2 to 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 +105°C and a minimum of 20°C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility of 0.0005g/cm^3.

2.4. Conductivity measurement

Conductivity measurements were carried out using Thermo Fisher Scientific/Eutech Instrument PC700 pH/mV/Conductivity meter. The instrument conductivity ranges from 0 to 2000 μS and 0 to 200.0 mS. The instrument has a full scale resolution of 0.5% and an accuracy of ±1%. Before and after measurements, the instrument was calibrated with KCℓ solution. The temperature of the sample was kept at 30 ± 0.1°C. Each measurement was repeated three times and the average values were calculated.

2.5. Infrared measurement

IR spectra were recorded using Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer in the range 400 – 4000 cm^{-1}. UV-vis spectra were recorded on a Perkin-Elmer lambda 9 UV-vis spectrometer.

2.6. NMR measurement

^{1}H-NMR spectra in acetone were measured using a Bruker Avariqance 300 NMR spectrometer operating at proton frequency of 300 MHz 75.48 MHz for ^{13}C; proton chemical shifts were recorded relative to an internal TMS standard.

2.7. 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 to 900°C.

2.8. Preparation of 1-Butyl-3-Methylimidazolium Bromide [BMIM][Br]

Equal molar amounts of bromobutane and 1-methylimidazole were added to a round-bottomed flask fitted with a reflux condenser for 24–72 h at 70 °C with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and ethyl acetate (a volume approximately equal to half that of the bottom phase) was added with thorough mixing. The ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this step was repeated twice. The solution was then washed with ethyl acetate to remove any unreacted material from the bottom phase. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 70 °C and stirring room temperature, depending on the amount of water present in that phase. Yield (86%). The ionic liquid was characterized by ^{1}H-and ^{13}C-NMR and by FTIR.

^{1}H NMR of the liquid sample (*d*-acetone, ppm) contains peaks at δ: 10.13 (s), 8.16 (d), 4.52 (t), 4.15 (s), 3.46 (s), 1.97 (p), 1.39 (q), and 0.94 (t). ^{13}C NMR results (ppm) include: δ: 206.88, 138.27, 124.59, 49.87, 36.9, 33.91, 30.86, 20.00 and 13.94. FTIR (neat liquid); ν/cm^{-1} 3081 Br, 2960 (s, aliphatic C-H stretch), 1625 (w, C=C), 1568 (s, sym. ring stretch), 1458 (s, sym ring stretch), 1133 (w, sym. ring stretch), 1374 (m, CH_3 bending vibration), 1165 (s, C−N vibration).

3. RESULTS AND DISCUSSION

Density and viscosity data for the ionic liquid 1-Butyl-3-methylimidazolium bromide are presented in figures 1 and 2.

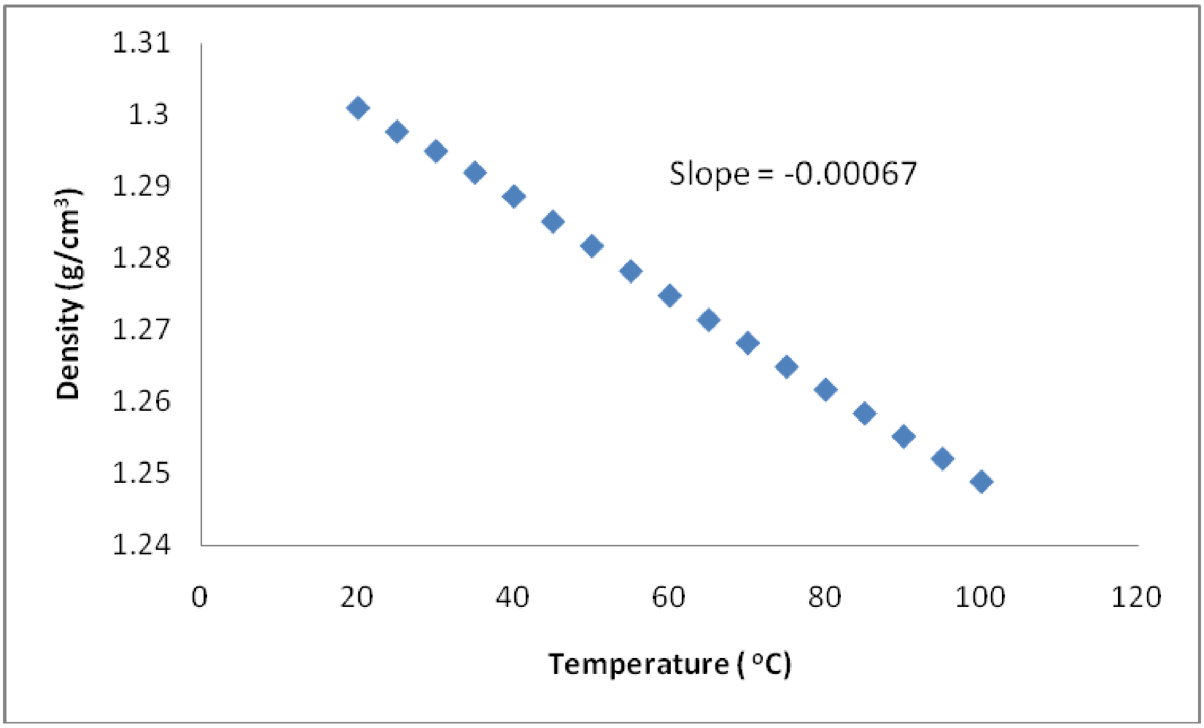

Figure 1. Density measurement of pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] as a function of temperature.

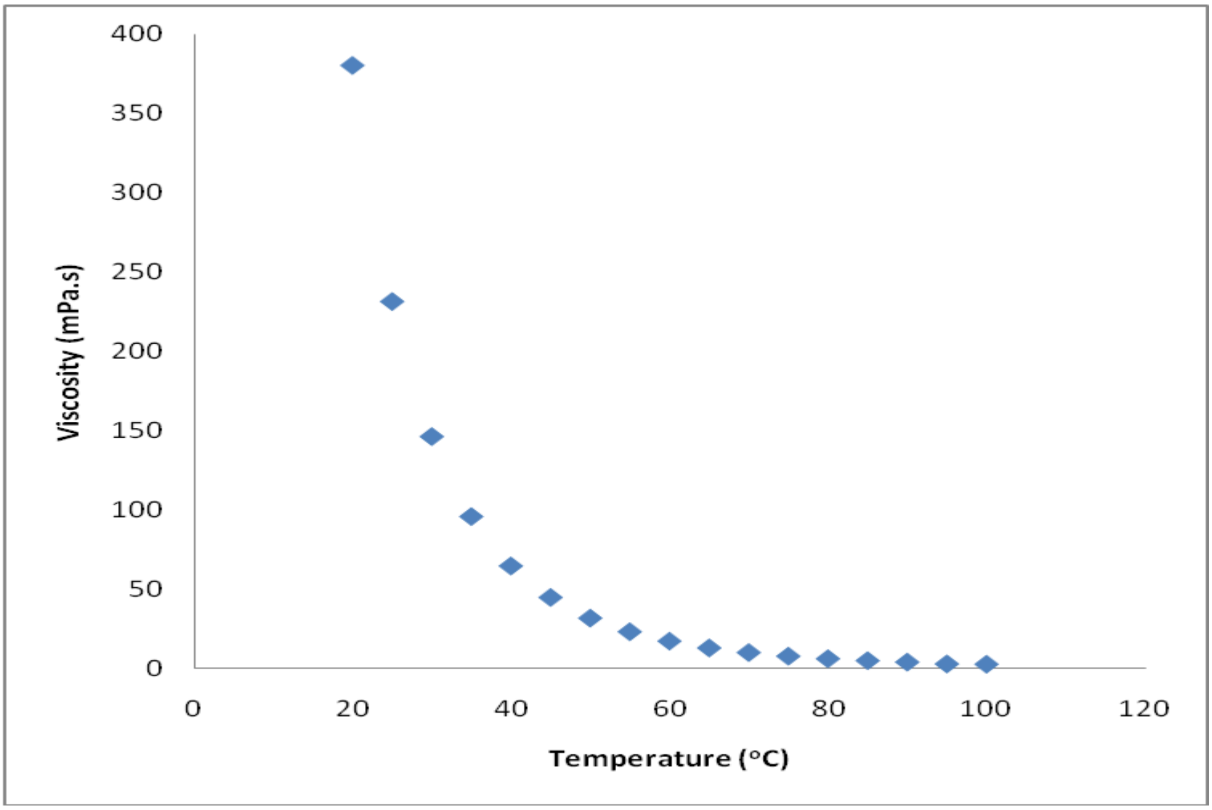

Figure 2. Viscosity measurement of pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] as a function of temperature.

Figure 1 show the density of the ionic liquid, 1-Butyl-3-methylimidazolium bromide, solution measured at several temperatures. The density measurement curve obtained is linear indicating that the molar mass of the bromide anion is what is responsible for the linearity obtained. This linear relationship has been observed by other researchers [38]. 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 [39]. 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 [40]. The viscosity of the ionic liquid measured at several temperatures from (293.15 to 373.15) K is presented in and figure 2. The viscosity decreased with increase in temperature, figure 2, it has been reported that temperature affects the viscosity of pure ionic liquid as well as ionic liquid saturated in water [40]. The temperature dependent viscosity plot for 1-Butyl-3-methylimidazolium bromide is presented by the Arrhenius plot of viscosity against temperature, figure 3. This is a non linear curve which is similar to that described for other ionic liquid [40].

The conductivity of the pure ionic liquid at 298 to 373 K is presented in figure 4. Conductivity increased with increase in temperature. This is however, a non linear increase as can be deduced from the graph. Conductivity of binaries at different temperatures were measured.

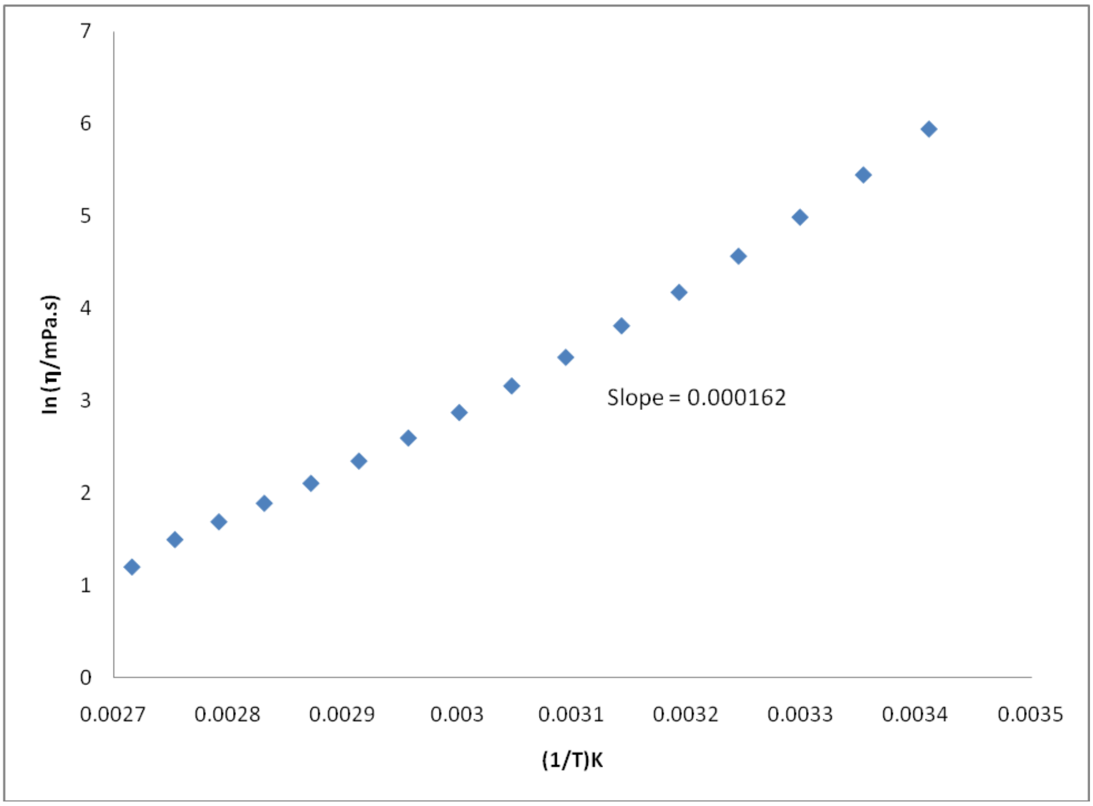

Figure 3. Arrhenius plot of viscosity of pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] as a function of inverse of temperature.

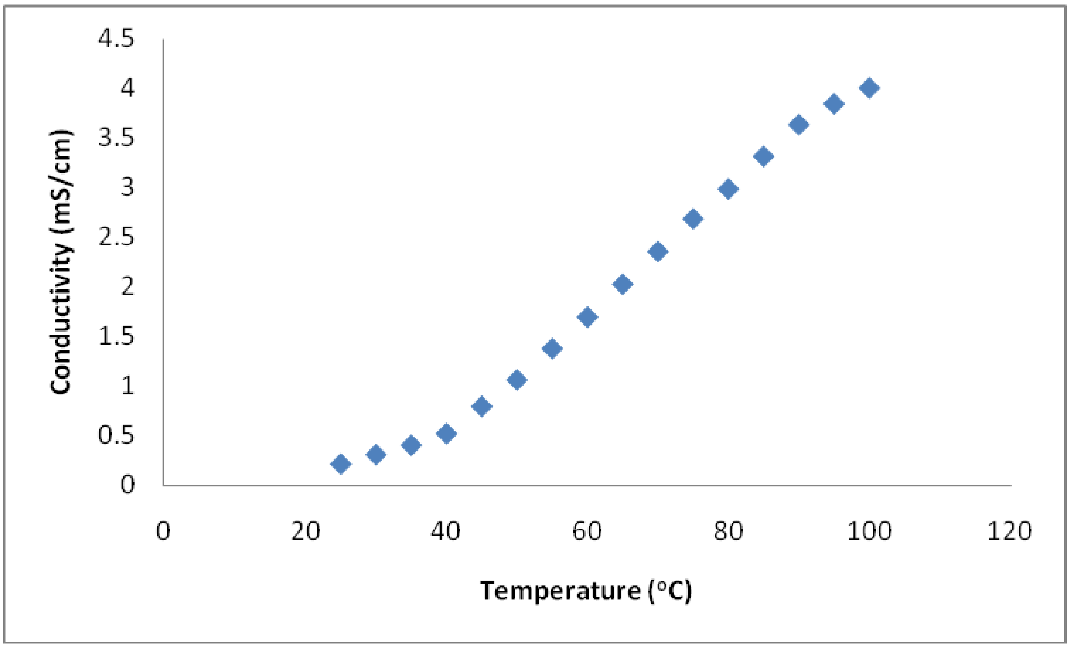

Figure 4. Plot of conductivity of pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] as a function of temperature.

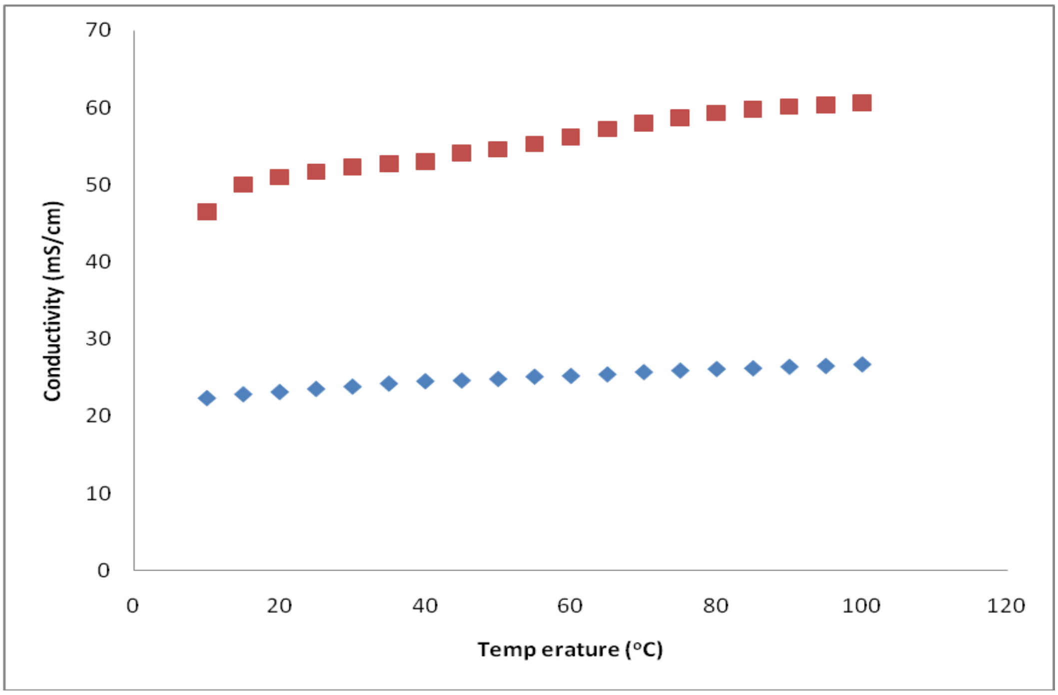

Figure 5. Plot of conductivity of water (♦) and pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] in water (■) as a function of temperature.

The volumes of ionic liquid and the various binaries were kept constant. The conductivity data of binary mixtures of the ionic liquid, 1-Butyl-3-methylimidazolium bromide, with solvents water, methanol, ethanol, acetonitrile and acetone over a wide range of temperature are presented. The conductivity of pure ionic liquid is affected by the addition of cosolvent, i.e. significant increase or decrease in the conductivity of ionic liquid is observed on addition of the cosolvent. The increase or decrease in conductivity depends on the solvent added and the extent of the resulting dissociation of ionic liquids into ions.

In this study, the conductivity of 1-Butyl-3-methylimidazolium bromide [BMIm][Br], with the cosolvents water, methanol, ethanol, acetonitrile and acetone were measured. The effect of the addition of each cosolvent is presented in figures 5 – 9. The main aim in these measurements is to provide results of modification of transport coefficient upon addition of a cosolvent.

The addition of water to the ionic liquid resulted to an increase in the conductivity of the mixture. The conductivity also increased with temperature, figure 5. Mixtures of ionic liquid and water display properties of concentrated salt solutions increase in conductivity. Conductivity increase is due to presence of water-rich regions in the mixture. Ionic liquid aqueous solution conductivity increases with increase in hydrophilic anions. It is expected that increasing the amount of water increases the diffusion constant and the energies of interaction between water and the ions of the ionic liquid are smaller than the ion-ion interactions. This results in an increase in conductivity. The addition of methanol as cosolvent to the ionic liquid caused a decrease in the electrical conductivity of the solution, figure 6. Conductivity measurement of pure methanol decreased with increase in temperature.

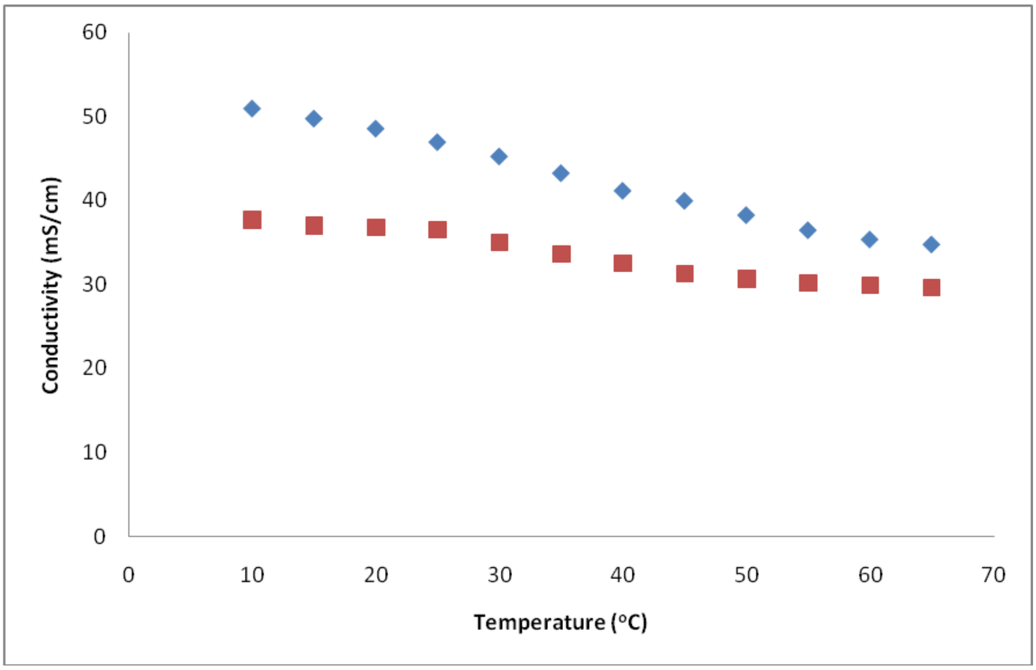

Figure 6. Plot of conductivity of methanol (♦) and pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] in methanol (■) as a function of temperature.

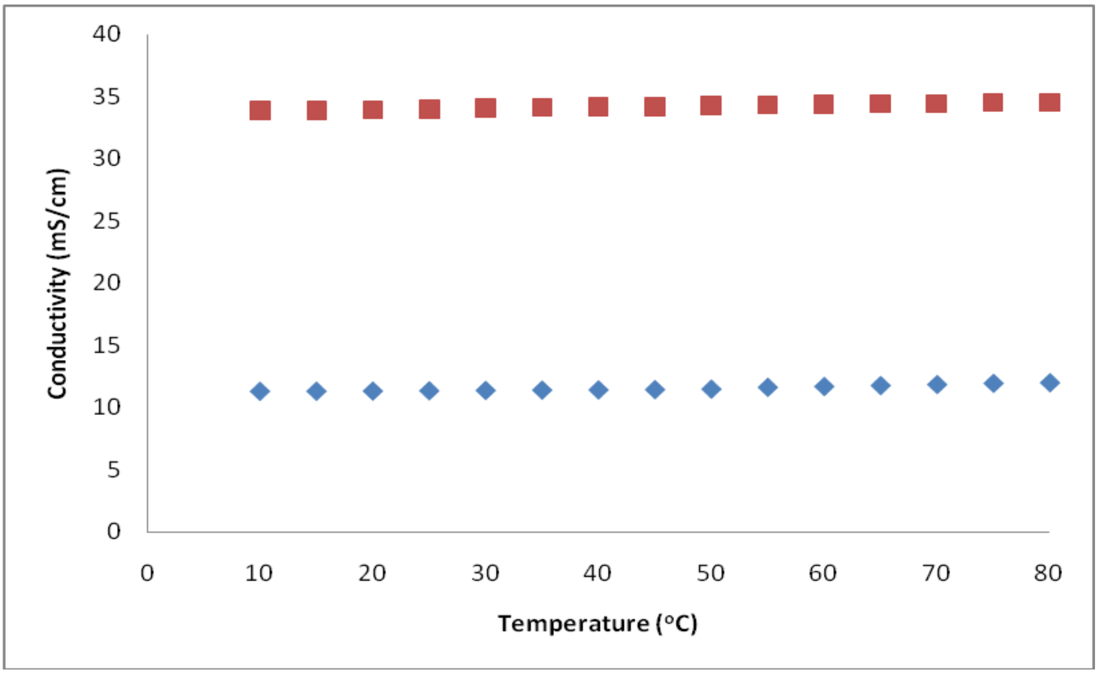

Figure 7. Plot of conductivity of ethanol (♦) pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] in ethanol (■) as a function of temperature.

Decrease in the conductivity of the mixture is less pronounced compared to decrease in conductivity of pure methanol with increase in temperature. This decrease in conductivity is as a result of the differences in polarities which must have resulted in different interactions with ions in the ionic liquid.

Addition of ethanol as cosolvent to the ionic liquid resulted in an increase in the electrical conductivity of the solution, figure 7, with reference to the pure solvent.

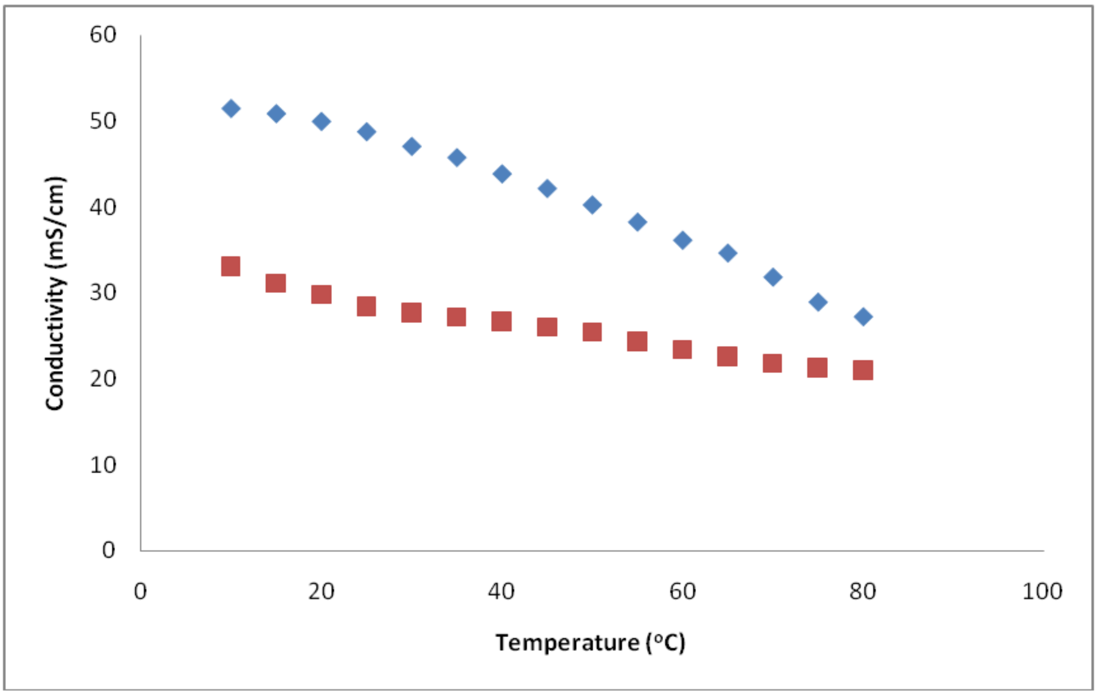

Figure 8. Plot of conductivity of acetonitrile (♦) pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] in acetonitrile (■) as a function of temperature.

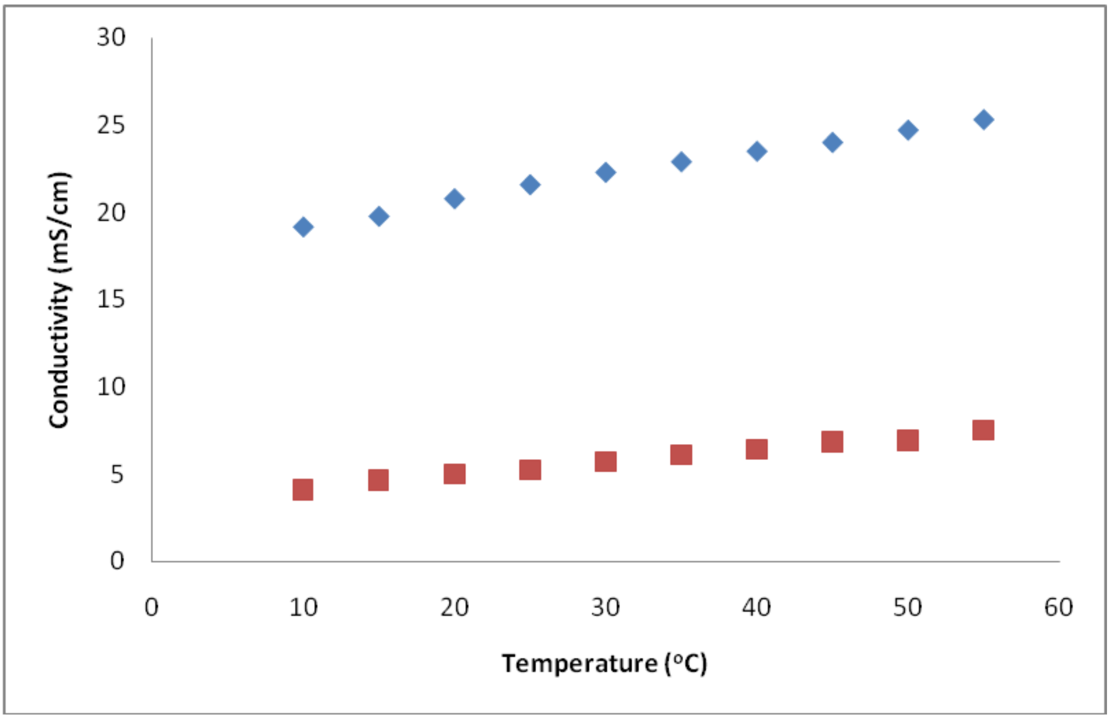

Figure 9. Plot of conductivity of acetone (♦) pure 1-butyl-3-methylimidazolium bromide [BMIm][Br] in acetone (■) as a function of temperature.

The conductivity measurement of pure ethanol increased slightly with increase in temperature and the conductivity of the solution increased with increase in temperature. The addition of the ionic liquid enhanced the ionic interactions in the solution. Conductivity of acetonitrile decreased with increase in temperature, figure 8, and the decrease is non linear. The addition of acetonitrile to the ionic liquid as cosolvent also resulted in a decrease in conductivity with increase in temperature which also non linear. The addition of acetone to the ionic liquid resulted in a decrease in the conductivity of the solution. Conductivity measurement for acetone was found to increase with increase in temperature. The conductivity of the solution of acetone and the ionic liquid increased with temperature, figure 9. These results show that the addition of a cosolvent to an ionic liquid has influenced the ionic association equilibrium of the ionic liquid. The thermodynamics properties of such solutions could be described as ion-solvent, ion-ion and solvent-solvent interactions [38].

Measurement of electrical conductivity of mixtures of the ionic liquid and the cosolvents water, acetonitrile and methanol against concentration at ambient temperature, is presented in table 1 and figure 10. The conductivity plot shows increase in conductivity with increase in concentration. By increasing the concentration of ionic liquid, ion association and relaxation effect occurs between anion and cation of ionic liquid, thus resulting in more aggregates of the ionic liquid dispersing in the cosolvent [41,42].

TGA and DTG analysis of the ionic liquid is presented in figure 11. The thermal stability was determined over a temperature range from of 30 – 800°C. The onset of thermal decomposition started at 305.42°C and at the weight of 111.506 mg. No further decomposition or degradation was observed. This gives a high thermal stability for the ionic liquid under study.

Table 1. Conductivity measurement of different concentrations of [BMIm][Br] in water, acetonitrile and methanol at ambient temperature.

Concentration (mol/dm^3)	Conductivity in H_2O (mS/cm)	Conductivity in CH_3CN (mS/cm)	Conductivity in MeOH (mS/cm)
12.348	63.5	33	43.8
6.174	54.5	30.2	35.3
3.087	46.9	27.1	28.2
1.543	39.9	24.6	24.4
0.772	35.2	22.1	21.2
0.386	31.3	20.3	18.58
0.193	28.1	17.96	16.5
0.096	25.6	17.02	15.15
0.048	23.4	16.09	12.6
0.024	21.6	15.78	11.3
0.012	19.3	15.02	10.6
0.006	18.6	14.4	9.5
0.003	17.26	13.6	8.8
0.0015	16.34	12.8	7.9

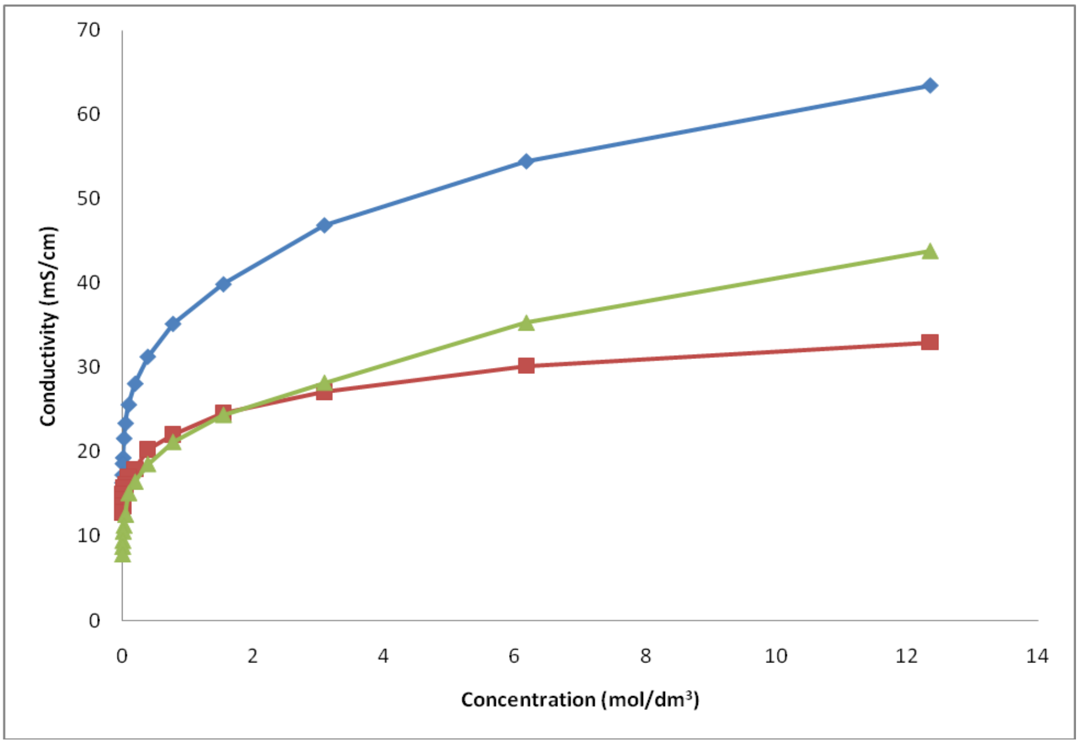

Figure 10. Plot of conductivity at different concentrations of [BMIm][Br] against the solvents water (♦), acetonitrile (■) and methanol (▲) at ambient temperature.

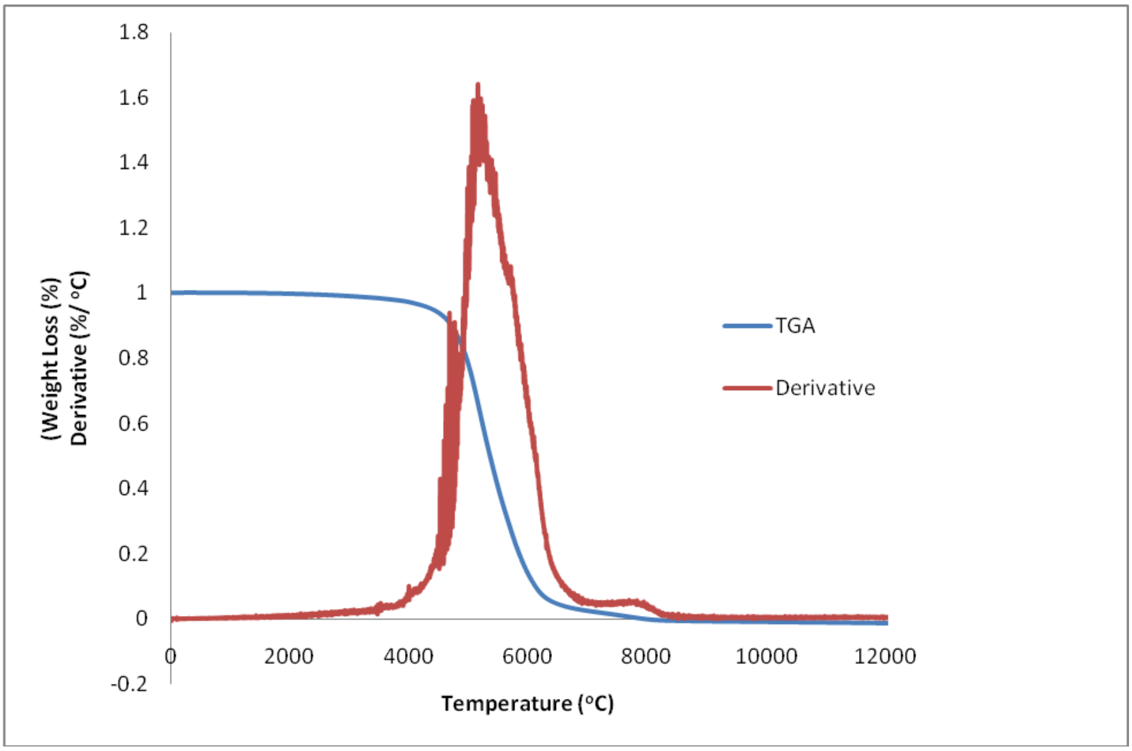

Figure 11. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis of [BMIm][Br].

Imidazolium salts have high thermal stability beginning to decompose around 400°C. Recent reports have shown that the presence of a halide anion reduces the thermal stability of an imidazolium ionic liquid with onset occurring at least at a temperature of about 100°C below other imidazolium salts. The derivative thermogravimetric analyses (DTG), of the ionic liquid indicate the presence of a single decomposition peak as observed in the TGA.

4. CONCLUSION

In this paper we present measurement of density, viscosity and electrical conductivity of 1-Butyl-3-methylimidazolium bromide. The density decreases monotonically and the viscosity decreases with increase in temperature. The electrical conductivity of the ionic liquid against temperature in different cosolvents show increases in conductivity with water and ethanol while conductivity decreased with methanol, acetonitrile and acetone. Conductivity measurement of binaries of the ionic liquid with water, acetonitrile and methanol increased with increase in concentration. Ionic liquid aqueous solution conductivity increases with increase in hydrophilic anions.

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