Temperature-dependent spectroscopic properties of imidazolium-based Ionic Liquids in the 100 MHz to 10 GHz microwave region

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Abstract - Microwave spectroscopic properties of imidazolium-based ionic liquids has been investigated in the 100 MHz to 10 GHz range over a range of temperature between 25 ºC and 125 ºC for characterising the dielectric and loss factor properties. The room temperature dielectric properties of the ionic liquids were found to decrease with increasing frequency of incident wave which may be attributed to a net drop in polarization, as some polarization mechanisms example interfacial and orientation polarization cease to contribute at higher frequencies. The dielectric properties are, however, enhanced at higher temperatures due to a decrease in relaxation time of polarization which is in good correlation with the Debye model of relaxation time for spherical dipoles. Amongst the four liquids investigated for the microwave induced physicochemical changes, the emim[SCN] liquid showed the lowest viscosity of 21 cP at room temperature, highest electrical conductivity of 22 mS/cm, susceptibility to microwave irradiation. By comparison, the bmim[HSO4] liquid exhibited the highest viscosity of 101cP at 80 ºC and the lowest electrical conductivity of 1.38 mS/cm when irradiated with the microwave irradiation. The relaxation time of molecular polarisation appears to be consistent with the Debye model for the viscous relaxation of ionic liquids investigated herein.

Index Terms - Ionic liquids, microwave absorption properties, loss factor.

I. INTRODUCTION

Ionic liquids (ILs) exhibit physical and chemical properties that make them useful for a variety of applications; these include high thermal stability, ionic conductivity, a large electrochemical window, low flammability and negligible vapour pressure [1, 2]. Ionic liquids exhibit good thermal stability and tend to decompose above 200 °C [3]. The room temperature conductivities of ionic liquids vary between 0.1 and 18 mScm^{-1}; with typical values of 10 mScm^{-1} for imidazolium cations [4]. One of the primary driving forces for research on ionic liquids is the perceived benefit of substituting traditional industrial solvents, most of which are volatile organic compounds (VOCs). The replacement of conventional solvents by ionic liquids is likely to reduce the emission of VOCs to the environment, and hence decrease the environmental impact due to the greenhouse gases [5].

Ionic liquids are designed with large organic cations, such as imidazolium ($C_3N_2H_4$) or pyridinium (C_5H_5N), with alkyl chain (C_nH_{2n+1}) substituents and anions such as trifluoromethylsulfonyl imide ((CF_3SO_2)$_2$N$^-$), chloride (Cl$^-$), nitrate (NO$_3^-$), Bromide (Br$^-$), hexafluorophosphate (PF$_6^-$) and tetrafluoroborate (BF$_4^-$) [6]. "The physicochemical properties of ILs are influenced by both their cationic and their anionic moieties" [7]. For example, the viscosity of 1-alkyl-3-methylimidazolium ($C_n$mim$^+$) cations with the same hexafluorophosphate (PF$_6^-$) anion increases as the length of the 1-alkyl chain of the cation increases. However, the density and surface tension decrease with increasing length of the 1-alkyl chain [8]. Moreover, in an ionic liquid the anionic moiety affects its water solubility. For instance, bmim[Cl] and bmim[BF$_4$] are both soluble in water, whereas the bmim[PF$_4$] and bmim[NTf$_4$] ILs are immiscible in water [9]. Different arrangement of cations and anions may yield different properties, thus ILs are termed "tailor-made" materials [10].

Over the years, ionic liquids have attracted extensive attention for research such as organic synthesis, process of green chemistry, catalysis, separation science, spectroscopy and many more! The extractive metallurgy industry is in urgent need for developing process technologies which might help in reducing the cost of energy consumption, waste generation and, therefore reduce the overall adverse environmental impact. The application of ILs as solvents for the extraction of metals has potential to offer a green alternative to conventional hydrometallurgical processes [11]. For example, the recovery of gold (Au) and silver (Ag) from mineral concentrates using ionic liquids was reported for the first time by Whitehead [12]. In this investigation 1-butyl-3-methyl-imidazolium hydrogen sulphate ionic liquid, bmim[HSO$_4$], was mixed with iron (III) sulphate oxidant and thiourea to oxidize gold and silver metals, which were selectively extracted from chalcopyrite at room temperature in 50 hours at efficiencies higher than 85% and 60%, respectively.

The reaction rate is strongly dependent on temperature because of the need to overcome the chemical activation barrier. In this respect, there have been a number of studies on reducing the leaching process time using microwave irradiation of the extraction medium. Although there have been a large number of investigations in this area, our focus is on micro-wave

assisted leaching for the digestion of biological, botanical, food and mineral materials for metal extraction and reclamation [13-19]. The interaction of microwave offers a fast heating process rate, and thereby increases the dissolution rate than in conventional heating [20]. In an attempt to reclaim metallic values from the electronic printed circuit boards. Kuo et al adopted, leaching techniques to extract heavy metals from the sludge of the printed circuit board process. A traditional acid extraction (TAE) method demonstrated that 74% of copper can be leached out from sludge of fine particle sizes using nitric acid after 18 hours treatment. By comparison, when the leaching was carried out by irradiating the medium with incident microwave at powers of 400W and 800 W, leaching efficiencies of 77% and 93% respectively, were achieved after 30 minutes. Evidence for enhanced kinetics of metal dissolution from the sludge is therefore indisputable in the presence of microwave radiation. [21].

In order to determine the suitability of the use of ionic liquids for the recovery of precious and transition metals (Cu,Ni) from the electronic wastes and mineral bodies, especially by microwave technique, the temperature dependence of microwave absorptive properties of four imidazolium-based ionic liquids, and their dielectric and spectroscopic properties in relation with the chemical structure have been investigated in this article and the results are reported herein.

II. EXPERIMENTAL

2.1 Ionic Liquids

Four different types of imidiazolium based liquids selected for investigation were: 1-methyl-3-propylimidazolium bis trifluoromethylsulfonyl imide, >98% ($mpim^+[N(CF_3SO_2)_2]^-$), 1-ethyl-3-methylimidazolium thiocyanate, 99%, ($emim^+[SCN]^-$), 1-butyl-3-methylimidazolium hydrogen sulphate, >95% ($bmim^+[HSO_4]^-$) and 1-Ethyl-3-methylimidazolium hydrogen sulphate, 95% ($emim+[HSO_4]^-$) procured from the Ionic Liquids Technologies (IOLITEC) GmbH, Germany. These liquids were analysed in the as-received form for their electrical conductivity and temperature-dependent microwave dielectric property. To prevent water hydration, the ionic liquids were kept in a desiccator inside the packaging with air tight bottles. The chemical structures of the ionic liquids used are shown in Figure 1 below.
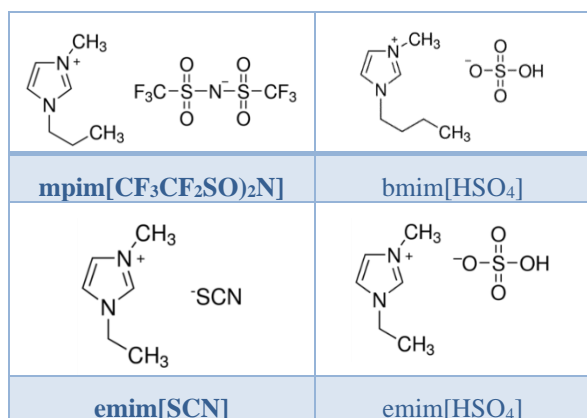

Figure 1: *Schematic structures and abbreviations of imidazolium ionic liquids investigated in this work.*

2.2 Electrical Conductivity Cell

The electrical conductivity of the ionic liquid was characterized using a home-made apparatus, shown below in *Figure 2*, in which two copper plates with dimensions (25mm x 25mm x 1.5 mm) spaced 10 mm apart, were positioned in a T-glass tube, with wall thickness of 3 mm and internal diameter of 38.1 mm. The cell was subsequently filled with ionic liquid and closed with 35mm x 40.5mm x 38.5 mm silicone rubber bung stoppers to contain the ionic liquid inside the glass tube. The terminals of the copper wire were connected to an electrical circuit, as shown in *Figure 2*, for characterising the resistivity of the medium by passing current for a given applied potential. By applying fixed AC voltage, the overall flow of current was recorded with increasing applied AC voltage. Using the Ohm's law method, the electrical resistivity of ionic liquids was characterized.
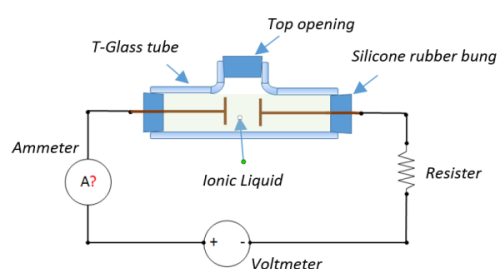

Figure 2 : *A T-glass tube with electrical circuit used for measuring the electrical conductivity of the imidazolium ionic liquids*

2.3 Measurements of Dielectric Properties

The frequency sweep measurements of the ionic liquids under study were carried out using an Agilent Technologies E8361A Performance Network Analyzer (PNA) which offers a combination of speed and precision, with a frequency range coverage from 10 MHz to 67 GHz, [22]. The experimental set up is shown in Figure 3, where a 25 ml glass beaker containing 10 ml of IL was placed on a digital hot plate. The PNA high temperature dielectric probe was positioned to just touch the IL on the surface, making sure that no bubbles were trapped underneath it. The hot plate was used to heat the IL for maintaining the isotherms at 25º, 50º, 100º and 125ºC. At each temperature, the properties of ILs were characterized by sweeping across the microwave frequency range from 100 MHz-10 GHz.
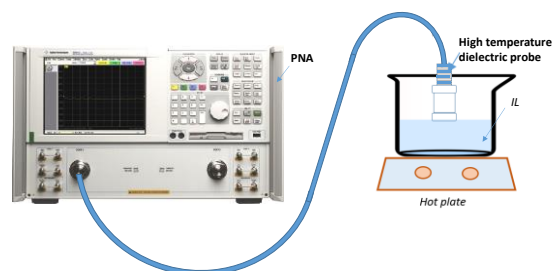

Figure 3: *The schematic illustration of the experimental set up for PNA frequency sweep mode measurements of microwave properties at an isotherm, maintained at (25, 50, 100 and*

125ºC) by using a hot plate. The microwave probe is shown as touching the IL liquid surface.

III.   RESULTS AND DISCUSSION

3.1 Comparison of Physical Properties of Ionic Liquids

Using the T-glass tube conductivity cell, the measured ionic conductivities of the ILs are compared in Table **1**. Other physical properties namely the molar weight, density and viscosity were taken from literature [23-27]. In this table, the measured electrical conductivity data using the apparatus in Figure 3 are compared with the data in literature, from which it is evident that the electrical conductivity decreases with increasing viscosity of the ionic liquids, which may be explained by using the Stoke-Einstein viscosity model and the Nernst-Einstein law [28]. In the Stoke-Einstein model expressed in equation 1, the molecular viscosity (η, P) is inversely related with the ionic or molecular diffusion coefficient (D, $m^2 s^{-1}$). Here k is the Boltzmann constant and T is the temperature in absolute scale. For ionic diffusion, the activated states must overcome the activation barrier. The ionic diffusion, however, is inversely dependent on the average spherical diameter (a, nm) of the molecule. On the basis of Stoke-Einstein model, a relationship between the apparent electrical conductivity of ILs and viscosity may be explained at a given temperature by using the classical ionic conductivity or diffusivity

$$D = \frac{kT}{6\pi\eta a} \qquad (1)$$

$$\sigma T = A(n_1 Z_1^2 e^2 D_1 + n_2 Z_2^2 e^2 D_2 + \cdots) \qquad (2)$$

The Nernst-Einstein law relates the total ionic conductivity (σ, S/m) of a conducting solvent with the diffusion coefficient (D, m^2/s) of the constituent ions, as expressed in equation 2, where A is a numerical factor and *n* and *Ze*, are, correspondingly, concentrations (ions/m^3) and charges (Coulombs) of constituent ions. In equation 3, which is obtained by comparing equations 1 and 2, an inverse relationship is apparent between conductivity and viscosity of the conducting medium irrespective of its composition and particular properties of the constituent ions [28].

$$\sigma T = \frac{kTAe^2}{6\pi\eta} \left(\frac{n_1 Z_1^2}{a_1} + \frac{n_2 Z_2^2}{a_2} \right) \qquad (3)$$

As the apparent viscosity of an ionically conducting medium increases the conductivity is expected to decrease, in accordance with the Stoke-Einstein and Nernst-Einstein models. The molecular thermal vibration (kT) in equations (1) and (3), therefore contributes to dispersion of molecular vibration modes contributing to overcoming the ionic conduction. Amongst the four ILs investigated, as evident in Table **1**, the $Bmim^+[HSO_4]^-$ IL has the highest viscosity of 164 cP at 80ºC, and consequently the lowest electrical conductivity of 1.34 mS/cm at room temperature. On the other end, the IL

$emim^+[SCN]^-$ exhibits high electrical conductivity of 22 mS/cm and low viscosity of 21 cP at 25 ºC.

Table 1: *A comparison of the physical properties of the four imidazolium ionic liquids. A^b[C] format: A is the measured/referenced value, b is the temperature and [C] refers to the referencing source. An inverse relationship is apparent between conductivity and viscosity of the conducting medium*

Ionic Liquids	Measured (25ºC)	Referenced			
	σ (mS/cm)	σ (mS/cm)	M (g/mol)	Density, ρ (g/cm³)	Viscosity, η (cP)
Emim [SCN]	22.00	21 [29]	169.25	1.12 [25]	21^{25} [29] 22^{25} [25]
Mpim [N(CF₃SO₂)₂]	4.40	4.35 [23]	405.34	1.47 [23, 24]	43.7^{25} [24] 43.94^{25} [23]
Emim [HSO₄]	1.38	-	208.24	1.36 [27]	101.2^{80} [27]
Bmim [HSO₄]	1.34	1.4 [26]	236.29	1.32 [26]	164^{80} [26] 1572^{24} [26]

3.2 Effect of frequency on Dielectric properties

Microwaves interact with dielectric materials either through conduction process or by polarization. Conduction involves the translation motion of free charges such as ions due to the internal field generated by the microwaves in the ionic liquid. Conduction losses occur when the moving ions collide with other species in the liquid. Polarization occurs when the charge complexes such as dipoles are induced to align in the direction of the microwave field. Polarization losses occur when frictional forces resist induced motions by the microwaves. Both conduction and polarization loss mechanisms dissipate heat into the system which results in volumetric heating. The degree of interaction of microwaves is related to the material's complex permittivity ε:

$$\varepsilon = \varepsilon_0(\varepsilon' - \varepsilon'') \qquad (4)$$

Where ε_0 is the permittivity of free space (ε_0= 8.86 x 10^{-12} F/m), the real part ε' is the relative dielectric constant and the imaginary part ε'' is the effective relative dielectric loss factor. The dielectric constant, ε', describes the polarizability of the molecules of IL by the applied electric field, whereas the dielectric loss factor, ε'', measures the efficiency with which the energy of the electromagnetic radiation is absorbed and converted into heat. Loss tangent (tan δ) is used commonly to describe these losses, which is defined as:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sigma}{2\pi f \varepsilon_0 \varepsilon'} \qquad (5)$$

Where σ is the total effective conductivity (S/m) caused by ionic conduction and displacement currents and f is the microwave frequency.

polarization mechanisms have frequency dependence and that is because of the mass associated with the charge dipoles and hence inherent inertia to movement. Also, the orientation and disorientation phenomenon of the dipoles due to the oscillating field of microwaves very much depends on the frequency. The timescales for the polarization and depolarization for electronic and atomic polarization is much faster compared to the timescale associated with the permanent dipole moments in molecules during orientation polarisation [30]. As a result, due to decreasing contributions of polarisation mechanisms as microwave frequency is increased, the total losses measured in all four liquids are seen to decrease with frequency as evident in Figure **4**.

3.3 Effect of temperature on Dielectric properties

The effect of temperature on the total dielectric losses can be understood by considering the effect of temperature on the two main mechanisms of microwave heating; conduction and polarization losses using the Debye model. The Debye model expressed in equation 7 directly relates the relaxation time of polarization (τ, s) and/or temperature (T, K) with the viscosity (ŋ, P) of the medium as shown in equation 7:

$$kT\tau = 4\pi r^3 ŋ \qquad (7)$$

Where k is the Boltzmann's constant (1.38×10^{-23} m^2 kg s^{-2} K^{-1}) and r is the radius of the dipolar molecule. The relaxation time of polarization measures the time it takes for a polarised dipole under an applied field to assume its original orientation when the applied field is removed. Assuming that the relaxation time of polarization is fixed in the Debye model, an increased temperature would directly increase the viscosity of the medium which would allow speedy movement of the both free and bound charges causing an increased conduction and number of collisions to result in conduction losses. The vibrational motion and internal kinetic energy of the dipoles would also increase to enhance phase lagging and polarization losses within the medium. Consequently, an overall increase in microwave dielectric properties with temperature observed as evident in Figure **5**.
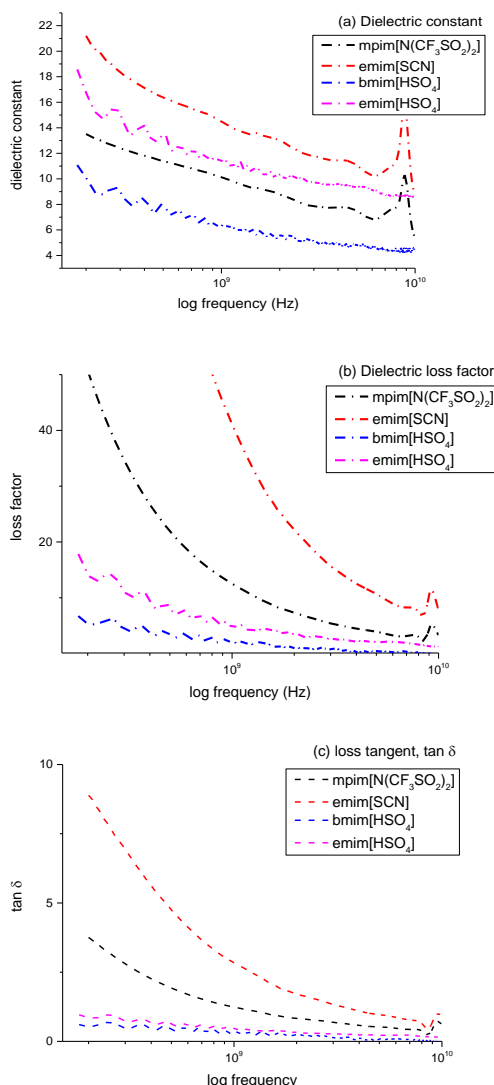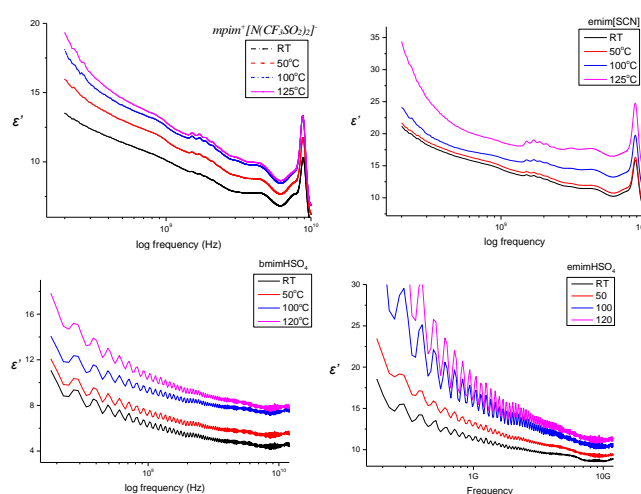
Figure 4: *Measured frequency sweep data for four imidazolium-based ionic liquids at room temperature, showing the frequency dependence of microwave absorption and permittivity dispersion. The loss tangent distribution is also shown in fig (c).*

From Figure **4**, it is obvious that the dielectric properties decrease with frequency which is in agreement with equation 5 where the loss tangent is inversely proportional to the microwave frequency. Various polarization mechanisms contribute to the total polarization effect of microwave irradiation. The most dominant is dipole rotation, also referred to as orientation polarization. Other polarization processes include electronic polarization, which results from the realignment of electrons around specific nuclei; atomic (ionic) polarization, which arises from the relative displacement of nuclei due to the unequal distribution of charge within the molecule; and interfacial polarization, also referred to as space charge or Maxwell-Wagner polarization, which occurs when there is a build-up of charges at the interfaces normally observed in amorphous or polycrystalline solids. These
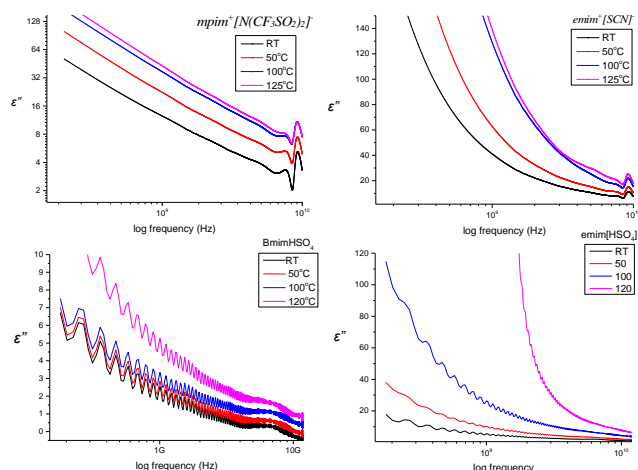
Figure 5: *A temperature-dependant frequency sweep reading of microwave properties at an isotherm, maintained at (25, 50, 100 and 125ºC) by using a hot plate. Both the microwave dielectric constant (top) and loss factor (bottom) increase as temperature is increased*

It can be easily understood that the more viscous the conducting medium the more time it takes for relaxation to occur due to stronger resistance by internal friction. It is apparent from Figure **6** that the slope of the curve representative of the IL's response to microwave irradiation is gentle for bmimHSO4 which is the most viscous compared to the others. EmimSCN with the lowest viscosity shows the steepest microwave dielectric response.
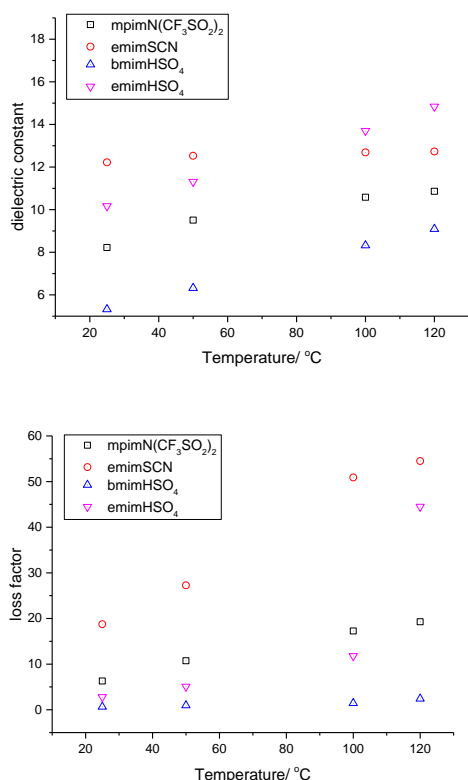

Figure 6: *Effect of temperature on the dielectric properties of the measured ionic liquids at 2.45 GHz frequency.*

IV.   CONCLUSION

In summary, the microwave spectroscopic properties of imidazolium-based ionic liquids were investigated in the 100MHz to 10GHz range over a range of temperature between 25 ºC and 125 ºC for characterising the dielectric and loss factor properties. The room temperature dielectric properties of the ionic liquids were found to decrease with increasing frequency of incident wave. This behaviour may be attributed to a net drop in polarization, as some polarization mechanisms (e.g. interfacial and orientation polarization) cease to contribute at higher frequencies. The dielectric properties are, however, enhanced at higher temperatures due to a decrease in relaxation time of polarization which is in good correlation with Debye's model of relaxation time for spherical dipoles. It is also observed that amongst the four liquids investigated, emim[SCN] ionic liquid with least viscosity of 21 cP at room temperature showed highest electrical conductivity of 22 mS/cm and susceptibility to microwave irradiation whereas bmim[HSO4], the most viscous liquid (101 cP at 80 ºC) showed the least electrical conductivity of 1.38 mS/cm and response to microwave irradiation. This final behaviour can be attributed to both the Debye's model where the relaxation time is directly proportional to the viscosity of the liquid medium, and ionic drift velocity, which is the average velocity that an ion attains due to an applied field.

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