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Dielectric Properties of Ionic Liquids Proposed to Be Used in Batteries

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1. Introduction

Ionic liquids (ILs) opened new technological possibilities (Marsh, 2004) at the end of the 1990s for many application fields (Mutelet & Jaubert, 2006) due to their special physical and chemical properties (Welton, 1999). They have several advantages compared to commercial organic solvents (Mutelet & Jaubert, 2006), or electrolyte liquids (Plechkova & Seddon, 2008) since they are liquid over a wide temperature range, easy to recycle, non-combustible (Matsumoto, 2005), non-flammable (Saruwatari, 2010), display wide electrochemical windows (Giroud, 2008), high inherent conductivities (Stracke, 2009), have negligible vapor pressure (Endres, 2008), high thermal (Wasserschied & Welton, 2007) and electrochemical stability (Arnold, 2004), tuneable physicochemical properties (Koel, 2008) and lack of reactivity in various electrochemical or industrial applications (Seddon, 2003).

Therefore ILs have been intensively studied recently as novel, much safer electrolyte materials (Sakaebe, 2007) for electrochemical devices (Ohno 2005) and energy storing devices, such as Li batteries for cellular phones (Xu, 2006), batteries for vehicles, fuel cells, supercapacitors (Sato, 2004), solar cells (Stathatos, 2005.), etc.

In order to decide whether an IL could be successfully used as electrolyte it is necessary to first gain enough information about the electrochemical properties, hence the dielectric behaviour of the selected liquid.

However, several methods have already been published about determination of the dielectric properties of ILs – generally characterized by the dielectric constant (ε') (Wakai, 2005) and by the dielectric loss factor (ε'') (Bright & Baker, 2006; Wakai, 2006), so far no measuring method was introduced. This can be explained by the fact that the dielectric properties of ionic liquids cannot be measured by classical methods due to their high conductivity (Krossing, 2006).

In this chapter we intend to describe a novel method and a self-designed microwave dielectrometric apparatus built to measure the (ε') and (ε'') values and the electrical conductivity (G) of several ionic liquids, which might be used as electrolyte in batteries, at 2.45 GHz and at different temperatures. Furthermore the connections between the structure of the investigated ionic liquids and the dielectric characteristics will be determined.

2. Ionic liquids used in batteries

The most investigated ILs for the use of batteries are composed of quaternary ammonium (Mastumoto, 2001), pyridinium (Xiao & Malhotra, 2005), pyrrolidinium (Forsyth, 2001), pyrazolium (Alarco, 2004), piperidinium (Sakaebe, 2005), imidazolium (Ito, 2000) cations and [BF$_4$]$^-$, [PF$_6$]$^-$ anions.

In 2000 Hagiwara and Ito (Hagiwara & Ito, 2000) reported a dramatic increase of activity in this field of research (Wilkes, 1982) and published several physical and chemical properties of ILs which could be used for electrolysis, electrochemical deposition and the production of batteries. They found that the investigated ILs possesssed many excellent characteristics as electrolytes.

Few years later Diaw and co-workers studied the temperature dependence of the electrochemical properties of ILs mixed with organic solvents used as electrolyte for lithium batteries. They concluded that this new system did not only permit the same amount of charging and discharging without significant loss in capacity as the commercial batteries, but it could also be used at higher temperature without any safety problems (Diaw, 2005).

Matsumoto and co-workers published the electrochemical properties of ILs built up of amide anions and aliphatic onium cations at the temperature of 25°C. They found that not only the physical but also the electrochemical properties of the ILs depend mainly on the type of anions and cations (Matsumoto, 2005). Also it was found that the introduction of alkoxy groups into the ILs might lower the viscosity hence increase the effectiveness of the battery based on such liquid (Matsumoto, 2000).

The electrochemical windows, feasibility of ILs and the cycle life of batteries prepared with ILs were studied by Yang and co-workers (Xu, 2006). It was concluded that the battery containing *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide as electrolyte base (Sakaebe & Matsumoto, 2003) had a wide potential-stable window (> 5.5 V) and that it showed stable efficiency of 90-92% after 10 cycles.

Sakaebe and co-workers investigated the advantages and drawbacks of ILs used in batteries. It was found that the application of ILs could lead to relatively high electrochemical window, excellent thermal stability and that this kind of cell design had to be customised for further development (Sakaebe, 2007).

Stracke and co-workers reported the successful application of ILs as electrolytes in a toxic compound free Leclanché batteries and found that higher ionic conductivities were related to higher Leclanché battery potentials (Stracke, 2009).

The electrochemical behaviour and ionic conductivity of IL electrolytes and the resistance of the battery cells were studied by Saruwatari and co-workers. Both the temperature and the chemical structure of ILs had an effect on the ionic conductivity data. The increase in resistance of electrolyte meant the decrease of the ionic conductivity of electrolyte. Furthermore the cell showed as large discharge capacity as 235mAhg^{-1} at 20°C (Saruwatari, 2010).

Sutto and co-workers prepared new type of batteries containing IL electrolyte and determined their ionic conductivity between 20°C and 100°C and carried out tests on measuring their capacity. It was demonstrated that new, environmentally sound energy storage devices could be developed with discharge voltages ranging up to 1.8 V depending on the used anode and cathode (Sutto, 2011).

Ionic conductivity, dynamic viscosity and electrochemical and thermal stability of several ILs were reported by Giroud and co-workers. Thermogravimetric investigations showed

that the IL solution were damaged above 450°C hence they could be used even for electric vehicle applications. It was also stated that the IL electrolyte showed better cycling performances than organic electrolyte and that operating potentials for IL electrolyte batteries might be higher than that of conventional lithium ion batteries (Giroud, 2008).

Most of the authors having studied the electrochemical properties of ILs and their possible application in batteries as electrolyte concluded that ILs could be successfully used to create new types of rechargeable systems or to even replace the standard lead-acid batteries.

3. Dielectric properties

3.1 Permittivity

The permittivity (ε) is a characteristic of a material, which describes how any electric field affects and is affected by a material (a dielectric medium). In nonconducting materials (insulators or dielectrics) charges do not move freely only might be slightly displaced from their equilibrium position (Heaviside, 2007). Permittivity is determined by the ability of a material to polarize in response to the field, and reduce the total electric field inside the material, hence it can be calculated by Equation 1, which gives the electric field of a point charge (Q) at the distance r from Q.

$$E = \frac{Q}{4\pi \cdot \varepsilon \cdot r^2} \rightarrow \varepsilon = \frac{Q}{4\pi \cdot E \cdot r^2} \tag{1}$$

Equation 2 gives the unit of ε, which is conventionally measured in farads per meter [F/m], or coulombs per volt-meter [C/Vm], as well.

$$[\varepsilon] = \frac{[Q]}{[E] \cdot [r^2]} = \frac{1As}{1\frac{V}{m} \cdot 1m^2} = 1\frac{As}{Vm} \tag{2}$$

3.2 Dielectric constant

For a given system the ratio of the electric flux density (D) to the electric field strength (E) is a constant, known as the absolute permittivity (Equation 3), which can also be defined as the product of the permittivity of free space (or vacuum permittivity) (ε_0) and the relative permittivity (ε_r), or sometimes also called as dielectric constant (ε') as shown in Equation 4 (Housecroft & Sharpe, 2005).

$$\varepsilon = \frac{D}{E} \tag{3}$$

$$\varepsilon = \varepsilon_0 \cdot \varepsilon_r \tag{4}$$

where the value of vacuum permittivity is; $\varepsilon_0 = 8.8541878176 \times 10^{-12}$ As/Vm (Fleisch, 12008).

The dielectric constant, or relative permittivity, which is the permittivity of a material relative to that of free space and equals to 1 for vacuum by definition. Due to ability of any material to polarize more than vacuum the dielectric constant of a given material is always higher than 1. The ε' is dimensionless since it is just a ratio of two similar quantities.

The most common application of dielectric materials is to increase the capacitance and maximum operating voltage of capacitors. The capacitance (ability to store charge) of a

parallel-plate capacitor (*C*) is proportional to the area of the plates (*A*) and the distance between the plates (*d*) and is given by Equation 5 (Carrier & Soga, 1999).

$$C_0 = \varepsilon_0 \frac{A}{d} \tag{5}$$

The capacitance of a capacitor is increased by placing a dielectric between the capacitor plates and is given by Equation 6 (Benenson, 2002).

$$C = \varepsilon \frac{A}{d} = \varepsilon_0 \varepsilon_r \frac{A}{d} \tag{6}$$

The dielectric constant (*ε′*) in reality is not always constant. In general, it can be different depending on the position in the medium, the frequency of the electric field, temperature, humidity, and other parameters.

3.3 Dielectric loss factor

When a capacitor of value *C* is connected to a generator of RMS voltage (*U*) at angular frequency (*ω*) will draw a current (*I*) according Equation 7.

$$I = jU\omega C \tag{7}$$

Supposing that the permittivity has an imaginary component and is written by Equation 8

$$\varepsilon_r = \varepsilon' - j\varepsilon'' \tag{8}$$

then substituting Equation 6 and Equation 8 into Equation 7 the current will be;

$$I = U\omega \frac{\varepsilon_0 A}{d} \left(j\varepsilon' + \varepsilon'' \right) \tag{9}$$

The first therm in parentheses shows the component of current in phase quadrature with the voltage as it would be in the case of lossless capacitors. The second term is a component in phase with the applied voltage and therefore it reperesents power dissipation (*P*), which is given by Equation 10.

$$P = U^2 \omega \frac{\varepsilon_0 A}{d} \varepsilon'' \tag{10}$$

where *ε″* is called the dielectric loss factor of a dielectric and it can quantify the power dissipation in a dielectric filled capacitor.

The dielectric loss angle (*δ*) is defined as the angle by which the resultant current is different from the ideal 90° phase angle relative to the voltage and is given by Equation 11 (Meredith, 1998).

$$tg\delta = \frac{\varepsilon''}{\varepsilon'} \tag{11}$$

3.4 Electrical conductivity

The electrical conductivity is a measure of how easy it is for an electrical current to flow through a material or how easily electrical charge may be transported through it. High value

corresponds to the materials that carry electrical currant easily and do not readily remain electrically charge. Due to this behaviour these material might be excellent candidates for electrolytes in certain batteries (Heiken, 1991). Electrical conductivity is defined by Ohm's law for direct current (Equation 12), measured in units of Siemens (S) and is given by the inverse of the resistance as shown in Equation 13 (Mohos, 2010).

$$U = IR \tag{12}$$

where U is voltage (V), I is current (A) and R is resistance (Ω).

$$G = \frac{1}{R} \tag{13}$$

4. Measurement methods for dielectric properties

Several different techniques have been developed for the determination of the dielectric constant and the dielectric loss factor of solid and liquid materials. The most commonly used ones are the following.

4.1 Perturbation technique

The perturbation technique is normally used in the case of homogeneous materials due to its simplicity, high temperature capability and easy data reduction (Tong, & Lentz, 1993). One of its greatest advantages is that it can be highly accurate in the determination of small loss factors. It is based on the measurement of either reflection coefficients or resonant frequencies (Sheen, 2009). In this later case the investigated materials are characterized to load a resonant cavity and the sample permittivity is evaluated from the shift of the resonant frequency value, compared to that of the empty cavity (Murthy & Raman, 1989). For the evaluation of dielectric properties of homogeneous dielectric materials a new, even more accurate perturbation technique has been developed where a special cavity has been designed with very small slot at the center of the broader side of the wave-guide in order to insert the sample (Kumar & Sharma, 2007).

4.2 Waveguide and coaxial transmission line method

The determination of dielectric constant and loss factor is based on the transmission line theory (Ebara, 2006). According to this theory the values of ε' and ε'' can be determined by measuring the phase and amplitude of reflected microwave signals both from a solid or liquid sample placed against the end of a short circuit transmission - waveguide or coaxial – line (Kozhevnikov, 2009). Charreyre and co-workers were among the first researchers who have described an apparatus designed to measure dielectric parameters by this technique (Charreyre, 1984).

4.3 Open-ended probe technique

In this case a coaxial line with a tip, which can sense the signal reflected from the investigated material, must be applied (Sheen & Woodhead, 1999). The tip is either in contact with the sample by touching the probe to a flat face of the solid material (Gardner & Anantaraman, 1995) or it is immersed into the liquid sample during the measurements (Guo, 2011). The dielectric properties are calculated from the phase and amplitude of the

reflected signal at the end of the open-ended coaxial line. This technique is valid for materials with loss factor higher than 1, between the frequencies of 915 and 2450 MHz.

4.4 Time domain spectroscopy method

Although, this method is rather expensive it is an excellent tool to investigate the interaction of the electromagnetic energy and materials over a wide frequency range (Afsar, 1986). The reflection characteristics of the investigated material are used to compute the dielectric properties. The measurement is very rapid and the accuracy is very high, within a few percent error range (Lee, 2003).

4.5 Free-space transmission technique

It is considered to be a non-destructive and contact-less measuring method, which is particularly suitable for determining the dielectric properties of materials at high temperature and for inhomogeneous dielectrics. It can also be easily implemented in industrial applications for continuous monitoring and control (Kraszewski, 1980). The accuracy of measurement depends mainly on the performance of the measuring system and the validity of the equations used for the calculation (Håkansson, 2007).

The above described conventional techniques to measure the dielectric properties of ionic liquids or electrolyte solutions mostly tend to fail because the samples are largely short circuited by the high electrical conductance (Wakai, 2005). Hence it is quite difficult to measure the dielectric constant and loss factor of conducting materials. The main challenge is to develop an accurate method for determining the dielectric properties of such materials while the method is not only effected by the frequency of interest, the required accuracy, the geometry of the sample holder (Roumeliotis & Kokkorakis, 1994) and the adequate modeling of the circuit, but also by the physical and electrical characteristics of the studied liquid (Venkatesh & Raghavan, 2005).

Therefore we intended and managed to design and build a so-called microwave dielectrometric measurement device in which - based on the compensation of phase change due to the microwave energy absorption of the liquid sample – the dielectric properties of ionic liquids can be successfully measured in a continuous and automatic way.

5. Experimental

5.1 Materials

All ILs used in this work were synthesized at the Research Institute of Chemical and Process Engineering, University of Pannonia, Hungary. Their names, structural formula and water content can be seen in Table 1. The water content of the ILs was measured by Karl-Fischer titration and the values ranged between 0.08% and 5.11% (w/w). After a 24 h long vacuum treatment all ILs contained less than 0.01% (w/w) water.

5.2 Experimental set-up

The schematic representation of the self-designed experimental set-up applied for automatic and online measurement of dielectric properties of well conducting liquids in a definite temperature range is shown in Figure 1. It is composed of the following devices and instruments; cylindrical sample holder unit, thermostat, peristaltic pump, waveguide, temperature sensor, displaceable piston, stepper motor, magnetron, detectors, control unit, and a PC.
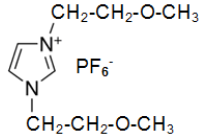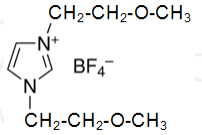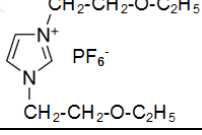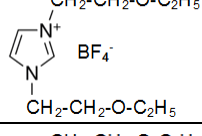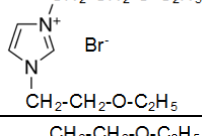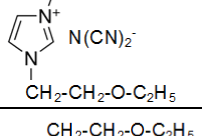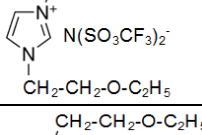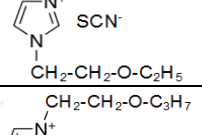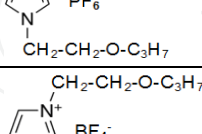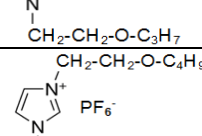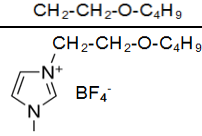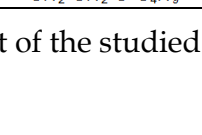
Ionic liquids			
Short name	Name	Structure	Water content(w/w%)
[DiEtMeIm][PF$_6$]	1,3-diethoxymethyl imidazolium hexafluorophosphate	CH_2-CH_2-O-CH_3 ... PF_6^- ... CH_2-CH_2-O-CH_3	5.11
[DiEtMeIm][BF$_4$]	1,3-diethoxymethyl imidazolium tetrafluoroborate	CH_2-CH_2-O-CH_3 ... BF_4^- ... CH_2-CH_2-O-CH_3	3.22
[DiEtEtIm][PF$_6$]	1,3-diethoxyethyl imidazolium hexafluorophosphate	CH_2-CH_2-O-C_2H_5 ... PF_6^- ... CH_2-CH_2-O-C_2H_5	1.58
[DiEtEtIm][BF$_4$]	1,3-diethoxyethyl imidazolium tetrafluoroborate	CH_2-CH_2-O-C_2H_5 ... BF_4^- ... CH_2-CH_2-O-C_2H_5	0.08
[DiEtEtIm][Br]	1,3-diethoxyethyl imidazolium bromide	CH_2-CH_2-O-C_2H_5 ... Br^- ... CH_2-CH_2-O-C_2H_5	0.76
[DiEtEtIm][N(CN)$_2$]	1,3-diethoxyethyl imidazolium dicyanamide	CH_2-CH_2-O-C_2H_5 ... $N(CN)_2^-$ ... CH_2-CH_2-O-C_2H_5	0.93
[DiEtEtIm][N(SO$_3$CF$_3$)$_2$]	1,3-diethoxyethyl imidazolium bis(trifluoromethyl sulfonyl) imide	CH_2-CH_2-O-C_2H_5 ... $N(SO_3CF_3)_2^-$ ... CH_2-CH_2-O-C_2H_5	1.17
[DiEtEtIm][SCN]	1,3-diethoxyethyl imidazolium thiocyanate	CH_2-CH_2-O-C_2H_5 ... SCN^- ... CH_2-CH_2-O-C_2H_5	0.88
[DiEtPrIm][PF$_6$]	1,3-diethoxypropyl imidazolium hexafluorophosphate	CH_2-CH_2-O-C_3H_7 ... PF_6^- ... CH_2-CH_2-O-C_3H_7	0.95
[DiEtPrIm][BF$_4$]	1,3-diethoxypropyl imidazolium tetrafluoroborate	CH_2-CH_2-O-C_3H_7 ... BF_4^- ... CH_2-CH_2-O-C_3H_7	2.27
[DiEtBuIm][PF$_6$]	1,3-diethoxybutyl imidazolium hexafluorophosphate	CH_2-CH_2-O-C_4H_9 ... PF_6^- ... CH_2-CH_2-O-C_4H_9	1.96
[DiEtBuIm][BF$_4$]	1,3-diethoxybutyl imidazolium tetrafluoroborate	CH_2-CH_2-O-C_4H_9 ... BF_4^- ... CH_2-CH_2-O-C_4H_9	2.35

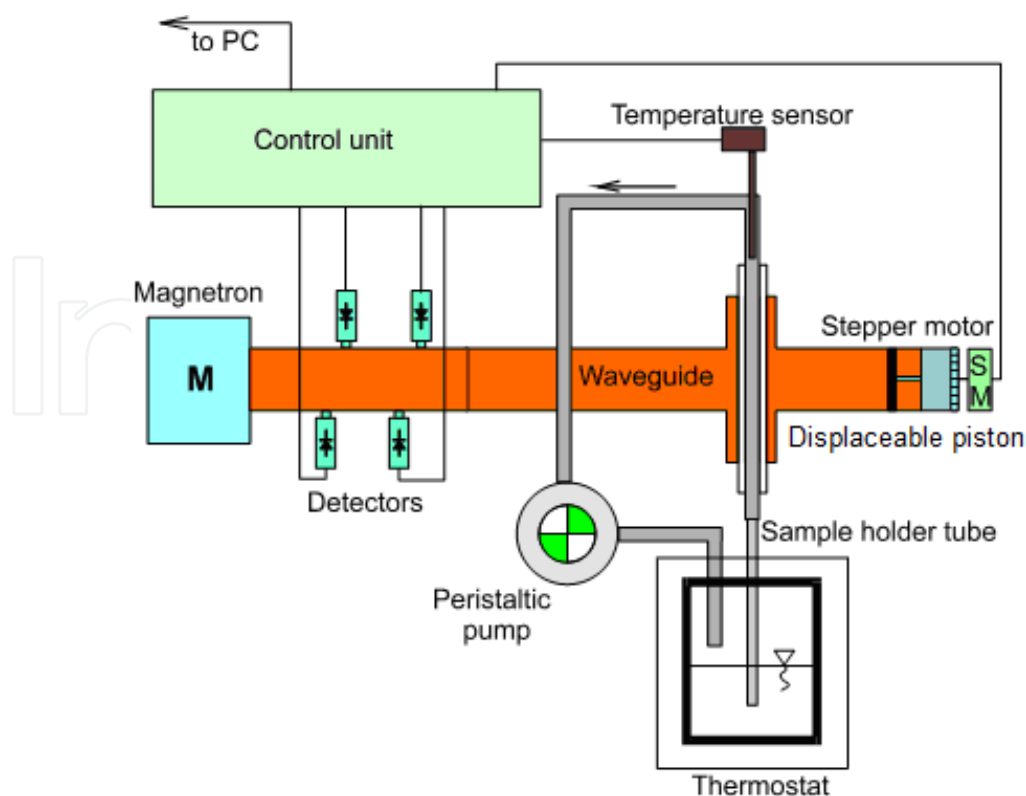Table 1. Name, structural formula and water content of the studied ionic liquids

Fig. 1. Scheme of the experimental set-up

The IL sample, which is placed in the thermostat to keep it at the desired constant temperature, is flown across the waveguide having a length of about 3λ through the sample holder tube with the help of a peristaltic pump. The electric energy is transformed into microwave energy by the magnetron. The stepper motor is controlled by a microprocessor control unit, which contains an Intel 8-bit microcontroller, 12 bit A/D converters for receiving the four diode-detector signals, a stepper motor driver and a RS-232 serial interface to connect it to the PC. The control unit collects the detector signals and the temperature data determined by the temperature sensor and sends them to the PC. Furthermore it controls the position of the short circuit displaceable piston on the basis of algorithm software elaborated for this purpose.

5.3 Measurement method

The method is based on the compensation of phase change due to the microwave energy absorption of the liquid sample. The short circuit piston situated behind the sample must be actuated for compensation. The energy conditions created by the wave front in the waveguide are measured by four diode-detectors. Based on the diode detector signals the wave-front pictures are developed in the transmission-line as it is represented on Figure 2. As it shown, essentially three arrangements can be formed.

Figure 2 a) shows the case when the sample holder is empty and the piston is at the position x_0, then a field maximum is detected by diode D_3. The short circuit piston must be moved to a distance $3/2\lambda$ from the diode detector D_1, and the signal of D_1- being at a distance $\lambda/4$ from the detector D_3 – exhibits a minimum. As a result of suitable geometric and electric arrangements, the signals of the detector D_2 and D_4 - which are placed with $\lambda/4$ spacing - are identical. The incorrect position of the short circuit piston is indicated by the difference

between D_2 and D_4. The differences between the signals determine the distance from the required position of the piston, while its sign refers to the direction where the short circuit piston must be moved. These latter detectors are applied to measure the equilibrium state, while D_1 and D_3 serve for the detection of the standing wave ratio.
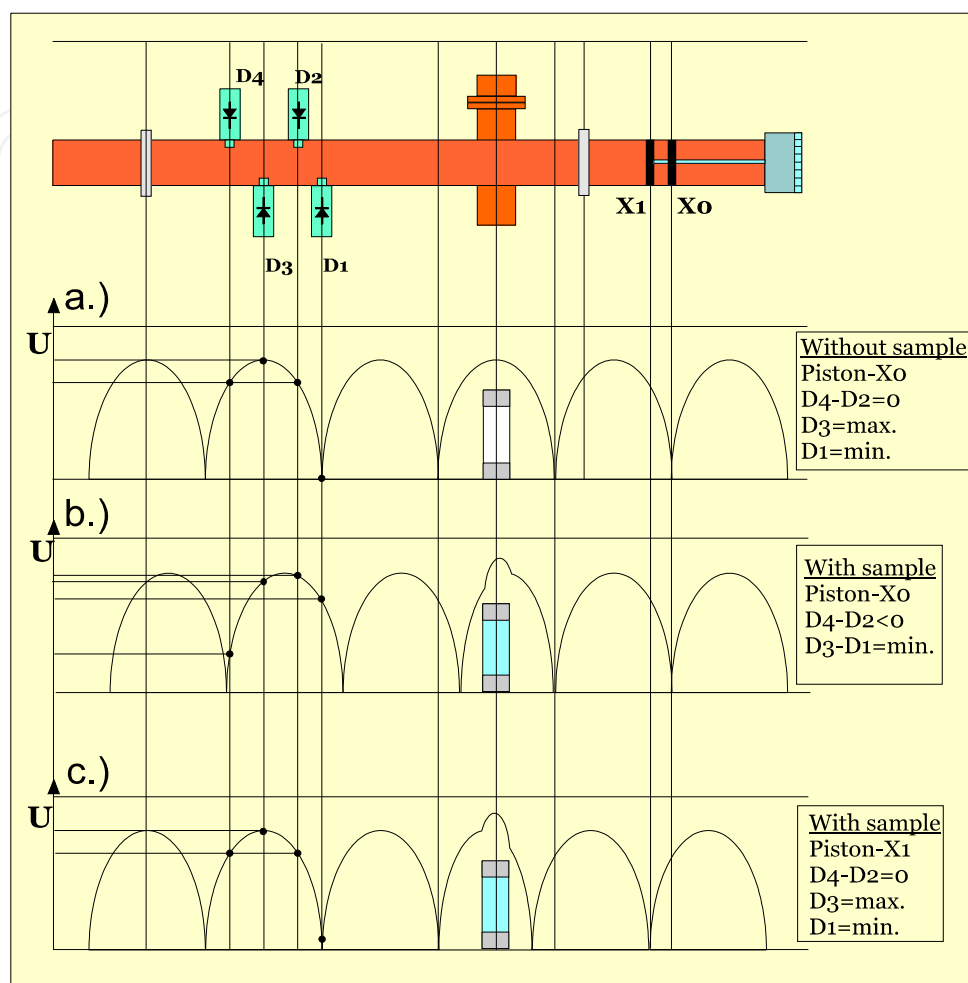

Fig. 2. a-c. Illustration of wave-fronts developed in the transmission line

Figure 2 b) shows the situation when the sample is introduced into the sample holder such a way, that the position of the piston remains unchanged. However, the reflection on the short circuit takes place in the same way as previously, the signals of the detectors are different from the previous state (demonstrated in Figure 2 a) when the shape of the wave-front formed in the transmission line is modified by the sample of dielectric properties. Due to the equilibrium shift between the D_2 and D_4 detectors, their signals become different and the quotient of the signals of D_1 and D_3 decreases because of the change of the traveling/reflected wave ratio, where the latter depends on the dielectric constant.

Figure 2 c) represents the state when the sample is still in the sample holder, but the equilibrium is restored by moving the short circuit piston. At the correct position of the piston the wave-front is restored to the state demonstrated in Figure 2 a). The position of the short circuit piston will be at a new x_1 position after the detector signals turn into the initial positions on the standing wave. The difference between position x_1 and x_0 (Δx) is used to calculate the dielectric constant ε' (Equation 14). The standing wave ratio is equivalent to the

quotient of the maximum and minimum values of the electromagnetic waves developed in the transmission line, which are measured by the detectors marked with odd numbers. When the sample holder is empty the standing wave ratio is equal to 1 at equivalent state ($D_2 = D_4$). When the sample is inserted into the sample holder the standing wave ratio increases and the calculation of the dielectric loss factor ε'' is based on the extent of this increase of the standing wave ratio (Equation 15).

$$\varepsilon' = 1 + \frac{a\lambda^2}{\lambda_T \pi^2 d^2} tg(\beta \cdot \Delta x) \tag{14}$$

where $\beta = 2\pi / \lambda_T$ and $\Delta x = x_1 - x_0$

$$\varepsilon'' = \frac{a\lambda^2}{\lambda_T \pi^2 d^2} \cdot \frac{1}{r} \tag{15}$$

where $1/r = \sqrt{(U_1/U_3)}$, a is the large waveguide dimension, d is the inner diameter of the sample holder λ and λ_T are wavelength in vacuum and in the waveguide, respectively, U_1/U_3 is the so called standing wave ratio, arising from D_1 and D_3 detector signals and Δx is the displacement of short circuit piston (Charreyre, 1984).

5.4 Determination of the dielectric constant, dielectric loss factor and the electrical conductivity of ionic liquids

Dielectric constants, dielectric loss factors and the temperature dependence of the dielectric properties of ionic liquids intended to be used in batteries were determined by the above described self-designed microwave dielectrometric apparatus (Figure 3) at the frequency of 2.45 GHz and at different temperatures (30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C and 120°C). The speed of the change in temperature depends on the electrical field strength in the material (E), the absorbed microwave power, (P_v) density (ρ), the specific heat capacity (C_p) and the dielectric loss factor ε'' and can be given by Equation 16 (Göllei, 2009). The electrical conductivity values (G) were calculated by Equation 12 and Equation 13.

$$\frac{\Delta T}{\Delta t} = \frac{P_v}{\rho C_p} = \frac{jE^2 f \varepsilon''}{\rho C_p} \tag{16}$$

6. Results and discussion

6.1 Effect of anion on the dielectric properties

The dielectric constant (E_1), dielectric loss factor (E_2) and electric conductivity (G) values of ILs built up of the same [DiEtEtIm] cation and six different anions ([PF$_6$], [BF$_4$], [Br], [N(CN)$_2$], [N(SO$_3$CF$_3$)$_2$] and [SCN]), at different temperatures between 30°C and 120°C are shown in Figure 4, Figure 5 and Figure 6, respectively.

It can be seen that while at the temperature of 30°C dielectric constants are similar for all ILs, ranging from 6 to 8, a slight increase of E_1 values can be seen with the increase in temperature up to 80°C. Above this temperature ILs containing different anions behave in a slightly different way; the E$_1$ values for [DiEtEtIm][N(CN)$_2$] and [DiEtEtIm][SCN] decrease, tha values for [DiEtEtIm][PF$_6$] sharply increase and the values for [DiEtEtIm][BF$_4$],

[DiEtEtIm][Br] and [DiEtEtIm][N(SO$_3$CF$_3$)$_2$] remain more or less the same between 80°C and 120°C. At 120°C temperature the highest dielectric constant 18.2 belongs to [DiEtEtIm][SCN] and the lowes, 5.6 to [DiEtEtIm][N(CN)$_2$].
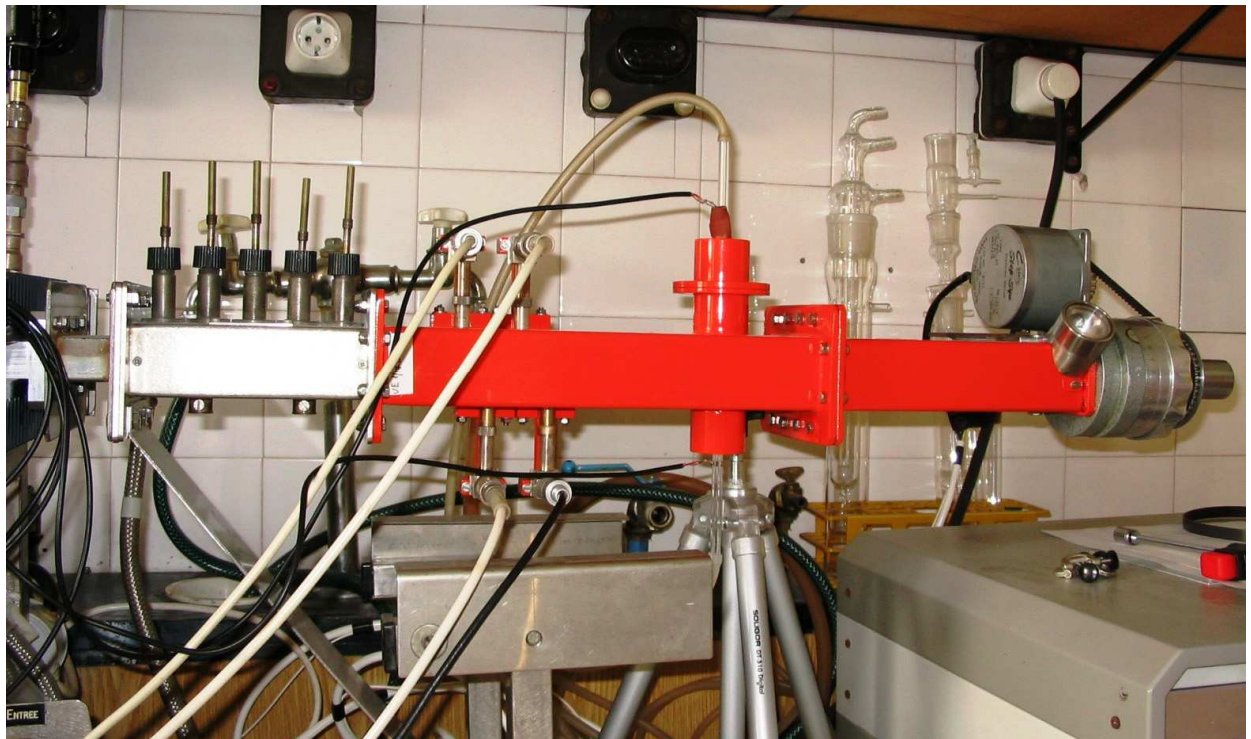

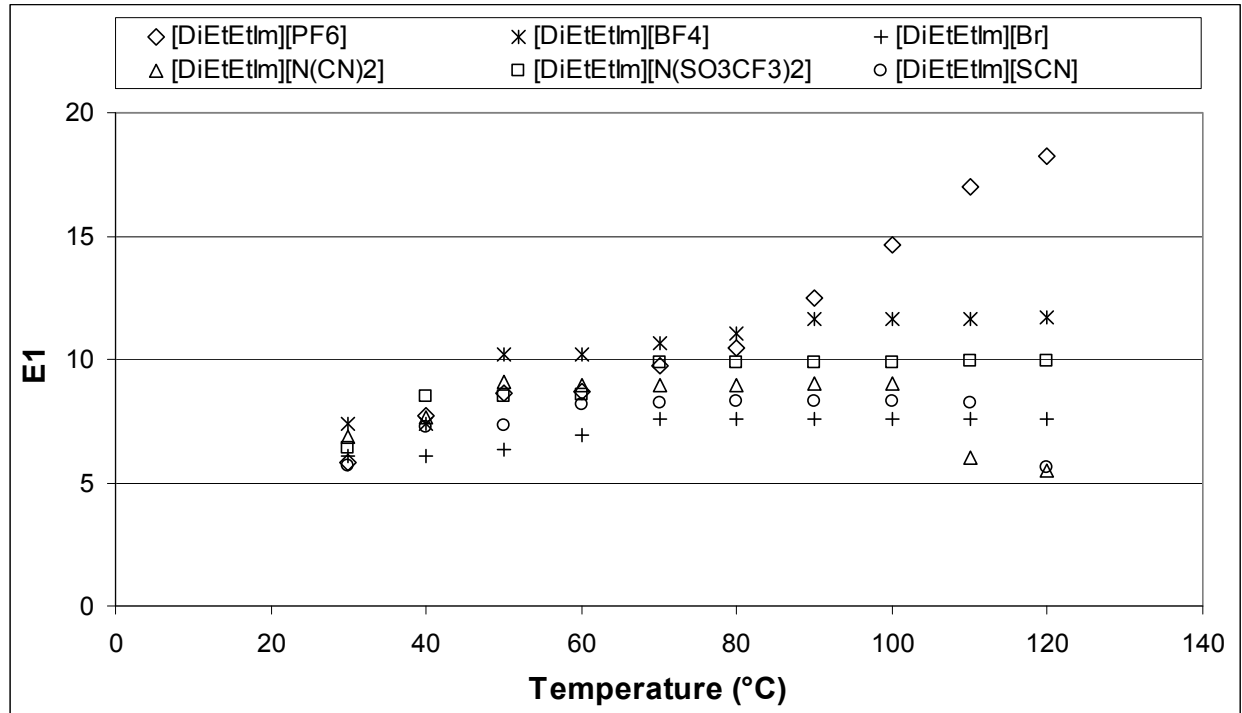Fig. 3. Picture of the microwave dielectrometric apparatus

Fig. 4. Dielectric constant of ILs containing common [DiEtEtIm] cation and different anions
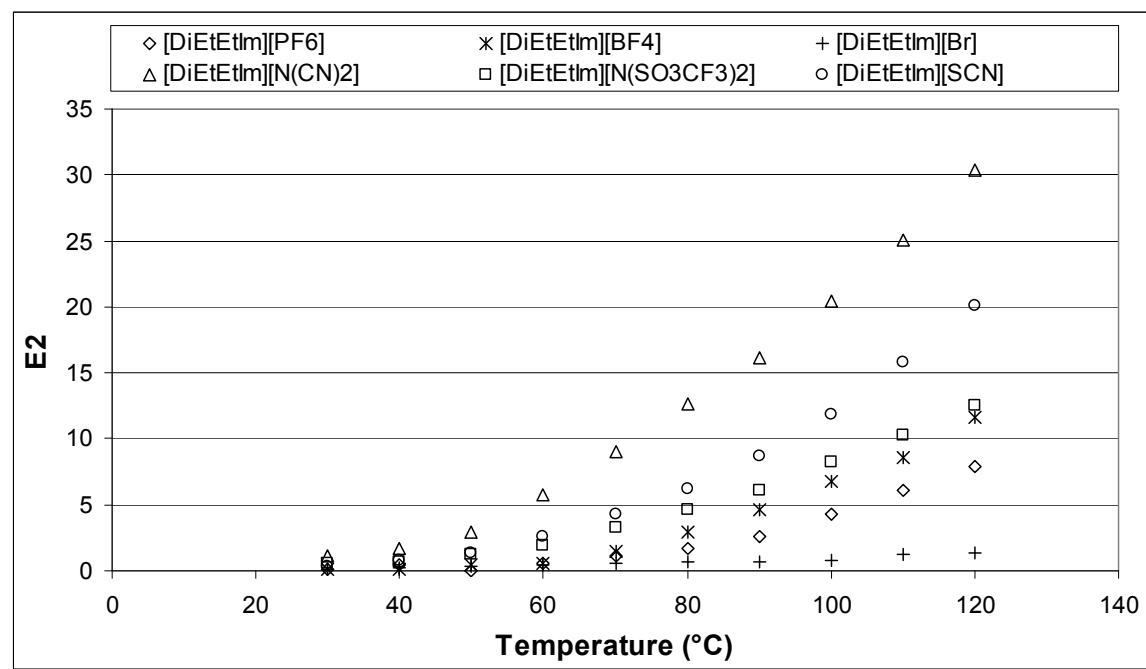
Fig. 5. Dielectric loss factor of ILs containing common [DiEtEtIm] cation and different anions

The dielectric loss values are almost the same and quite low for all six ILs at the temperature of 30°C. Except for the E_2 of [DiEtEtIm][Br], which reaches only the value of 2 at 120°C, the dielectric loss of the other five investigated ILs increase constantly with higher temperature. It is interesting to note that the highest E_2 value belongs to the [DiEtEtIm][N(CN)$_2$] IL, which has the lowest E_1 value.
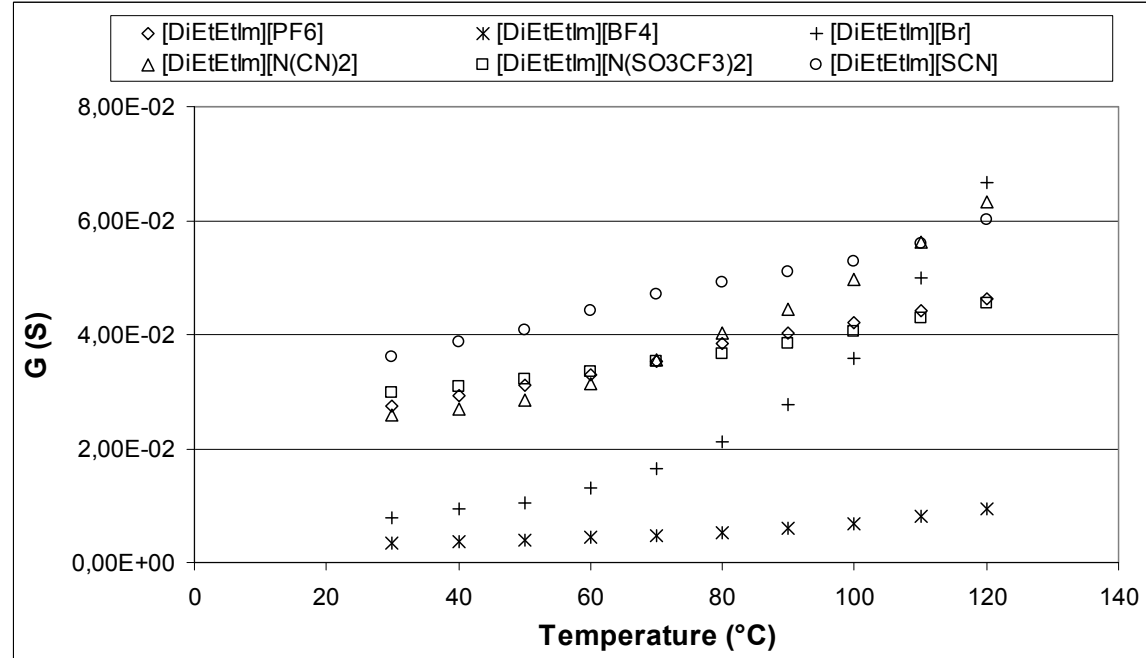
Fig. 6. Electrical conductivity of ILs containing common [DiEtEtIm] cation and different anions

At the initial 30°C temperature the lowest electric conductivity value of 3×10^{-3} S is exhibited by [DiEtEtIm][BF$_4$], followed by [DiEtEtIm][Br] with the value of 8×10^{-3} S and then the other three ILs around 3×10^{-2} S and finally by the [DiEtEtIm][SCN] with 3.8×10^{-2} S. The conductivity of [DiEtEtIm][Br] and [DiEtEtIm][PF$_6$] show a steep increase, while that of the other ILs indicate only a slight increase with the increase in temperature between 30°C and 120°C. The G values of [DiEtEtIm][PF$_6$], [DiEtEtIm][N(SO$_3$CF$_3$)$_2$], [DiEtEtIm][N(CN)$_2$] and [DiEtEtIm][SCN] are more than four times higher than that of water at the initial temperature and further increase at elevated temperatures. The [DiEtEtIm][BF$_4$] has extremely low conductivities, at the temperature range between 30°C and 120°C they hardly reach that of water. However, the conductivity values for [DiEtEtIm][Br] exceed that of water at elevated temperature, at the general operation temperature of batteries it shows extremely low values. Therefore neither of these ILs should be considered as candidates for elctrolytes.

It is worth noticing that the ILs containing the same cation and different anions have quite different E_1 values, and that their E_2 values become more distinct with the increase in temperature between the temperature range of 80°C and 120°C.

It can be concluded that there might be a connection between the dielectric constant, dielectric loss factor and electrical conductivity of the investigated ILs and the structure of the ILs but the connection is not yet correctly defineable and further experiments should be carried out in this field.

6.2 Effect of cation on the dielectric properties

The dielectric constant (E_1), dielectric loss factor (E_2) and electrical conductivity (G) values of ILs built up of the same [PF$_6$] anion and six different cations containing alkyl chains with different lengths ([DiEtMeIm], [DiEtEtIm], [DiEtPrIm] and [DiEtBuIm]) at different temperatures between 30°C and 120°C are shown in Figure 7, Figure 8 and Figure 9, respectively.

The dielectric constants for [DiEtEtIm][PF$_6$], [DiEtPrIm][PF$_6$] and [DiEtBuIm][PF$_6$] exhibit more or less the same values around 5 and that of [DiEtMeIm][PF$_6$] is four times higher at 30°C. With the increase in temperature the E_1 values of [DiEtMeIm][PF$_6$] and [DiEtEtIm][PF$_6$] successively increase, while in the case of [DiEtPrIm][PF$_6$] and [DiEtBuIm][PF$_6$] a sudden break can be noticed in the constant values between 50°C and 70°C. This might be associated with some sudden changes in the structure of the ILs or in the physicochemical interactions between the ions.

Similarly to the dielecetric constant, the highest dielectric loss of 4.3 belongs to [DiEtMeIm][PF$_6$], while the other ILs have more than four times lower E_2 values. With increasing temperature between the range of 30°C and 120°C the dielectric loss value of [DiEtMeIm][PF$_6$] shows a sharp increase, the values for [DiEtEtIm][PF$_6$] and [DiEtBuIm][PF$_6$] moderately increase and the increase of [DiEtPrIm][PF$_6$] E_2 value exhibits such a sudden change in the values between 100°C and 110°C as it is shown in the case of E_1.

The highest 2.9×10^{-2} S electrical conductivity value belongs to [DiEtMeIm][PF$_6$] followed by the 2.8×10^{-2} S of [DiEtBuIm][PF$_6$] then by the 4.4×10^{-2} S value for [DiEtPrIm][PF6] and finally by the 3.8×10^{-2} S for [DiEtBuIm][PF$_6$] at 30°C. The conductivity of the former two ILs sharply increase, while those of the latter two ILs show only a slight increase with increasing temperature.

It is worth noticing that the [DiEtMeIm][PF$_6$], which contains the shortest alkyl chain in its cation, exhibits the highest E_1, E_2 and G values, hence in the case of ILs containing the same

[PF$_6$] anion it can be stated that the cation has an effect on the dielectric constant and the dielectric loss factor of the investigated liquids. Furtehrmore it can be concluded that the [DiEtMeIm][PF$_6$] and [DiEtetIm][PF$_6$] ILs seem to be the most adequate for battery applications, however further investigation must be carried out.
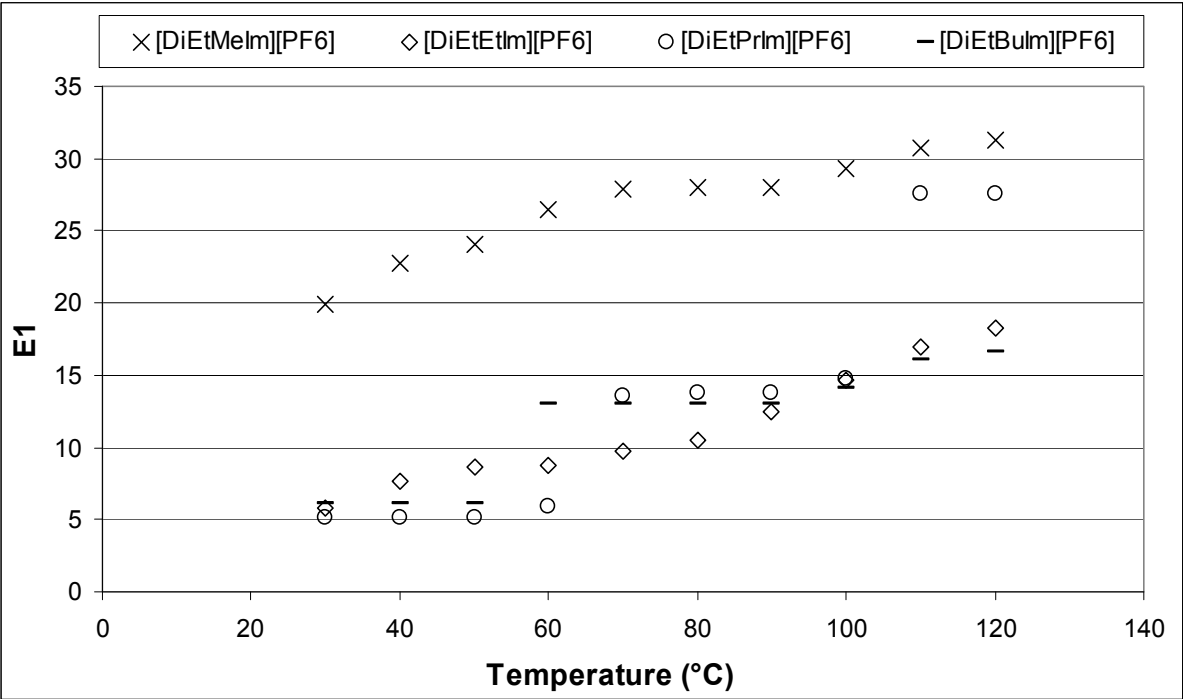

Fig. 7. Dielectric constant of ILs containing common [PF$_6$] anion and different cations
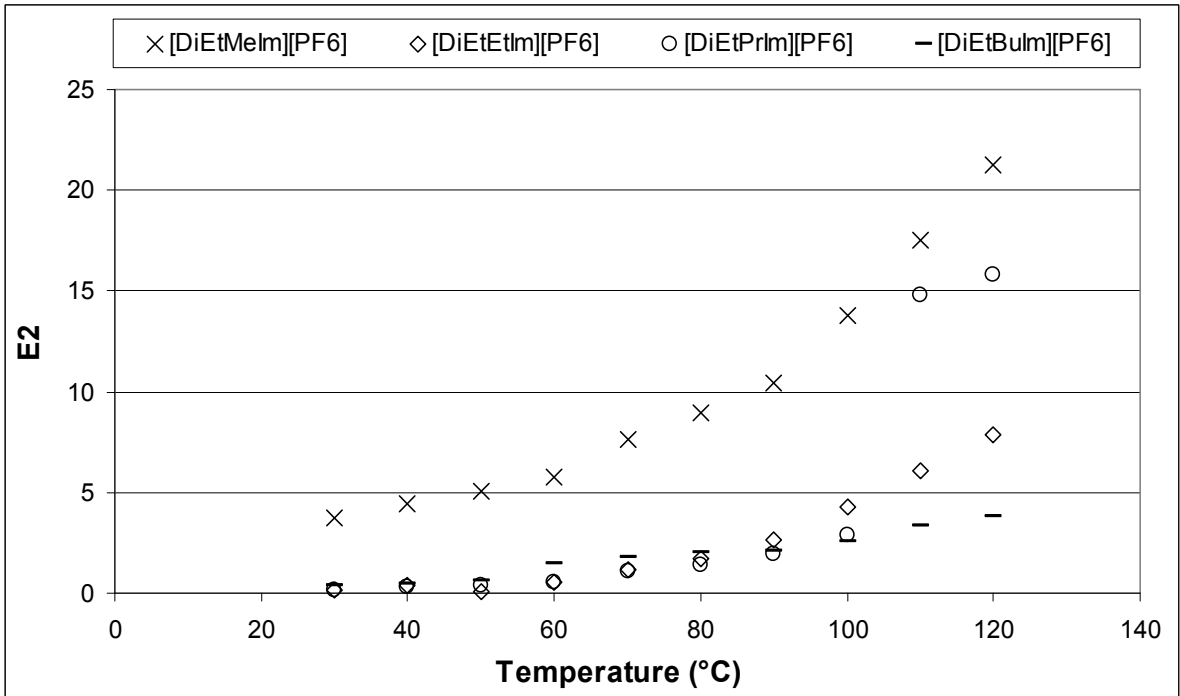

Fig. 8. Dielectric loss factor of ILs containing common [PF$_6$] anion and different cations
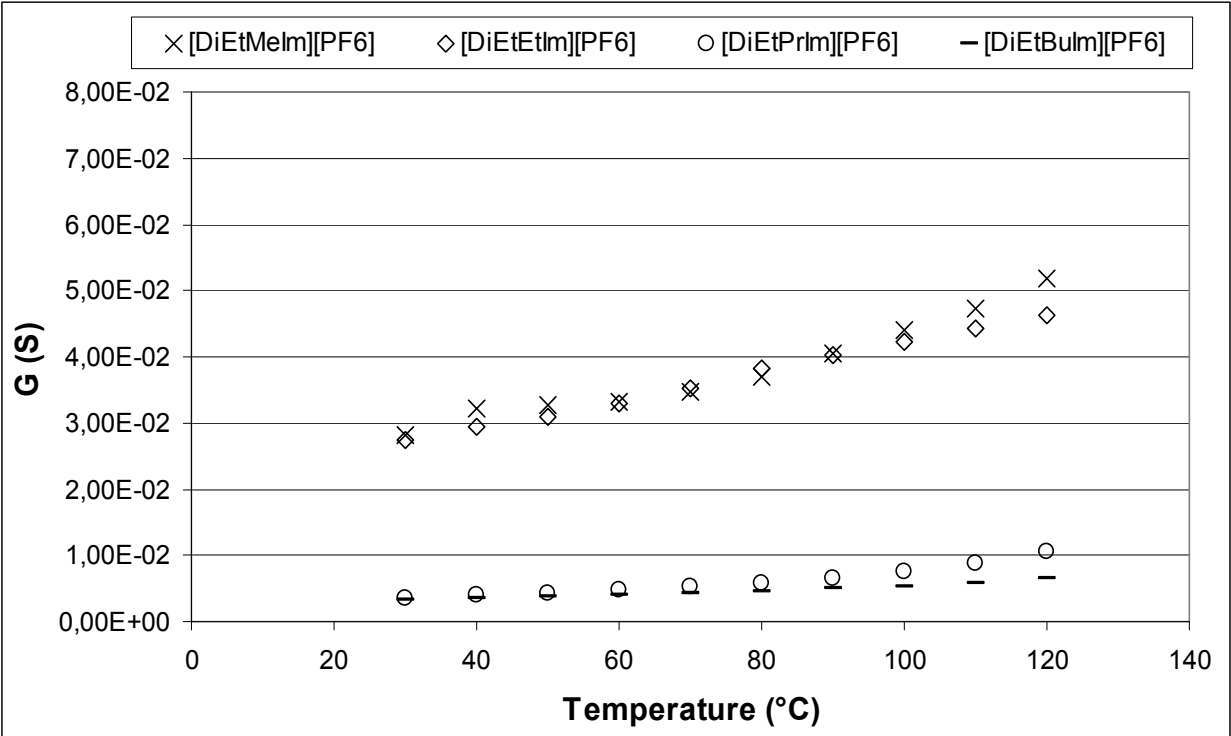
Fig. 9. Electrical conductivity of ILs containing common [PF$_6$] anion and different cations

The dielectric constant (E_1), dielectric loss factor (E_2) and electrical conductivity (G) values of ILs built up of the same [BF$_4$] anion and six previously described cations containing alkyl chains with different lengths ([DiEtMeIm], [DiEtEtIm], [DiEtPrIm] and [DiEtBuIm]) at different temperatures between 30°C and 120°C are shown in Figure 10, Figure 11 and Figure 12, respectively.

At the initial measuring temperature of 30°C all four of the studied ILs have similar dielectric constants around 7. With the increase in temperature the E_1 values for [DiEtMeIm][BF$_4$], [DiEtEtIm][BF$_4$] and [DiEtPrIm][BF$_4$] slightly increase up to 13, while the dielectric constant for [DiEtBuIm][BF$_4$] shows a sudden break at 90°C and at 120°C it reaches the value as high as 27. This could be explained with some sudden changes in the structure of the ILs or in the physicochemical interactions between the anion and the cation. Excluding the results for [DiEtBuIm][BF$_4$] the values at elevated temperature show that the highest E_1 value belongs to [DiEtMeIm][BF$_4$], followed by [DiEtEtIm][BF$_4$] and then by the [DiEtPrIm][BF$_4$], hence the dielectric constant increases with the decrease in the alkyl chain length of the cation.

It can be seen that all of the ILs have similar dielectric loss factor values at 30°C and sharply increase with the increase in temperature. Similar to E_1 the E_2 value of [DiEtBuIm][BF$_4$] shows a sudden change between the temperature range of 80°C and 90°C. At higher temperatures the highest dielectric loss factor of 19 belongs to [DiEtBuIm][BF$_4$], followed by [DiEtMeIm][BF$_4$], [DiEtEtIm][BF$_4$] and then by the [DiEtPrIm][BF$_4$]. Therefore it can be said that the longer the alkyl chain length in the IL cation, the highest the E_2 values are.

It is important to notice that the E_1 and E_2 values of ILs containing cation with longer alkyl chains tend to exhibit a sudden break and increase at elevated temperatures.
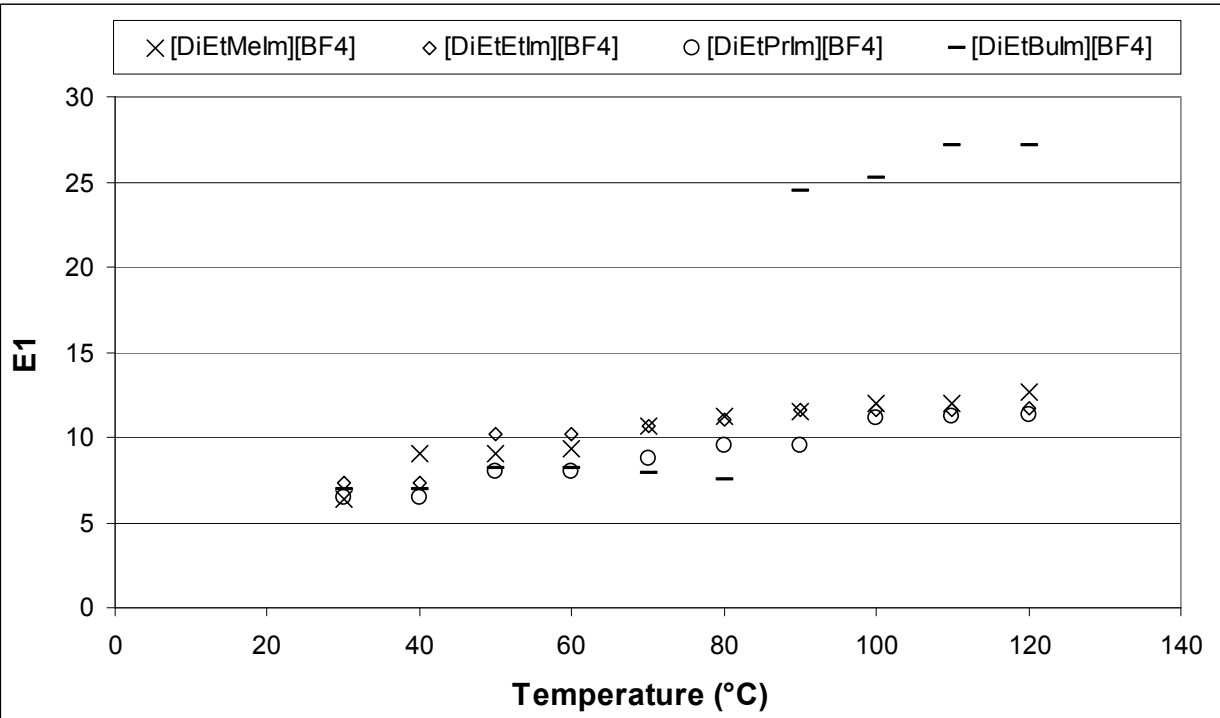
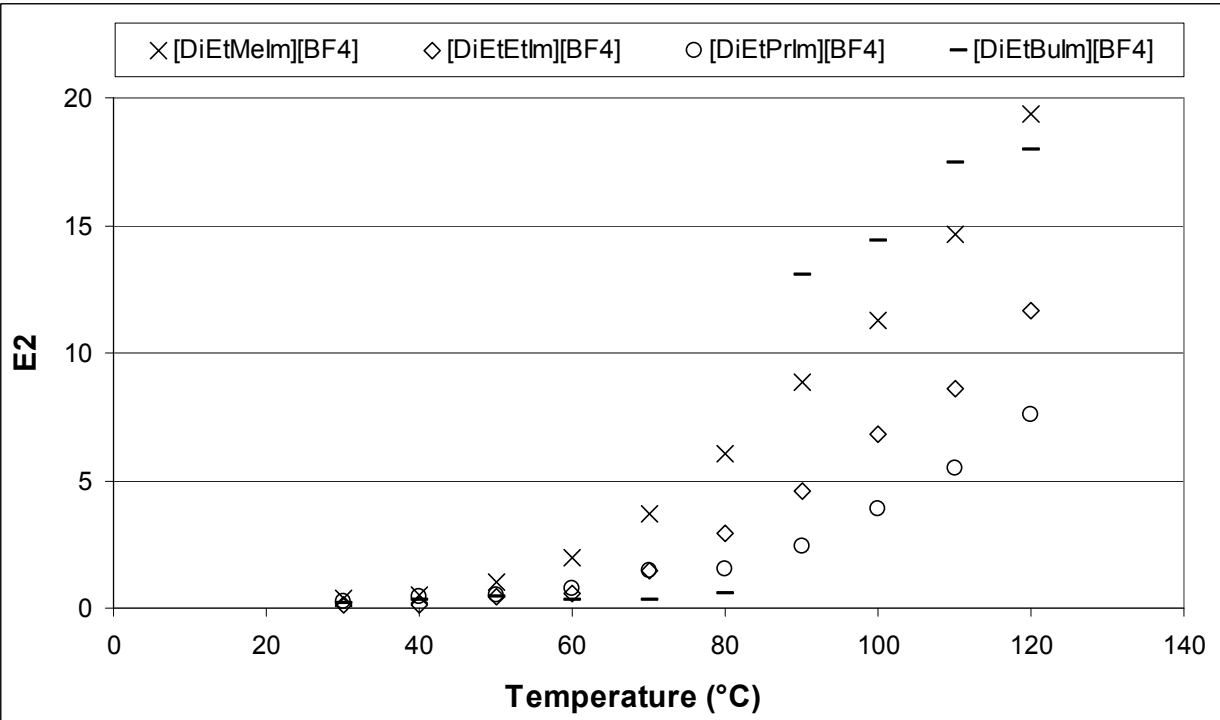Fig. 10. Dielectric constant of ILs containing common [BF₄] anion and different cations

Fig. 11. Dielectric loss factor of ILs containing common [BF₄] anion and different cations
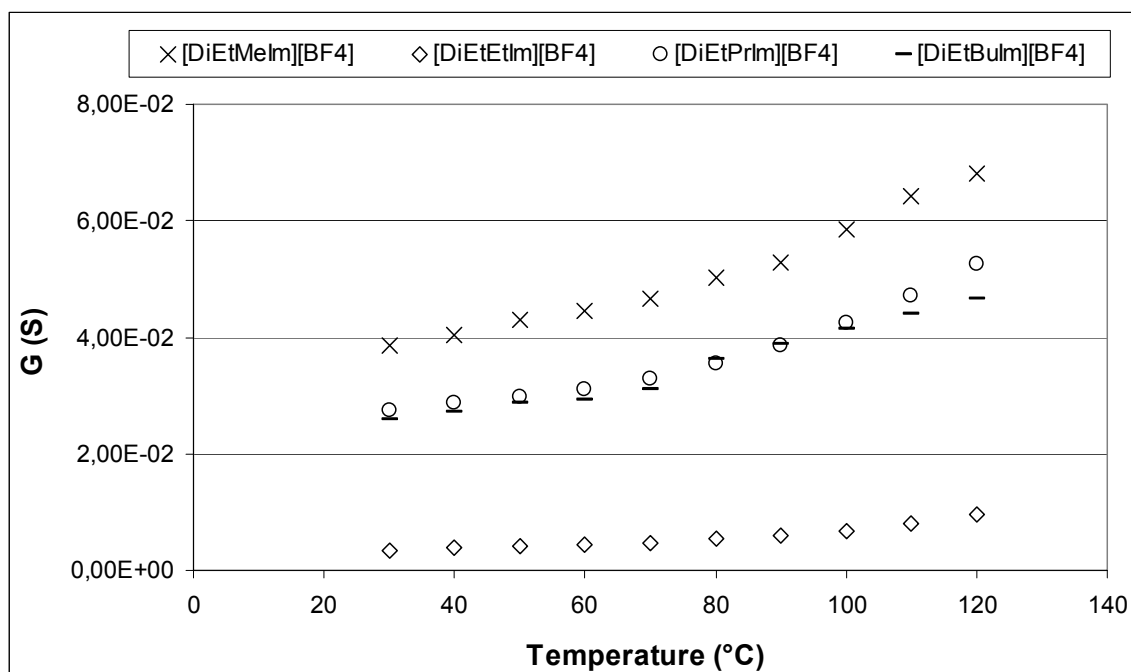
Fig. 12. Electrical conductivity of ILs containing common [BF$_4$] anion and different cations

The highest electrical conductivity of 3.94×10^{-2} S belongs to [DiEtMeIm][BF$_4$], the [DiEtPrIm][BF$_4$] and [DiEtBuIm][BF$_4$] ILs have the second highest G values of about 2.8×10^{-2} S and the lowest 3×10^{-3} S conductivity is exhibited by [DiEtEtIm][BF$_4$] at the temperature of 30°C. With the increase in temperature the electrical conductivity values of [DiEtEtIm][BF$_4$] moderately and those of the other three examined ILs sharply increase.

It is worth noticing that excluding the results of [DiEtEtIm][BF$_4$], which has a surprisingly low conductivity compared to the other three studied ILs, the *G* values increase along with the decrease in the alkyl chain length of the IL's cation. Therefore it can be stated that there might be a similar connection between the chemical structure of the cation and the dielectric properties of the ILs containing common [BF$_4$] anion as it has been shown for the ILs built up of the common [PF$_6$] anion.

Taking into account the dielectric constant, dielectric loss and electrical conductivity results of all the investigated ILs it can be concluded that the alkyl chain length of the cation and the structure of the anion strongly influence the dielectric properties of the ILs and that the highest *G* value is exhibited by the [DiEtMeIm][BF$_4$] IL at 30°C temperature, hence it is the most suitable candidate for battery applications. Furtermore it can be stated that implementing the knowledge about the connection between the IL structure and the dielectric properties another ILs should be studied in order to select the ones most adequate for electrolyte application.

7. Conclusion

Due to the special characteristics of ILs, such as wide electrochemical windows, high inherent conductivities, high thermal and electrochemical stability, tuneable physicochemical properties, etc., they might be excellent candidates for environmentally sound, green electrolites in batteries. In order to decide whether they could be successfully applied it is essential to gain information about their dielectric properties.

However, several techniques have already been published about determination of the dielectric properties of ILs, so far no measuring methods were introduced due to the fact that such measurements cannot be realized by classical methods because of the high conductivity of ILs.

In this chapter first a self-designed microwave dielectrometric apparatus and a novel method for the measurement of the dielectric properties of ILs were described, then the dielectric constant, dielectric loss factor and electrical conductivity of several ILs were measured. Furthermore the connections between the structure of the investigated ionic liquids and the dielectric characteristics were determined.

It was concluded that there was a certain connection between the structure of the investigated ILs and that this knowledge was worth implementing in studying further ILs that might be applied as novel, environmentally sound electrolytes.

8. Acknowledgement

9. References

Afsar, M.N., Birch, J.R., Clarke, R.N., Chantry, G.W. (1986). The measurement of properties of materials. *IEEE Transactions on Instrumentation and Measurement,* 74., 1., 183-199., 0018-9456

Alarco, P.J., Yaser, A.L., Ravet, N., Armand, M. (2004). Lithium conducting pyrazolium imides plastic crystals: a new solid state electrolyte matrix. *Solid State Ionics*, 172., 1-4., 53-56., 0167-2738

Arnold, C.B. Sutto, T.E. Kim, H.K. Pique, A. (2004). Direct-write laser processing for miniature electrochemical systems. *Laser Focus World*, 40., 5., 9-12., 1043-8092

Benenson, W., Harris, J.W., Stocker, H., Lutz, H. (2002). *Handbook of Physics*, Springer-Verlag New York, Inc., ISBN: 0-387-95269-1, New York, USA

Bright, F., Baker, G.A. (2006). Comment on "How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-based Ionic Liquid by Microwave Dielectric Spectroscopy". *The Journal of Physical Chemistry B*, 110., 11., 5822-5823., 1520-6106

Carrier, M., Soga, K. (1999). A four terminal measurement system for measuring the dielectric properties of clay at low frequencies. *Engineering Geology*, 53., 2., 115-123., 0013-7952

Charreyre, M., Thiebaut, J., Roussy, G. (1984). Permittivity measurement of materials during high-power microwave irradiation and processing. *Journal of Physics E: Scientific Instruments*, 17., 8., 678-682., 0022-3735

Diaw, M., Chagnes, A., Carré, B. Willmann, P., Lemordant, D. (2005). Mixed ionic liquid as electrolyte for lithium batteries. *Journal of Power Sources*, 146., 1-2., 682-684., 0378-7753

Ebara, H., Inoue, T., Hashimoto, O. (2006). Measurement method of complex permittivity and permeability for a powdered material using a waveguide in microwave band. *Science and Technology of Advanced Materials*, 7., 1., 77-83., 1468-6996

Endres, F., Abbott, A.P., MacFarlane, D.R. (2008). *Electrodeposition from Ionic Liquids*, Wiley-VCH Verlag GmbH & Co. KGaA, ISBN: 978-3-527-31565-9, Weinheim, Germany

Fleisch, D. (2008). *A Student's Guide to Maxwell's Equations*, Cambridge University Press, ISBN: 978-0-521-87761-9, Cambridge, UK

Forsyth, S., Golding, J., MacFarlane, D.R., Forsyth, M. (2001). N-methyl-N-alkylpyrrolidinium tetrafluoroborate salts: ionic solvents and solid electrolytes. *Electrochimica Acta*, 46., 10-11., 1753–1757., 0013-4686

Gardner, C.L., Anantaraman, A.V. (1995). Measurement of membrane conductivities using an open-ended coaxial probe. *Journal of Electroanalytical Chemistry*, 395., 1-2., 1995, 67-73., 1572-6657

Giroud, N.M., Rouault, H., Chainet, E., Poignet, J.C. (2008). Ionic liquids based electrolytes for lithium ion battery. *ECS Meeting Abstracts*, 802., 3044., 1091-8213

Göllei, A., Vass, A., Pallai, E., Gerzson, M., Ludányi, L., Mink, J. (2009). Apparatus and method to measure dielectric properties (ε′ and ε″) of ionic liquids. *Review of Scientific Instruments*, 80., 4., 0034-6748

Guo, W., Liu, Y., Zhu, X., Wang, S. (2011). Temperature-dependent dielectric properties of honey associated with dielectric heating. *Journal of Food Engineering*, 102., 3., 209-216., 0260-8774

Hagiwara, R., Ito, Y. (2000). Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *Journal of Fluorine Chemistry*, 105., 2., 221-227., 0022-1139

Håkansson, E, Amiet, A., Kaynak, A. (2007). Dielectric characterization of conducting textiles using free space transmission measurements: Accuracy and methods for improvement. *Synthetic Metals*, 157., 24., 1054-1063., 0379-6779

Heaviside, O. (2007). *Electromagnetic Theory, Volume I.*, Cosimo, Inc., ISBN: 978-1-60206-271-9, New York, USA

Heiken, G.H., Vaniman, D.T., French, B.M. (1991). *LUNAR sourcebook; a user's guide to the moon*, Press Syndicate of the University of Cambridge, ISBN: 0-521-33444-6, Melbourne, Australia

Housecroft, C.E., Sharpe, A.G. (2005) *Inorganic chemistry*, 2nd Edition, Pearson Education Limited, ISBN: 978-0-13-039913-7, Essex, England

Ito, K., Nishina, N., Ohno, H. (2000). Enhanced ion conduction in imidazolium-type molten salts. *Electrochimica Acta*, 45., 8-9., 1295–1298., 0013-4686

Koel, M. (2008). *Ionic liquids in Chemical Analysis*, CRC Press Taylor & Francis Group, ISBN: 1420046462, USA

Kozhevnikov, N.O. (2009). Applying the transmission line theory to study ungrounded horizontal loop self-transients. *Russian Geology and Geophysics*, 50., 3., 222-233., 1068-7971

Kraszewski, A.W. (1980). Microwave aquametry-A review. *Journal of Microwave Power and Electromagnetic Energy*, 15., 4., 209-220., 0832-7823

Krossing, I., Slattery, J.M., Daguenet, C., Dyson, P.J., Oleinikova, A., Weingartner, H. (2006). Why are ionic liquids liquid? A simple explanation based on lattice and

solvation energies. *Journal of the American Chemical Society*, 128., 41., 13427-13434., 0002-7863

Kumar A., Sharma, S. (2007). Measurement of dielectric constant and loss factor of the dielectric material at microwave frequencies. *Progress In Electromagnetics Research,* 69., 47-54., 1559-8985

Lee, K.-S., Lu, T.-M., Zhang, X.-C. (2003). The measurement of the dielectric and optical propertiesof nano thin films by THz differential time-domain spectroscopy. *Microelectronics Journal*, 34., 1., 63-69., 0026-2692

Marsh, K.N., Boxall, J.A., Lichtenthaler, A. (2004). Room temperature ionic liquids and their mixtures-a review. *Fluid Phase Equilibria*, 219., 1., 93-98., ISSN: 03783812

Mastumoto, H., Kageyama, H., Miyazaki, Y. (2001). Room temperature molten salts based on tetraalkylammonium cations and bis(trifluoromethylsulfonyl)imide. *Chemistry Letters*, 30., 2., 182-183., 0366-7022

Matsumoto, H., Sakaebe, H., Tatsumi, K. (2005). Preparation of room temperature ionic liquids based on aliphatic onium cations and asymmetric amide anions and their electrochemical properties as a lithium battery electrolyte. *Journal of Power Sources*, 146., 1-2., 45-50., 0378-7753

Matsumoto, H., Yanagida, M., Tanimoto, K., Kojima, K., Tamiya, Y., Miyazaki, Y. (2000). Highly conductive room temperature molten salts based on small trimethylalkylammonium cations and bis(trifluoromethylsulfonyl)imide. *Chemistry Letters*, 29., 8., 922., 0366-7022

Meredith, R. (1998). *Engineers' handbook of industrial microwave heating*, The Institution of Electrical Engineering, ISBN: 0 85296 916 3, London, United Kingdom

Mohos, F. (2010). *Confectionery and Chocolate Engineering; Principles and Applications*, John Wiley & Sons Ltd, ISBN: 978-1-4051-9470-9, West Sussex, United Kingdom

Murthy, V.R.K., Raman, R. (1989). A method for the evaluation of microwave dielectric and magnetic parameters using rectangular cavity perturbation technique. *Solid State Communication*, 70., 8., 847–850., 0038-1098

Mutelet, F., Jaubert, J.N. (2006). Accurate measurements of thermodynamic properties of solutes in ionic liquids using inverse gas chromatography. *Journal of Chromatography A* 1102., 1-2., 256-267., 00219673

Ohno, H. (2005). *Electrochemical Aspects of Ionic Liquids*, 2nd Ed., John Wiley and Sons, Inc., ISBN: 978-0-471-64851-2, Hoboken, New Jersey, USA

Plechkova, N.V., Seddon, K.R. (2008). Applications of ionic liquids in the chemical industry. *Chemical Society Reviews,* 37., 1., 123-150., 0306-0012

Roumeliotis, J.A., Kokkorakis, G.C. (1994). Resonant frequencies in an electromagnetic cylindrical/spherical cavity with an internal off-axis small dielectric sphere. *Electromagnetics*, 14, 195-215, 0272-6343

Sakaebe, H. Matsumoto, H. (2003) N-Methyl-N-propylpiperidinium bis (trifluoromethane-sulfonyl)imide (PP 13-TFSI) - novel electrolyte base for Li battery. *Electrochemistry Communications*, 5., 7., 594–598., 1388-2481

Sakaebe, H. Matsumoto, H., Tatsumi, K. (2005). Discharge–charge properties of Li/LiCoO$_2$ cell using room temperature ionic liquids (RTILs) based on quaternary ammonium

cation – Effect of the structure. *Journal of Power Sources*, 146., 1-2., 693-697., 0378-7753

Sakaebe, H., Matsumoto, H., Tatsumi, K. (2007). Application of room temperature ionic liquids to Li batteries. *Electrochimica Acta*, 53., 3., 1048-1054., 0013-4686

Saruwatari, H., Kuboki, T., Kishi, T., Mikoshiba, S., Takami, N. (2010). Imidazolium ionic liquids containing LiBOB electrolyte for lithium battery. *Journal of Power Sources*, 195., 5., 1495-1499., 0378-7753

Sato, T., Masuda, G., Takagi, K. (2004). Electrochemical properties of novel ionic liquids for electric double layer capacitor applications. *Electrochimica Acta*, 49., 21., 3603-3611., 0013-4686

Seddon, K.R. (2003). Ionic liquids: A taste of the future. *Nature Materials*, 2., 6., 363-365., 1476-1122

Sheen, J. (2009). Measurements of microwave dielectric properties by an amended cavity perturbation technique. *Measurement*, 42., 1., 57-61., 0263-2241

Sheen, N.I., Woodhead, I.M. (1999). An open-ended coaxial probe for broad-band permittivity measurement of agricultural products. *Journal of Agricultural Engineering Research*, 74., 2., 1999, 193-202. 0021-8634

Stathatos, E. Lianos, P. Jovanovski, V., Orel, B. (2005). Dye-sensitized photoelectrochemical solar cells based on nano-composite organic-inorganic materials. *Journal of Photochemistry and Photobiology A: Chemistry*, 169., 1., 57–61., 1010-6030

Stracke, M.P., Migliorini, M.V., Lissner, E., Schrekker, H.S., Dupont, J., Gonçalves, R.S. (2009). Imidazolium ionic liquids as electrolytes for manganese dioxide free Leclanché batteries. *Applied Energy*, 86., 9., 1512-1516., 0306-2619

Sutto, T.E., Duncan, T.T., Wong, T.C., McGrady, K. (2011). Ionic liquid batteries: Chemistry to replace alkaline/acid energy storage devices. *Electrochimica Acta*, 56., 9., 3375-3379., 0013-4686

Tong, C.H., Lentz, R.R. (1993). Dielectric properties of bentonite pastes as a function of temperature. *Journal Food Processing and Preservation*, 17., 2., 139-145., 0145-8892

Venkatesh, M.S., Raghavan, G.S.V. (2005). An overview of dielectric properties measuring techniques. *Canadian Biosystems Engineering*, 47., 7., 15-30., 1492-9058

Wakai, C., Oleinikova, A., Ott, M., Weingartner, H. (2005). How polar are ionic liquids? Determination of the static dielectric constant of imidazolium-based ionic liquid by microwave dielectric spectroscopy. *The Journal of Physical Chemistry B*, 109., 36., 17028-17030., 1520-6106

Wakai, C., Oleinikova, A., Weingartner, H. (2006). Reply to "Comment on "How polar are ionic liquids? Determination of the static dielectric constant of an imidazolium-based ionic liquid by microwave spectroscopy"". *The Journal of Physical Chemistry B*, 110., 11., 5824., 1520-6106

Wasserschied, P., Welton, T. (2007). *Ionic Liquids in Synthesis*, VCH–Wiley, ISBN: 978-3-527-31239-9, Weinheim, Germany

Welton, T. (1999). Room-temperature ionic liquids, solvents for synthesis and catalysis. *Chemical Reviews*, 99., 8., 2071-2083., 0009-2665

Wilkes, J.S., Levisky, J.A., Wilson, R.A., Hussey, C.L. (1982). Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for

electrochemistry, spectroscopy and synthesis. *Inorganic Chemistry*, 21., 3., 1263-1264., 0020-1669

Xiao, Y., Malhotra, S.V. (2005). Friedel-crafts acylation reactions in pyridinium based ionic liquids, *Journal of Organometallic Chemistry*, 690., 15., 3609-3613., 0022-328X

Xu, J., Yang, J., NuLi, Y., Wang, J., Zhang, Z. (2006). Additive-containing ionic liquid electrolytes for secondary lithium battery. *Journal of Power Sources* 160., 1., 621-626., 0378-7753
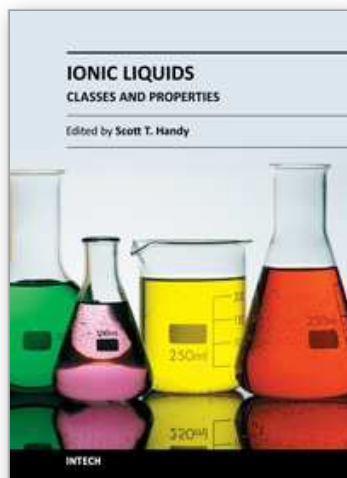
Ionic Liquids - Classes and Properties

Edited by Prof. Scott Handy

Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanimide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determinination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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