Dielectric Properties of Ionic Liquids

A Dissertation Submitted to the Faculty of Chemistry and Biochemistry, Ruhr University Bochum, for the degree of Dr.rer.nat.

By

Mianmian Huang

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To

My family
Acknowledgments

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Overview

Within the scope of this thesis frequency dependent dielectric relaxation spectroscopy between 0.3 MHz to 20 GHz has been used to characterize a number of ionic liquids.

Ionic liquids are receiving ever-increasing interest owing to their unique properties. As a new class of materials, ionic liquids are finding more and more applications in both industrial and scientific fields, as electrolytes, solvents, extraction media, co-catalysts etc. Due to their special structure ionic liquids are estimated to have $10^{18}$ different species and are regarded as potential novel solvents. More interesting is that ionic liquids can be tuned to suit different applications by changing their ion combinations. To predict the properties of ionic liquids, a systematic understanding of the interaction mechanisms between the ions is required. One of the most important properties of a solvent is polarity; a common scale of polarity relies on dielectric constant, which in case of ionic liquids can be measured by dielectric relaxation spectroscopy.

In the first chapter, ionic liquids are introduced. First, the history of ILs and some of their applications are summarized; after a brief description of the synthesis of ILs the main part of this chapter focus on their chemical and physical properties, including thermal properties, viscosity, self-diffusion coefficient, polarity and electrochemical properties.

Besides dielectric parameters, there are many other scales to describe solvent polarity. In the second chapter some of these methods, such as absorption and fluorescence spectroscopy, chromatography and electron paramagnetic resonance spectroscopy, are introduced, discussing the concepts and basic theoretical background.

The third chapter deals with the theory of dielectric relaxation. It begins with a description of materials in the static electric field, followed by a discussion of dielectrics in time dependent fields; finally different dielectric relaxation processes are introduced.

Details of experimental setups can be found in chapter four. Two dielectric spectrometers with different frequency ranges have been used. The components of the
measurement setups are introduced and the measurement technique is shortly described.

In the next chapter, results of dielectric relaxation spectroscopic measurements of ionic liquids are presented. First of all, the method to analyze the dielectric spectrum of ionic liquids is described in detail. Different series of ionic liquids have been measured, which are divided into aprotic ionic liquids, special anion based ionic liquids and protic ionic liquids. The dielectric relaxation parameters are evaluated, including static dielectric constant, dielectric relaxation strength and relaxation time. The results are discussed and comparisons with data from some other measurement techniques are made. Notably, some of the ionic liquids were purchased, whereas others were synthesized in the lab. The synthesis processes are described.

In the last chapter, the major results of the work are summarized and the future perspectives of the dielectric spectroscopy of ionic liquids are discussed.
Chapter 1  Introduction to Ionic Liquids

About 15 years ago, research on ionic liquids was a relatively unknown field of chemistry. In the years between 1986 and 1997 there were fewer than 25 papers on ionic liquids published each year. Since then, this field grows exponentially. There were more than 4000 papers on the topic published in 2009 and over 2000 in the first six months in 2010! So, what is an ionic liquid? And why does an ionic liquid exist? Nowadays the generally accepted definition of an ionic liquid (IL) is a salt with a low melting point, normally below the boiling point of water, typically close to room-temperature. For the classical salts, the melting points are much higher, e.g. for NaCl, which melts at 801°C. So the ionic liquids are “molten salts”, but there are many other synonyms used for ionic liquids, such as liquid organic salts, liquid electrolytes, ionic melts, ionic fluids (IF), fused salts (FS), liquid salts and ionic glasses.

![Fig.1.1 Common cations of ionic liquids. (1) 1-ethyl-3-methylimidazolium, (2) 1-butyl-3-methylimidazolium, (3) choline, (4) 2-hydroxyethylammonium, (5) 1-butylpyridinium, (6) 1-ethyl-1-methylpyrrolidinium.](image-url)
**Fig. 1.2** Common anions of ionic liquids. (1) hexafluorophosphate, (2) tetrafluoroborate, (3) bis(trifluoromethylsulfonyl)imide, (4) triflate, (5) nitrate, (6) formate, (7) thiocyanate.

As salts ionic liquids consist only of ions, mostly of an organic cation and an inorganic polyatomic anion. Some common component ions are listed in Fig.1.1-1.2. Since there are many known cations and anions, the potential number of ionic liquids is huge. Besides, the physical and chemical properties of different compositions vary tremendously. However, there is so far not yet a well established fundamental understanding of the relationships between the structure and property of ionic liquids. Thus, the determinations of their physical and chemical properties are mandatory.
1.1 History

Ionic liquids can be viewed as materials with a long history. The first ionic liquid reported in the literature was ethanol-ammonium nitrate with a melting point of 52-55 °C, which was synthesized by S. Gabriel and J. Weiner in 1888 [Gabriel, 1888 #1]. One of the earliest truly room temperature ionic liquids was ethyl-ammonium nitrate with the melting point of 12 °C, synthesized in 1914 by Paul Walden [Walden, 1914 #2]. Another key step in ionic liquid research was the work of J. Yoke at Oregon State University in 1960s. He found that solid copper(I) chloride and alkyl ammonium chloride formed a liquid at room temperature when they were mixed together [Yoke, 1963 #3]. In the 1970s Jerry Atwood and his group at the University of Alabama discovered and characterized a series of unusual compounds, which were denoted as liquid clathrates. These compounds are composed of a salt with an aluminium alkyl compound and one or more aromatic molecules. They are now recognized as ionic liquids, but not strictly because of the aromatic molecules [J.D.Atwood, 1976 #4; L.Atwood, 4 496 744`, 1981 #5]. All these works form the very first story of ionic liquids, but none of these materials was direct related to the presently used generation of ionic liquids.

The impetus of the present developments was the problem of using high temperature molten salts in the thermal batteries. Some 40 years ago, these traditional chloroaluminate molten salts, such as LiCl or KCl mixed with AlCl₃, were called ‘low temperature molten salts’. They were used as electrolytes and were heated by pyrotechnic procedures, when the batteries were activated. With a temperature of 375-550°C, these batteries were just too hot to handle. To develop a molten salt electrolyte operated at a much lower temperature was the goal of an Air Force Academy group in the 1960s and 1970s. Lowell A. King chose the little-known alkali chloride-aluminium chloride system [John, 2002 #6].

In 1978, the chemical and physical properties of a 1-butylpyridinium chloride-aluminium chloride mixture (BPC-AlCl₃) were measured and published [R.J.Gale, 1978 #7; J.C.Nardi, 4 122 245`, 1978 #8], which is marked as a start of the modern era of ionic liquids, because for the first time a wider audience of chemists started to take interest in these totally ionic, completely nonaqueous new solvents [John, 2002 #6; Peter, 2008 #9]. However, BPC-AlCl₃ is not a room-temperature liquid (Mp. 40°C) and the alkylpyridinium cation is relatively easy to reduce [John, 2002 #6]. More attractive candidates are dialkylimidazolium
salts. Over the time, the chemical and physical properties of these chloroaluminate ionic liquid were determined and also some of the applications as solvent and catalyst were discovered [Fannin, 1984 #10; Fannin, 1984 #11; Boon, 1986 #12]. As a disadvantage, these ionic liquids are reactive with water, and thus, they can only be handled inside the glove box. In the 1990s, a numbers of ionic liquids based on imidazolium cations and different anions such as tetrafluoroborate, hexafluorophosphate, nitrate were developed, which were more stable towards hydrolysis [J.S.Wilkers, 1992 #13; Carlin, 1996 #14]. These developments are the beginning of the booming current research on ionic liquids.

The research on ionic liquids now develops in many directions: from the ionic liquids which consist of halogen containing anions such as [AlCl₄]⁻, [PF₆]⁻, [BF₄]⁻ or [TfO]⁻ and imidazolium or pyridinium cations to halogen-free ionic liquids [Wasserscheid, 2002 #15]; from pure ionic liquids to IL-based mixed solvents, both aqueous or non-aqueous [Heintz, 2005 #16]; from aprotic ionic liquids to protic ionic liquids [Belieres, 2007 #17]; from laboratory to industry.

1.2 Applications

Ionic liquids are finding more and more applications in both scientific and industrial areas. Here are just some examples.

Back to the 1980s, the ionic liquids were developed as a new class of electrolytes in thermal batteries [Wilkes, 1982 #18]. In 2009 the U.S. Department of Energy awarded a 5,13-million-dollar research grant toward development of a metal-air battery using ionic liquids, replacing aqueous solutions as an electrolyte. This metal-air ionic liquid battery is supposed to have up to 11 times the energy density of the best lithium-ion technologies whereas the costs reduce to less than one-third [2009 #19].

The first industrial application of an ionic liquid was the BASIL (Biphasic Acid Scavenging utilizing Ionic Liquid) process, which was developed by BASF in 2003. This process is used for the synthesis of alkoxyphenylphosphines. During the synthesis the HCl is formed as a by-product. The conventional way to scavenge this acid is to use tertiary amine to form solid salts, which lead to a suspension of the reaction mixture. Unlike in the laboratory, it is expensive and time-consuming on the industrial scale to extract the desired product from this suspension. In the BASIL process, the ionic liquid
precursor is used as base, which forms an ionic liquid as a second phase after the reaction with HCl, so that the separation becomes easy. With this process the space/time yield of the reaction has been increased by a factor of 80,000 to 690,000 kg m$^{-3}$h$^{-1}$.

Ionic liquids are well known as “green solvents” mainly because of their low vapor pressures. Instead of traditional organic solvents or extraction media, the use of ionic liquids largely reduces the loss of solvent caused by evaporation, so that the resulting environmental damages can be avoided. More important, ionic liquids are able to act as co-catalysts in organic synthesis, which not only offer new opportunities to perform known reactions, but even meet specific synthesis needs with tailored ionic liquids. Aqueous/organic systems have been used to the hydrogenation and hydroformylation of unsaturated substrates catalyzed by transition-metal complexes, but the reaction rate was too low. Compared to these systems, ionic liquids are able to dissolve organic substrates and they provide a polar but weakly coordinating medium for transition-metal-catalysts that are stable in water. Using ionic liquid the reaction rates and selectivities could be enhanced [Chauvin, 1996 #20; Carmichael, 1999 #21].

Besides the transition-metal-mediated catalysis there are many other organic reactions, which employ ionic liquids. By using ionic liquids as polar media in the scandium triflate catalyzed Diels-Alder reaction one can facilitate the catalyst recovery and increase the reaction rate and selectivity [Song, 2001 #22]. It has been demonstrated that some of the Friedel-Crafts reactions like acylations and sulfonylations can be carried out in ionic liquids with the best regioselectivities and rates [Adams, 1998 #23; Nara, 2001 #24]. In the three-component Mannich reactions of aldehydes, amines, and ketones, acidic ionic liquids were successfully used as solvents and catalysts, so that higher yields were obtained [Zhao, 2004 #25].

Since the late 1990s, ionic liquids have been applied in the electrodeposition of metals [Zhao, 1997 #26]. Ionic liquids have high solubility of metal salts and are able to electrodeposit metals which are impossible to reduce in aqueous solutions; furthermore, they can be used to engineer redox chemistry and control the metal nucleation characteristics [Andrew P., 2006 #27]. Ionic liquids have been used as media in the synthesis of nanoparticles [Mudring, 2009 #28], both metallic [Dupont, 2002 #29] and as semiconductors [Endres, 2002 #30] exploiting their wide electrochemical windows and high polarities. Besides, the low interfacial tensions of ionic liquids render high nucleation rates and small nanostructures possible; most important, some of the ionic liquids form extended H-
bonded systems, and these highly structured liquids have a strong effect on the morphology of the nanoscale structures.

Currently, ionic liquids are widely applied in most sub-disciplines of analytical chemistry, including extraction[Li, 2009 #31], gas chromatography[Yao, 2009 #32], liquid chromatography and capillary electrophoresis[Berthod, 2008 #33], sensors[A.Kamio, 2008 #34], and as matrixes in MALDI mass spectrometry[I.A.Crank; D.W.Armstrong, 2009 #35] or as pairing reagents in ESI-MS[R.J.Soukup-Hein, 2007 #36].

In polymer science, ionic liquids are used as plasticizers and solvents for polymerization processes and as key components in new classes of polymer gels[Lu, 2009 #37]. Supercapacitors are energy storage and conversion systems of high power for many applications. Equipped with ionic liquids as solvent-free electrolytes, safe high-energy supercapacitors can prevent from sacrificing power capability and cycling stability[Mastragostino, 2009 #38].

Because of their unusual solvation characteristics, ionic liquids are proposed to be unique solvents for biomolecules such as proteins. They are used as media for biocatalytic reactions[Peter, 2008 #9], biosensors[Ohno, 2003 #39], protein stabilization[Baker, 2004 #40; Constantinescu, 2009 #41] and biopreservation[Majewski, 2003 #42]. In biomedicine, ionic liquids are considered to have potential to advance formulation science for protein-based pharmaceutical preparations and cellular therapies[Gloria, 2009 #43].

Other applications of ionic liquids include robust electrolytes for photoelectrochemical cells, such as dye-sensitized solar cell[Grätzel, 2009 #44]. In another interesting application the ionic liquid is coated with colloidal silver particles to become a highly reflective material that could be used as a liquid mirror of a space telescope[Soukup-Hein, 2007 #45].

More applications and recent research on the development of ionic liquids can be found in the book of “Ionic Liquids in Synthesis”, “Ionic Liquids: From Knowledge to Application” and “An Introduction to Ionic Liquids”.[Peter, 2008 #9][Plechkova, 2009 #168][Freemantle, 2010 #169]

### 1.3 Synthesis

The preparation of ILs presents no significant difficulties, even in large quantities. For non-protic ILs, the synthesis requires generally two steps: the alkylation of a tertiary amine by alkyl halide, followed by the exchange of the halide anion with the
corresponding anion to get the desired product [Mickiko Hirao, 2000 #46]. Protic ionic liquids are formed by proton transfer between a Brønsted acid and a Brønsted base through the acid-base neutralization reaction [Angell, 2007 #47]. Since the presence of certain impurities can lead to a radical change of the chemophysical properties, the purification of ionic liquids is always an important part of the synthesis. The impurities can be the compounds originating from starting materials through oxidation or thermal degradation, the unreacted starting materials, halide impurities, acidic impurities, and water, which is the most common impurity in ILs, even in hydrophobic ones. [Peter, 2008 #9]

To minimize the impurities, there are some options. First, the use of clean materials, which means all the starting materials should be purified before synthesis; second, the reaction should be carried out under inert gas such as nitrogen; third, the reaction temperature should be kept as low as possible, especially for the acid-base neutralization; finally, one has to dry the ILs after the synthesis, e.g. over a week in cold trap with vacuum pump, and before the direct use, normally at 70°C in vacuum for 48 hours.

1.4 Chemical and physical properties

Ionic liquids are receiving more and more interest because of their unique properties. Based on these properties, a multitude of applications is being developed. Although ionic liquids are applied in many fields and considered to be very potential to meet the special needs for different projects, the lack of systematic and mechanistic understanding of the properties is a bottleneck for progress. However, the research on ionic liquids is still in the early stage, and for the most common used ionic liquids, some properties are now widely examined.
1.4.1 Thermal properties

1.4.1.1 Measurement technique

The most common techniques which are used to measure the thermal properties of a material are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC measures the difference of heat, which is required to increase the temperature of a sample and a reference as a function of temperature. Using this technique, phase transitions such as fusion, crystallization and the glass transition can be observed. The principle of this technique is that, for phase transitions, the sample and different amounts of heat will be needed to establish the same temperature, more by exothermic process such as fusion, less by endothermic process such as crystallization. An alternative to DSC is differential thermal analysis (DTA), in which same heat flow is enforced instead the same end temperature. Similar information is provided by both DSC and DTA.

TGA measures the changes in weight of sample in relation to temperature. It is widely used to determine the degradation, absorbed moisture content, and the decomposition points.

It is always beneficial to combine both techniques, DSC and TGA, to get the thermal information about materials, and interpretation of the results is easier.

1.4.1.2 Melting, Crystallization and glass-transition temperatures

The thermal behaviors of ILs are complex and can be largely different. ILs have by definition a melting point below 100°C; actually they cover a broad range of melting temperature, from below room temperature to above 100°C. The combination of Volume Based Thermodynamics (VBT) and quantum chemical calculations can be used for understanding of the low melting points of ILs compared to classical salts[Ingo Krossing, 2007 #48; Weingärtner, 2008 #49]. At the melting temperature, the Gibbs free energy of fusion Δ\text{fus}G_m is zero; for a given temperature, the sign of Δ\text{fus}G_m indicates the favored state: positive for solid and negative for liquid. The Born-Fajans-Haber cycle provides basic insights into the processes that control the phase transition. Δ\text{fus}G_m equals the sum of the Gibbs
energy of lattice $\Delta_{\text{latt}} G_m$ and the Gibbs energies of solvation of cation and anion, $\Delta_{\text{solv}} G_m(A^+)$ and $\Delta_{\text{solv}} G_m(X^-)$ in the IL. At room temperature negative $\Delta_{\text{fus}} G_m$ result from small lattice enthalpies and large entropy changes, indicate that the favored liquid state comes from large size and conformational flexibility of the ions.

Many factors have been discussed that influence the melting points [H. Ohno, 2002 #50; Urszula Domanska, 2005 #51; H. Ohne, 2004 #52; Dzyuba, 2002 #53] of ILs. The dominant force in ILs is the Columbic attraction between ions. The lattice energy of ionic solids depends on the product of net ion charges, the ion-ion separation and the packing efficiency of the ions. Change in size, shape and character of the component ions influences the melting temperature. Generally, large ions tend to lower the melting points, e.g. for [EtMelm]X- $T_m$ decreases in the series [Cl-]>[NO₃-]>[BF₄-]>[Tf₂N]- [H. Ohno, 2006 #54] and for tetraalkylammonium bromide salts, $T_m$ decreases with increasing cation size [Peter, 2008 #9]. Also the shape of the ions is important: increasing the symmetry of the ions or changing from planar ions to spherical ions increases $T_m$ by enabling more efficient ion-ion packing in the crystal cell, which, for example, renders $T_m$ of imidazolium salts lower than of tetraalkylammonium salts. For the imidazolium ionic liquids with alkyl chains [CₙMeI₄]$, T_m$ decreases with increasing chain length for 4<n<12; for n>12, $T_m$ starts to increase with increasing chain length and the phase diagrams become complicated.

**Fig. 1.4.1** Born-Fajans-Haber cycle in solid (s), liquid (l) and gaseous (g) states for calculating $\Delta_{\text{fus}} G_m$.

The cold crystallization temperature is defined as the onset of an exothermic peak on heating from a supercooled liquid state to a crystalline solid state. Typically the actual
crystallization temperatures of ILs are 30-60K lower than equilibrium melting points, which indicates a slow crystallization rate and a fairly stable supercooled state\cite{Tokuda,2004}. For the ILs with low melting points, the crystallization is not very favoured because of the low lattice energy mentioned above. Instead cooling ILs from the liquid state to a low temperature causes glass formation, which preferably happens by rapid cooling. The glass transition is indicative of the cohesive energy within the IL, which is decreased by repulsive Pauli forces and increased by the attractive Coulomb and van der Waals interactions\cite{Xu,2003}. Through the modification of the cation and anion component can usually influence the glass temperature like melting point. For most of the ILs, the glass temperatures are very low, varies from -20 to -120°C.

Concern about the phase transition, three types of the behavior could be summarized. First kind of ILs have distinct freezing point on cooling and melting point on heating; crystallize with no glass formation, e.g. [BuMeIm][TfO]. The second kind of ILs has no true phase transitions. On cooling there only forms an amorphous glass, upon heating the liquid is recovered, and there is no well-defined melting point or freezing point, e.g. in [BuMeIm][Br]. The third group of ILs form glasses by supercooling and crystallize by heating, followed by a melting transition, e.g. [BuMeIm][PF₆]. \cite{Fredlake,2004}

**1.4.1.3 Decomposition Temperature**

To determine the thermal stabilities of ILs thermogravimetric analysis (TGA) can be used. Very little weight loss before decomposition confirms the negligible vapour pressures of ILs, which facilitates their handling as solvents and forms one of the basic requirements for the “green” nature. Traditional molten salts form tight ion pairs in the vapour phase; in contrast, the ion pair formation in the ILs is energetically restricted because of the reduced Columbic interactions, which leads to low vapour pressures of ILs. Therefore the decomposition temperatures of ILs are usually related to the upper limit of their liquid range.

A lot of decomposition temperatures $T_d$ of ILs were determined\cite{Kosmulski,2003,Ngo,2000,Drummond,2008}, usually up to 500°C. Table 1.4.1 lists decomposition temperatures of some ILs. In fact, thermal decomposition is strongly dependent on the structure of ILs and varies with different cation-anion combination. Generally it can be concluded:
i) Compared to ammonium cations the imidazolium cations tend to be thermally more stable, e.g. $T_d$ of [BuMeIm][BF$_4$] is 403°C, whereas $T_d$ of [BuMeNH$_2$][BF$_4$] is 350°C and $T_d$ of [tert-BuNH$_3$][BF$_4$] is 243°C;

ii) The thermal stability of the imidazolium salts increases with increasing linear alkyl substitution;

iii) Variation of the anion types follow the relative stabilities: [PF$_6$]$^-$ > [Tf$_2$N]$^-$ > [BF$_4$]$^-$ > [Br]$^-$ > [Cl]$^-$, e.g. $T_d$ of [EtMeIm][Br] is 311°C and $T_d$ of [EtMeIm][Cl] is 281°C;

iv) Protonic ILs have generally lower $T_d$ than non-protonic ILs because of the shifts in the proton transfer equilibrium between the salt form and acid/base pairs, e.g. [BuMeIm][Tf$_2$N] with 423°C and [BuNH$_3$][Tf$_2$N] with 352°C. $T_d$ of tributylammonium nitrate is even as low as 120°C.

**Table 1.4.1** Decomposition temperatures of some ILs. [Huddleston, 2001 #62; Belieres, 2007 #17; Fernicola, 2006 #63; Ngo, 2000 #64; Poole, 2004 #65; H. Tokuda, 2004 #55]

<table>
<thead>
<tr>
<th>IL</th>
<th>$T_d$/°C</th>
<th>IL</th>
<th>$T_d$/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuMeIm][Tf$_2$N]</td>
<td>423</td>
<td>[BuNH$_3$][Tf$_2$N]</td>
<td>352</td>
</tr>
<tr>
<td>[BuMeIm][TfO]</td>
<td>409</td>
<td>[tert-BuNH$_3$][TfO]</td>
<td>243</td>
</tr>
<tr>
<td>[BuMeIm][BF$_4$]</td>
<td>403</td>
<td>[BuMeNH$_2$][BF$_4$]</td>
<td>350</td>
</tr>
<tr>
<td>[Im][BF$_4$]</td>
<td>363</td>
<td>[NH$_4$][TfO]</td>
<td>225</td>
</tr>
<tr>
<td>[BuMeIm][PF$_6$]</td>
<td>433</td>
<td>[BuNH$_3$][BF$_4$]</td>
<td>310</td>
</tr>
<tr>
<td>[EtMeIm][Br]</td>
<td>311</td>
<td>[Bu$_3$NH][NO$_3$]</td>
<td>120</td>
</tr>
<tr>
<td>[EtMeIm][Cl]</td>
<td>281</td>
<td>[HOEtNH$_3$][HCO$_2$]</td>
<td>150</td>
</tr>
</tbody>
</table>
1.4.2 Viscosity and self-diffusion coefficient

Fluids resist the relative motion of immersed objects as well as to the motion of layers with differing velocities within them. Viscosity is the internal property of a fluid that describes resistance to flow. There are two quantities that are called viscosity: the dynamic viscosity ($\eta$) is expressed in SI units of Pascal second ($Pa\cdot s$) or in the older cgs system in poise ($P$) ($1P = 0.1Pa\cdot s$). By contrast the kinematic viscosity ($\nu$) is expressed in the SI systems in terms of $m^2/s$ or in the cgs systems in terms of Stokes ($St$) ($1 St = 10^{-4} m^2\cdot s^{-1}$). The relationship between dynamic viscosity ($\eta$) and kinematic viscosity ($\nu$) and density ($\rho$) is as follows:

$$\nu = \frac{\eta}{\rho} \quad (1.4.1)$$

Formally, the viscosity is the ratio of the shearing stress, which is the pressure exerted on the surface of a fluid in the lateral or horizontal direction, to the velocity gradient in a fluid. For straight, parallel and uniform flow, the shear stress between layers is proportional to the velocity gradient in the vertical direction to the layers; the constant of proportionality is the fluid viscosity. The fluids with this kind of behaviour are called Newtonian fluid (named after Isaac Newton). By contrast, non-Newtonian fluids have a more complicated relationship between shear stress and velocity gradient than simple linearity. Many fluids are Newtonian type, such as water, hydrocarbons and oils; fluids like polymer solutions, blood, and ketchup are non-Newtonian. The popular ILs are recognized as Newtonian fluids, and there are no data so far for non-Newtonian ILs.

1.4.2.1 Measurement methods

There are three major measurement methods to determine the viscosity of ILs based on falling balls, capillary flow and rotational techniques. The construction of a falling ball viscometer can be easily described as a vertical glass tube and a ball with known size and density. In the measurement the ILs to be examined are filled into the glass tube and stay stationary in the tube; the ball is dropped carefully through the IL. With a correct selection, the ball reaches its terminal velocity, which can be measured by the time it
takes to pass two marks on the tube. Using Stroke’s Law the dynamic viscosity of IL can be calculated:

$$\eta = \left( \frac{2}{9} \right) \left( \frac{\rho_s - \rho}{v} \right) g R^2$$

(1.4.2)

$\rho_s$ is the density of the ball, $\rho$ is the density of the IL, $g$ is the gravity constant, $R$ is the radius of the ball, $v$ is the terminal velocity of the ball. Commonly, the falling ball viscometer is calibrated with a standard fluid which has a similar viscosity to the IL of interest to get an instrument constant $k$; the kinematic viscosity of IL is then given by:

$$v = k(\rho_s - \rho)\theta$$

(1.4.3)

$\theta$ is the falling time between two marks on the glass tube. Generally the falling ball viscometer is used for the ILs in the viscosity range of $10^{-3}$ to $10^7$ $P$.\[2000 \#66\]

The glass capillary viscometer is also known as U-tube viscometer or Ostwald viscometer. It consists of a glass U-tube with a capillary section between two bulbs, one is higher on one arm, and the other one is lower down one another arm. In the measurement the fluid is drawn into the upper bulb using a vacuum, then allowed to flow down through the capillary into the lower bulb. The time required for the test liquid to flow through the capillary between two marked points is measured. The kinematic viscosity can be calculated using:\[2000 \#66\]

$$\nu = \left[ \frac{\pi g}{128} \left( \frac{z_1 - z_2}{LV_0} \right) D^4 \right] \Delta t$$

(1.4.4)

where $(z_1, z_2)$ is the change of the height, $D$ is the capillary inner diameter, $L$ is the length of the capillary, and $V_0$ is the volume between the fiducial marks. With known density of the fluid the dynamic viscosity can also be calculated. This kind of viscometer is used for the ILs with the viscosity range of $4 \cdot 10^{-3}$ to $1.6 \cdot 10^2$ St or $6 \cdot 10^{-3}$ to $2.4 \cdot 10^2$ P.

The last widely used viscometer is the rotational viscometer. The idea of this kind of viscometer is that the torque required to turn an object in a fluid is a function of the viscosity of that fluid. Two main elements of rotational viscometer are a rotating element and a fixed element, which could be concentric cylinders, cone and plate and parallel disks. By measurement the test fluid is placed in the space between the two
elements and the torque transferred is measured, and then the viscosity of the fluid can be calculated. Take the concentric cylinder as an example:

$$\eta = \left[ \frac{(\beta^2 - 1)}{\left(4 \pi R_2^2 L_e\right)} \right] \cdot \frac{T}{\omega_2^2} \quad (1.4.5)$$

where $\beta$ is the ratio of the cylinder radii, $R_2$ is the radius of the outer cylinder, $L_e$ is the effective length of the cylinder, $T$ is the torque, and $\omega_2$ is the rotational speed of the outer cylinder.

### 1.4.2.2 Viscosity of ionic liquids

Viscosity is a key transport property of ionic liquids, which has a great influence on the rate of mass transport. High viscosities form barriers for many of their applications and slow down the rate of the chemical reactions, which are diffusion controlled. As a group, ILs tend to have higher viscosities than conventional molecular solvents, and the value of the viscosity varies tremendously with chemical structure, composition, temperature and the presence of solutes of impurities. At room temperature, the viscosities of ILs range from low to 5 cP to more than 1000 cP. Some viscosities are listed in the table 1.4.2.

**Table 1.4.2**  Viscosities of some ILs compared with water and organic solvents at room-temperature. [1992-1993 #67; Seddon Kenneth, 2002 #68]

<table>
<thead>
<tr>
<th>IL</th>
<th>$\eta / \text{cP}$</th>
<th>Liquid</th>
<th>$\eta / \text{cP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMeIm][BF$_4$]</td>
<td>67</td>
<td>water</td>
<td>0.894</td>
</tr>
<tr>
<td>[EtMeIm][PF$_6$]</td>
<td>371</td>
<td>ethanol</td>
<td>1.074</td>
</tr>
<tr>
<td>[HeMeIm][NO$_3$]</td>
<td>804</td>
<td>castor oil</td>
<td>985</td>
</tr>
<tr>
<td>[HeMeIm][Cl]</td>
<td>18000</td>
<td>glycerol</td>
<td>1490</td>
</tr>
</tbody>
</table>
As mentioned above, there are many factors that influence the viscosities of ILs. First of all is the temperature. The viscosity of a liquid decreases as the temperature increases. It is also true for ILs. [Baker, 2001 #69; Ghatee, 2010 #70; Ghatee, 2010 #71]. Figure 1.4.2 shows the temperature dependence of the viscosity of two typical salts of [BuMeIm][PF_6] and [BuMeIm][BF_4] in a logarithmic plot of $\eta$ versus the inverse temperature $1/T$. It is commonly observed, that the viscosities of ILs exhibit non-Arrhenius temperature dependence [H.Tokuda, 2004 #55; H. Tokuda, 2005 #72; Seddon Kenneth, 2002 #68]. The curved shape of the logarithmic plot classifies ILs as so-called fragile liquids.

![Figure 1.4.2](image)

**Fig. 1.4.2** Temperature dependence of the viscosity of [BuMeIm][PF_6] and [BuMeIm][BF_4]. [Seddon Kenneth, 2002 #68]

The viscosities of ILs are influenced by the component cations and anions. Generally, the tetraalkylammonium-based ILs are more viscous than alkylimidazolium-based ILs; for instance, the viscosities of most alkylimidazolium Tf_2N ILs are below 100 cP, while those of most tetraalkylammonium Tf_2N ILs are above 100 cP. Within a series of ILs containing the same anion the trend is: larger alkyl substituents on the imidazolium or ammonium cation lead to higher viscosities; for instance, with the same anion of [Tf_2N]: the value of viscosity follow the order [C_8MeIm]^+ > [C_6MeIm]^+ > [C_4MeIm]^+ > [C_2MeIm]^+ [H.Tokuda, 2005 #72]. For the ILs with the same cation, vary the anionic species clearly change the viscosities of ILs; generally it follow the order: [Tf_3C]^− > [PF_6]^− > [(C_2F_5SO_2)_2N]^− > [BF_4]^− > [CF_3SO_3]^− ≈ [CF_3CO_2]^− > [Tf_2N]^− > [(CF_3SO_2)(CF_3CO)N]^− [H.Tokuda, 2004 #55; Jin, 2007 #73].

Interesting is that the presence of OH group leads to a large increase in viscosity. For
example, at 25°C the viscosity of [BuMeIm][Tf₂N] is 49 cP and the viscosity of [HOEtMelm][Tf₂N] is almost doubled to 91 cP; with two OH groups the effect is much more dramatic: compare the N-propyl-N-methylpyrrolidinium Tf₂N with 54 cP and N-1,2-propanediol-N-methyl-pyrrolidinium Tf₂N with 1500 cP. [Lin, 2007 #73]

1.4.2.3 Self diffusion coefficient

According to IUPAC definition, self-diffusion coefficient is the diffusion coefficient $D_i^*$ of species $i$ when the chemical potential gradient equals zero. It is linked to the diffusion coefficient $D_i$ by the equation:

$$D_i^* = D_i \frac{\partial \ln c_i}{\partial \ln a_i}$$

(1.4.6)

where $a_i$ is the activity of the species $i$ in the solution and $c_i$ is the concentration of $i$.

For ILs, the pulsed gradient spin echo PGSE-NMR is a common method used to determine the self-diffusion coefficient, which allows evaluation of the diffusivity of ions without the use of additional probe molecules.

For the diffusion of a sphere of radius $r$ in a hydrodynamic continuum of viscosity $\eta$, the diffusion–viscosity relationship is often described by the Stokes–Einstein (SE) equation:

$$D = \frac{k_B T}{\xi \pi \eta r}$$

(1.4.7)

The coupling factor $\xi$ accounts for the different hydrodynamic boundary conditions at the interface between the diffusing sphere and the viscous medium.

In low-viscosity ILs at 25°C, the self-diffusion coefficients of the cations and anions are of the order of $10^{-11}$ m² s⁻¹. Those of simple molecular liquids are of the order of $10^{-9}$ - $10^{-10}$ m² s⁻¹.[H.Tokuda, 2005 #72; H.Tokuda, 2004 #55]. The self-diffusion coefficients are also temperature dependent; the values decrease with the increasing temperature. With the same anion, e.g. [Tf₂N]⁻, the sum of the cationic and anionic diffusion coefficients for the imidazolium-based ILs follows the order: [C₂MeIm]⁺ > [C₃MeIm]⁺ > [C₄MeIm]⁺ > [C₆MeIm]⁺ >
\([\text{C}_8\text{MeIm}]^+\); with the same cation, e.g. \([\text{BuMeIm}]^+\), the sum follows the order: 
\([\text{(CF}_3\text{SO})_2\text{N}]^- > [\text{CF}_3\text{CO}_2]^- > [\text{CF}_3\text{SO}_3]^- > [\text{BF}_4]^- > [\text{PF}_6]^-.\)

### 1.4.3 Polarity

In the chemical reactions, solvent effects are widely discussed and have powerful influence on the rate, equilibria and outcome of the reactions. Thus the choice of the right solvent for the reaction is a key topic. One of the most important properties, which classify the solvents, is the polarity. As a “designer solvent”, the polarity of an IL also helps to predict the solubility, miscibility and distribution equilibria. However, the solvent polarity describes the global solvation capability, which results from complex molecular interactions. There are many experimental methods to characterize the solvation polarity, each scale highlights different facet of these interactions. Some methods are listed as followed and more discussions about these methods are followed in the next two chapters.

- Dielectric spectroscopy
- Absorption spectra
- Fluorescence spectra
- Electron spin resonance spectroscopy
- Chromatography
- Solvent effects upon chemical reactions

The most common scale used to describe the polarity is the static dielectric constant \((\varepsilon_s)\). Because the direct measurement of \(\varepsilon_s\) requires a non-conducting medium, which for ILs is not available, conventional methods are not suitable for the measuring of \(\varepsilon_s\) of ILs. However, through the measuring of frequency dependent dielectric permittivity and extrapolation to zero frequency the dielectric constants of electrolyte solutions can be determined. As discussed earlier, most ILs are fluids of relatively low viscosity. Then, the frequency-dependent behaviour falls into microwave range, from about 100MHz to
Table 1.4.3 summarizes some dielectric constants of imidazolium based ILs.

Table 1.4.3  Dielectric constants of some imidazolium-based ILs at 298.15K

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>IL</th>
<th>$\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMeIm][BF$_4$]</td>
<td>12.9</td>
<td>[BuMeIm][BF$_4$]</td>
<td>11.7</td>
</tr>
<tr>
<td>[EtMeIm][Tf$_2$N]</td>
<td>12.3</td>
<td>[BuMeIm][Tf$_2$N]</td>
<td>11.6</td>
</tr>
<tr>
<td>[EtMeIm][TfO]</td>
<td>15.1</td>
<td>[BuMeIm][TfO]</td>
<td>13.2</td>
</tr>
</tbody>
</table>

1.4.4 Electrochemical properties

As mentioned, the research on ionic liquids began with their applications as electrolytes in batteries. The discussion of the electrochemical properties of ILs, such as electrochemical potential window and conductivity, is steadily growing. The electrochemical potential window is the range of voltages over which the substance is electrochemical inert, which means that it does not get oxidized or reduced. In case of ILs, the electrochemical stability depends chiefly on the resistance of the cation to reduction and the resistance of the anion to oxidation.

The most common method to measure the potential window of ILs is cyclic voltammetry (CV). This method uses a three-electrode system with a reference electrode, a working electrode and a counter electrode. The potential is measured between the reference electrode and the working electrode; the current is measured between the working electrode and the counter electrode. Due to the oxidation and the reduction of the substance, the current can rise dramatically and reach thresholds. The electrochemical potential window is the difference between the oxidative and reductive potential limits. The results of the measurement can be affected by some factors, such as the choice of working electrode and the impurities in the ILs. Common materials of the working electrode are glassy carbon, platinum and tungsten; the potentials of same substance measured with different working electrode are not the same value, differ in the range of
±0.2 V. The impurities in ILs can have a pronounced impact on the electrochemical window. For example, the potential of vacuum dried [BuMeIm][Tf₂N] is 4.3 V, whereas without drying is 2.9 V; the dried [BuMeIm][BF₄] is 5.1 V, without drying is 4.0 V [O’Mahony, 2008 #78].

With the variation of the component cations and anions, the electrochemical windows of ILs change to a certain extent, from about 2 V to over 6 V. Comparison of ILs with similar anions, the electrochemical stability of cations follows the order: pyridinium < imidazolium < sulfonium < pyrrolidinium < ammonium [S. Yeon, 2005 #79; T. Sato, 2004 #80; Z. Zhou, 2005 #81]. Because of the uncertainties by the measurements, the effect of the changing alkyl substituents on the electrochemical window of cations is difficult to determine; however, for the imidazolium-based ILs, when the 2-position of the imidazolium ring is capped by an alkyl group, the stability of the cation increases clearly. It is proposed that the limiting reaction of the imidazolium cations is the reduction of ring protons to molecular hydrogen [G. Gray, 1996 #82], and the 2-position is the most acidic hydrogen; the substitution of the alkyl group at that position actually improve the reductive stability of the imidazolium cation. The anion stability towards oxidation follows the order: halides (Cl⁻, F⁻, Br⁻) < fluorinated ions ([PF₆]⁻) < triflate/triflyl ions ([CF₃SO₂]⁻; [(CF₃SO₂)₂N]; [(C₂F₅SO₂)₂N]; [(CF₃SO₂)₃C]⁻) ≈ fluoroborates ([BF₄]⁻) [S. Yeon, 2005 #79; T. Sato, 2004 #80; Z. Zhou, 2005 #81].

The ionic conductivities of ILs play an important role in their electrochemical applications. The most common determine technique for the ILs is the impedance bridge, which uses a two-electrode cell to carry out the measurements. The conductivity of an electrolyte shows the available charge carriers and their mobility. Although ILs are composed entirely of ions, their conductivities are not that high as expected. Possible explanations could be the ion pairing, ion aggregation and reduced ion mobility due to the large ion size. Generally the conductivities of ILs at room temperature fall into the range of ~20 mS cm⁻¹; exceptions are ILs with the [(HF)₂₃F]⁻ anion, which have the conductivities at room temperature higher than 100 mS cm⁻¹. Unlike other properties, the conductivities of ILs are not clearly correlated to the type and size of the ions. Large size of cation leads to lower conductivity probably due to the reduced mobility; in case of anion, there is no clear relationship between the size and conductivity.
The electrical conductivity is strongly dependent on temperature, so is that of ILs, too. With increasing temperature, the conductivities of ILs rise and often exhibit classical Arrhenius behaviour above room temperature. The degree of change in conductivity with temperature varies depending on the ionic liquids. Through Walden's rule, the conductivity and viscosity are often combined:

\[ \Lambda \eta = \text{constant} \]  

(1.4.8)

where \( \Lambda \) is the molar conductivity given by:

\[ \Lambda = k \frac{M}{\rho} \]  

(1.4.9)

where \( k \) is the absolute conductivity, \( M \) is the molecular weight and the \( \rho \) is the density. Ideally, the Walden Product \( (\Lambda \eta) \) remains constant for a given ionic liquid, regardless of temperature. With increasing size of cation, the Walden product decreases; the size of anion shows no clear correlation to the Walden product. Plotting the molar conductivity \( (\Lambda) \) instead the absolute conductivity can normalize the effects of molar concentration and density on the conductivity, and give a better indication of the number of mobile charge carriers in an ionic liquid. [Peter, 2008 #9]
Chapter 2  Polarity Measurement Techniques for Ionic Liquids

It is well known to every chemist that the rates and equilibria of chemical reactions are solvent-dependent. The selection of an appropriate solvent for a reaction is part of the chemist’s workmanship. Early in the 1860s, the influence of solvents on the rates of chemical reactions was discovered by Berthelot and Péan de Saint-Gilles [Berthelot, 1862 #83] and followed by the work done by Menshutkin in 1890s [Menshutkin, 1890 #84]. The influence of solvents on the position of chemical equilibrium was noted with the discovery of keto-enol tautomerism in 1,3-dicarbonyl compounds, which was independently done by Claisen [Claisen,1896#85], Knorr [Knorr L.,1896#86] and Wislicenus [Wislicenus,1896#87]. With the development of modern detection techniques, the solvent effects were characterized for more and more chemical reactions.

The understanding of these effects relies on the concept of solvent polarity. All these effects result basically from the different solvation, which depends on the intermolecular forces between solute and surrounding solvent molecules. The intermolecular forces can be divided into non-specific forces, such as electrostatic forces arising from the Coulomb forces between charged ions and dipolar molecules and polarization forces arising from dipole moments induced in molecules by the nearby ions or dipolar molecules; and specific forces, such as hydrogen-bonding between hydrogen-bond donor and hydrogen-bond acceptor, and electron-pair donor/electron-pair acceptor forces. [C. Reichardt, 1994 #88]

Therefore, it is difficult to define the term of solvent polarity. A commonly accepted definition is the overall solvation capability of solvents, which in turn depends on the action of all possible intermolecular interactions between solute ions or molecules and solvent molecules. Thus, the solvent polarity actually cannot be described quantitatively with single solvent parameters. This leads to the development of various empirical solvent polarity scales based on carefully selected, well-understood and strongly solvent-dependent model chemical reactions or spectral absorptions.

In case of ILs, many methods have been applied to determine their solvent polarities. Some of these techniques will be shortly introduced in this chapter, including the basic principles behind them and part of the results.
2.1 Absorption and fluorescence spectroscopy

It has long been known that the absorption or emission spectra of chemical compounds could be influenced by the surrounding solvents due to the solvent polarity, which lead to changes in position, intensity and shape of absorption or emission bands; this phenomenon is called solvatochromism. With increasing solvent polarity negative solvatochromism leads to hypsochromic (blue) shift of the absorption band and the positive solvatochromism leads to bathochromic (red) shift. The polarities of the ground and exited state of a light-absorbing molecule (chromophore) are different; the change of solvent polarity will change the solvation of the molecules with different electronic states and thus the energy gap between these electronic states. When the ground-state molecules are better stabilized with increasing solvent polarity, it leads to negative solvatochromism; on the contrast, if the exited-state molecules are better stabilized, it results in positive solvatochromism. The solvatochromic effects depend on the chemical structure and the physical properties of the chromophore and the solvent molecules. Generally, dye molecules with a large change in their permanent dipole moment upon excitation exhibit a strong solvatochromism and the ability of the solute to donate or to accept hydrogen bonds to or from surrounding solvent molecules determines the extent and sign of its solvatochromism. [C.Reichardt, 1994 #88]

The empirical parameters of solvent polarity measured with absorption or emission spectroscopy are normally determined by means of solvatochromic compounds. The first solvatochromic dye used for the numbers of polarity determinations was Nile Red(1) [Carmichael, 2000 #89], and more and more dyes have been applied, such as Reichardt's dye(3) [C.Reichardt, 2005 #90; Fletcher, 2001 #91], pyrene(2) [Fletcher, 2001 #91], 4-nitroaniline(5) [L.Crowhurst, 2003 #92], N,N-diethyl-4-nitroaniline(4) [L.Crowhurst, 2003 #92], 3-(4-amino-3-methyl-phenyl)-7-phenyl-benzo-[1,2-b:4,5-b']-di furan-2,6-dione(7) [A.Oehlke, 2006 #93], 4-tert-butyl-2-(dicyano methylene)-5-[4-(diethylamino) benzyl idene]-$\Delta^3$-thiazoline(6) [A.Oehlke, 2006 #93], which are shown in Fig.2.1.1.
Fig. 2.1.1 Molecular structures of the solvatochromic dyes (1) Nile Red, (2) Pyrene, (3) Reichardt’s dye, (4) N,N-diethyl-4-nitroaniline, (5) 4-nitroaniline, (6) 4-tert-butyl-2 (dicyano methylene)-5-[4-(diethylamino) benzylidene]-Δ3-thiazoline, (7) 3-[4-amino-3-methyl-phenyl]-7-phenyl-benzo-[1,2-b:4,5-b’]-difuran-2,6-dione.

Depending on these solvatochromic compounds, which have been used as potential empirical solvent polarity indicators, distinct spectroscopically derived scales of solvent polarity have been established. In case of ILs, the common scales used are the $\pi^*$ scale of Kamlet and Taft [Kamlet, 1977 #94; Abboud, 1977 #95], the $E_{\text{Rf}(30)}$ scale of Dimroth and Reichardt [K.D., 1963 #96] and its normalized form $E_{\text{Rf}}^N$ scale introduced by Reichardt and Harbusch-Görnert [E.Harbusch-Görnert, 1983 #97].
2.1.1 The $\pi^*$, $\alpha$ and $\beta$ scales

Most of the scales are based on data for a single spectral parameter, which are somewhat inadequate in the correlation analysis of other solvent-dependent processes because of the complicated solute/solvent interactions. It is known that the empirical parameters describing solvent polarity can be understood as the result of linear free-energy relationships [Reichardt, 1979 #98]. Kamlet and Taft [Kamlet, 1976 #99; Kamlet, 1977 #94; Taft, 1976 #100] established a system, using the solvatochromic comparison of effects on the UV/Vis spectra of a set of closely related dyes that were selected to test particular solvent properties. This system includes three parameters, $\pi^*$, $\alpha$, and $\beta$.

The $\pi^*$ scale is based on solvent-induced shifts of the longest wavelength $\pi \rightarrow \pi^*$ absorption band of nitroaromatic indicators. The electronic transition is connected with an intramolecular charge transfer from the electron-donor part, such as OMe, NR$_2$, alkyl, to the electron acceptor part, such as NO$_2$, COC$_6$H$_5$ through the aromatic system. Therefore, the exited state is more dipolar than the ground state. Seven nitroaromatics have been employed in the initial construction of the $\pi^*$ scale and the value was normalized and averaged to give $\pi^* = 0.00$ for cyclohexane and $\pi^* = 1.00$ for dimethyl sulfoxide [Kamlet, 1977 #94]. The $\alpha$- and $\beta$- scales are based on the hydrogen-bonding effect.

In case of a solvent as hydrogen-bond acceptor interacting with the dye molecule, such as 1a in Fig. 2.1.2, an electronic transition from a hydrogen-bonded ground state to an excited state would lead to a hydrogen-bond strengthening in the electronic excitation (1b in Fig. 2.1.2), corresponding to a lowering in electronic transition energy, which leads to a bathochromic effect [Kamlet, 1976 #99]. In case of a solvent acting as hydrogen-bond donor to the dye molecule, such as 2a in Fig. 2.1.3, the electronic transition leads to charge delocalization from the phenoxide oxygen into the pyridinium ring and then to the attached phenyl groups (2b, Fig. 2.1.3). Thus, the hydrogen-bonding to phenoxide oxygen should stabilize the ground state relative to the excited state, which results in a hypsochrimic effect [Taft, 1976 #100].
The \( \pi^* \) scale is an index of solvent dipolarity/polarizability, measuring the ability of the solvent to stabilize a charge or a dipole by virtue of its capacity for orientation and induction interactions; \( \alpha \) characterizes the hydrogen bond acidity scale, which describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond; \( \beta \) defines the hydrogen bond basicity scale, which reflects the ability of solvent to accept a proton in a solute-to-solvent hydrogen bond. These solvatochromic parameters were correlated with linear solvation energy relationships (LSER), a simplified form is shown in eqn. (2.1.1) [Kamlet, 1983 #101]

\[
\nu_{\text{max}} (\text{probe}) = \nu_{\text{max}, 0} + a \alpha + b \beta + s \pi^*
\]  

(2.1.1)

\( \nu_{\text{max}}(\text{probe}) \) is the position of the UV/Vis absorption band of the solvatochromic indicator, which is measured in the respective environment. The factors \( a, b \) and \( s \) are solvent-independent correlation coefficients. The three parameters of \( \pi^*, \alpha, \) and \( \beta \) are roughly normalized to a range from 0 to 1. The parameters of some organic solvents are listed in table 2.1.1.
**Table 2.1.1** Solvatochromic parameters of some organic solvents. [Kamlet, 1983 #10; Reichardt, 1994 #88]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\pi^*$</th>
<th>$\beta$</th>
<th>$\alpha$</th>
<th>$E_{T}^{\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.006</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.27</td>
<td>0.47</td>
<td>0.00</td>
<td>0.117</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.71</td>
<td>0.48</td>
<td>0.08</td>
<td>0.350</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.75</td>
<td>0.31</td>
<td>0.19</td>
<td>0.460</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.54</td>
<td>0.77</td>
<td>0.83</td>
<td>0.654</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.60</td>
<td>0.62</td>
<td>0.93</td>
<td>0.762</td>
</tr>
</tbody>
</table>

This system has been applied to separate non-specific effects of the local electric field from hydrogen-bonding effects of ILs. Some of the results are listed in *table 2.1.2*. Since the experiment results depend to some extent on the dyes used in the measurements, the data listed here focus on the values obtained from a single set of dyes for a better comparison: dye (5) (*Fig 2.1.1*) for the determination of $\pi^*$, dye (3) for the determination of $\alpha$, dye (4) for the determination of $\beta$.

**Table 2.1.2** Solvatochromic parameters of some ILs. [Crowhurst, 2003 #102]

<table>
<thead>
<tr>
<th>IL</th>
<th>$\pi^*$</th>
<th>$\beta$</th>
<th>$\alpha$</th>
<th>$E_{T}^{\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuMeMelm][BF$_4$]</td>
<td>1.083</td>
<td>0.363</td>
<td>0.402</td>
<td>0.576</td>
</tr>
<tr>
<td>[BuMeMelm][Tf$_2$N]</td>
<td>1.010</td>
<td>0.239</td>
<td>0.381</td>
<td>0.541</td>
</tr>
<tr>
<td>[BuMePy][Tf$_2$N]</td>
<td>0.954</td>
<td>0.252</td>
<td>0.427</td>
<td>0.544</td>
</tr>
<tr>
<td>[BuMelm][BF$_4$]</td>
<td>1.047</td>
<td>0.376</td>
<td>0.627</td>
<td>0.670</td>
</tr>
<tr>
<td>[BuMelm][Tf$_2$N]</td>
<td>0.984</td>
<td>0.243</td>
<td>0.617</td>
<td>0.644</td>
</tr>
<tr>
<td>[BuMelm][TfO]</td>
<td>1.006</td>
<td>0.464</td>
<td>0.625</td>
<td>0.656</td>
</tr>
</tbody>
</table>

**$\pi^*$ values**
The absorption spectroscopy measures the differential stabilization of the more polar excited state with respect to the ground state of the dye. In the experiment, the $\pi^*$ value is derived from the change in the energy of absorption maximum of the dye which is
induced by the local electric field caused by the solvent. In organic molecular solvents, the $\pi^*$ value reflects the dipolarity/polarizability of the solvent; while in case of ILs, the possible ion-dye coulombic interactions should be taken into consideration. That may explain the common high values of $\pi^*$ of the ILs compared to the organic molecular solvents.

Compared to ammonium salts, the $\pi^*$ values of imidazolium salts are lower; the charge on the imidazolium ring is delocalized, which leads to a reduction in the coulombic attraction. Within the ammonium series, the $\pi^*$ values of monoalkylammonium salts are higher than those of quaternary ammonium salts; probably it is easier for the charge centre on the cation of the monoalkylammonium salts to approach the dye molecules than that of the quaternary ammonium salts because of the steric hindrance.[Poole, 1989 #103]

It can be seen that the $\pi^*$ value decreases with the delocalization of charge on the anion over more atoms due to the decrease in the strength of Coulombic interactions. For ILs with triflate anions, the values are unusual; considering the dipolar nature of triflate, the $\pi^*$ values should be higher than that of the ILs with tetrafluoroborate and hexafluorophosphate anions, but the experimental results were opposite.[Crowhurst, 2003 #102; Weingärtner, 2009 #77] In case of cations, longer alkyl chain on the imidazolium ring lead to a decrease in the $\pi^*$ value due to delocalization of charge[Peter, 2008 #9]; but the substitution of alkyl group in the 2-position in the imidazolium ring instead of proton leads to an increase of $\pi^*$ values. Thus, with a proper consideration of the uncertainty in the $\pi^*$ values, the trend of the influences of cation and anion on the dielectric effect is not very clear. High values suggest strong orientation and induction interactions, but the change with the structure variation is small.

$\alpha$ values

The $\alpha$ values for the ILs are largely determined by the nature of the cation, by means of the availability of hydrogen-bond donor sites. It is no surprise that the monoalkylammonium salts with 3 protons on the cations have the highest $\alpha$ values, ranging from 0.8-1.1; and tetraalkylammonium salts have the lowest $\alpha$ values, below 0.3; imidazolium salts are ranked in the middle, ranging from 0.3-0.8. It is long known that all three protons on the imidazolium ring are acidic[Elawi, 1995 #104], the most acidic proton is on the 2-position on the ring, which explains the decreasing of $\alpha$ value with the alkyl group substitution on the imidazolium ring.
Although the α value relates mainly to the cation of the IL, the influence from the anion can also be seen. With a common cation, such as [BuMeIm]⁺, there is small decrease of α with the increasing hydrogen-bonding acceptor ability of the anion, e.g. from [BF₄]⁻ to [[TfO]⁻]. A probable explanation could be the competition between anion and probe dye for the proton or the direct interactions between anion and dye.[L.Crowhurst, 2003 #92].

β values
The β scale is a measure of the hydrogen bond basicity of the solvent. For ILs, the values should be moderate and dominated by the nature of anions; the basicity increases with decreasing strength of the conjugate acids. Since the conjugate acids are normally strong, low values of the basicity of the anions are expected, compared to other solvents. In fact, the experiment results show values of ILs close to other molecular solvents. The data also indicate an influence of cations on the basicity of IL anions, but there is no clear trend described due to the limited data.

2.1.2 The $E_T(30)$ and $E_T^N$ scales

The $E_T(30)$ scale is based on the negatively solvatochromic pyridinium N-phenolate betaine dye (3 in Fig.2.1.1) as probe molecule. It is defined as the molar electronic transition energies ($E_T$) of dissolved dye 3, measured in kilocalories per mole (kcal/mol) at room temperature (25°C) and normal pressure (1 bar), according to the eqn.(2.1.2)[Reichardt, 1994 #88]:

$$E_T(30) = \frac{hc\nu_{\text{max}}N_A}{(2.8591\times10^{-3})\lambda_{\text{max}}} = \frac{28591}{\lambda_{\text{max}}(nm)}$$

(2.1.2)

where $\nu_{\text{max}}$ is the frequency and $\lambda_{\text{max}}$ the wavelength of the maximum of the longest wavelength, intramolecular charge-transfer $\pi-\pi^*$ absorption band of dye 3. The structure of this dye was first published by Christian Reichardt in 1963[Dimroth, 1963 #105] with a formula number of 30 added for distinction from similar dyes. It is called “Reichardt’s dye”.

Due to the highly dipolar electronic ground state of $\mu = 15D$ and less dipolar electronic excited state of $\mu = 6D$, Reichardt’s dye has the longest wavelength absorption band,
which leads to the largest solvatochromic shifts of 375 nm, from $\lambda_{\text{max}} = 810$ nm in diphenyl ether (the least polar solvent in which the dye is sufficiently soluble) to $\lambda_{\text{max}} = 453$ nm in water (the most polar solvent in which the dye is scarcely soluble). It can register the effect of solvent dipolarity and hydrogen bonding interactions mainly with hydrogen bond donors. In 1983, the dimensionless normalized scale $E_T^N$ was introduced with $E_T^N=1.00$ for water and $E_T^N=0.00$ for TMS as reference of the scale, according to the eqn.2.1.3:

$$E_T^N = \frac{E_T\text{(solvent)} - E_T\text{(TMS)}}{E_T\text{(water)} - E_T\text{(TMS)}} \tag{2.1.3}$$

The $E_T^N$ scale has been applied to numbers of ILs, the values of some organic solvents and ILs are listed in table 2.2.1. It can be seen that the values are more sensitive to the cations than to the anions; since the positive charge of the dye is delocalized and sterically shielded, the interactions with hydrogen bond acceptors are difficult to be detected. Similar to the $\pi^*$ values, the monoalkylammonium salts have the highest value above 0.9, tetraalkylammonium salts have the lowest below 0.5 and in between lie the imidazolium salts. From the data of imidazolium salts with a proton in 2-position and those with methyl group instead, the hydrogen bond donor properties of these cations are clearly established.

### 2.1.3 Fluorescence spectroscopy

Fluorescence spectroscopy has also been applied to determine the polarity of ILs using polycyclic aromatic hydrocarbon (PAH), such as pyrene (2, Fig 2.1.1). Unlike other solvatochromic molecules, these PAHs do not exhibit spectral frequency shifts but a variation in the ratio of emission band intensities that has been correlated with the polarity of the PAH immediate environment. Pyrene is one of the most widely used neutral fluorescence probes and its emission spectrum shows a significant enhancement in the 0 - 0 vibronic band intensity in the presence of polar solvents. Based on this
emission response of an empirical relationship between solvent polarity and the pyrene spontaneous emission band ratio has been established. This scale is defined as $I_I/II$ emission intensity ratio. Band $I$ corresponds to a $S_1(v = 0) \rightarrow S_0(v = 0)$ transition and band $III$ corresponds to a $S_1(v = 0) \rightarrow S_0(v = 1)$ transition. The $py$ scale was suggested to be explained in terms of vibronic coupling. The dipolar nature of the solvent medium determines the extent to which the formation of an induced dipole moment is formed by vibrational distortion(s) of the nuclear coordinate. The increasing value of $I_I/II$ emission intensity ratio indicates the increasing solvent polarity. The important intermolecular process that gives rise to the $py$ scale is the interaction between the solvent dipole and solute induced dipole.\[Street, 1986 #108;Karpovich, 1995 #109\]

\[\text{Fig.2.1.4} \quad \text{Electronic transition energy level diagram.}\]

However, the measurement results are surprising. The common $py$ values of ILs show high polarity, compared to that deduced from other polarity measurement methods. \([\text{BuMeIm}][\text{PF}_6]\) has a high value of the $I_I/II$ emission intensity ratio (1.84), higher than methanol (1.50), similar to acetonitrile (1.88), even comparable to water (1.96). A probable explanation of this high value is the high sensitivity of the spectrum of pyrene to spurious HF, which might be found in $[\text{PF}_6]$- ionic liquids. Interesting is that, the $py$ scale can be related to $\varepsilon$ and $n$ by

$$I_I/II = A + Bf(\varepsilon, n^2) \quad (2.1.4)$$

where $f(\varepsilon, n^2)$ is the dielectric cross term and given by\[^Baker, 2001 #110\]

$$f(\varepsilon, n^2) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \left(\frac{n^2 - 1}{2n^2 + 1}\right) \quad (2.1.5)$$
The spectrum shifts of another fluorescence probe PRODAN can also be related by

\[
SS = \frac{2\Delta f}{hc\alpha} (\mu_E - \mu_G) + \text{const.}
\]  

(2.1.6)

where \( h \) is Planck’s constant, \( c \) is the speed of light, \( a \) is the cavity radius swept out by the PRODAN molecule, \( \mu_E \) is the PRODAN’s excited-state dipole moment, \( \mu_G \) is PRODAN’s ground-state dipole moment, and \( \Delta f \) is the solvent’s orientational polarizability, which is given by[\text{Baker, 2001 #110}]

\[
\Delta f = \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) - \left( \frac{n^2 - 1}{2n^2 + 1} \right)
\]  

(2.1.7)

Based on these two probes, Baker et al. estimated \( \varepsilon \approx 11.4 \) for [BuMeIm][PF₆][\text{Baker, 2001 #110}], which is in good agreement with the data measured by dielectric spectroscopy.

### 2.2 Chromatographic Measurements

Another multi-parameter scale to describe the polarity of ILs is based on gas-liquid chromatographic measurements using ILs as stationary phase. Separation in gas-liquid chromatography is founded on the fact that the solutes interact to different extents with the stationary liquid phase. The principal interactions that affect the solubility of a solute in a liquid phase, e.g., retention, are dispersion, induction, orientation, and donor-acceptor interactions, including hydrogen bonding[\text{Poole, 1989#111}]. To analyse the contribution of the various intermolecular interactions to the singular observed value of the retention parameter Abraham’s cavity model of solvation[\text{Abraham, 1993 #112}] has been used[\text{F.Poole, 1995 #113}]. In this model, two Gibbs energy related steps for the transfer of a solute from a gas state to the solvent are assumed: (1) creation of a cavity in the solvent to accommodate the solute, which is endoergic due to the overcome of self-association of the solvent; (2) incorporation of the solute in the cavity. The exergonic process is due to the interaction of the solute molecule with the surrounding solvent molecules. The total Gibbs energy change can be represented by the sum of individual Gibbs energy contributions to the solvation process, as described by the eqn.(2.2.1):

\[
\log K_e = c + rR_z + s\pi_2'' + a\alpha_2'' + b\beta_2'' + l\log L^{16}
\]  

(2.2.1)
where \( c \) is a constant; \( K_L, R_2, \pi_2^H, \alpha_2^H, \beta_2^H, \) and \( L^{16} \) are solvation parameters derived from equilibrium measurements and refined by multiple linear regression analysis on solvents of assumed characteristic properties: \( K_L \) is the solute gas-liquid partition coefficient, \( R_2 \) is the solute excess molar refraction, \( \pi_2^H \) is the effective solute dipolarity/polarizability parameter, \( \alpha_2^H \) is the effective hydrogen-bond acidity, \( \beta_2^H \) is the effective hydrogen bond basicity and \( L^{16} \) is the gas-liquid partition coefficient on hexadecane at 25°C; \( r, s, a, b, l \) are solvent parameters: \( r \) is the ability of the solvent to interact with solute through \( \pi \)- and \( n \)-electron pairs, \( s \) refers to the contribution of solvents to the dipole-dipole and dipole-induced dipole interactions, \( a \) is the hydrogen bond basicity of the solvent, \( b \) is the hydrogen bond acidity of the solvent, \( l \) incorporates contributions from solvent cavity formation and dispersion interactions and indicates how well the solvent will separate members of a homologous series. In Table 2.2.1 lists the characteristic solvent constants of some ILs.

**Table 2.2.1 Characteristic solvent constants for the ILs** [Poole, 1995 #113; Anderson, 2002 #114]

<table>
<thead>
<tr>
<th>IL</th>
<th>c</th>
<th>r</th>
<th>s</th>
<th>a</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Bu}_4\text{N}][\text{NO}_3]^{\text{a}})</td>
<td>-0.829</td>
<td>0.145</td>
<td>1.864</td>
<td>3.535</td>
<td>0.453</td>
</tr>
<tr>
<td>([\text{Bu}_4\text{N}][\text{TfO}]^{\text{a}})</td>
<td>-0.522</td>
<td>0</td>
<td>1.579</td>
<td>2.135</td>
<td>0.416</td>
</tr>
<tr>
<td>([\text{Bu}_4\text{P}][\text{NO}_3]^{\text{b}})</td>
<td>-0.758</td>
<td>0.183</td>
<td>1.829</td>
<td>3.538</td>
<td>0.412</td>
</tr>
<tr>
<td>([\text{BuMeIm}][\text{TfO}]^{\text{b}})</td>
<td>-2.764</td>
<td>0</td>
<td>1.386</td>
<td>2.353</td>
<td>0.485</td>
</tr>
<tr>
<td>([\text{BuMeIm}][\text{BF}_4]^{\text{b}})</td>
<td>-2.724</td>
<td>-0.141</td>
<td>1.365</td>
<td>1.660</td>
<td>0.473</td>
</tr>
<tr>
<td>([\text{BuMeIm}][\text{TF}_2\text{N}]^{\text{b}})</td>
<td>-3.130</td>
<td>0</td>
<td>1.596</td>
<td>1.551</td>
<td>0.487</td>
</tr>
<tr>
<td>([\text{BuMeMeIm}][\text{TF}_2\text{N}]^{\text{b}})</td>
<td>-3.152</td>
<td>0.092</td>
<td>1.581</td>
<td>1.566</td>
<td>0.478</td>
</tr>
<tr>
<td>([\text{BuMePy}][\text{TF}_2\text{N}]^{\text{b}})</td>
<td>-2.920</td>
<td>0</td>
<td>1.442</td>
<td>1.547</td>
<td>0.484</td>
</tr>
</tbody>
</table>

*a* Data measured at 121°C;  
*b* Data measured at 100°C.

In terms of polarity, the typical range for the solvent constants (\( s \) value) of non-ionic solvents is 0-1.90 [Abraham, 1990 #115; Abraham, 1991 #116]. The large \( s \) values of ILs indicate significant capacity for dipole-dipole and dipole-induced dipole interactions. In the measurements data of Poole, the tetraalkylammonium and tetraalkylphosphonium salts were found to be no hydrogen bond acids, but strong hydrogen bond bases. The basicity depends largely on the anion; the cation has little influence on it. Interestingly, compared with non-ionic polar solvents, the tetraalkylammonium and tetraalkyl-
phosphonium salts with non-associating anions have surprisingly large $I$ constants, which is unusual among the polar solvents. Compared to ammonium based ILs, imidazolium based ILs have relatively smaller $s$ values and hydrogen bond basicity. The dipolarity and the hydrogen bond basicity of ILs with the same cation and different anions are quite different, while the changing of cation has little effect on them. Anions have a clearly dominant influence on the dipolarity and hydrogen bond basicity.

2.3 Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance spectroscopy (EPR) also called electron spin resonance spectroscopy (ESR) has also been applied to assess the polarity of ILs. EPR is used to investigate paramagnetic species, which have one or more unpaired electrons, including organic and inorganic free radicals, triplet states or inorganic complexes with a transition metal ion. EPR was first discovered by the Soviet physicist Yevgeny Konstantinovich Zavoisky in 1944. The basic principles of EPR are very similar to the NMR, except that it detects the signal from the excited electron spins instead of the atomic nuclei spins. The limitation to paramagnetic species makes EPR to be a special technique, since ordinary chemical solvents and matrices do not give rise to EPR spectra.

Every electron has a magnetic moment and spin quantum number $s = 1/2$, with magnetic components $m_s = +1/2$ and $m_s = -1/2$. In the presence of an external magnetic field, the electron’s magnetic moment aligns itself either parallel ($m_s = -1/2$) or antiparallel ($m_s = +1/2$) to the field, each alignment having a specific energy and the difference between energy levels is $\Delta E = g_s \mu_B B_0$ (Fig.2.3.1). The unpaired electron can move between these two energy levels by absorbing or emitting corresponding energy, so that the resonance takes place when the electromagnetic radiation of energy $\varepsilon = h \nu$ corresponds to the energy difference $\Delta E$. 


Fig. 2.3.1 Energy-level diagram for two electron spin states.

When there are nuclei with magnetic spins nearby the unpaired electron, the interaction between the electron spin and nuclear spin results in additional energy states, which is reflected in the spectra by multiple lines and the spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei. That is called hyperfine coupling and the hyperfine coupling constant of a nucleus is directly related to the spectral line spacing. It has been known that the $^{14}$N isotropic hyperfine splitting constant, $a_N$ of certain nitroxide free radicals are affected by interactions between the radical and the surrounding solvent including dipolar aprotic interactions, hydrogen bonding and complex formation.[Strehmel, 2006#117] For the nitroxide functional group there are two canonical structures in terms of valence bond,[Knauer, 1976 #118] (Fig. 2.3.2)

Fig. 2.3.2 Two canonical structures of nitroxide

The greater the polarity of a solvent the more structure $b$ is favoured, increasing the electron density on oxygen and the spin density on nitrogen. The nitrogen hyperfine splitting constant $a_N$ is a solvent polarity parameter for cases in which the nitroxide functional group is used as a solvent polarity probe. For the polarity determination of ILs, some spin probes have been used, such as 2,2,6,6-tetraethylpiperidine-1-oxyl (TEMPO), 4-amino-2,2,6,6-tetraethylpiperidine-1-oxyl (ATEMPO), 4-hydroxy-2,2,6,6-tetraethylpiperidine-1-oxyl (TEMPOL) and 4-trimethylammonium-2,2,6,6-tetraethylpiperidine-1-oxyl (CAT-1), showed in Fig. 2.3.3.
Another information provided by EPR is the rotational correlation time $\tau_r$, which is derived from the average rotational diffusion rate constant $\bar{R}$ according to eqn. (2.3.1)\footnote{Strehmel, 2006 #117}

$$\tau_r = 10^{-\bar{R}} \quad (2.3.1)$$

where $\bar{R}$ is defined as the geometric mean of the rate constants for rotational diffusion about the x-, y- and z-axes of the molecular diffusion frame. Some of the results are listed in table 2.3.1.

**Table 2.3.1 EPR Constants of ATEMPO in ILs and molecular solvents\footnote{Kawai, 2004 #119}**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$a_N / G$</th>
<th>$\tau_r / \text{ns}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>16.99</td>
<td>–</td>
</tr>
<tr>
<td>Ethanol</td>
<td>16.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzene</td>
<td>15.53</td>
<td>0.02</td>
</tr>
<tr>
<td>[BuMeIm][BF$_4$]</td>
<td>16.26</td>
<td>1.4</td>
</tr>
<tr>
<td>[BuMeIm][PF$_6$]</td>
<td>16.30</td>
<td>0.94</td>
</tr>
<tr>
<td>[EtMeIm][TfO]</td>
<td>16.32</td>
<td>0.83</td>
</tr>
<tr>
<td>[NR$_4$][BF$_4$]</td>
<td>16.02</td>
<td>0.54</td>
</tr>
<tr>
<td>[NR$_4$][Tf$_2$N]</td>
<td>16.02</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Since the EPR spectra of different spin probes in the same solvent are different, data in table 2.3.1 are from measurements with same spin probe, ATEMPO for example. The data shows that, the polarity of imidazolium based ILs are similar to that of ethanol but the relaxation times are much longer; the variation of cation has stronger effects on the polarity of ILs than the changing of anions; the relaxation time depends largely on the structure not only of cation but also anion. So far EPR has been used to study a small numbers of ILs. Systematic information about the polarity of ILs by EPR spectroscopy are not yet clear.

### 2.4 Comparison of polarity scales

Polarity of solvents is complex. This term takes all the possible microscopic properties, which are responsible for the interactions between solvent and solute molecules into account, Coulombic, inductive, dispersion, hydrogen bonding, electron pair donor and acceptor forces and so on. Lots of methods have been applied to develop empirical solvent polarity scales for a better understanding of the effects of the solvents in the different applications and an accurate prediction which allows to select the solvents. Ionic liquids are a new class of solvent, which are very different from the traditional molecular ones; their polarity is not easy to determine and to evaluate, every method reflects a different part of the overall interactions, which makes a comparison of different polarity scales difficult.

The polarity determinations of ILs by means of solvatochromic probes are generally easy to perform and the values largely depend on the dye molecules. Each dye probe is sensitive to a particular kind of interactions. The zwitterionic Reichardt's dye is more sensitive to the hydrogen bond donor ability of the solvent; the $E_{T}^{N}$ values are largely cation-controlled. Neutral probes like Nile Red are more sensitive to changes in solvent dipolarity/polarizability; but the $\pi^*$ scale reflects not only the dipolarity/polarizability of the solvent, but also the ion-dye interactions.

The advantage of using GC to determine the polarity of ILs is that the quantities needed are small and the measurement can easily done over a wide range of temperatures. The
polarity scale from GC measurements is also a multi-parameter scale. Similar to the π* value, the high dipolar parameter s is probably due to the extra contribution from ion-ion and ion-dipole interactions.

In both experiments, the hydrogen bond basicities of ILs are showed to be controlled by anion. The agreement is worse for the hydrogen bond acidities. In GC measurements the hydrogen bond acidities are largely affected by anion, while in Kamlet-Taft measurements the cation plays an important role.

The py scale of the fluorescence spectroscopy is based on the effects from the polar solvents on the radiative transition rate of the (0,0) band in fluorescence. The polar solvents enhance the oscillator strength of symmetry-forbidden transitions through a reduction of local symmetry[A.Winnik, 1985 #120]. The mechanism for that remains unclear, which makes it difficult to interpret the results of the measurements.

EPR spectroscopy provides another polarity scale using spin probes. The results show different trends of polarity for different probes; the hyperfine coupling constants of TEMPO and TEMPOL dissolved in the ILs do not depend on the structure of the ILs, while the results of CAT-1 strongly depend on structural variation of the ILs. Interesting is that the values from the measurement with ATEMPO correlate very well with the $E_t(30)$ scale.

Many of these polarity methods use probes molecules and the polarity scale depends to a certain extent on the choice of the probe.[Strehmel, 2006 #121] Each scale maps a different contribution; the choice of an appropriate polarity scale and probe depends on the solute of interest and on the projected applications of ILs. Comparison of these scales may not be very helpful to draw the whole picture of the polarity of ILs, but are helpful to get a further understanding of the solvent-solute interactions.
Chapter 3 Dielectric Relaxation Theory

The most common polarity scale relies on the static dielectric constant $\varepsilon$. In case of ILs, the traditional standard methods are not available for the determination of dielectric constants due to their intrinsic electrical conductance. However, this quantity can be derived from microwave dielectric relaxation spectroscopy [Weingärtner, 2001 #76; Daguenet, 2006 #75; Schrödle, 2006 #74; Ingo Krossing, 2007 #48; Huang, 2008 #122; Weingärtner, 2009 #77].

Dielectric relaxation is a many particle phenomenon; it can be used as a suitable tool to get insight into specific molecular interactions in polar liquids. Dielectric relaxation parameters describe the behaviour of certain relaxing moieties, which generally consist of a number of molecules correlated by short range interactions. The history of dielectric theory can be traced back to the pioneering work of Faraday [Faraday, 1837 #123] and Maxwell [J.C. Maxwell, 1865 #124; J.C. Maxwell, 1868 #125] and later work by Clausius-Mossotti [R. Clausius, 1879 #126; P.F. Mossotti, 1847 #127], and Lorentz-Lorenz [L. Lorenz, 1880 #128; H.A. Lorentz, 1880 #129; H.A. Lorentz, 1952 #130]. The present interpretation of the dielectric parameters correlated to the molecular structures is based upon the theory of Debye [P. Debye, 1929 #131] and subsequent refinements.

In this chapter there will be a brief introduction of the dielectric relaxation theory relevant to the measurement technique and current study.

3.1 Matter in the static electric field

3.1.1 The dielectric constant

The dielectric constant, also called “relative dielectric permittivity”, is a measure of the ability of a material to store a charge from an applied electromagnetic field and then transmit that energy. It can be defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. Consider a condenser consisting of two parallel conducting plates, each of area $A \text{ cm}^2$, at a distance apart $d \text{ cm}$. With a potential difference $V$ applied across the plates, which acquires charges $+Q$ and $-Q$ per
unit area with the surface density of charge of \( \sigma \), the condenser in vacuum has then the capacitance given by

\[
C_0 = \frac{Q}{V} = \frac{\varepsilon_0 A}{d}
\]

(3.1.1)

where the \( \varepsilon_0 \) is the dielectric constant in vacuum. Inside the condenser the intensity of the electric field between the plates is

\[
E_0 = 4\pi \sigma
\]

(3.1.2)

**Fig.3.1.1 Dielectrics in a condenser.**

Filling the space between two plates with some isotropic material, the condenser keeps charging under the same potential difference \( V \) with the capacity of the condenser of

\[
C = \frac{Q + P}{V} = \frac{\varepsilon_0 A}{d} + \varepsilon P
\]

(3.1.3)

where \( P \) is the polarization of material under the influence of electric field, \( \varepsilon \) is the dimensionless dielectric constant or the relative permittivity, defined by

\[
\varepsilon = \frac{C}{C_0}
\]

(3.1.4)

When the charges on the plates remain unchanged, the strength of the electric field decreases to
3.1.2 Polarizations

When placing a material between the plates of the condenser, the strength of the field decreases, which could be effected by charging the surface of the dielectric opposite each condenser plate with a charge of opposite sign to that on the plate. The surface density of this charge is produced by an induced charge shift throughout the dielectric, and is called polarization. It is given by

\[ \varepsilon \sigma = E \]  

(3.1.5)

Different types of polarization can be classified. When placing a non-polar medium into the condenser, under the influence of electric field two effects give rise to the polarization: 1) the displacement of the electrons relative to the nucleus, called electronic polarization; 2) the displacement of the atoms relative to one another, called atomic polarization. When placing a polar medium into the condenser, another type of polarization will occur in addition, called orientational polarization, which is due to orientation of the molecular dipole in the field. A schematic representation of these three types of polarization is shown in Fig.3.1.2.

The total polarization can be given by:

\[ P_{\text{total}} = P_e + P_a + P_{or} \]  

(3.1.7)

where \( P_e \) is the electronic polarization, \( P_a \) the atomic polarization and \( P_{or} \) the orientational polarization; the \( P_e \) and \( P_a \) is due to distortion of the molecule by the field and collectively called induced polarization \( P_{ind} \). Under the electric field with the field strength of \( E \), the correlation between dielectric constant \( \varepsilon \) and the polarization \( P \) can be given by:

\[ P_{\text{total}} = \varepsilon_0(\varepsilon - 1)E \quad P_{or} = \varepsilon_0(\varepsilon - \varepsilon_\infty)E \quad P_{ind} = \varepsilon_0(\varepsilon_\infty - 1)E \]  

(3.1.8)
3.1.3 **Induced dipole and permanent dipole**

An electric dipole is formed by a separation of positive and negative charges. The induced dipole is generated by induced polarization; in electric field, a non-polar molecule can also have an induced dipole moment, which is proportional to the local electric field. Assuming a sphere with radius $r$ of a continuous isotropic dielectric, the volume of the sphere is

$$V = \frac{4\pi r^3}{3} \quad (3.1.9)$$

When applying a constant field with moderate strength to the sphere, according to eqn.(3.1.6) it is given by

$$\overline{m_{\text{ind.}}} = PV = \frac{(\varepsilon - 1)r^3}{3} E = \alpha E_{\text{loc}} \quad (3.1.10)$$

where $m_{\text{ind.}}$ is the average induced dipole moment, $\alpha$ is the polarizability of the molecule. $\alpha$ is a constant, which is characteristic of the substance in an isotropic
condition. The local electric field is the addition of external electric field $E$ and the field arises from neighbour dipoles. In case of gases, the distances between molecules are too large for imposing influences of dipoles on one another, so that the local electric field is mainly determined by the applied external field. In dense media, the contributions from the neighbouring dipoles must be accounted for. The local electric field is then given by:

$$E_{\text{loc}} = E + f \cdot \frac{P}{\varepsilon_0}$$  \hspace{1cm} (3.1.11)

where $f$ is a de-electrification factor. In a sphere, which is centered on the selected molecule, the de-electrification factor is equal to $1/3$ \cite{H.A.Lorentz,1890}, so the local field is, according to eqn.(3.1.8), given by:

$$E_{\text{loc}} = E + \frac{P}{3\varepsilon_0} = \frac{\varepsilon + 2}{3} E$$  \hspace{1cm} (3.1.12)

Substitution of expression (3.1.10) for $E$ and rearrangement gives

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\alpha}{r^3}$$  \hspace{1cm} (3.1.13)

The average induced dipole moment is then given by:

$$m_{\text{ind.}} = \frac{P}{N} = \frac{P \cdot M}{\rho \cdot N_A} = \alpha \left(E + \frac{1}{3} \frac{P}{\varepsilon_0}\right)$$  \hspace{1cm} (3.1.14)

Substitution of expression (3.1.8) for $E$ gives

$$\frac{P \cdot M}{\rho \cdot N_A} = \alpha \left\{ \frac{P}{\varepsilon_0 (\varepsilon - 1)} + \frac{1}{3} \frac{P}{\varepsilon_0} \right\} = \frac{P(\varepsilon + 2)}{3 \varepsilon_0 (\varepsilon - 1)} \alpha$$  \hspace{1cm} (3.1.15)

So the molar Clausius-Mosotti formula is expressed by:

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\[ \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{1}{N_{\alpha}} \frac{A}{3 \varepsilon_0} \]  

(3.1.16)

Polar molecules have a permanent dipole moment. Without the electric field, permanent dipoles in an isotropic material are statistically orientated; when the electric field is applied, the dipoles orientate themselves in direction along to the electric field. This mechanism results in orientational polarization, which is the major source of the total polarization. This orientation is against the Brownian motion. The final polarization is the result of the competition. By the orientation the potential energy of the molecule is \(-\mu E \cos \theta\) with \(\theta\) as the angle between the axis of its dipole and the direction of electric field, while the thermal energy is \(kT\). According to Boltzmann’s law, the total number of molecules obtained by integration over all possible directions is \(\int Ae^{(\mu E/kT)\cos \theta} d\Omega\), and the total moment in the direction of the field is \(\int Ae^{(\mu E/kT)\cos \theta} \mu \cos \theta d\Omega\). The average moment per molecule in the direction of the field is

\[
\bar{m} = \frac{\int Ae^{(\mu E/kT)\cos \theta} \mu \cos \theta d\Omega}{\int Ae^{(\mu E/kT)\cos \theta} d\Omega}
\]  

(3.1.17)

Substituting \(a=\mu E/kT\), integrating numerator and denominator and simplifying the expression leads to

\[
\frac{\bar{m}}{\mu} = \langle \cos \theta \rangle = \coth a - \frac{1}{a} = L(a)
\]  

(3.1.18)

\(L(a)\) was derived by Langevin\(^{[P.\text{Langevin, 1905 #132}]}\). When \(L(a)\) is plotted against \(a\), the curve is linear for very small values of \(a\), for large values, \(L(a)\) approaches 1. For small field intensities the average moment in the direction of the field is proportional to the field, while for large field intensities saturation effects occur. In actual dielectric measurements, the field strengths are within the range of small field intensities. For small values of \(a\), the function can be expressed as \(L(a) = a/3\). So that

\[
\bar{m} = \frac{\mu \cdot a}{3} = \frac{\mu^2 E}{3kT}
\]  

(3.1.19)
Fig.3.1.3 The Langevin function

Adding contributions from this orientational dipole moment to those from the induced moment, the total mean moment in the direction of the electric field is given by:

$$ \langle m \rangle = \alpha E + \frac{\mu^2 E}{3kT} = \left( \alpha + \frac{\mu^2}{3kT} \right) E $$

(3.1.20)

where $\alpha$ is the polarizability by distortion and $\mu^2/3kT$ the polarizability by orientation. Replacing $\alpha$ given by eqn.(3.1.16) by the total polarizability leads to the Debye-equation[P.Debye, 1912 #133]:

$$ \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{1}{3} \frac{N_A}{\varepsilon_0} \left( \alpha + \frac{\mu^2}{3kT} \right) $$

(3.1.21)

3.1.4 Onsager's reaction field

For gases and very dilute solutions the Debye equation is a good approximation, but it is impossible to apply it to solutions with considerable polarity. The complexity of the
molecular shapes and the inadequacy of the Lorentz treatment of the local electric field acting on the molecules lead to problems in calculating the total dipole moment of polar liquids. The re-examination by Onsager of the problem for the internal field has led to important advances of dielectric theory.

In Onsager’s model, it is assumed that a rigid dipole of moment $m$ is in a cavity of radius $r$ in an unpolarized medium of constant dielectric constant $\varepsilon$. In an electric field $E$, the total electric moment per molecule is

$$m = \mu + \alpha E$$  \hspace{1cm} (3.1.22)

Treating the dipole as a point singularity of the electric field, situated at the centre of the cavity, the following expressions are obtained

$$m^* = \frac{3\varepsilon}{2\varepsilon + 1}m$$  \hspace{1cm} (3.1.23)

$$R = \frac{2(\varepsilon - 1)m}{(2\varepsilon + 1)r^3}$$  \hspace{1cm} (3.1.24)

where $m^*$ is the external moment of the immersed dipole, which determines the force the dipole exert upon a distance charge in the dielectric. $R$ - called reaction field - measures the electric field which acts upon the dipole as a result of the electric displacements induced by its own presence.

Considering the modification of the homogeneous field $E$ by the introduction into the dielectric of an empty spherical cavity, it is given by:

$$M = \frac{\varepsilon - 1}{2\varepsilon + 1}Er^3$$  \hspace{1cm} (3.1.25)

$$G = \frac{3\varepsilon}{2\varepsilon + 1}E$$  \hspace{1cm} (3.1.26)

where $M$ is the electric moment of the spherical region, $G$ is the cavity field.

The total electric field acting upon a spherical polar molecule in a polarized dielectric combines the results for the dipolar molecule in the unpolarized dielectric and the
spherical cavity in the polarized dielectric, thus consisting of the reaction field and the cavity field. It is then given by:

$$E_{\text{loc}} = G + R = \frac{3\epsilon}{2\epsilon + 1}E + \frac{2(\epsilon - 1)}{(2\epsilon + 1)\mu^2}m$$  \hspace{1cm} (3.1.27)

This equation describes the condition for equilibrium in the environment of the molecule, and the eqn. (3.1.22) gives the condition for internal equilibrium of the molecule. Combination of eqn (3.1.13) with eqn (3.1.22) and substitution in eqn (3.1.13) by the Maxwell relation \cite{Maxwell} \(\epsilon = \epsilon^2 = \epsilon_{\infty}\) then yields

$$m = \frac{(\epsilon + 2)(2\epsilon + 1)}{3(2\epsilon + \epsilon_{\infty})} \mu + \frac{\epsilon(\epsilon_{\infty} - 1)}{2\epsilon + \epsilon_{\infty}}\mu^3 E$$  \hspace{1cm} (3.1.28)

In combination with the Debye equation the dipole moment is then given by

$$\mu^2 = \frac{9kT\epsilon_0}{N_A} \frac{(\epsilon - \epsilon_{\infty})(2\epsilon + \epsilon_{\infty})}{\epsilon(\epsilon_{\infty} + 2)^2}$$  \hspace{1cm} (3.1.29)

### 3.2 Dielectrics in time-dependent fields

The dielectric behaviour discussed above applies to materials in static electric fields, in which the dielectric is in equilibrium with the external applied field. When a harmonic alternating electric field is applied, a lag in the attainment of equilibrium can be observed. This lag is commonly referred to relaxation, which is defined as the lag in the response of a system to change in the forces to which it is subjected. \cite{Kauzmann}

Dielectric relaxation is the exponential decay with time of the polarization in a dielectric when an externally applied field is removed.
Fig. 3.2.1 Dependence of the polarization on the changing of the external field.

Fig. 3.2.1 shows the dependence of the polarization on the changing on the external field. When the electric field is on \((t_1)\), an induced polarization forms instantaneously, while the orientation polarization responds slowly and lags behind the rise of the electric field. A periodic field is described by

\[ E = E_0 e^{i\omega t} \]  

where \(E_0\) is independent of time \(t\), and \(\omega\) is the angular frequency with \(\omega = 2\pi \nu\). Then

\[ P_{or}(t) = A \cdot e^{i\omega t} \]  

When the field is removed, the polarization process can be described as

\[ \frac{d\bar{P}_{or}}{dt} = \frac{\bar{P}_{or}(0) - \bar{P}_{or}(t)}{\tau} = \frac{1}{\tau} \left( \bar{P}_{or} - \bar{P}_{or}(t) \right) \]  

where \(\tau\) is the relaxation time, which is defined as the time in which this polarization is reduced to \(1/e\) times its original value. So the decay function for the orientation polarization can be expressed by:
When the polar molecules are very large, or the frequency of the alternating field is very high, or the viscosity of the medium is very great, the rotation of the molecules is not sufficiently rapid for the attainment of equilibrium with the field. The polarization then acquires a component out of phase with the field, and the displacement current acquires a conductance component in phase with the field, which leads to thermal dissipation of energy. [C.P.Smyth, 1955 #136] In a condenser, the total current is the sum of the charging current and the loss current, the loss angle $\delta$ is defined as

$$\tan \delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'}$$

(3.2.5)

where $\varepsilon'$ is the measured dielectric constant of the material and $\varepsilon''$ is the loss factor.

Fig.3.2.2 Diagram of loss angle and complex dielectric constant.

A complex dielectric constant is then defined as:

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

(3.2.6)

$\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts, which can be connected by Kramers-Kronig relations and give:
\[ \varepsilon'(f) - \varepsilon_\infty = \frac{2}{\pi} \int_0^\infty \varepsilon''(f) F dF \quad (3.2.7) \]

\[ \varepsilon''(f) = -\frac{2}{\pi} \int_0^\infty (\varepsilon'(f) - \varepsilon_\infty) dF \quad (3.2.8) \]

where \( F \) is a dummy variable supplementing the frequency \( f \). By Laplace transformation of the decay function \( (3.2.4) \) the Debye equations can be given by:

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_m - \varepsilon_\infty}{1 + i \sigma \tau} \quad (3.2.9) \]

\[ \varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_m - \varepsilon_\infty}{1 + i \sigma \omega \tau^2} \quad (3.2.10) \]

\[ \varepsilon''(\omega) = \frac{(\varepsilon_m - \varepsilon_\infty) \omega t}{1 + \sigma^2 \omega^2 \tau^2} \quad (3.2.11) \]

\( \varepsilon' \) is called dispersion and \( \varepsilon'' \) is called absorption. Their frequency-dependent behaviour is shown in Fig. 3.2.2.

At low frequency the dielectric constant is close to static value. With increasing frequency, the orientation polarization is unable to catch up with the changing field, the contribution drops off and the dielectric constant remains close to \( \varepsilon_\infty \). For example, for small molecules in liquids of low viscosity, the time required for the dipole or orientation polarization process is about \( 10^{-11} \) to \( 10^{-10} \) seconds, corresponding to frequencies in the microwave region. When the frequency keeps increasing, the contribution from atomic polarization drops off, since the required time for this process is about \( 10^{-12} \) to \( 10^{-14} \) s, corresponding to the frequency of infrared light. The electronic polarization is the most rapid process and the time required is about \( 10^{-15} \) s, which corresponds to the frequency of ultraviolet light.
Fig. 3.2.3 *Frequency response of dielectric mechanisms.*

The Maxwell relation gives $\varepsilon_\infty$ as:

$$\varepsilon_\infty = n^2$$  \hspace{1cm} (3.2.12)

where $n$ is the refractive index, which is ordinarily measured for visible light, and the refraction of which is due primarily to the displacement of electrons. Considering the contribution from atomic polarization, $\varepsilon_\infty$ is generally given by:

$$\varepsilon_\infty = 1.05n^2$$  \hspace{1cm} (3.2.13)

### 3.3 Non-Debye relaxation process

The Debye equations describe the ideal relaxation process, in which the molecule is assumed to have spherical shape; rotation is about one axis and only one relaxation time is recorded. Most of the actual relaxation processes are not ideal. If a molecule is not
spherical, the processes of orientation by rotation about different axes should require
different relaxation times. Taking for example an alcohol, the relaxation process could be described through the addition of up to three different Debye processes:

\[
e^* = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_1}{1 + (i\omega\tau_1)} + \frac{\varepsilon_\infty - \varepsilon_2}{1 + (i\omega\tau_2)} + \frac{\varepsilon_\infty - \varepsilon_3}{1 + (i\omega\tau_3)}
\]

(3.3.1)

**Fig.3.3.1** Real part of the trimodal relaxation

**Fig.3.3.2** Imaginary part of the trimodal relaxation
Variations in the local environment of the molecules should give rise to variations in the relaxation times. A useful empirical relation developed by K.S.Cole and R.H.Cole [R.H.Cole, 1941 #137] results in a modification of Debye equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_\infty}{1 + (i\omega\tau_\theta)^{1-\alpha}}$$  \hspace{1cm} (3.3.2)

where $\tau_\theta$ is the most probable relaxation time, corresponding to the frequency at which $\varepsilon''=\varepsilon''_{\text{max}}$; $\alpha$ is an empirical constant with values between 0 and 1, measures the distribution of the relaxation times. For $\alpha=0$ this equation reduces to Debye equation with a single relaxation time.

The real and imaginary parts of the dielectric constant derived from the Cole-Cole formulation are:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_\infty}{2} \left( 1 - \frac{\sinh [(1-\alpha)\ln(\omega\tau_\theta)]}{\cosh [(1-\alpha)\ln(\omega\tau_\theta)] + \sin \frac{\pi\alpha}{2}} \right)$$ \hspace{1cm} (3.3.3)

$$\varepsilon'' = \frac{\varepsilon_\infty - \varepsilon_\infty}{2} \left( \frac{\cos \frac{\pi\alpha}{2}}{\cosh [(1-\alpha)\ln(\omega\tau_\theta)] + \sin \frac{\pi\alpha}{2}} \right)$$ \hspace{1cm} (3.3.4)

The Cole-Cole equation can be viewed as presenting a distribution of relaxation times in the form of:

$$f(\tau) = \frac{\sin \alpha \pi}{2\pi} \cosh \left( (1-\alpha)\ln \frac{\tau}{\tau_\theta} \right) - \cos(\alpha \pi)$$ \hspace{1cm} (3.3.5)

The Cole-Cole equation is valid for the systems which show a uniform, symmetrical distribution of relaxation times. For the systems with non-symmetrical distribution of relaxation times, R.H.Cole and D.W.Davidson [D.W.Davidson, 1951 #138] modified the model obtaining:
\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1+i\omega\tau_0)^\beta} \]  

(3.3.6)

where \( \beta \) is denoted as Cole-Davidson asymmetry parameter with the value between 0 and 1. For \( \beta=1 \) the equation reduces to Debye equation. The real and imaginary parts of the dielectric constant derived from the Cole-Davidson formulation are:

\[ \varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\cos \beta \varphi \cos \varphi \beta \]  

(3.3.7)

\[ \varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty)\cos \beta \varphi \sin \varphi \beta \]  

(3.3.8)

where, \( \varphi = \arctan \omega \tau \). The Cole-Davidson equation can be viewed as representing a distribution of relaxation times in the form of:

\[ f\left(\frac{\tau}{\tau_0}\right) = \frac{\sin \beta \pi}{\pi} \left(\frac{\tau}{\tau_0 - \tau}\right)^\beta \]  

(3.3.9)

**Fig. 3.3.3** Real part of the Cole-Cole function
**Fig. 3.3.4** Real part of the Cole-Davidson function.

The empirical combination of the Cole-Cole and Cole-Davidson equations is proposed by Havriliak and Negami (HN)\(^{[S. Negami, 1967 \#139]}\) and is given:

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_\infty}{(1 + (i\omega\tau_0)^{-\alpha})^\beta} 
\]  

(3.3.10)

When \(\beta = 1\) the HN equation reduces to a Cole-Cole equation, and when \(\alpha = 0\), it reduces to Cole-Davidson one. The real and imaginary parts are given by:

\[
\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_\infty - \varepsilon_\infty) \cdot \frac{\cos \beta \phi}{\{1 + 2(\alpha \tau_0)^{-\alpha} \sin \frac{\pi \alpha}{2} + (\alpha \tau_0)^{2(\alpha - 1)}\}^\frac{\beta}{2}} 
\]  

(3.3.11)

\[
\varepsilon''(\omega) = (\varepsilon_\infty - \varepsilon_\infty) \cdot \frac{\sin \beta \phi}{\{1 + 2(\alpha \tau_0)^{-\alpha} \sin \frac{\pi \alpha}{2} + (\alpha \tau_0)^{2(\alpha - 1)}\}^\frac{\beta}{2}} 
\]  

(3.3.12)
where the $\phi$ can be expressed by:

$$
\phi = \arctg \left[ \left( \sigma \tau_0 \right)^{1-\alpha} \frac{\cos \frac{\pi \alpha}{2}}{1 + \left( \sigma \tau_0 \right)^{1-\alpha} \sin \frac{\pi \alpha}{2}} \right]
$$

(3.3.13)
Chapter 4  Experimental Setup

The measurement of the dielectric properties of conducting materials like ionic liquids is a difficult task. In non-glassy (low viscosity) ILs, the essential portion of the reorientational dynamics of ions falls into the picosecond to nanosecond regime, which corresponds to the microwave and radio frequency region (0.001GHz ~ 100GHz) of the electromagnetic spectrum. Conventional techniques fail because the samples are largely short-circuited by the high electrical conductance. Pilot studies show that, microwave dielectric spectroscopy can be a suitable tool to measure the dielectric constant (ε’) and loss factor (ε’’ ) of highly conducting ionic liquids and other ionic solvents\cite{Weingärtner, 2001 #76; Weingärtnert, 2009#77; Huang, 2008#122; Schrodle, 2006#74]. This method is based on coaxial transmission line and wave guide techniques, which form basically a reflection/transmission type spectroscopy and provide frequency coverage up to several GHz. In the current study, reflection type of spectroscopy is used to measure the dielectric properties of series of ILs. Depending on the frequency regime, it is divided into a low-frequency part and high-frequency part; both will be introduced in this chapter. Besides, a brief introduction of Karl-Fischer Coulometer, which is used to determine the water content in ILs and in other solvents, will be inclusive in this chapter.

4.1 High frequency dielectric spectrometer (50 MHz ~ 20 GHz)

For measurements of dielectric spectra at high frequency, a reflection dielectric spectrometer with open-ended coaxial probe technique is employed.

4.1.1 Open-ended coaxial probe technique

A typical coaxial probe system consists of a vector network analyzer, a coaxial probe and an external computer. This technique represents a coaxial line equipped with a tip that
senses the signal reflected from the investigated material. During the measurement of dielectric properties the tip is immersed into the liquid sample. The complex permittivity is measured and calculated with an automated network analyzer from the phase and amplitude of the reflected signal at the end of the open-ended coaxial line inserted into the sample. By the measurement, errors can be caused through density variations in material, as well as bubbles between the end of the coaxial probe and the sample.

**Fig.4.1.1 Coaxial probe system.**

### 4.1.2 Dielectric probe Kit

The probe kit used is 85070E from Agilent Technologies with high temperature design. It features a hermetic glass-to-metal seal and is resistant to corrosive or abrasive chemicals. The temperature range of the probe is from −40℃ to +200℃ and frequency range of 50MHz to 20GHz.

By measurement, the probe is connected with a cable to the network analyzer; the other end of the probe is fixed in a glass cell which contained the sample to be measured with
the probe immersing into it. The glass cell together with the probe is kept in a thermostat with the temperature range of 0°C to 90°C with an accuracy of ±0.01°C.

Fig. 4.1.2 Dielectric probe kit.

4.1.3 The Network Analyzer

One of the most fundamental concepts of network analysis involves incident, reflected and transmitted waves traveling along transmission lines. Network analysis is concerned with the accurate measurement of the ratios of the reflected signal to the incident signal, and the transmitted signal to the incident signal. Fig.4.1.3 shows the principle of measurement in analogy with light waves. The network analyzer used in high-frequency spectrometer is the Hewlett-Packard HP8720C apparatus. It analyzes the
reflected wave in terms of phase and amplitude. Fig.4.1.4 is the generalized block diagram of a network analyzer, showing the major signal-processing sections. The analyzer comprises mainly a microwave signal source for stimulus, signal separation devices, receivers that down convert and detect the signals, and a processor/display for calculating and reviewing the results. In the measurements, the reflected waves will be recorded and converted into complex dielectric spectra by using suitable conversion algorithms, which in the current work is the Nicolson-Ross method [D.K. Misra, 1987 #141].
4.1.4 Calibration and measurement

Before carrying out measurements on any liquid samples, a standard calibration of the vector probe is required. This is done for the whole frequency with three known standards: air (open circuit), short circuit and pure deionized water or user defined solutions, depending on the nature of the sample under test. The calibration must be refreshed with air between the different measurements, which ensures that the existing calibration is retained for the whole period of the measurements.

In the measurements signals at 1000 frequency points between 50 MHz and 20 GHz are usually recorded and then sampled by the network analyzer and converted to complex dielectric spectra. The resulting data triples \((\nu, \varepsilon', \varepsilon'')\) for the frequency, real part and imaginary part can be then fitted to different relaxation models described in the previous chapter.

4.2 Low frequency dielectric spectrometer (0.3 MHz ~ 1300 MHz)

In the low frequency dielectric spectrometer a “coaxial /circular wave guide” method, which is developed by the group of Kaatze\cite{U.Kaatze, 1995 #142; O.Göt mann, 1996 #143; U.Kaatze, 1997 #144; U.Kaatze, 2006 #145}, is employed. The sample holder in this method is a home made “cut-off” cell, which can be represented by a lumped circuit, shown in Fig.4.2.1. The main part of the cell is a coaxial/circular wave guide transition and the wave guide is excited below the cut-off frequency \(\gamma_c\) of the transverse electromagnetic waves. The radius of the stainless steel cylinder, which holds the sample, determines the critical measurements frequency region. For the samples without loss \((\varepsilon''=0)\), the cut-off frequency is given by the relation

\[
\nu_c = \frac{C}{2.61R_o\sqrt{\varepsilon'}}
\]  

(4.2.1)
where \( C \) is the speed of the light, \( R_0 \) the radius of tube which holds the liquid sample and \( \varepsilon' \) is the real part of dielectric constant. [Padmanabhan, 2007 #146]

![Schematic diagram of the lumped circuit model](image)

**Fig.4.2.1 Schematic diagram of the lumped circuit model.** [A.Knocks, 2001 #147]

Two frequency regions are available for the measurements, 0.3MHz to 100MHz and 0.3MHz to 1300MHz. Calibration for this experimental set-up requires two steps. The first is the calibration of the network analyzer (Agilent Technologies 8712ES) using an open circuit and short circuit. The second step is the measurements with air and water for the calculation of the reflection coefficient of empty cell (i.e. air) and the reference liquid. The reflection coefficients obtained are stored in the program that converts the reflection coefficient into the corresponding relative permittivity as a function of frequency.

The reflection coefficient of the sample after the measurement will then be sampled by the network analyzer and converted to complex dielectric spectra using the values of reflection coefficient of air and water. The programs used were developed in our group by Dr. Alla Oleinikova. The resulting data triples \((\nu, \varepsilon', \varepsilon'')\) for the frequency, real part and imaginary part can be then fitted to different relaxation models described in the previous chapter.

### 4.3 Karl-Fischer coulometer
Since water is an important impurity in the ionic liquids and can largely influence the measurement results, the water content determination is then a must step before the spectroscopic measurements. The Karl Fisher titration is a technique for the determination of moisture content developed by Karl Fischer. The fundamental principle behind it is based on the Bunsen Reaction between iodine and sulfur dioxide in an aqueous medium. Karl Fischer modified this reaction and used it for the determination of water in a non-aqueous system containing an excess of sulfur dioxide. He used a primary alcohol (methanol) as the solvent, and a base (pyridine) as the buffering agent. Basically the reaction follows the equation

\[
ROH + SO_2 + R'N \rightarrow [R'NH]SO_2R + H_2O + I_2 + 2R'N \rightarrow 2[R'NH]I + [R'NH]SO_4R
\]

The alcohol reacts with sulfur dioxide and base to form an intermediate alkylsulfite salt, which is then oxidized by iodine to an alkylsulfate salt. This oxidation reaction consumes water. Water and iodine are consumed in a 1:1 ratio in the reaction. Once all of the water present is consumed, the presence of excess iodine is detected voltametrically by the titrator’s indicator electrode. That signals the end-point of the titration. The amount of water present in the sample is calculated based on the concentration of iodine in the Karl Fisher titrating reagent and the amount of Karl Fisher Reagent consumed in the titration.

*Fig.4.3.1 831 KF coulometer. (Metrohm AG)*
To determine trace amounts of water in a sample one can use coulometric or volumetric titration. The current study used 831 KF coulometer by Metrohm AG with determination range from 10 μg to 200 mg H₂O with a resolution of 0.1 μg H₂O, which is shown in Fig.4.3.1. The set-up contains mainly a coulometer, a titration vessel equipped with an indicate electrode, a generator electrode and a drying tube filled with molecular sieve (0.3nm). The vessel is fixed on a stirring bar with adjustable stirring rate. In the coulometric KF titration the required iodine is contained in electrolyte and generated electrochemically *in situ* during titration. Water is quantified on the basis of the total charge passed \(Q\), as measured by current \(I\) and time(seconds), according to the following relationship

\[
Q = 1 \text{ C (Coulomb)} = 1 \text{ A} \times 1 \text{ s}, \text{ where } 1\text{mg H}_2\text{O} = 10.72 \text{ C}
\]

For the titration two electrolytes (both from Fischer Scientific) should be filled, 80-100ml anolyte into the titration vessel and 5ml catholyte into the generator electrode. Before the titration the trace water inside the vessel and electrolytes must be consumed. When it is ready, the sample is added injected into the vessel and the weight of sample is inputted. The results come out in ppm of weight.
Chapter 5  Microwave Dielectric Dpectroscopy of Ionic Liquids

As neoteric materials and “green” solvents in chemical technology, ionic liquids are receiving more and more attention. By using of ILs, a significant barrier is the absence of understanding how the structure of ILs affects its physical properties and solvent strength. The latter can be simply indicated by polarity and polarizability. Previous work showed that dielectric relaxation spectroscopy can be used to determine the solvent strength of ILs. In this chapter, the interpretation of the dielectric spectra of ILs will be introduced as well as some experiment details, and the measurement results of neat ILs will be discussed.

5.1 Microwave dielectric spectrum

In microwave frequency range, the possible contributions to the complex dielectric function \( \Sigma^*(\nu) \) originate from different processes: (a) microscopic fluctuations of molecular dipoles (rotational contributions); (b) the propagation of mobile charge carriers (translational contributions); (c) the separation of charges at interfaces (Maxwell-Wagner polarization). Ionic liquids are charged systems, the contribution from rotation and translation can not be separated experimentally. The complex dielectric function can be expressed either by the complex dielectric permittivity or by complex dielectric conductivity. At non-zero frequency the permittivity and conductivity are coupled, while at zero frequency are decoupled and turn to be static dielectric constant and direct current conductivity. The latter one is independently measurable, the complex dielectric function can be then expressed by

\[
\Sigma^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) + \frac{\sigma}{i2\pi\nu\varepsilon_0} \tag{5.1.1}
\]
where $\sigma$ is dc conductivity; the last term is a diverging low-frequency response of imaginary part, called “ohmic loss”. The complex dielectric permittivity is expressed by [Böttcher, 1972 #149; Böttcher, 1978 #150]

$$
\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) = \varepsilon_\infty + \Delta\varepsilon'(\nu) - i\Delta\varepsilon''(\nu) + \frac{\sigma}{i2\pi\nu\varepsilon_0}
$$

where $\varepsilon_\infty$ is the high frequency limit of the real part. The key interest focus on the relaxational terms of $\Delta\varepsilon'(\nu)$ and $\Delta\varepsilon''(\nu)$. It is shown in the dielectric spectrum, with increasing frequency, the real part $\varepsilon'(\nu)$ decreases step-like whereas the imaginary part $\varepsilon''(\nu)$ exhibits a maximum (Fig.5.1.1). The essential quantities which characterize the dielectric relaxation process can be extracted from this behavior.

Fig.5.1.1 Frequency-dependent dielectric absorption.

Fig.5.1.2 shows a dielectric spectrum of [EtMeIm][Tf$_2$N] as example, $\varepsilon'(\nu)$ is the dielectric dispersion, $\varepsilon''(\nu)$ is the dielectric loss with ohmic loss and $\Delta\varepsilon''(\nu)$ is corrected imaginary part with ohmic loss being cut off. Static dielectric constant $\varepsilon_s$ is defined as the zero-frequency limit of the real part and can be extrapolated

$$
\varepsilon_s = \lim_{\nu \to 0} \varepsilon'(\nu)
$$

(5.1.3)
The characteristic relaxation time \( \tau \) of the fluctuating dipoles is related to the frequency of maximal loss \( \nu_m \)

\[
\tau = \frac{1}{2\pi \nu_m}
\]  

(5.1.4)

Fig. 5.1.2 Real part, imaginary part and conductance-corrected imaginary part of the dielectric spectrum of [BuMelm][Tf₂N]. [Daguenet, 2006 #75]

For the given viscosities of ILs, all the relevant dynamical processes stay at nanosecond to picosecond time scales; the dispersion curve reaches its low-frequency limit in the experiment frequency window. The accuracy of dielectric constant depends largely on whether there is sufficient part of the low frequency plateau of the dielectric dispersion spectrum be recorded by experiment. Note that for highly conducting ILs, the presence of large effects due to electrode polarizations makes the extraction of relaxational terms difficult, as shown in Fig. 5.1.3.
Fig. 5.1. Dielectric dispersion under the presence of electrode polarization. Top: Analog dielectric dispersion; Bottom: dielectric dispersion of [Bu₄N][Al(OR)₄].

The frequency range of current study is from 0.3MHz to 20GHz. In this range, the data fitted very well to a bimodal model with a dominant primary relaxation process and a weak secondary process at higher frequency. To parameterize the primary relaxation mode of ILs, recent work [Hunger, 2009 #151; Buchner, 2009 #152; Turton, 2009 #153] showed that the symmetrical Cole-Cole (CC) distribution is more suitable than asymmetrical Cole-Davidson (CD) relaxation time distribution. The weak secondary mode is difficult to characterize; however, in the frequency range under test a simple Debye term is adequate to describe the high-frequency mode. Eventually, the fitting of the spectrum
yielded terms from a combination of two processes. In this work, for all ILs the overall fitting equation is the combination of a Cole-Cole function plus a Debye function given by

$$
\varepsilon^*(\nu) = \varepsilon_\infty + \frac{S_{CC}}{1 + (i2\pi \nu \tau_{CC})^{\alpha}} + \frac{S_D}{1 + i2\pi \nu \tau_D} \tag{5.1.5}
$$

$$
\varepsilon'(\nu) = \varepsilon_\infty + \frac{S_{CC}}{2} \left[ \frac{1 - \sinh(1 - \alpha) \ln(2\pi \nu \tau_{CC})}{\cosh\left((1 - \alpha)\ln(2\pi \nu \tau_{CC}) + \frac{\pi \alpha}{2}\right)} \right] + \frac{S_D}{1 + \left(2\pi \nu \tau_D\right)^2} \tag{5.1.6}
$$

$$
\varepsilon''(\nu) = \frac{\cos \frac{\pi \alpha}{2}}{2} \left[ \frac{\cosh\left((1 - \alpha)\ln(2\pi \nu \tau_{CC}) + \frac{\pi \alpha}{2}\right)}{1 + \left(2\pi \nu \tau_D\right)^2} \right] + \frac{S_D \cdot \pi \nu \tau_D}{1 + \left(2\pi \nu \tau_D\right)^2} \tag{5.1.7}
$$

For a spectrum describable by equation above, the static dielectric constant is given by the sum of the amplitudes, $$\varepsilon_s = \varepsilon_\infty + S_{CC} + S_D.$$  

### 5.2 Dielectric relaxation measurements of aprotic ionic liquids

Ionic liquids can be divided into two subsets, aprotic ILs and protic ILs. Previous research work on ILs mainly focused on aprotic ones. In this section, the dielectric behavior of series of aprotic ILs measured will be discussed. To get a comprehensive understanding as far as possible, the systems were chosen to cover the general types of ILs. The salts involve alkyl-substituted imidazolium (Im), pyrrolidinium (Pyr), pyridinium (Py) and alkylammonium cations; the anions include tetrafluoroborate(BF_4), hexafluorophosphate(PF_6), bis(trifluoromethylsulfonyl)amide(TfE_N), trifluoromethylsulphonate (triflate(TfO)), dicyanamide (DCA), dimethylphosphate ([MeO]_2PO_2), butylsulfate (BuOSO_3), diethylphosphate ([EtO]_2PO_2), ethylsulfate (EtSO_3), hydrogensulfate (HOSO_3), octylsulfate (OcSO_3) and thiocyanate (SCN). The structures
and origins of all the ILs studied can be found in appendixes. All the ILs were dried for 48 hours at 70°C and 10⁻⁵ bar before being measured.

### 5.2.1 The static dielectric constant

As mentioned above, the spectra were fitted with the model equation of Cole-Cole-Debye (eqn.5.1.5), \( \varepsilon_s \) is obtained by zero-frequency extrapolation. Depending on the low-frequency spectrum, the estimated accuracy of \( \varepsilon_s \) is typically of the order of ±0.3-1.0. All measurements were carried out at 298.15 K except that [EtMelm][PF₆] was measured at 338.15 K. Fig. 5.2.1 shows an example of the dielectric dispersion spectrum of [EtMelm][TfO] at 298.15K and the fit to the Cole-Cole-Debye model.

![Dielectric dispersion spectrum of [EtMelm][TfO] at 298.15K. The curve shows the fit to eqn.(5.1.6).](image)

**Fig.5.2.1** Dielectric dispersion spectrum of [EtMelm][TfO] at 298.15K. The curve shows the fit to eqn.(5.1.6).

*Table 5.2.1*-5.2.4 summarizes the dielectric constants of some widely used aprotic ILs under test. Since ILs are charged systems, their polarities are expected to reach a high value. By contrast, the results for dielectric constants range from 12.0 to 35.0, which are substantially lower than those of common polar solvents like acetonitrile (\( \varepsilon_s = 37 \)), and therefore classify ILs as moderate polar solvents. The main contribution to the dielectric
constant is the dipole orientation; the large molar volumes of the bulky ions, compared to traditional molecular solvents, lead to low dipole concentrations, which could be one reason of the low dielectric constants.

**Anion dependence of dielectric constant**

*Table 5.2.1* Dielectric constants $\varepsilon_s$ of 1-ethyl-3-methylimidazolium ILs at 298.15K ([EtMelm][PF$_6$] at 338.15K). The comparison lists normalized polarity parameters $E^T_N$ and normalized dipolarity parameters $\pi^*$.

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>$E^T_N$</th>
<th>$\pi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMelm][PF$_6$]</td>
<td>13.0 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][Tf$_2$N]</td>
<td>12.0 ± 0.3</td>
<td>0.676$^a$</td>
<td>0.970$^b$</td>
</tr>
<tr>
<td>[EtMelm][TfO]</td>
<td>16.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][EtOSO$_3$]</td>
<td>35.0 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][BuOSO$_3$]</td>
<td>30.0 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][OcOSO$_3$]</td>
<td>12.0 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm]HOSO$_3$</td>
<td>18.4 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][SCN]</td>
<td>13.7 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EtMelm][(EtO)$_2$PO$_2$]</td>
<td>16.9 ± 0.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Data from Ref.[Weingärtner, 2009 #77];
$^b$ Data from Ref.[Tokuda, 2006 #154].

The *Table 5.2.1* summarizes the dielectric constants of aprotic ILs with [EtMelm]$^+$ as a common cation. Changing the anion, the dielectric constant of [EtMelm]$^+$ salts considerably over the range of aprotic ILs. For the anions with symmetric structure, such as [BF$_4$]$^-$, [PF$_6$]$^-$ and [Tf$_2$N]$^-$, which lack a permanent dipole moment, the contribution to the dielectric constant mainly comes from the cation and the values from these ILs are closely together. With the increasing polarity of anions, the dielectric
constant of ILs increases. The highest value among measured ILs is 35.0 for [EtMeIm][EtOSO₃]. For alkylsulfate salts, the value of the dielectric constant decreases significantly with increasing alkyl chain in the anion ([EtOSO₃] > [BuOSO₃] > [OcOSO₃]), which also shows the effect of anion on the total dielectric constant. It should be noted that a low accuracy may result from the extrapolation of the spectra of [EtMeIm][EtOSO₃] and [EtMeIm][BuOSO₃], since part of the spectrum falls below 200 MHz, which make the fitting difficult due to electrode polarization effect.

Table 5.2.2 summarizes the dielectric constants of aprotic ILs with [BuMeIm]+ cations. Similar to the [BuMeIm]+ salts, the dielectric constant of ILs with symmetric anions are closely together and normally of low value. The anion of [TfO]⁻ is asymmetric and therefore has a larger dipole moment than [BF₄]⁻, [PF₆]⁻ and [Tf₂N]⁻, so that a higher dielectric constant of [BuMeIm][TfO] is expected than that of [BuMeIm][BF₄], [BuMeIm][PF₆] and [BuMeIm][Tf₂N], as in [EtMeIm]+ salts, but the measured results show little difference. Due to concern about the accuracy, the trend is not clear.

For comparison the normalized polarity parameters $E_N^T$ and normalized dipolarity parameters $\pi^*$ are also listed in the table. The polarity parameters have been defined and discussed in Chapter 2. Both parameters classify ILs as highly polar solvents; the normalized polarity parameters $E_N^T$ of ILs are higher than that of acetonitrile, close to ethanol; the normalized dipolarity/polarizability parameters $\pi^*$ of ILs are higher than that of general molecular solvents, the values are close to the value observed for water. An explanation of the highly $\pi^*$ values of ILs was proposed by Weingärtner [Weingärtner, 2009 #77]. The dielectric constant reflects the dipole-dipole interactions and polarizability effects, while the dipolarity parameters $\pi^*$ indicate the ability of solvents to induce a dipole in a solute; in case of ILs, the ion-ion and ion-dipole interactions due to the local electric field could contribute the $\pi^*$ value.
Table 5.2.2 Dielectric constants $\varepsilon_s$ of 1-butyl-3-methylimidazolium ILs at 298.15K. To compare lists normalized polarity parameters $E^T_N$ and normalized dipolarity parameters $\pi^*$.

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>$E^T_N$</th>
<th>$\pi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuMelm][BF$_4$]</td>
<td>$13.9 \pm 0.5$</td>
<td>0.670 $^a$</td>
<td>1.047 $^a$</td>
</tr>
<tr>
<td>[BuMelm][PF$_6$]</td>
<td>$14.0 \pm 0.8$</td>
<td>0.669 $^a$</td>
<td>1.032 $^a$</td>
</tr>
<tr>
<td>[BuMelm][Tf$_2$N]</td>
<td>$14.0 \pm 1.0$</td>
<td>0.644 $^a$</td>
<td>0.984 $^a$</td>
</tr>
<tr>
<td>[BuMelm][TfO]</td>
<td>$12.9 \pm 0.5$</td>
<td>0.656 $^a$</td>
<td>1.006 $^a$</td>
</tr>
</tbody>
</table>

$^a$ Data from Ref.[Weingärtner, 2009 #77].

Cation dependence of the dielectric constant

Table 5.2.3 summarizes the dielectric constants of aprotic ILs with [Tf$_2$N]⁻ as a common anion. The $\varepsilon$ values of the salts fall into a narrow range of 12.0~15.2. Compared to the anion variation, the differences of dielectric constant for [Tf$_2$N]⁻ based ILs with different cations are small, which indicates that dielectric constants of aprotic ILs are more sensitive to anion variation than to cation variation. It is notable that with increasing 1-alkyl chain the $\varepsilon$ value increases slightly. The polarity parameters $E^T_N$ also listed in the table illustrate the anion dependence. It is seen that the $E^T_N$ parameter is more sensitive to the cation variation. This can be traced back to the ionic structure of the dye. Reichardt’s dye is a zwitterionic compound (Fig.2.1.3). Compared to the negative charge at the oxygen, the positive charge is delocalized over the aromatic rings; thus, the dye-anion interactions are much weaker than dye-cation interactions and the $E^T_N$ value is mainly cation-controlled. [Weingärtner, 2009 #77]
**Table 5.2.3** Dielectric constants $\varepsilon_s$ of *bis(trifluoromethylsulfonyl)amide* ILs at 298.15K. For comparison the table lists normalized polarity parameters $E_N^{T}$ and normalized dipolarity parameters $\pi^*$. 

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>$E_N^{T}$</th>
<th>$\pi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMeIm] [Tf$_2$N]</td>
<td>12.0 ± 0.3</td>
<td>0.676$^{a)}$</td>
<td>0.970$^{b)}$</td>
</tr>
<tr>
<td>[EtMeMelm][Tf$_2$N]</td>
<td>12.8 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PrMeIm][Tf$_2$N]</td>
<td>13.3 ± 0.3</td>
<td>0.654$^{a)}$</td>
<td></td>
</tr>
<tr>
<td>[BuMeIm] [Tf$_2$N]</td>
<td>14.0 ± 1.0</td>
<td>0.596$^{a)}$</td>
<td>0.984$^{a)}$</td>
</tr>
<tr>
<td>[BuMeMelm][Tf$_2$N]</td>
<td>14.0 ± 0.5</td>
<td>0.546$^{a)}$</td>
<td></td>
</tr>
<tr>
<td>[PeMeIm] [Tf$_2$N]</td>
<td>15.0 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BuPy] [Tf$_2$N]</td>
<td>15.2 ± 0.3</td>
<td>0.648$^a$</td>
<td>1.01$^b$</td>
</tr>
<tr>
<td>[PeMePyr] [Tf$_2$N]</td>
<td>12.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PeEt$_3$N] [Tf$_2$N]</td>
<td>12.5 ± 0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a)$ Data from Ref.[Weingärtner, 2009 #77];  
$^b)$ Data from Ref.[Tokuda, 2006 #154].

**ILs based on methyl-substituted imidazolium cations**

1-alkyl-3-methylimidazolium is an aromatic cation with a delocalized 3-center-4-electron configuration across the N1-C2-N3 moiety, a double bond between C4 and C5 and a weak delocalization in the central region[Weingärtner, 2008 #49]. C2 is positively charged owing to the electron deficit in the C=N bond, whereas C4 and C5 are practically neutral[Weingärtner, 2008 #49]. It has been proved experimentally that all three protons at C2, C4 and C5 are acidic, and the C2 proton is more potential to be a hydrogen bond donor towards anions[Elaiwi, 1995 #104].

Table 5.2.4 summarizes the dielectric constants of ILs based on methyl-substituted imidazolium cations. Replacement of the proton at C2 position yields [EtMeMelm]$^+$ and [BuMeMelm]$^+$ cations; replacement of the protons at C2, C4 and C5 positions yields [BuMe$_4$Im]$^+$ cation. The former was obtained from IoLiTec (Denzlingen, Germany), the latter were synthesized.
The results are surprising. In case of [Tf$_2$N]$^-$ salts, with more methyl groups connected to the imidazolium ring, the dielectric constant increases. In case of [PF$_6^-$] and [BF$_4^-$] salts the results are opposite; with more methyl groups on the imidazolium ring, dielectric constant decreases. Especially by [BuMeIm][PF$_6^-$], when the C2 proton is replaced by a methyl group, the value of $\varepsilon_s$ decreases from 14.0 down to 9.4.

**Table 5.2.4 Dielectric constants $\varepsilon_s$ of ILs with methyl-substituted imidazolium cations at 298.15K.**

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMeIm][Tf$_2$N]</td>
<td>12.0 ± 0.3</td>
</tr>
<tr>
<td>[EtMeMeIm][Tf$_2$N]</td>
<td>12.8 ± 0.3</td>
</tr>
<tr>
<td>[BuMeIm][PF$_6$]</td>
<td>14.0 ± 0.8</td>
</tr>
<tr>
<td>[BuMeMeIm][PF$_6$]</td>
<td>9.4 ± 0.8</td>
</tr>
<tr>
<td>[BuMeIm][Tf$_2$N]</td>
<td>14.0 ± 1.0</td>
</tr>
<tr>
<td>[BuMeMeIm][Tf$_2$N]</td>
<td>14.0 ± 0.5</td>
</tr>
<tr>
<td>[BuMe$_4$Im][Tf$_2$N]</td>
<td>15.0 ± 0.8</td>
</tr>
<tr>
<td>[BuMeIm][BF$_4$]</td>
<td>13.9 ± 0.5</td>
</tr>
<tr>
<td>[BuMeMeIm][BF$_4$]</td>
<td>13.3 ± 0.5</td>
</tr>
<tr>
<td>[BuMe$_4$Im][BF$_4$]</td>
<td>12.0 ± 0.5</td>
</tr>
</tbody>
</table>

**5.2.2 Cole-Cole dielectric relaxation strength**

The dielectric constant is the sum of different contributions. Separating the ionic and electronic displacement polarizations and the unknown high frequency secondary mode, the Cole-Cole dielectric relaxation strength can be obtained as
\[ S_{CC} = \varepsilon_s - \varepsilon_\infty \cdot S_D \]

*Table 5.2.5* summarizes the Cole-Cole dielectric amplitude of the aprotic ILs under test. The highest value of 26.0 is shown by \([\text{EtMelm}][\text{EtOSO}_3]\), and lowest value of 5.5 is shown by \([\text{BuMeMelm}][\text{PF}_6]\). Generally, for the ILs with symmetrical anions (\([\text{BF}_4^-],[\text{PF}_6^-],[\text{Tf}_2\text{N}^-]\)), \(S_{CC}\) increases with increasing alkyl chain length in the imidazolium ring, \([\text{EtMelm}][\text{Tf}_2\text{N}] < [\text{PrMelm}][\text{Tf}_2\text{N}] < [\text{BuMelm}][\text{Tf}_2\text{N}] < [\text{PeMelm}][\text{Tf}_2\text{N}], [\text{EtMelm}][\text{PF}_6] < [\text{BuMelm}][\text{PF}_6]\).

*Table 5.2.5* Cole-Cole dielectric relaxation strength.

<table>
<thead>
<tr>
<th>IL</th>
<th>(S_{CC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{EtMelm}][\text{PF}_6])</td>
<td>7.9</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{TfO}])</td>
<td>8.9</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{EtOSO}_3])</td>
<td>26.0</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{BuOSO}_3])</td>
<td>21.3</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{OcOSO}_3])</td>
<td>6.3</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{HOSO}_3])</td>
<td>10.9</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{SCN}])</td>
<td>7.5</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{(EtO)}_2\text{PO}_2])</td>
<td>11.3</td>
</tr>
<tr>
<td>([\text{EtMelm}][\text{Tf}_2\text{N}])</td>
<td>6.4</td>
</tr>
<tr>
<td>([\text{EtMeMelm}][\text{Tf}_2\text{N}])</td>
<td>7.1</td>
</tr>
<tr>
<td>([\text{BuMelm}][\text{BF}_4])</td>
<td>9.2</td>
</tr>
<tr>
<td>([\text{BuMeMelm}][\text{BF}_4])</td>
<td>9.0</td>
</tr>
<tr>
<td>([\text{BuMelm}][\text{PF}_6])</td>
<td>9.8</td>
</tr>
</tbody>
</table>
5.2.3 Dielectric relaxation time

It is a common experience that the relaxation time can be correlated with the macroscopic viscosity. Table 5.2.6 lists the Cole-Cole dielectric relaxation time $\tau_{cc}$, distribution parameter $\alpha$ and viscosities of the ILs. The central relaxation time $\tau_{cc}$ and the distribution parameter $\alpha$ were obtained by fitting process according eqn.(5.1.5-5.1.7); The sources of the viscosity values are from references and ionic liquids database given at the bottom of the table.

<table>
<thead>
<tr>
<th>IL</th>
<th>$\tau_{cc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuMeMelm][PF$_6$]</td>
<td>5.5</td>
</tr>
<tr>
<td>[BuMelm][Tf$_2$N]</td>
<td>9.2</td>
</tr>
<tr>
<td>[BuMelm][Tf$_2$N]</td>
<td>8.8</td>
</tr>
<tr>
<td>[BuMe$_3$Im][Tf$_2$N]</td>
<td>10.6</td>
</tr>
<tr>
<td>[BuMelm][TfO]</td>
<td>8.1</td>
</tr>
<tr>
<td>[PrMelm][Tf$_2$N]</td>
<td>8.5</td>
</tr>
<tr>
<td>[PeMelm] [Tf$_2$N]</td>
<td>10.2</td>
</tr>
<tr>
<td>[BuPy] [Tf$_2$N]</td>
<td>11.6</td>
</tr>
<tr>
<td>[PeMePyr] [Tf$_2$N]</td>
<td>7.6</td>
</tr>
<tr>
<td>[PeEt$_3$N] [Tf$_2$N]</td>
<td>8.2</td>
</tr>
<tr>
<td>[BuMePyr][DCA]</td>
<td>10.9</td>
</tr>
<tr>
<td>[MeMelm][(MeO)$_2$PO$_2$]</td>
<td>21.3</td>
</tr>
</tbody>
</table>
Fig. 5.2.1 shows the plot of relaxation time against viscosity, taking viscosity data from the literature. The definition of the viscosity and experimental methods for determining the viscosity have been described in Chapter 2.

The relationship between the relaxation time and solvent viscosity is obvious. Generally, a high viscosity leads to slow relaxation processes reflected by a longer relaxation time; a linear correlation between relaxation time and viscosity can be found in the low viscosity range (in the blue square frame), which is in good agreement with results obtained by Buchner et al[Stoppa, 2008 #155].

Fig.5.2.1 Cole-Cole relaxation time $\tau_{CC}$ [ps] of the ILs plotted against the viscosity $\eta$ [mPa·s].

Besides viscosity, another essential factor that influences the relaxation time is the structure and size of the ions. The figure shows a clear trend: the longer the alkyl chain in the imidazolium ring, the longer is the relaxation time, e.g. $[\text{EtMeIm}][\text{Tf}_2\text{N}] < [\text{PrMeIm}][\text{Tf}_2\text{N}] < [\text{BuMeIm}][\text{Tf}_2\text{N}] < [\text{EtMeMeIm}][\text{Tf}_2\text{N}] < [\text{PeMeIm}][\text{Tf}_2\text{N}]$; a long chain slows down the rotational processes due to the steric hindrance. Most of the ILs with $[\text{Tf}_2\text{N}]$ anion have low viscosity (<120 mPa·s) and the relaxation time ranges from 75 ps to 515 ps.
Among the ILs under test, the shortest relaxation time was obtained for [EtMeIm][PF₆] with 45 ps; the salt is solid at room temperature and melts at 307.1K, the determination was carried out at 343.15K; the low viscosity and fast relaxation process result from the high temperature. The highest value was obtained for [EtMeIm][BuOSO₃] with 1824 ps. Interestingly, with a common cation [EtMeIm]+, the relaxation time of sulfate salts has does not depend markedly on the anion size, [EtMeIm][EtOSO₃] < [EtMeIm][OcOSO₃] < [EtMeIm][BuOSO₃].

Concerning the ILs based on methyl-substituted imidazolium cations, regardless of viscosity the trend of relaxation time contradicts expectation. In case of [Tf₂N]- salts, [EtMeIm][Tf₂N] < [EtMeMeIm][Tf₂N], [BuMeIm][Tf₂N] < [BuMeMeIm][Tf₂N] < [BuMe₄Im][Tf₂N], the relaxation process slows down with increasing viscosity and cation size, as expected. In case of [PF₆]- salts, [BuMeIm][PF₆] > [BuMeMeIm][PF₆], the weakness of hydrogen bonding of the C2 proton towards anions replacement might be an explanation, since the ion pair size is reduced, which leads to a faster relaxation process. In case of [BF₄]- salts, [BuMeIm][BF₄] < [BuMe₄Im][BF₄] < [BuMeMeIm][BF₄], the results may indicate the competition between influences from viscosity, ion size and hydrogen bonding.

Table 5.2.6 Dielectric relaxation time \( \tau_{cc} \), distribution parameter \( \alpha \) and viscosities of the ILs.

<table>
<thead>
<tr>
<th>IL</th>
<th>( \tau_{cc} ) [ps]</th>
<th>( \alpha )</th>
<th>( \eta ) [mPa·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtMeIm][PF₆]</td>
<td>45</td>
<td>0.39</td>
<td>23(^{e)})</td>
</tr>
<tr>
<td>[EtMeIm][Tf₂O]</td>
<td>83</td>
<td>0.23</td>
<td>42(^{e)})</td>
</tr>
<tr>
<td>[EtMeIm][EtOSO₃]</td>
<td>784</td>
<td>0.17</td>
<td>150(^{e)})</td>
</tr>
<tr>
<td>[EtMeIm][BuOSO₃]</td>
<td>1824</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>[EtMeIm][OcOSO₃]</td>
<td>850</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>[EtMeIm]HOSO₃</td>
<td>1000</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>[EtMeIm][SCN]</td>
<td>81</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>[EtMeIm][(EtO)₂PO₂]</td>
<td>1000</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>[EtMeIm][Tf₂N]</td>
<td>94</td>
<td>0.14</td>
<td>37d)</td>
</tr>
<tr>
<td>[EtMeMeIm][Tf₂N]</td>
<td>118</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>[BuMeIm][BF₄]</td>
<td>259</td>
<td>0.49</td>
<td>114c)</td>
</tr>
<tr>
<td>[BuMeMeIm][BF₄]</td>
<td>462</td>
<td>0.47</td>
<td>456e)</td>
</tr>
<tr>
<td>[BuMe₄Im][BF₄]</td>
<td>393</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>[BuMeIm][PF₆]</td>
<td>406</td>
<td>0.44</td>
<td>196c)</td>
</tr>
<tr>
<td>[BuMeMeIm][PF₆]</td>
<td>295</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>[BuMeIm][Tf₂N]</td>
<td>314</td>
<td>0.32</td>
<td>54d)</td>
</tr>
<tr>
<td>[BuMeMeIm][Tf₂N]</td>
<td>400</td>
<td>0.36</td>
<td>118d)</td>
</tr>
<tr>
<td>[BuMe₄Im][Tf₂N]</td>
<td>403</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>[BuMeIm][TfO]</td>
<td>226</td>
<td>0.16</td>
<td>81c)</td>
</tr>
<tr>
<td>[PrMeIm][Tf₂N]</td>
<td>141</td>
<td>0.36</td>
<td>53d)</td>
</tr>
<tr>
<td>[PeMeIm][Tf₂N]</td>
<td>515</td>
<td>0.44</td>
<td>70d)</td>
</tr>
<tr>
<td>[BuPy][Tf₂N]</td>
<td>75</td>
<td>0.40</td>
<td>60e)</td>
</tr>
<tr>
<td>[PeMePyr][Tf₂N]</td>
<td>218</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>[PeEt₃N][Tf₂N]</td>
<td>403</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>[BuMePyr][DCA]</td>
<td>266</td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>
5.3 Dielectric relaxation measurements of [Al(hfip)$_4$]$^{-}$-based ionic liquids

It is known that cation-anion interactions may play an important role for the physical properties of ILs. For example, weak anion-cation interaction can lead to low viscosities of molten salts\cite{Krossing2006}. The strength of this interaction is correlated with the coordination ability and Lewis basicity of the anion\cite{Krossing2004}. Tetra(hexafluoroisopropoxy)aluminate ([Al(hfip)$_4$]$^{-}$) is a weakly coordinating anion (Fig.5.3.1), which can be used to stabilize reactive cations\cite{Raabe2009}. Thus, the ILs with [Al(hfip)$_4$]$^{-}$ as common anion have low viscosities and the cation modification has no substantial influence over the viscosity, which makes this new class of ILs an interesting candidate for testing hydrodynamic models of rotational dynamics.

![Fig.5.3.1 Schematic representation of the [Al(hfip)$_4$]$^{-}$ anion](image)

\[ [\text{MeMeIm}]\{[(\text{MeO})_2\text{PO}_2]\] 696 0.19

c) Data from Ref.\cite{H.Jin2008}; d) Data from Ref.\cite{Daguenet2006};
e) Data from "Ionic Liquids Database- (ILThermo)". (http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix)
5.3.1 Synthesis

In this work, a series of ILs with [Al(hfip)$_4$]$^-$ as common anion were studied. These ILs were synthesized by the group of I. Krossing at the Albert-Ludwig-University in Freiburg. The anion metathesis was carried out in absolute CH$_2$Cl$_2$, using Li[Al(hfip)$_4$] and methylimidazolium halides (Cl$^-$ or Br$^-$) as starting materials. The reaction was conducted for 24 hours at room temperature, followed by filtration of the reaction mixture and removal of CH$_2$Cl$_2$. Products were rinsed with n-hexane and dried for 24 hours under vacuum. Since [Al(hfip)$_4$]$^-$ is water-sensitive, all the steps were conducted under inert conditions. Details of the synthesis can be found in Ref. [Bulut, 2010 #159].

5.3.2 Dielectric measurements and data evaluation

All the ILs were tested at temperature of (343.1±0.2) K, which is well above their melting temperatures. The working frequency range is from 50MHz up to 20GHz. Fig.5.3.2 shows the experimental recorded real- and total imaginary part of complex dielectric function of [BuMeMorph][Al(hfip)$_4$].

The spectra were fitted to the Cole-Cole-Debye function (5.1.5). Dielectric relaxation probes the collective response of all dipoles, and so does the relaxation time $\tau_{CC}$ obtained through fitting. By contrast, hydrodynamic theory relates the single-particle reorientation time $\tau_{rot}$ to the viscous friction exerted by the surrounding medium[Date, 1981 #160]. Thus, to apply the hydrodynamic relations, $\tau_{CC}$ needs first to be converted to $\tau_{rot}$. The conversion between $\tau_{CC}$ and $\tau_{rot}$ is given by [Glarum, 1960 #161]

$$\tau_{rot} = \left(\frac{2\varepsilon + \varepsilon_{\infty}}{3\varepsilon}\right)^{\frac{1}{n}} \tau_{CC}$$ (5.3.1)

where it is estimated that $\varepsilon_{\infty} \approx n^2 \approx 2$, as predicted by the Maxwell-relation.
Fig. 5.3.2 Real part and total imaginary part of the frequency-dependent complex dielectric function of [BuMeMorph][Al(hfip)$_4$] at 343.1 K.

Hydrodynamic theory relates single-particle reorientation time $\tau_{rot}^L$ to the bulk viscosity $\eta$ through the Stokes-Einstein-Debye equation\cite{Dote1981}

$$\tau_{rot}^L = \frac{6\eta V_{\text{eff}}}{L(L+1)kT}$$

where $L$ denotes the rank of the spherical harmonics associated with the dynamical probe, for dielectric processes $L=1$; $V_{\text{eff}}$ is the effective hydrodynamic volume of the rotating particle. $V_{\text{eff}}$ can be related to the geometric volume $V$ of the particle by a coupling factor $f$ ($0 \leq f < 1$) with $V_{\text{eff}} = fV$. For a rotating ellipsoid $f$ depends on the hydrodynamic boundary condition, the orientation of the dipole axis and the aspect ratio of the ellipsoid\cite{Youngren1975}. For isotropic rotation, $f=1$ indicates a sticky hydrodynamic boundary condition, $f=0$ indicates a slip condition\cite{Huang2010}. 

5.3.3 Discussion

Table 5.3.1 summarizes the parameters describing dielectric relaxation behavior of [Al(hfip)$_4$]- based ILs. $V_{cation}$ is the volume of the cation; $f$ as coupling factor is calculated by $f = \frac{V_{eff}}{V_{cation}}$.

The dielectric constants of these ILs fall into a range from 12.6 to 18.4. Generally, with increasing ion size, the dielectric constant decreases. Within the imidazolium based ILs, the trend is very clear. Fig 5.3.3 plots the dielectric constant versus the imidazolium cation, with increasing alkyl chain length dielectric constant increases; substitution of the proton at C2 position with methyl group, dielectric constant increase, which is similar to the [Tf$_2$N]$^-$ based ILs.

The collective relaxation time of these ILs ranges from 161 ps to 900 ps. Within the imidazolium based ILs, the longer the alkyl chain length, the longer is the relaxation time, although the viscosity does not show a cation dependent trend. For the ILs with methyl group substituent at C2, an increasing viscosity and ion size slow down the relaxation processes. Interestingly, [Bu$_4$N][Al(hfip)$_4$] has highest viscosity and largest ion size among these ILs, whereas its relaxation time is smaller than that of other ILs.

\[ \text{Fig.5.3.3 Cation-dependent dielectric constant of imidazolium based ILs.} \]
**Table 5.3.1** Dielectric relaxation parameters of [Al(hfip)$_4$]-based ILs at 343.1K.

<table>
<thead>
<tr>
<th>ILs</th>
<th>$\varepsilon_s \pm 0.3$</th>
<th>$S_{CC}$ [ps]</th>
<th>$\tau_{CC}$ [ps]</th>
<th>$\alpha$</th>
<th>$\tau_{rot}$ [ps]</th>
<th>$V_{eff}$ [$10^{-30}$m$^3$]</th>
<th>$V_{cation}$/$f$ [$10^{-30}$m$^3$]</th>
<th>$f$</th>
<th>$\eta^f$ [mPa∙s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AlMeIm][Al(hfip)$_4$]</td>
<td>17.0</td>
<td>12.0</td>
<td>804</td>
<td>0.30</td>
<td>252</td>
<td>41.9</td>
<td>167</td>
<td>0.251</td>
<td>9.5</td>
</tr>
<tr>
<td>[EtMelm][Al(hfip)$_4$]</td>
<td>12.6</td>
<td>8.1</td>
<td>161</td>
<td>0.26</td>
<td>45</td>
<td>6.9</td>
<td>149</td>
<td>0.046</td>
<td>10.3</td>
</tr>
<tr>
<td>[EtMeMelm][Al(hfip)$_4$]</td>
<td>17.7</td>
<td>14.2</td>
<td>178</td>
<td>0.29</td>
<td>53</td>
<td>7.0</td>
<td>173</td>
<td>0.041</td>
<td>11.9</td>
</tr>
<tr>
<td>[BuMelm][Al(hfip)$_4$]</td>
<td>14.4</td>
<td>9.4</td>
<td>280</td>
<td>0.19</td>
<td>47</td>
<td>8.2</td>
<td>197</td>
<td>0.042</td>
<td>9.0</td>
</tr>
<tr>
<td>[BuMeMelm][Al(hfip)$_4$]</td>
<td>18.4</td>
<td>14.9</td>
<td>440</td>
<td>0.20</td>
<td>75.5</td>
<td>12.4</td>
<td>218</td>
<td>0.057</td>
<td>9.6</td>
</tr>
<tr>
<td>[BuMeMorph][Al(hfip)$_4$]</td>
<td>16.5</td>
<td>11.6</td>
<td>714</td>
<td>0.23</td>
<td>158</td>
<td>20.1</td>
<td>222</td>
<td>0.091</td>
<td>12.4</td>
</tr>
<tr>
<td>[BuPy][Al(hfip)$_4$]</td>
<td>16.5</td>
<td>11.6</td>
<td>253</td>
<td>0.18</td>
<td>37</td>
<td>5.8</td>
<td>192</td>
<td>0.030</td>
<td>10.0</td>
</tr>
<tr>
<td>[BuMePyr][Al(hfip)$_4$]</td>
<td>16.6</td>
<td>11.3</td>
<td>232</td>
<td>0.13</td>
<td>16</td>
<td>1.9</td>
<td>213</td>
<td>0.009</td>
<td>13.1</td>
</tr>
<tr>
<td>[HeMelm][Al(hfip)$_4$]</td>
<td>17.5</td>
<td>12.9</td>
<td>900</td>
<td>0.22</td>
<td>183</td>
<td>28.9</td>
<td>244</td>
<td>0.118</td>
<td>10.1</td>
</tr>
<tr>
<td>[Bu$_4$N][Al(hfip)$_4$]</td>
<td>12.7</td>
<td>9.4</td>
<td>260</td>
<td>0.32</td>
<td>93</td>
<td>9.7</td>
<td>391</td>
<td>0.025</td>
<td>15.1</td>
</tr>
</tbody>
</table>

f) Data from Ref. [Bulut, 2010 #159].
Converting the collective relaxation time $\tau_{cc}$ to single particle reorientation time $\tau_{rot}$, the values become up to an order of magnitude smaller. The correction according to eqn. 5.3.1 largely removes the variation of $\tau_{cc}$ along the homologous cation series \cite{Huang2010}. According to hydrodynamic models, $\tau_{rot}$ is related to the viscosity $\eta$, thus effective hydrodynamic volumes $V_{eff}$ were deduced. A plot the single particle reorientation time $\tau_{rot}$ against effective hydrodynamic volume $V_{eff}$, yields a almost straight line (Fig. 5.3.4).

![Graph](image_url)

**Fig. 5.3.4** Effective hydrodynamic volume dependent single particle reorientation time of ILs.

The calculated effective volumes are extraordinarily low, which is reflected by the coupling factor $f$. The low values of the coupling factor $f$ indicate almost frictionless rotation, which corresponds to almost perfect slip condition in hydrodynamic theory. An exception is [AlMeIm][Al(hfip)$_4$], the value is much higher than that of other ILs. The special structure of functional side chain with double bond of the methylimidazolium cation probably generates largely different conditions, which is also reflected by other dielectric relaxation parameters.
5.4 Dielectric relaxation measurements of protic ionic liquids

Ionic liquids can be divided into two broad categories, aprotic ionic liquids (AILs) and protic ionic liquids (PILs). In the last two sections the dielectric relaxation behavior of some aprotic ionic liquids were discussed; in this section the results obtained from some protic ionic liquids will be presented.

The first reported PIL was ethanolammonium nitrate described in 1888 by Gabriel [Gabriel, 1888 #1], which is also the first IL discovered; the best known PILs is ethylammonium nitrate, which was first reported in 1914 by Walden [Walden, 1914 #2]. PILs are produced through proton transfer from a Brønsted acid to a Brønsted base. A key feature is that all PILs have a proton available for hydrogen bonding and usually result in a non-negligible vapor pressure [Drummond, 2008 #61].

The most commonly used cations in PILs include primary, secondary or tertiary ammonium ions, 1-alkylimidazolium or 1,2-dialkyylimidazolium ions, caprolactam and guanidinium ions (Fig.5.4.1). A large variety of anions can be coupled with these cations, including both, organic or inorganic anions.

![Fig.5.4.1](image)

**Fig.5.4.1** Cations used in PILs, (a) ammonium cations ($R_1,R_2,R_3$ can be hydrogen atoms), (b)1-alkylimidazolium cation, (c)1,2-dialkyylimidazolium cation, (d)caprolactam, (e)1,1,3,3-tetramethylguanidinium.
From the study of AILs, the dielectric constants fall into a narrow range and are lower than those of common polar solvents. In molecular solvents, high dielectric constants are usually obtained from hydrogen bonded structures, since the orientational correlation between dipoles in hydrogen bonded configurations can enhance the macroscopic dielectric polarization [Blösch, 1973; H. Weingärtner, 2006]. PILs are therefore interesting candidates.

### 5.4.1 Synthesis of PILs

In the work, series of PILs with and without additional hydroxyl groups in alkyl chains were under test; the hydroxyl ammonium ILs were synthesized in our laboratory. *Schema 5.4.1* illustrates the formation of hydroxyl PILs; *table 5.4.1* lists the starting materials and products.

**Scheme 5.4.1** Formation of the hydroxyl ammonium ionic liquids.

![Scheme 5.4.1](image)

*R_1, R_2, R_3*: H or HOOC_H_F*  
*R*: H, CH_3, and CH_3CH(OH)*

**Table 5.4.1** Starting materials and products of synthesis.

<table>
<thead>
<tr>
<th>Brønsted base</th>
<th>Brønsted acid</th>
<th>PILs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-aminoethanol [HOEtNH_2]</td>
<td>Formic acid [HCOOH]</td>
<td>2-hydroxyethylammonium formate [HOEtNH_2][HCO_2]</td>
</tr>
<tr>
<td>2-aminoethanol [HOEtNH_2]</td>
<td>Acetic acid [CH_3COOH]</td>
<td>2-hydroxyethylammonium acetate [HOEtNH_2][CH_3CO_2]</td>
</tr>
<tr>
<td>2-aminoethanol [HOEtNH_2]</td>
<td>Lactic acid [C_2H_4(OH)COOH]</td>
<td>2-hydroxyethylammonium lactate [HOEtNH_2][C_2H_4(OH)CO_2]</td>
</tr>
<tr>
<td>2-aminoethanol [HOEtNH_2]</td>
<td>Nitric acid [HNO_3]</td>
<td>2-hydroxyethylammonium nitrate [HOEtNH_2][NO_3]</td>
</tr>
<tr>
<td>Triethanolamine [(HOEt)_3N]</td>
<td>Formic acid [HCOOH]</td>
<td>Trihydroxyethylammonium formate [(HOEt)_3N][HCO_2]</td>
</tr>
</tbody>
</table>
Hydroxyl ammonium ILs were prepared by neutralization of ethanolamine in ethanol with different acids [Yuan, 2007]. The synthesis procedure of 2-hydroxyethylammonium lactate as an example is described in detail below.

1) 0.5 mol of 2-aminoethanol was dissolved in 100 ml absolute ethanol and the mixture was loaded into a 500 ml flask; the flask was placed in a room-temperature water bath and equipped with a reflux condenser under vigorous stirring;

2) 0.5 mol of lactic acid was dissolved in 100 ml absolute ethanol; the mixture was added drop wise to the flask in about 2 hours; the reaction was conducted for 2 hours at room temperature;

3) The solvent was removed by evaporation under vacuum; products were rinsed with 100 ml absolute ethanol; after evaporation the products were dried for 4 days in condensation trap under vacuum.

4) The products were characterized through NMR spectroscopy; the water content of the ILs were controlled by Karl-Fischer (KF) titration.

All the synthesis steps were carried out under inert gas protection to reduce the water content in the ILs as far as possible. The synthesis of other hydroxyl PILs followed almost in the same routine, except that the starting materials were of formic acid and nitric acid; since both acids are strong acids, their reactions with bases were highly exothermic. Thus the reactions were carried out with in an ice-water bath.

It should be noted that, the 2-hydroxyethylammonium formate is commercially available; the NMR spectrum obtained from the synthesized ILs and that from the purchased ILs were almost identical.

### 5.4.2 Dielectric relaxation measurements of PILs

All PILs are liquid at room temperature; thus all the measurements were carried out at 298.15K. Dielectric spectra of the PILs were recorded in the frequency range from 0.3 MHz to 1.3 GHz and from 50 MHz to 20 GHz. The final spectra are combinations of
these two individual records, the overlapping part was used to control the consistency. Like in the case of AILs, the dielectric dispersion and absorption of the PILs were fitted to the Cole-Cole-Debye function. Fig 5.4.2 shows the differences between normal PILs and PILs with functional hydroxyl group.
5.4.3 Discussion

Dielectric constant

The PILs without hydroxyl group studied are based on the [HCO$_2$]$^-$ anion. Table 5.4.2 lists the dielectric constant and relaxation strength of these four PILs. From the earlier work, the dielectric constants of ILs fall into a narrow range of low values; the results obtained from PILs vitiate this impression. Compared to AILs, the dielectric constants of PILs are generally high, with values up to 41. The hydrogen bonded structure substantially enhances the dielectric polarization. With increasing alkyl chain length dielectric constants decrease to a large extent, the size of cation has key influence on it. If one compares the value for [EtNH$_3$][HCO$_2$] to that of [EtNH$_3$][NO$_3$] ($\varepsilon_s \approx 26.2$) [Weingärtner, 2001 #77], the anion appears to play a minor role; despite the lack of dipole moment of [NO$_3$]$^-$ the dielectric constant does not markedly differ from that of the corresponding PIL with the dipolar anion of [HCO$_2$]$^-$.  

---

Fig.5.4.2 Dielectric relaxation spectra of PILs at 298.15K.
Table 5.4.2 Dielectric constants $\varepsilon_s$ and relaxation strengths $S_{CC}$ of protic ionic liquids without a functional group at the alkyl chain at 298.15K.

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>$S_{CC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MeNH$_3$][HCO$_2$]</td>
<td>41.0 ± 0.3</td>
<td>31.7</td>
</tr>
<tr>
<td>[EtNH$_3$][HCO$_2$]</td>
<td>31.5 ± 0.3</td>
<td>22.5</td>
</tr>
<tr>
<td>[BuNH$_3$][HCO$_2$]</td>
<td>23.0 ± 0.5</td>
<td>16</td>
</tr>
<tr>
<td>[MePyr][HCO$_2$]</td>
<td>22.9 ± 0.3</td>
<td>13.3</td>
</tr>
</tbody>
</table>

The value of dielectric constant keeps increasing, when the alkyl chain in the ammonium cation is terminated by a hydroxyl group. Table 5.4.2 lists the dielectric constants and relaxation strengths of these PILs. Terminated by a hydroxyl group, the dielectric constant of IL increases up to 61. Values of this order of magnitude are only reached by a few, mainly protic solvents ($\varepsilon_s$(water) ≈ 78.3, 298.15K). It should be noted that the molecular volume of [HOEtNH$_3$][HCO$_2$] is 89.4 cm$^3$mol$^{-1}$, which means that the high value of its dielectric constant is generated by a cation density which is roughly by a factor of five lower than the dipole density in water. The dominant influence of cation on the dielectric constant is particularly visible by tracing the differences of the values between [HOEtNH$_3$][HCO$_2$], [HOEtNH$_3$][CH$_3$CO$_2$] and [HOEtNH$_3$][NO$_3$]. For comparison table 5.4.3 lists three other ILs with hydroxyl groups at the side chain; higher dielectric constants than observed for normal AILs indicate the dramatic role of functionalization by hydroxyl groups for the dielectric behavior of ILs.

Surprisingly, in the case of [HOEtNH$_3$][C$_2$H$_4$(OH)CO$_2$], the value of the dielectric constant jumps up to 85.6, which is much higher than observed for other hydroxyethylammonium salts, and even higher than observed for of water. The peculiarity of the lactate salt is the hydroxyl group in the alkyl chain of the anion, which largely raises the polarity of the anion, leading to the extraordinarily high value of the dielectric constant. Because the dielectric relaxation process of [HOEtNH$_3$][C$_2$H$_4$(OH)CO$_2$] occurs in a lower frequency range than relaxation of other ILs, a large part of the low-frequency plateau was beyond the experimental, resulting in a high inaccuracy by the dielectric constant.
By replacement of the protons in the ammonium cation by a hydroxyethyl group one obtains a family of trihydroxyethylammonium-based PILs. The resulting decrease of the dielectric constant probably reflects the largely increasing cation size. Compared to [(HOEt)$_3$NH][CH$_3$CO$_2$], the high value for [(HOEt)$_3$NH][C$_2$H$_4$(OH)CO$_2$] emphasizes again the peculiarity of the lactate anion.

**Table 5.4.3** Dielectric constants $\varepsilon_s$ and relaxation strength $S_{cc}$ of protic ionic liquids with functional group at 298.15K ([Et(OH)Me$_3$N]([MeO)$_2$PO$_2$] at 338.15K).

<table>
<thead>
<tr>
<th>IL</th>
<th>$\varepsilon_s$</th>
<th>$S_{cc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HOEtNH$_3$][HCO$_2$]</td>
<td>61.0 ± 0.8</td>
<td>55.1</td>
</tr>
<tr>
<td>[HOEtNH$_3$][CH$_3$CO$_2$]</td>
<td>58.3 ± 0.3</td>
<td>49.7</td>
</tr>
<tr>
<td>[HOEtNH$_3$][NO$_3$]</td>
<td>60.9 ± 0.3</td>
<td>51.9</td>
</tr>
<tr>
<td>[HOEtNH$_3$][C$_2$H$_4$(OH)CO$_2$]</td>
<td>85.6 ± 2.0</td>
<td>78.6</td>
</tr>
<tr>
<td>[(HOEt)$_3$NH][CH$_3$CO$_2$]</td>
<td>31.0 ± 0.3</td>
<td>24.1</td>
</tr>
<tr>
<td>[(HOEt)$_3$NH][C$_2$H$_4$(OH)CO$_2$]</td>
<td>59.7 ± 0.5</td>
<td>54.2</td>
</tr>
<tr>
<td>[HOEtMeIm][BF$_4$]</td>
<td>23.3 ± 0.8</td>
<td>18.9</td>
</tr>
<tr>
<td>[EtMe(OH)Py][EtOSO$_3$]</td>
<td>35.0 ± 1.0</td>
<td>25.2</td>
</tr>
<tr>
<td>[Et(OH)Me$_3$N][(MeO)$_2$PO$_2$]</td>
<td>43.6 ± 0.8</td>
<td>34.1</td>
</tr>
</tbody>
</table>

**Relaxation time**

**Table 5.4.4** lists the relaxation time, distribution parameter, single particle reorientation time, effective hydrodynamic volume and the viscosity of the PILs with and without hydroxyl group.

For the PILs without hydroxyl group, the relaxation time increases with increasing cation size, as well as with the viscosity; so do the single particle reorientation time and effective hydrodynamic volume. Surprisingly, the calculated single particle reorientation...
time of $[\text{MeNH}_3][\text{HCO}_2]$ with 0.7 ps, which is the most fast process known for ILs; the small effective hydrodynamic volume can be seen as signal of rotation with vanishing friction.

In case of ILs with hydroxyl group, the viscosities are higher and the single particle reorientation times are longer than those of ILs without hydroxyl group, which may resulted from hydrogen bonded network in the ILs, when the data from $[\text{Al(hfip)}_4]$-based ionic liquids are also concerned.

Within the PILs with hydroxyl group, situations become complicated. For the hydroxyethylammonium ILs, the most viscous liquid is $[\text{HOEtNH}_3][\text{C}_2\text{H}_4(\text{OH})\text{CO}_2]$, which can be attributed to the strong hydrogen bonded network; $[\text{HOEtNH}_3][\text{CH}_3\text{CO}_2]$ has a much lower viscosity and shorter single particle reorientation time. Surprisingly, its collective relaxation time is close to that of $[\text{HOEtNH}_3][\text{C}_2\text{H}_4(\text{OH})\text{CO}_2]$. In fact, $[\text{HOEtNH}_3][\text{NO}_3]$ has a relative low viscosity, but the large effective hydrodynamic volume compare to its ion size indicates a frictional rotation. Further understanding of the dielectric relaxation behaviour of this kind of ILs requires much more microscopic information from other spectroscopies.

<table>
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<tr>
<th>$\text{ILs}$</th>
<th>$\tau_{cc}[\text{ps}]$</th>
<th>$\alpha$</th>
<th>$\eta[\text{mPa} \cdot \text{s}]$</th>
<th>$\tau_{\text{rot}}[\text{ps}]$</th>
<th>$V_{\text{eff}}[10^{-30}\text{m}^3]$</th>
</tr>
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<tbody>
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<td>$[\text{MeNH}_3][\text{HCO}_2]$</td>
<td>86</td>
<td>0.08</td>
<td>17$^{g)}$</td>
<td>0.7</td>
<td>5.6</td>
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<tr>
<td>$[\text{EtNH}_3][\text{HCO}_2]$</td>
<td>309</td>
<td>0.11</td>
<td>32$^{g)}$</td>
<td>10.3</td>
<td>44.1</td>
</tr>
<tr>
<td>$[\text{BuNH}_3][\text{HCO}_2]$</td>
<td>815</td>
<td>0.16</td>
<td>70$^{g)}$</td>
<td>84.4</td>
<td>165.3</td>
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<tr>
<td>$[\text{Mepy}][\text{HCO}_2]$</td>
<td>141</td>
<td>0.14</td>
<td></td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>$[\text{HOEtNH}_3][\text{HCO}_2]$</td>
<td>629</td>
<td>0.25</td>
<td>220$^{g)}$</td>
<td>132.6</td>
<td>83.1</td>
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<tr>
<td>$[\text{HOEtNH}_3][\text{CH}_3\text{CO}_2]$</td>
<td>7117</td>
<td>0.26</td>
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<td>1597.5</td>
<td>312.4</td>
</tr>
<tr>
<td>$[\text{HOEtNH}_3][\text{NO}_3]$</td>
<td>2702</td>
<td>0.48</td>
<td>113$^{g)}$</td>
<td>1201.1</td>
<td>1457.0</td>
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<td>6943</td>
<td>0.30</td>
<td>1324$^{g)}$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.29</td>
<td>342(^{\text{b)}})</td>
<td>1478.5</td>
<td>592.6</td>
</tr>
<tr>
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<td>------</td>
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<td>--------</td>
</tr>
<tr>
<td>((\text{HOEt})_3\text{N})\text{[CH}_3\text{CO}_2\text{]})</td>
<td>5364</td>
<td>0.29</td>
<td>342(^{\text{b)}})</td>
<td>1478.5</td>
<td>592.6</td>
</tr>
<tr>
<td>((\text{HOEt})_3\text{N})\text{[C}_2\text{H}_4\text{(OH})\text{CO}_2\text{]})</td>
<td>(5 \times 10^4)</td>
<td>0.41</td>
<td>455(^{\text{b)}})</td>
<td>(1.94 \times 10^4)</td>
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<td>((\text{HOEtMeIm})\text{[BF}_4\text{]})</td>
<td>419</td>
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<tr>
<td>((\text{EtMe(OH)Py})\text{[EtOSO}_3\text{]})</td>
<td>1368</td>
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<td></td>
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<tr>
<td>((\text{Et(OH)Me}_3\text{N})\text{[(MeO)]}_3\text{PO}_2\text{]})</td>
<td>1236</td>
<td>0.24</td>
<td>250.8</td>
<td></td>
<td></td>
</tr>
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</table>

\(^{\text{g)}}\text{Data from Ref. [Greaves, 2006 #167].}\)
\(^{\text{h)}}\text{Data from Ref. [Yuan, 2007 #166].}\)
Within the scope of this thesis, a series of homogenous ionic liquids were studied by means of frequency dependent dielectric relaxation spectroscopy in microwave range between 0.3 MHz and 20 GHz.

The microwave dielectric spectrum is recorded in form of the complex dielectric permittivity, which is separated into its real part $\epsilon'(\nu)$ and imaginary part $\epsilon''(\nu)$. Spectral analysis indicated a combination of two processes, represented by a model based on a Cole-Cole relaxation time distribution supplemented by a high-frequency correction modelled by a Debye function. In this way, the static dielectric constant, relaxation strength, relaxation time and distribution parameter are obtained.

Ionic liquids are divided into two families, non-protic ILs and protic ILs. The static dielectric constants of protic ILs are commonly higher than those of non-protic ILs; the hydrogen bonded structure substantially enhances the dielectric polarization. The values of non-protic ILs are generally lower than $\varepsilon_{st} = 30$. In case of normal protic ILs alued up to 41 were reached. Protic ILs with functional hydroxy groups showed even higher values, culminating in a value of 85.6 for $[\text{HOEtNH}_3][\text{C}_2\text{H}_4\text{(OH)CO}_2]$. Obviously, the hydroxyl group in the alkyl chain of the anion highly raises the polarity of the anion, thus increasing the dielectric constant.

For non-protic ILs, dielectric constants $\varepsilon_{st}$ are more sensitive to anion variation than to cation variation; with the increasing 1-alkyl chain on the imidazolium ring the value of $\varepsilon_{st}$ increases slightly; similar results are also obtained for $[\text{Al(hfip)}_4]$- based ILs. ILs based on methyl-substituted imidazolium cations do not show a clear tendency. Unlike the non-protic ILs, the sensitivity of dielectric constants $\varepsilon_{st}$ of protic ILs to anions and cations are quite unsystematic.

The data of central relaxation time of ILs show a linear-like correlation to the viscosities in the low viscosity range. Another essential factor that influences the relaxation time is the structure and size of the ions; the longer the alkyl chain in the imidazolium rings, the longer is the relaxation time.
In summarizing the experimental results dielectric relaxation spectroscopy is a powerful tool for characterizing the dielectric behaviour of ILs, including information on the solvent polarity provided by the dielectric constant. Polarity reflects a complex interplay of all intermolecular interactions. Different experiments highlight different facets. The dielectric constant of ILs mainly reflects the reorientational dipolar polarization of the ions. Comparing the polarity parameters from different experimental methods can help to learn more about the many molecular facets.

Another interesting information involved in dielectric spectra concerns solvation dynamics. This thesis focuses mainly on neat ILs. For a better understanding of solvation dynamics, it could be helpful to expand the dielectric experiments to aqueous solutions of ILs and to mixtures of ILs with organic solvents.

In the thesis, most the measurements were carried out at room temperature. The temperature dependent dielectric behaviour of ILs might reveal more information on the ILs properties.

Notably, a more general picture of the static and dynamic solvation properties of ILs requires a combination of dielectric spectroscopy with other techniques, both experimental and computational.
Appendix A: List of references

147. A.Knocks, PhD dissertation, 2001(Ruhr University Bochum).
### Appendix B: Dielectric parameters and source of ionic liquids

<table>
<thead>
<tr>
<th>$T / K$</th>
<th>$IL$</th>
<th>$\varepsilon_s$</th>
<th>$S_{CC}$</th>
<th>$\tau_{CC}$ / [ps]</th>
<th>$\alpha$</th>
<th>Source</th>
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<td>343.15</td>
<td>[EtMeIm][PF$_6$]</td>
<td>13.0 ± 0.5</td>
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<td>45</td>
<td>0.39</td>
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<td>83</td>
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<td>784</td>
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<td>298.15</td>
<td>[EtMeIm][EtO$_2$PO$_2$]</td>
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<td>1000</td>
<td>0.28</td>
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<td>10.6</td>
<td>403</td>
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<td>$S_{CC}$</td>
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<tr>
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<td>[EtMeMeIm][Al(hfip)$_4$]</td>
<td>17.7 + 0.3</td>
<td>14.2</td>
<td>178</td>
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<tr>
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<tr>
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<td>[HeMeIm][Al(hfip)$_4$]</td>
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<td>12.7 + 0.3</td>
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<td>[MeNH$_3$][HCO$_2$]</td>
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### Appendix C: Lists of ion structures

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<tr>
<th>Cation</th>
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<tr>
<td>[MeMeIm]</td>
<td>1,3-dimethylimidazolium</td>
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<td>[EtMeIm]</td>
<td>1-ethyl-3-methylimidazolium</td>
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<td>[PrMeIm]</td>
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<td>[AlMeIm]</td>
<td>1-allyl-3-methylimidazolium</td>
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<td>[BuMeIm]</td>
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<td>[PeMeIm]</td>
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<td>[HeMeIm]</td>
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<td>Symbol</td>
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<td>[CH₃CO₂]</td>
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<td>[C₂H₄(OH)CO₂]</td>
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</table>
[[(MeO)₂PO₂] Dimethylphosphate

[[EtO]₂PO₂] Diethylphosphate

[Al(hfip)₄] Tetra(hexafluoroisopropoxy) aluminate
Curriculum Vitae

Personal details

Name: Mianmian Huang
Date of birth: 26.12.1978 in P.R.Chian, Fujian

Primary and secondary education

1985 – 1991 Primary School, China
1991 – 1997 Secondary School, China

Academic education

1997 - 2001 Bachelor of Science in Chemical Engineering (Biotechnology)
Nanjing University of Science and Technology in China

2003 – 2005 Bachelor of Science in Chemistry,
Ruhr University Bochum
“Infarotspektroskopische Untersuchung von Van-der-Waals-Komplex ArCO”

2005 – 2006 Master of Science in Chemistry,
Ruhr University Bochum
“Dielektrische Spektroskopie an ionischen Flüssigkeiten”
Research experience

2006 Research assistant, Physical Chemistry II, Ruhr University Bochum

2006 – 2010 PhD studies in Physical chemistry, Ruhr University Bochum
“Dielectric properties of ionic liquids”

Publications

Huang, M. M. and H. Weingärtner
*Protic Ionic Liquids with Unusually High Dielectric Permittivities.*

Mian-Mian Huang, Safak Bulut, Ingo Krossing, and Hermann Weingärtner
*Communication: Are hydrodynamic models suited for describing the reorientational dynamics of ions in ionic liquids? A case study of methylimidazolium tetra(hexafluoroisopropoxy)aluminates*  

S. Bulut, P. Klose, M.-M. Huang, H. Weingärtner, P. J. Dyson, G. Laurenczy, C. Friedrich, J. Menz, K. Kümmerer, and I. Krossing
*Synthesis of Room Temperature Ionic Liquids with the weakly coordinating [Al(ORF)4]--Anion (RF = C(H)(CF3)2) and the Determination of their Principal Physical Properties*  
Mian-Mian Huang, Karola Schneiders, Peter S. Schulz, Peter Wasserscheid and Hermann Weingärtner

*Ion Speciation Driving Chirality Transfer in Imidazolium-based Camphorsulfonate Ionic Liquids.*

PCCP, online available DOI: 10.1039/c0cp01120g.

Mian-Mian Huang, Yanping Jiang, Padmanabhan Sasisanker, Gordon W. Driver, Hermann Weingärtner

*Static relative dielectric permittivities of ionic liquids at 25 °C*

Submitted to Journal of Chemical and Engineering Data.