

9 Dielectric Properties of Ionic Liquids: Achievements So Far and Challenges Remaining

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ABSTRACT

The static dielectric constant of an ionic liquid is not measurable by conventional methods because the samples are largely short-circuited by their intrinsic electrical conductance. It is, however, possible to determine this quantity by recording the frequency-dependent dielectric dispersion curve in the microwave regime, followed by extrapolation to quasi-static conditions. This review compiles the information on static dielectric constants available from such experiments, and discusses trends in the cation and anion dependence. The results classify most aprotic ionic liquids as moderately polar solvents with dielectric constants of the order of $\epsilon = 10\text{--}12$; protic ionic liquids, however, exhibit much higher values.

9.1 INTRODUCTION

Many innovative applications of ionic liquids benefit from the possibility of optimising their solvent properties by cation and anion variation [1–3]. Such modifications can dramatically affect the outcome and rate of chemical reactions. An understanding of these phenomena requires the characterisation and understanding of solvation, solvation dynamics, and their effects on reactants and transition states. The frequency-dependent dielectric response and its

zero-frequency limit—the relative static dielectric permittivity or “static dielectric constant”—reveal important facets of these properties [4, 5].

The dielectric response can be probed by dielectric relaxation spectroscopy (DRS), which measures the response of the dielectric polarisation of a sample to an electric field [6, 7]. In uncharged volatile organic compounds (VOCs), dielectric relaxation is driven by rotational motions of dipolar species, henceforth briefly denoted as “dipolar” processes. In electrically conducting systems, the dielectric response is also affected by translational motions of the charged species, henceforth denoted as “ionic” processes. In the case of complex ions, which possess an electric dipole moment, the dielectric response is partly dipolar and partly ionic.

In the case of VOCs and ionic liquids of low viscosity, a large portion of the dipolar and ionic dynamics driving dielectric relaxation occurs on the nano-second to sub-picosecond timescale, which corresponds to the microwave and far-infrared (FIR) regions of the dielectric spectrum. While the microwave region is captured by well-established experimental techniques [6], FIR methods are currently only available in a few specialised laboratories.

The range of broadband microwave spectra roughly extends from 1 MHz to several tens of gigahertz. The location of the dielectric modes in this regime usually depends on the viscosity η of the sample. Because high viscosities form barriers for most applications, interest usually focusses on low-viscosity ionic liquids [1–3]. For low-viscosity VOCs at ambient conditions, η is typically of the order of 1 mPa s (=1 cP), and the slowest component of dipolar dynamics occurs on the timescale of a few picoseconds. Thus, the relevant dielectric modes are usually centred at the upper edge of the microwave regime, say, above 10 GHz. By contrast, under ambient conditions, the lowest viscosities of ionic liquids are of the order of several tens of mPa s [1, 3], which is one to two orders of magnitude higher than the viscosities of simple VOCs. Accordingly, modes in ionic liquids are shifted to lower frequencies.

Although the basic DRS techniques are the same for VOCs and ionic liquids, two features render applications to ionic liquids particularly difficult [4, 5]: first, the direct current (DC) electrical conductivity contributes to the dielectric spectrum and superimposes upon the processes of interest. Second, conducting samples give rise to polarisations at the interface between the liquid and the sample cell, usually called “electrode polarisations.” Both effects rapidly increase with decreasing frequency, obscuring low-frequency spectra [4, 5, 8]. Despite these aberrant perturbations, DRS has for a long time provided unique information on the structure and dynamics of conducting electrolyte solutions [5]. We have shown in a pilot study of ethylammonium nitrate [9] that DRS can be beneficially applied to ionic liquids as well.

As a particularly interesting aspect, the low-frequency tail of the dielectric spectrum of an ionic liquid provides experimental access to its static dielectric constant, ε [10, 11]. For conducting media, standard capacitance methods for determining ε fail because the ionic liquid short-circuits the sample cell. If a

sufficiently large segment of the frequency-dependent dielectric response is covered, ε can be determined by zero-frequency extrapolation [10].

This overview spotlights the achievements made so far in characterising and understanding dielectric properties of ionic liquids, and on the challenges remaining, with a major focus on studies from the author's laboratory.

9.2 A GLANCE AT DIELECTRIC THEORY OF ELECTRICALLY CONDUCTING SYSTEMS

For VOCs, the interpretation of dielectric spectra benefits from experience over many years [7], and the outcomes of experiments usually match quite well with intuition. The dielectric behaviour of ionic liquids is more subtle. To avoid misconceptions, such as the belief that the static dielectric constant of an ionic liquid is infinite [12], a glance at the dielectric theory of electrically conducting systems is mandatory before discussing the dielectric properties of ionic liquids in detail.

DRS measures the interaction of a sample with an oscillating, low-amplitude electric field. The field-induced dielectric polarisation reflects the fluctuation of the total, that is, macroscopic electric dipole moment, $\mathbf{M}(t)$, of the sample (bold quantities denote vectors). The fluctuations of $\mathbf{M}(t)$ can be of different origins:

1. In VOCs, $\mathbf{M}(t)$ fluctuates due to orientational motions of the molecular dipoles, while translational motions do not contribute directly. Note that there are indirect translational contributions because collision-induced and interaction-induced high-frequency contributions will affect the macroscopic electric dipole moment. These features render DRS as a key method for studying the orientational dynamics of VOCs [7, 13]. The results are readily described in terms of a frequency-dependent dielectric permittivity.
2. In simple molten salts, such as NaCl, the individual ions lack a permanent electric dipole moment, so that orientational polarisation is absent. In the case of charged species, translational dynamics, however, affect $\mathbf{M}(t)$, leading to a frequency-dependent electrical conductivity [14]. Moreover, one expects interaction-induced high-frequency contributions to $\mathbf{M}(t)$.
3. Ionic liquids with dipolar ions share properties of VOCs and simple molten salts; that is, relaxation is partly dipolar and partly ionic [15].

Because the dielectric modes lack specificity to these mechanisms, their correct assignment is highly challenging. Molecular dynamics (MD) simulations can assist interpretation, but adequate simulations are still scarce [15–18]. Dielectric theory [6, 7] starts with Maxwell's equations, which have to be

supplemented by materials equations, namely the frequency-dependent relative dielectric permittivity, Equation (9.1),

$$\varepsilon^*(\nu) = \varepsilon_r'(\nu) - i\varepsilon_r''(\nu) \quad (i^2 = -1), \quad (9.1)$$

and the frequency-dependent electrical conductivity, Equation (9.2),

$$k^*(\nu) = \kappa'(\nu) - i\kappa''(\nu). \quad (9.2)$$

The real parts of the two quantities reflect the in-phase response of the sample to the oscillating field; the imaginary parts reflect the out-of-phase response. At finite frequencies, the dipolar and ionic contributions, $\kappa^*(\nu)$ and $\varepsilon^*(\nu)$, are coupled and merge to a generalised dielectric function, Equation (9.3),

$$\Sigma^*(\nu) = \Sigma'(\nu) - i\Sigma''(\nu). \quad (9.3)$$

Experiments probe the propagation of electromagnetic waves in the sample, which can be expressed in terms of $\Sigma^*(\nu)$. The real part, $\Sigma'(\nu)$, of the complex dielectric function is denoted as *dielectric dispersion*. In essence, $\Sigma'(\nu)$ indicates how far the sample polarisation is able to follow the oscillating field. The imaginary part, $\Sigma''(\nu)$, denoted as *dielectric loss*, reflects the absorption of electromagnetic radiation by the sample. Dispersion and loss are linked through the Kramers–Kronig relation [6, 7]. In principle, therefore, it is possible to obtain the complete information either from the dispersion curve $\Sigma'(\nu)$ or from the loss signal $\Sigma''(\nu)$. However, for reasons of experimental accuracy, it is often preferable to synchronously record and analyse both $\Sigma'(\nu)$ and $\Sigma''(\nu)$.

At zero-frequency, $\varepsilon^*(0)$ and $\kappa^*(0)$ become decoupled, and are real quantities. The latter property enables the definition of the static dielectric constant in terms of the zero-frequency limit, Equation (9.4),

$$\varepsilon^*(0) = \Sigma'(0) \equiv \varepsilon, \quad (9.4)$$

of the dispersion curve [6, 7]. The corresponding zero-frequency limit of the conductivity, Equation (9.5),

$$\kappa^*(0) = \kappa'(0) \equiv \kappa_{\text{DC}}, \quad (9.5)$$

yields the DC conductivity, which is measurable by standard conductance methods. Because κ_{DC} is independently measurable, it is convenient to decompose $\kappa^*(\nu)$ according to Equation (9.6):

$$\kappa^*(\nu) = \kappa_{\text{DC}} + \kappa_{\text{ex}}^*(\nu). \quad (9.6)$$

The excess term, $\kappa_{\text{ex}}^*(\nu)$, captures all the frequency-dependent contributions to the conductance. This separation yields the working Equation (9.7) [6]:

$$\Sigma^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) - i\kappa_{\text{DC}}/2\pi\nu\varepsilon_0. \quad (9.7)$$

In the limit $\nu \rightarrow 0$, the ν^{-1} -dependent term in Equation (9.7), called *Ohmic loss*, causes the measured imaginary part $\Sigma''(\nu)$ to diverge. ε_0 is the permittivity of the vacuum. The Ohmic loss can be experimentally corrected for because κ_{DC} is independently measurable. Alternatively, it can be extracted from the low-frequency branch of $\Sigma''(\nu)$, where only the ν^{-1} -dependent contribution survives.

The non-divergent parts, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$, in Equation (9.7) are of the form defined in Equations (9.8):

$$\varepsilon'(\nu) = \varepsilon'_r(\nu) - i\kappa_{\text{ex}}''(\nu)/2\pi\nu\varepsilon_0 \quad (9.8a)$$

and

$$\varepsilon''(\nu) = \varepsilon_r''(\nu) - i\kappa_{\text{ex}}'(\nu)/2\pi\nu\varepsilon_0. \quad (9.8b)$$

Despite the conductance correction in Equation (9.7), the residual terms in Equation (9.8a) and Equation (9.8b) still involve conductance contributions that are related to frequency-dependent deviations from the DC conductance, usually denoted as *conductance dispersion*. To a first approximation, it is often assumed that in the megahertz/gigahertz regime, the conductivity is a frequency-independent constant equal to κ_{DC} . In the latter case, the real part, $\Sigma'(\nu) \cong \varepsilon'(\nu)$, and the conductance-corrected imaginary part, $\varepsilon''(\nu) \cong \Sigma''(\nu) - \kappa_{\text{DC}}/2\pi\nu\varepsilon_0$, involve only dipolar contributions.

It is mandatory to note alternative, but fully interchangeable, representations of the experimental spectra in terms of the complex conductivity, Equation (9.9),

$$\kappa^*(\nu) = i2\pi\nu\varepsilon_0\varepsilon^*(\nu), \quad (9.9)$$

or in terms of the dielectric modulus, defined as the inverse permittivity [19], Equation (9.10),

$$M^*(\nu) = 1/\varepsilon^*(\nu). \quad (9.10)$$

These representations are widely used for describing relaxation in solid and glassy ionic conductors [6, 20]. In the latter case, the permittivity $\varepsilon^*(\nu)$ and, in particular, its real part, $\varepsilon'(\nu)$, are seldom considered, although they can shed light on interesting facets of the data not captured by the alternative representations [21]. The preference of the permittivity formalism in most studies of low-viscosity ionic liquids is founded in the key role ascribed to dipolar, as opposed to ionic, relaxation mechanisms in the microwave regime [4, 5]. In a few cases, the conductance [22, 23] and modulus representations [24] have been applied to ionic liquids as well.

In concluding this theoretical digression, some key features may be pinpointed:

1. By contrast to VOCs on the one hand, and simple molten salts on the other, the dielectric response of an ionic liquid has both dipolar and ionic components.
2. In the limit of $\nu \rightarrow 0$, the measured imaginary part, $\Sigma''(\nu)$, of the complex dielectric function shows a divergence founded in the contribution from the DC conductivity. This divergence can be removed by correction for the Ohmic loss, but the corrected spectrum is still affected by conductance dispersion.
3. The real part, $\Sigma'(\nu)$, is not affected by the DC conductivity and is non-divergent. Because the static dielectric constant is defined by the zero-frequency limit of $\Sigma'(\nu)$, it is well defined and finite, while in VOCs only dipolar processes contribute to ϵ , for a conducting liquid ϵ involves ionic contributions.

9.3 PHENOMENOLOGICAL DESCRIPTION OF DIELECTRIC SPECTRA OF IONIC LIQUIDS

9.3.1 Microwave Spectra

The vast majority of DRS studies concern the microwave regime, where experimental methods are well established and now largely benefit from general progress in measurement technology. Above all, the availability of vectorial network analysers up to several tens of gigahertz facilitates methods such as the coaxial reflection technique, applied by us [4]. Although the experimental methods are the same for VOCs and ionic liquids, the Ohmic loss and electrode polarisation render dielectric studies of conducting ionic liquids challenging.

As a prototypical example for low-viscosity ionic liquids [4, 25–29], Figure 9.1 shows the measured real and imaginary parts of the complex permittivity of $[\text{C}_2\text{mim}][\text{OTf}]$ at 25 °C [30]. Visual inspection of $\Sigma''(\nu)$ reveals the ν^{-1} divergence of the Ohmic loss. Distinct relaxation processes only become visible in the conductance-corrected spectrum, $\epsilon''(\nu) = \Sigma''(\nu) - \kappa_{\text{DC}}/2\pi\nu\epsilon_0$. At low frequencies, $\epsilon''(\nu)$ is a very small fraction of $\Sigma''(\nu)$, thus imposing a low-frequency limit for an accurate extraction of $\epsilon''(\nu)$.

In the simplest case, dielectric relaxation is exponential in the time domain, as for example predicted by the well-known Debye model of diffusive reorientational dynamics. Exponential relaxation is commonly denoted as the “Debye process” [6, 7]. Fourier–Laplace transformation of an exponential relaxation process in the time domain leads to a Lorentzian spectral shape of the corresponding permittivity contribution in the frequency domain, $\Delta\epsilon^*(\nu)$, which is characterised by the relaxation amplitude S and the Debye relaxation time τ_{D} , Equation (9.11),

$$\Delta\epsilon^*(\nu) = S/(1 + i2\pi\nu\tau_{\text{D}}). \quad (9.11)$$

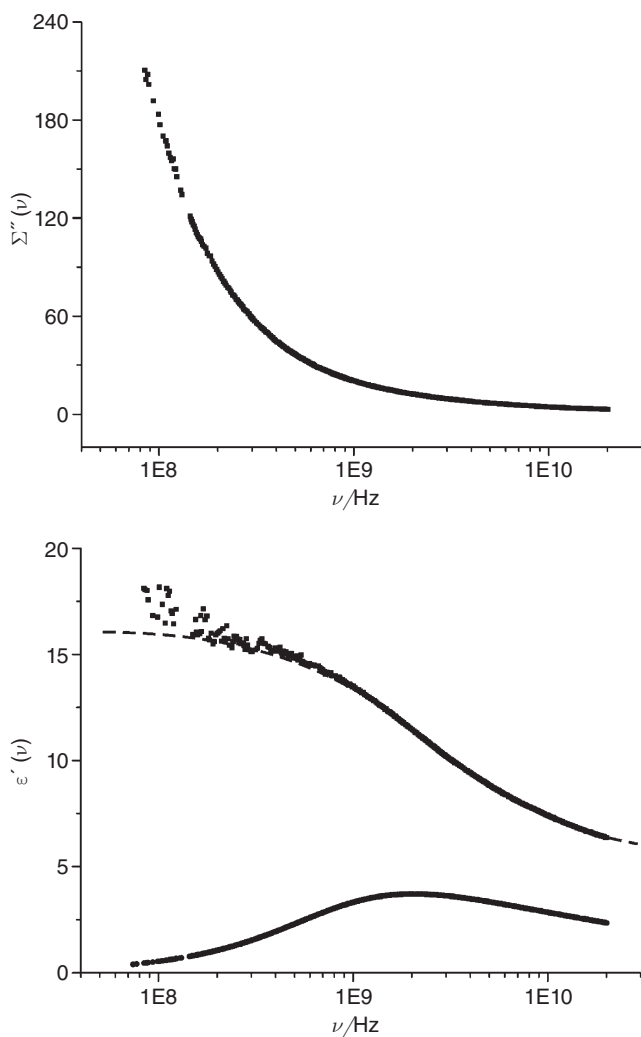


Figure 9.1 Real part (dielectric dispersion) $\epsilon'(\nu)$, total imaginary part (dielectric loss) $\Sigma''(\nu)$, and conductance-corrected imaginary part $\epsilon''(\nu) = \Sigma''(\nu) - \kappa_{DC}/2\pi\nu\epsilon_0$ of the frequency-dependent complex dielectric function of $[\text{C}_2\text{mim}][\text{OTf}]$ at 25°C . The increase in $\epsilon'(\nu)$ at low frequencies relative to the dashed line reflects the onset of electrode polarisation effects.

However, compared with the predictions from Equation (9.11), the decay of $\varepsilon'(\nu)$ and the loss signal $\varepsilon''(\nu)$ are largely broadened. For low-viscosity VOCs, such a broadening is not typical.

Another special feature of dielectric spectra of ionic liquids concerns the existence of pronounced high-frequency processes. For $\nu \rightarrow \infty$, the intermolecular dynamics ceases, but dielectric dispersion is still affected by non-relaxing intramolecular contributions, mainly due to ion polarisability. Izgorodina et al. [31] have shown that calculated ion polarisabilities correlate well with the optical refractive index of the sample, n , so that in case of ionic liquids, the polarisability contribution does not differ substantially from that of VOCs.

In most VOCs, high-frequency extrapolation of the measured dispersion curves $\varepsilon'(\nu)$ yields a high-frequency limit of $\varepsilon_\infty \cong n^2 \cong 2$, as predicted by the Maxwell relation [7]. By contrast, microwave spectra of ionic liquids usually extrapolate to values well above n^2 [4, 9, 25–27]. The difference $\varepsilon_\infty - n^2$ indicates that microwave experiments do not capture the complete intermolecular dynamics, presumably due to processes in the terahertz regime. This conjecture [9] is now well confirmed by experiments in the terahertz regime [32–37]. Taken together, microwave spectra of ionic liquids are rationalised by a broad low-frequency mode, superimposed by weak wings of terahertz processes, and in some cases by weak modes at intermediate frequencies.

In analogy to well-established procedures for describing spectral broadenings in viscous VOCs [6, 7, 13], in initial work on ionic liquids [4, 5] it was tempting to parameterise the low-frequency mode by an asymmetrical distribution of relaxation times, adopting the Cole–Davidson (CD) model [6, 7, 13]. There is, however, mounting evidence [27, 33] that, after proper correction for high-frequency processes, a symmetrical distribution of relaxation times according to the Cole–Cole (CC) model [6, 7, 13] is more apt. The CC function, Equation (9.12),

$$\Delta\varepsilon^*(\nu) = S/\{1 + (i2\pi\nu\tau)^{1-\alpha}\}, \quad (9.12)$$

implies a symmetrical broadening of the Lorentzian signal characterised by an exponent $0 \leq \alpha < 1$. In the Debye limit, $\alpha = 0$. Such a spectral shape is mainly suggested by a comparative analysis of dielectric and optical Kerr effect (OKE) spectra [27, 33].

There are other approaches for spectral parameterisation of broadened processes. Non-exponential relaxation in the time domain is often described by the Kohlrausch–Williams–Watts (KWW) stretched exponential function [6, 7, 13]. The KWW function has, for example, been used for representing time-dependent relaxation functions of ionic liquids deduced from MD simulations [16, 38]. Unfortunately, it does not possess an analytical Fourier–Laplace transform, which complicates the analysis of spectra in the frequency domain. For ionic liquids, correlations of the KWW parameters with those of the CC/CD distributions were considered by Schröder and Steinhauser [38].

Some comments on the chosen parameterisation are mandatory:

1. Because both the CD and CC models are empirical, their application is neither founded in theory nor does the spectral shape guide molecular interpretation.
2. The statistical quality of the CC and CD fits does not allow a clear-cut conclusion in favour of one of the models [27]. The rationale is founded in the fact that the wings of high-frequency processes obscure the spectral shapes.
3. The change in parameterisation indicates the importance of low-frequency contributions that are not accounted for by the CD model, which approaches Debye behaviour at the low-frequency side. It is likely that these long-time processes are founded in the micro-heterogeneous structure of the ionic liquids [33].
4. The two models exhibit different asymptotic behaviour as $\nu \rightarrow 0$. As an aberrant consequence, some reported dielectric constants need re-evaluation.

9.3.2 Terahertz Spectra

Only a few groups have so far studied the sub-picosecond part of the dielectric response. Sub-picosecond dynamics can be probed by conventional FIR spectroscopy [36, 37], but the experimental capabilities now greatly benefit from advances in femtosecond laser pulse technology [39], which permit probing of the femtosecond dielectric response by terahertz time domain spectroscopy (TDS) [32–35].

The terahertz spectra exhibit a wide range of behaviour. As an example, Figure 9.2 shows the conductance-corrected dielectric loss spectrum of ethylammonium nitrate, where a strong microwave process [9] is supplemented by a mode near 1.7THz [35]. At higher frequencies, FIR spectra identify further processes [35, 37]. The comparatively simple spectrum contrasts, for example, to the spectrum of $[\text{C}_4\text{mim}][\text{BF}_4]$, where many overlapping relaxation processes render the dielectric loss remarkably persistent up to the terahertz regime [5, 32].

9.4 MOLECULAR PROCESSES AFFECTING THE DIELECTRIC RESPONSE

9.4.1 Dipolar Processes

Depending on the timescale, the dielectric response of an ionic liquid can be driven by dipolar as well as ionic mechanisms. The lack of specificity to these mechanisms renders the assignment of the dielectric modes difficult. Interpretations typically resort to general knowledge about the structure and dynamics

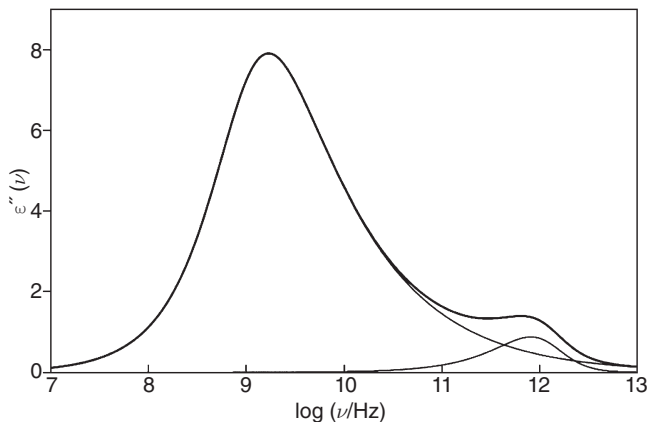


Figure 9.2 The “complete” conductance-corrected dielectric loss spectrum $\varepsilon''(\nu)$ of ethylammonium nitrate at 25 °C constructed from microwave [9] and terahertz-TDS data [35]. The spectrum is deconvoluted into a broad-end low-frequency process and a high-frequency process. The low-frequency process is fitted by a symmetrical CC relaxation time distribution. The high-frequency process is fitted by a damped harmonic oscillator.

of ionic liquids [1–3], specifically designed MD simulations [15–18], comparison with other spectroscopic data [28, 33, 40], and long-standing experience on dielectric processes in VOCs [7] and electrolyte solutions [5].

On very short timescales, dipolar processes are founded in the librational dynamics of the molecular ions. The spectral assignment of terahertz modes to librational processes is, however, difficult because a multitude of (translational) intermolecular vibrations of the ions in the cage of their neighbours can contribute to the same spectral region. Compared with these intermolecular vibrations, contributions of librational motions to the dielectric spectrum seem less relevant.

There is consensus that the dominant mode in the megahertz/gigahertz regime mainly reflects the co-operative reorientation of dipolar cations [4, 25–29], as confirmed by comparison with magnetic relaxation data [28, 40], OKE spectra [33], and MD simulations [16–18]. At a first glance, this dominant mode resembles the reorientational relaxation of dipolar species in VOCs, but some observations make a strong case against a detailed analogy:

- Comparison of dielectric and OKE spectra [33] indicates that cation reorientation occurs via large-angle jumps.
- Hydrodynamic approaches, which successfully describe dipole reorientation in VOCs, fail to rationalise the observed rotational modes in ionic liquids [4, 27, 41], although they reasonably account for translational diffusion of the ions [42, 43].

- For VOCs, non-exponential relaxation is usually observed in viscous and glassy states, where it signals relaxation in a spatially heterogeneous environment. In ionic liquids, non-exponential relaxation also occurs in low-viscosity systems.

In ionic liquids, non-exponential relaxation seems to reflect spatial heterogeneity resulting from the existence of meso-scale hydrophilic and hydrophobic domains in the ionic liquid structure [1–3]. The existence of such domains is key to the highly amphiphilic properties of ionic liquids, which can, for example, incorporate apolar molecules in hydrophobic domains and polar molecules in hydrophilic domains. By variation of the hydrophobic side chains of 1,3-dialkylimidazolium ionic liquids, Mizoshiri et al. [29] have estimated the local dielectric constant of hydrophilic domains in aprotic ionic liquids to be of the order of $\varepsilon = 20$, and that of hydrophobic domains to be of the order of $\varepsilon = 2.5$.

It is an open question how far these heterogeneous structures are related to the observed jump reorientation and to the failure of hydrodynamic approaches for ion reorientation. In low-viscosity VOCs, the low-frequency modes normally reflect small-angle diffusive reorientation and are well described by hydrodynamic approaches.

The failure of hydrodynamic models was noted in several papers [4, 26, 27] and recently studied in detail for ionic liquids containing the tetra(hexafluoroisopropoxy)aluminate(III) ($[\text{Al}(\text{hfp})_4]^-$) anion [41]. Because the viscosities of $[\text{Al}(\text{hfp})_4]^-$ ionic liquids are low, and cation modification does not substantially change the viscosity [44], this novel class of ionic liquids provides excellent candidates for testing hydrodynamic theories.

Hydrodynamics links the single-particle reorientation time τ_{rot} of a particle at temperature T to the bulk viscosity η of the surrounding medium, resulting in the well-known Stokes–Einstein–Debye (SED) equation, and its descendants [45]:

$$\tau_{\text{rot}} = 3V_{\text{eff}}\eta f/k_{\text{B}}T, \quad (9.13)$$

where V_{eff} is the effective (“hydrodynamic”) volume of the rotating particle, k_{B} is the Boltzmann constant, and f is a coupling factor that accounts for the hydrodynamic boundary conditions at the surface of the rotating particle. The effective volumes, V_{eff} , obtained from the dielectric relaxation times (after correction for co-operative effects) are at least two orders of magnitude smaller than the geometric volumes of the cations [41]. NMR relaxation data [40] show that this failure is founded in the rotational dynamics of the cations, and not special to dielectric relaxation. Instead of discussing this effect in terms of the anomalously small volume, it could also be seen as a local viscosity that is much smaller than that of the bulk. The results imply an almost frictionless cation reorientation, which is consistent with the meso-structure, and may be related to ion reorientation by large-angle jumps.

Spectral contributions by dipolar anions are far more difficult to assess. Halide ions and anions of high molecular symmetry, such as $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$, are dielectrically inactive. Other dipolar anions result in unexpectedly weak dielectric modes, if these are detectable at all [4, 5]. An example is $[\text{C}_2\text{mim}][\text{OTf}]$, where a weak mode at the upper edge of the spectrum in Figure 9.1 accounts, at least in part, for the asymmetric shape of the loss curve $\varepsilon''(\nu)$ [30].

Notable exceptions are alkyl sulfates such as $[\text{C}_2\text{mim}][\text{C}_2\text{H}_5\text{SO}_4]$, which exhibit unusually high static dielectric constants [11]. Spectral analysis shows that these are caused by a strong mode near 10 GHz, which is not present in other ionic liquids [46]. While it seems inescapable to attribute this mode to anion reorientation, the fast relaxation and the low amplitudes of anion contributions in other ionic liquids are not clear.

Other candidates for dipolar relaxation are long-lived ion pairs (and higher dipolar ion clusters). Ion pairing in ionic liquids is a much debated issue [1–3]. By analysis of the conductance–ion diffusion relationship, Watanabe and coworkers [42, 43] have concluded that a notable fraction of ions contribute to mass transport, but not to charge transport, as is expected for cations and anions forming neutral ion pairs.

In dielectric spectra, ion pairs should reveal themselves by intense modes because oppositely charged ions at contact give rise to very high electric dipole moments. Ion-pair modes are well documented for salts in solvents of low and moderate polarity, and make DRS a powerful tool for ion-pair spectroscopy [5, 47, 48]. By contrast, there is no evidence for such modes in neat ionic liquids [4, 5]. Obviously, cation–anion configurations, which cause the observed reduction in the conductance of neat ionic liquids, do not survive on the timescale of molecular reorientation, signalling lifetimes of less than ~ 10 ps. Ion-pair modes have, however, indeed been identified on short timescales in the terahertz regime [36]. There is also no convincing evidence for contributions of larger ion clusters. Note that such aggregates are dielectrically invisible, if the ions are involved in symmetric clusters with low or vanishing total electric dipole moments.

9.4.2 Ionic Processes

Ionic contributions to the dielectric response may result from ion migration, as reflected by the frequency-dependent electrical conductivity $\kappa^*(\nu)$. As expanded upon in detail in the theoretical section (Section 9.2), it is convenient to separate $\kappa^*(\nu)$ into the Ohmic loss due to the DC conductivity and residual effects due to conductance dispersion. The latter phenomenon is little understood. Its relevance depends on the time/frequency range under consideration:

- In the terahertz regime, translational processes due to intermolecular vibrations of ions in the cage of their neighbours are well established.

- In the microwave (megahertz/gigahertz) region, experiments and simulations do not decisively indicate conductance dispersion. If present, the measured dielectric loss will capture these ionic contributions.
- In the kilohertz regime and below, electrode polarisation has so far prevented any decisive experiments.

The relevance of intermolecular vibrations for dielectric spectra is well established by terahertz-TDS/FIR spectroscopy. An illustrative example is the mode at 1.7 THz in Figure 9.2, which was assigned to an intermolecular bending vibration in the hydrogen-bonded network of [EtNH₃][NO₃] [35, 37]. More complex spectra, for example, of [C₄mim][BF₄], obviously reflect a superposition of many vibrational modes [5, 33]. It seems that in the terahertz region, dielectric spectra are highly specific to the ionic liquids, presumably due to the sensitivity of the intermolecular vibrations to local ionic liquid structures. The presence of these translational modes in the terahertz regime is confirmed by computation [15, 17, 18, 36, 38]. In VOCs, intermolecular vibrations are dielectrically inactive, except for interaction-induced contributions in the terahertz regime, which can be significant [7].

As noted earlier, relaxation in the microwave regime should mainly reflect dipolar reorientation of the ions. It may, however, be speculated that the broad modes also cover conductance dispersion. Nevertheless, it seems that to a first approximation, the conductivity in the megahertz/gigahertz regime can be treated as a frequency-independent constant equal to the DC conductivity. The same conclusion can be drawn from simulated dielectric spectra of ionic liquids [16]. For molten NaCl [17], where the dielectric response is purely ionic and conductance dispersion is not superimposed by processes due to dipolar ions, MD simulations by Song [17] also do not signal conductance dispersion in the microwave regime [17].

Conductance dispersion in the megahertz/gigahertz or sub-megahertz region may be expected on grounds of the retarded response of the ionic environment to the motion of a central ion. This effect, occasionally denoted as “space charge polarisation” [12], resembles the *ion cloud relaxation* predicted in the case of dilute electrolyte solutions by Debye and Falkenhagen (DF), as early as in 1928 [49]. Meanwhile, DF theory has been extended to concentrated solutions [50, 51]. Debye and Falkenhagen have conjectured that, in an electric field, the Debye–Hückel (DH) ion cloud cannot follow immediately a moving ion and becomes asymmetric, which retards the motion of the ion. In an oscillating electric field, this effect depends on frequency.

Ion cloud relaxation is experimentally well established for solutions of multiply charged macro-ions, such as polyelectrolytes like DNA, where it gives rise to a strong mode in the kilohertz region [52, 53]. Ion cloud relaxation of much lower magnitude—and located in the megahertz regime (~25 MHz)—has been observed in the case of ionic micelles [54, 55]. In electrolyte solutions, such as NaCl–H₂O, ion cloud relaxation is theoretically expected in the

megahertz/gigahertz regime, but it is fair to say that the reported evidence is very weak [56–58], presumably due to very low amplitudes in systems of low nett charge.

The predictive power of these results for neat ionic liquids is very limited. The concept of a DH-type ion cloud implies a monotonously decreasing charge density of the counterions around a central ion, as opposed to the oscillating charge density of charge-ordered layers of cations and anions in ionic liquids [3]. There is a DF-type theory for dielectric processes in solid and glassy ion conductors [59] that successfully rationalises conductance dispersion in terms of the structural relaxation of the environment after the jump of an ion to a different position [60]. It does not seem possible to infer from this theory the magnitude and timescale of conductance processes in the fluid regime of ionic liquids of low viscosity.

9.5 RELATION TO SOLVATION DYNAMICS

The characterisation and understanding of the dielectric response are crucial for an understanding of the solvation dynamics of ionic liquids, which plays a key role in reactions involving charge rearrangements. Solvation dynamics can be probed by solvation spectroscopy (time-resolved fluorescence spectroscopy), which uses solvatochromic dyes for observing the solvent reorganisation after excitation of the probe's dipole moment by photons [18, 61]. Solvation dynamics should be closely related to the dielectric response.

Maroncelli's group has used dielectric continuum theory for computing solvation spectra of ionic liquids from dielectric spectra. By contrast to successful calculations for VOCs, such models have failed for ionic liquids [62]. This shortcoming may be due to several reasons, such as the lack of knowledge on the high-frequency (terahertz) portion of the spectra, limitations of continuum dielectric theory, or a different relevance of translational versus rotational dynamics for the dielectric and solvation responses. Song [17] has recently proposed a DH-type continuum model for ion concentrations up to neat ionic liquids, which offers the prospect of a better understanding of the role of the dielectric response in charge-controlled chemical reactions.

9.6 THE STATIC DIELECTRIC CONSTANT OF IONIC LIQUIDS

Dielectric relaxation spectroscopy is especially useful for determining static dielectric constants of conducting liquids [10, 11]. For VOCs, the prominent role of ϵ for assessing and modelling solvent properties is well recognised. The definition of ϵ in terms of the zero-frequency limit of the frequency-dependent dielectric dispersion curve yields a recipe for determining ϵ of conducting liquids, where conventional capacitance methods fail. Because ϵ is the sum of

TABLE 9.1 Reported Experimental Static Permittivities of [C₄mim][BF₄]

Method	Frequency	ϵ	Reference
DRS	200 MHz–20 GHz	14.0 (11.7)	[10]
DRS	200 MHz–89 GHz	14.6 (12.2)	[31] ^a
DRS	1 MHz–20 GHz	14.1	[28]
Terahertz-TDS	100–1200 GHz	6.7	[37]
Waveguide	2.45 GHz	8.7	[62]
Voltammetry	50 kHz	68.89	[63]
Capacitance	1–3 MHz	1600	[64]

^a Recalculated from Reference 16.

the amplitudes of all contributing dielectric modes, in contrast to most other polarity probes, one can trace the mechanisms of the underlying processes. Such procedures have been exploited for more than 50 years for characterising static dielectric constants of electrolyte solutions, as, for example, documented in the 1973 monograph by Hasted [63].

For obvious reasons, static dielectric constants of ionic liquids measured by DRS are at least by an order of magnitude less accurate than data for VOCs obtained by conventional methods. Table 9.1 compares ϵ values for [C₄mim][BF₄] at, or near, 25 °C. To obtain a common basis, DRS results in earlier studies have been re-extrapolated in terms of the CC model. On this common basis, the results of three independent DRS experiments [10, 28, 32] agree to within 4%. By comparison, extrapolation of ϵ from terahertz-TDS data [34] does not capture the complete dielectric response. A single-point experiment at 2.45 GHz [64] does not reflect static conditions. Voltammetry [65] and capacitance measurements [66] have also yielded unreliable results.

As a matter of concern, in DRS experiments, “static” refers to processes on the nanosecond timescale. Even in the most favourable case, where the dispersion curve was not perturbed by electrode polarisation down to 3 MHz [9], static conditions only refer to processes on a timescale shorter than 100 ns. While the absence of slower dynamics seems plausible for rotational motions, low-frequency translational contributions due to conductance dispersion cannot be excluded *a priori*.

The challenge is to discriminate electrode polarisation effects from sample-specific low-frequency conductance dispersion. Electrode polarisation is apparatus specific and can be identified (and sometimes reduced) by choosing a suitable geometry and material of the sample cell. While in some experiments electrode polarisation was observed at 100 MHz or even beyond (see also Figure 9.1) [4, 5], experiments by Nakamura and Shikata imply a lower bound for meaningful spectra of 20 MHz [28]. Input impedance measurements with a special sample cell enabled us to record the dielectric spectrum of [EtNH₃][NO₃] to 3 MHz without interference from electrode polarisation [9]. These experiments do not provide evidence that processes in low-viscosity ionic

liquids at the lower edge of the microwave regime are overlooked in experiments above 100 MHz.

The situation is different in the kilohertz region and below, where electrode polarisation rapidly increases with decreasing frequency. For example, in impedance measurements extending below the kilohertz regime, electrode polarisation has exceeded the sample-specific modes by up to five orders of magnitude [8]. The resulting dramatic increase in the dispersion curve should not be confused [12] with generic dielectric processes in ionic liquids. Perhaps temperature variation, as performed by Kremer's group [22, 23], can create conditions where conductance effects can be distinguished from systematic and spurious effects due to electrode polarisation.

Disregarding the speculations about low-frequency ionic processes, Table 9.2, Table 9.3, and Table 9.4 summarise static dielectric constants extrapolated by the CC model [67], superseding values published in earlier work [11]. Typically, the corrected values exceed earlier results extracted by the CD model [4, 10, 11, 26] by 10%, which does not alter the basic physical conclusions.

Table 9.2 and Table 9.3 show that, for some widely used aprotic ionic liquids with weakly polar or non-polar anions such as $[\text{NTf}_2]^-$ or $[\text{BF}_4]^-$, the static dielectric constants at 25 °C exhibit moderate values of $\epsilon = 12\text{--}18$. In these cases, the main contribution to ϵ results from the dipolar cations. Ionic liquids with higher dielectric constants can be designed by using highly polar anions, such as $[\text{C}_2\text{H}_3\text{SO}_4]^-$ (Table 9.3) [11, 46].

For protic ionic liquids based on monoalkylammonium, $[\text{RNH}_3]^+$, ions, ϵ shows moderate increases relative to aprotic ionic liquids. On the other hand, hydroxy-functionalisation of alkyl chains can lead to dramatic increases in ϵ , as seen by comparison of results for ethylammonium ionic liquids with results for 2-hydroxyethylammonium ionic liquids in Table 9.4. The high static dielec-

TABLE 9.2 Cation Dependence of the Static Dielectric Constants of Aprotic Ionic Liquids at 25 °C, Exemplified by Salts with Bis((trifluoromethyl)sulfonyl)amide $[\text{NTf}_2]^-$ as a Common Anion

Cation	ϵ
$[\text{C}_2\text{mim}]^+$	12.0, ^a 12.3 ^b
$[\text{C}_3\text{mim}]^+$	13.3 ^a
$[\text{C}_4\text{mim}]^+$	14.0, ^a 13.7 ^b
$[\text{C}_5\text{mim}]^+$	15.0 ^a
$[\text{C}_4\text{py}]^+$	15.2 ^a
$[\text{C}_4\text{mpyr}]^+$	14.7 ^a

^a Reference 30, data recalculated from spectra in Reference 4.

^b Reference 28.

TABLE 9.3 Anion Dependence of the Static Dielectric Constants of Aprotic Ionic Liquids at 25 °C, Exemplified by Salts With [C₂mim]⁺ as a Common Cation

Anion	ϵ
[N(CN) ₂] ⁻	11.7 ^a
[NTf ₂] ⁻	12.0, ^b 12.3 ^c
[BF ₄] ⁻	14.5, ^a 13.6 ^c
[SCN] ⁻	13.7 ^b
[OTf] ⁻	16.5 ^b
[C ₄ H ₉ SO ₃] ⁻	30.0 ^b
[C ₂ H ₅ SO ₃] ⁻	35.0, ^b 35.5 ^d

^a Reference 27.^b Reference 30.^c Reference 28.^d Reference 46.**TABLE 9.4 Static Dielectric Constants of Some Protic Ionic Liquids at 25 °C [30]**

Ionic liquid	ϵ
[C ₂ H ₅ NH ₃][NO ₃]	26.2
[C ₂ H ₅ NH ₃][HCO ₂]	31.5
[C ₄ H ₉ NH ₃][HCO ₂]	23.0
[HOC ₂ H ₄ NH ₃][NO ₃]	60.9
[HOC ₂ H ₄ NH ₃][HCO ₂]	61.0
[HOC ₂ H ₄ NH ₃][lac]	85.6

Reference 30; part of the data supersede values quoted in Reference 68.

tric constants of 2-hydroxyethylammonium ionic liquids resemble the high values observed for water or strongly hydrogen-bonded VOCs, such as amides, where dipole correlations cause a pronounced increase in ϵ [7].

The dielectric constant is an important measure of the solvation capability, which may be compared with results deduced from other polarity probes. Well-known polarity probes are, for example, UV-Vis and fluorescence spectra of solvatochromic dyes, liquid-liquid distribution coefficients, inverse gas chromatography, and solvent effects on certain chemical reactions [69]. These probes reflect different facets of the solute-solvent interactions. The resulting empirical or semi-empirical polarity scales range from simple one-parameter approaches to multi-parameter representations, for example, based on linear free energy relationships [3, 11, 69, 70].

Many polarity parameters for ionic liquids have been transcribed into effective dielectric constants using correlations between ε and other measures of the polarity, which were established from data for VOCs. When the first experimental values of the static dielectric constant of aprotic ionic liquids became available [10], we immediately noted that these were lower than estimated from most other polarity probes. The experimental values of the order of $\varepsilon = 12\text{--}18$ correspond to dielectric constants of alcohols of intermediate chain length such as pentanol. Most other probes suggest values for ionic liquids of the order of $\varepsilon = 30\text{--}40$, resembling those of polar VOCs such as methanol, ethanenitrile, and dimethyl sulfoxide [11]. The difference results from the fact that the static dielectric constant is a bulk property, while other polarity parameters reflect local probes, often purposely designed to map specific interactions such as the hydrogen-bonding ability of the cation or anion. Obviously, the dielectric constants do not correlate with these parameters.

One of the challenges is to relate the static dielectric constant to the molecular dipole moments of the ions. The static dielectric constant, or more accurately the sum of the amplitudes of the dipolar contributions, is related to the mean square fluctuation $\langle M^2 \rangle$ of the total electric dipole moment $M(t)$ of the sample. $\langle M^2 \rangle$ can be broken down into an effective molecular dipole moment. Assuming, for simplicity, that only the cation contributes to the static dielectric constant, as encountered in many cases, $\langle M^2 \rangle$ can be transcribed into an effective molecular dipole moment μ_{eff} by the Kirkwood formula, Equation (9.14) [7],

$$\langle M^2 \rangle = N\mu_{\text{eff}}^2 = Ng_{\text{K}}\mu_0^2, \quad (9.14)$$

where μ_0 is the dipole moment of the isolated molecule and the Kirkwood factor g_{K} reflects orientational correlations of the dipoles. For VOCs, this type of analysis has been performed in numerous cases [7].

Unfortunately, such procedures cannot be applied to ionic liquids in a straightforward manner because the dipole moment of a charged particle is ill defined [71]. It can be shown that the static dielectric constant and the mean squared total electric dipole moment $\langle M^2 \rangle$ are invariant against the origin of the atomic coordinates, but the molecular dipole moment μ_0 and the Kirkwood factor g_{K} depend on the origin chosen [15]. It is therefore only possible to calculate from ε an unambiguous value of the effective dipole moment. If one applies standard procedures devised for VOCs, then one finds for aprotic ionic liquids values of the order of $\mu_{\text{eff}} = 3\text{--}6\text{D}$ ($1\text{D} = 3.3 \times 10^{-30}\text{Cm}$) [27], which corresponds to highly dipolar VOCs. At a first glance, this seems to contradict the observed low dielectric constants, but the low ε values just reflect the low dipole densities caused by the large molar volumes of the bulky ions.

Again, there is no clear correlation of μ_{eff} with reported polarity parameters. This finding is not surprising for those polarity probes that map specific interactions such as the hydrogen-bonding (donating or accepting) ability of the ions. However, there is also no clear correlation of μ_{eff} with values

[70] for the semi-empirical Kamlet–Taft π^* parameter [72], which is said to reflect the combined effect of electrostatic interactions and electronic polarisability.

Finally, we mention yet another difference between ionic liquids and VOCs. While, for VOCs, dielectric continuum theory provides a surprisingly good representation of their solvation properties, it is often inadequate for assessing solvation properties of ionic liquids on a quantitative level. A typical example is the solvent effect on chemical reactions. Transition state theory yields an expression for the rate constant in terms of two barriers, namely the intrinsic reaction barrier, $\Delta G_{\text{in}}^\ddagger$, and the solvent reorganisation barrier, $\Delta G_{\text{solv}}^\ddagger$ [69]. The latter is defined as the difference in free energy of solvation between the transition state and the reactants.

In a dielectric continuum approach, $\Delta G_{\text{solv}}^\ddagger$ is given by the Born solvation free energy, which depends on the static dielectric constant of the surrounding medium through an expression of the general form $(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)$ [69]. Experimental static dielectric constants predict, for simple imidazolium salts, values of $\Delta G_{\text{solv}}^\ddagger \cong 5\text{--}7 \text{ kJ} \cdot \text{mol}^{-1}$, while experimental determinations of $\Delta G_{\text{solv}}^\ddagger$ from fluorescence Stokes shift data yield $\Delta G_{\text{solv}}^\ddagger = 10\text{--}15 \text{ kJ} \cdot \text{mol}^{-1}$ [73]; that is, electrostatics can account for only 30–50% of the solvent reorganisation barrier.

9.7 CONCLUSIONS

In the microwave regime, the spectra of low-viscosity ionic liquids at 25 °C show quite common features. By contrast, terahertz spectra indicate a much more specific behaviour, presumably because intermolecular vibrations are highly specific to local interactions. The goal in writing this account has been to spotlight these dielectric properties from the experimental perspective and to highlight differences to dielectric properties of VOCs.

Although at ambient conditions the microwave portion of the dielectric response is experimentally well characterised for many ionic liquids, fundamental questions remain. One pressing problem concerns the detailed origin of the extraordinarily fast reorientation of the cations, and of the still faster reorientation and low relaxation amplitudes exhibited by many anions. Another challenge concerns the description of the dielectric response in terms of molecular dipole moments because, for charged species, the electric dipole moment cannot be defined in an unambiguous manner.

To complete the dielectric spectra of ionic liquids, it would be necessary to extend the experiments at their low-frequency edge, say, below 1 MHz; however, in this range, electrode polarisation and the high Ohmic loss so far have prevented meaningful experiments. The question for processes at lower frequencies is key to the extrapolation of the static dielectric constant of ionic liquids. To the best of the present knowledge, there is no evidence for such contributions, so that the assumption of such processes is speculative.

Space limitations have prompted us to limit the discussion to neat ionic liquids of low viscosity near 25 °C. Exciting developments are expected from an extension of DRS to a wider temperature range [32], which should also provide a link to glassy dynamics [22–24]. For example, the temperature dependence of the static dielectric constant needs accurate and systematic characterisation. Another exciting perspective is founded in an extension of DRS to mixtures between ionic liquids and VOCs, as some applications, such as chemical reactions or separation processes, concern mixtures of ionic liquids with VOCs [1–3, 48].

It seems that the proper characterisation and thorough understanding of dielectric spectra of ionic liquids will keep experimentalists and theoreticians busy for the foreseeable future.

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REFERENCES

- 1 Wasserscheid, P. and Welton, T. (eds.), *Ionic Liquids in Synthesis*, 2nd ed. (Wiley-VCH, Weinheim, 2008).
- 2 Plechkova, N. V., Rogers, R. D. and Seddon, K. R. (eds.), *Ionic Liquids: From Knowledge to Application*, ACS Symp. Ser., Vol. 1030 (American Chemical Society, Washington D. C., 2009).
- 3 Weingärtner, H., Understanding ionic liquids at the molecular level: Facts, problems, and controversies, *Angew. Chem. Int. Ed.* **47**, 654–670 (2008).
- 4 Daguene, C., Dyson, P. J., Krossing, I., Oleinikova, A., Slattery, J., Wakai, C., and Weingärtner, H., The dielectric response of ionic liquids, *J. Phys. Chem. B.* **110**, 12682–12688 (2006).
- 5 Buchner, R., and Hefter, G., Interactions and dynamics in electrolyte solutions by dielectric spectroscopy, *Phys. Chem. Chem. Phys.* **11**, 8984–8999 (2009).
- 6 Kremer, F., and Schönhals, A., *Broadband Dielectric Spectroscopy* (Springer, Berlin, 2003).
- 7 Böttcher, A. V. J., and Bordewijk, P., *Theory of Dielectric Polarization*, Vol. 2 (Elsevier, Amsterdam, 1978).
- 8 Leys, J., Wübberhorst, M., Menon, C. P., Rajesh, R., Thoen, J., Glorieux, C., Nockemann, P., Thijs, B., Binnemans, K., and Longuemart, S. J., Temperature dependence

- of the electrical conductivity of imidazolium ionic liquids, *J. Chem. Phys.*, **128**, paper No. 064509 (2008).
- 9 Weingärtner H., Knocks, A., Schrader, W., and Kaatz, U., Dielectric spectroscopy of the room temperature molten salt ethylammonium nitrate, *J. Phys. Chem. A.* **105**, 8646–8650 (2001).
 - 10 Wakai, C., Oleinikova, A., Ott, M., and Weingärtner, H., How polar are ionic liquids? Determination of the static dielectric constant by microwave dielectric spectroscopy, *J. Phys. Chem. B.* **109**, 17028–17030 (2005).
 - 11 Weingärtner, H., The static dielectric constant of ionic liquids, *Z. Phys. Chem.* **220**, 1395–1405 (2006).
 - 12 Chiappe, C., Malvaldi, M., and Pornelli, C. S., Ionic liquids: Solvation ability and polarity, *Pure Appl. Chem.* **81**, 767–776 (2009).
 - 13 R. H. Cole, Dielectrics in physical chemistry, *Annu. Rev. Phys. Chem.* **40**, 1–29 (1989).
 - 14 Hansen, J.-P., and McDonald, I. R., Statistical mechanics of dense ionized matter. 4. Density and charge fluctuations in a simple molten salt, *Phys. Rev. A* **11**, 2111–2123 (1975).
 - 15 Schröder, C., and Steinhauser, O., On the dielectric conductivity of molecular ionic liquids, *J. Chem. Phys.* **131**, paper No. 114504 (2009).
 - 16 Schröder, C., Wakai, C., Weingärtner, H., and Steinhauser, O., Collective rotational dynamics of ionic liquids: A computational and experimental study of 1-butyl-3-methylimidazolium tetrafluoroborate, *J. Chem. Phys.* **126**, paper no. 084511 (2007).
 - 17 Song, X., Solvation dynamics in ionic fluids. An extended Debye-Hückel dielectric continuum model, *J. Chem. Phys.* **131**, paper no. 044503 (2009).
 - 18 Shim, Y., and Kim H. J., Dielectric relaxation, ion conductivity, solvent rotation and solvation dynamics in a room temperature ionic liquid, *J. Phys. Chem. B* **112**, 11028–11038 (2008).
 - 19 Moynihan, C. T., Boesch, L. P.; Laberge, N. L., Decay function for the electric field relaxation in vitreous ionic conductors, *Phys. Chem. Glasses* **14**, 122–125 (1973).
 - 20 Howell, F. S., Bose, R. A., Macedo, P. B., and Moynihan, T. C., Relaxation in a glass-forming molten salt, *J. Phys. Chem.* **78**, 639–648 (1974).
 - 21 Ngai, K. L., and Rendell, R. W., Interpreting the real part of the dielectric conductivity contributed by mobile ions in ionically conducting media, *Phys. Rev. B* **61**, 9393–9398 (2000).
 - 22 Sangoro, J., Sergej, A., Naumov, S., Galvosas, P., Kärger, J., Wespe, C., Bordusa, F., and Kremer, F., Charge transport and mass transport in imidazolium-based ionic liquids, *Phys. Rev. E*, **77** paper no. 051202 (2008).
 - 23 Jacob, C., Sangoro, J. R., Serghei, A., Naumov, S., Korth, Y., Kärger, J., Friedrich, C., and Kremer, F., Charge transport and glass dynamics in imidazole based liquids, *J. Chem. Phys.* **129**, paper no. 234511 (2008).
 - 24 Ito, N., and Richert, R., Solvation dynamics and electric field relaxation in an imidazolium-PF₆ ionic liquid: From room temperature to the glass transition, *J. Phys. Chem. B.* **111**, 5016–5022 (2007).
 - 25 Schrödle, S., Annat, G., MacFarlane, D. R., Forsyth, M., Buchner, R., and Hefter, G., Broadband dielectric response of the ionic liquid N-methyl-N-ethylpyrrolidinium dicyanamide, *Chem. Comm.* 1748–1750 (2006).

- 26 Weingärtner, H., Sasisanker, P., Daguene, C., Dyson, P. J., Krossing, I., Slattery, J., and Schubert, T., The dielectric response of room temperature ionic liquids: Effect of cation variation, *J. Phys. Chem. B* **111**, 4775–4780 (2007).
- 27 Hunger, J., Stoppa, A., Schrödle, S., Hefter, G., and Buchner, R., Temperature dependence of the dielectric properties and dynamics of ionic liquids, *ChemPhysChem* **10**, 723–733 (2008).
- 28 Nakamura, K., and Shikata, T., Systematic dielectric and NMR study of the ionic liquid 1-alkyl-3-methylammonium, *ChemPhysChem.*, **11**, 285–294 (2010).
- 29 Mizoshiri, M., Nagao, T., Mizoguchi, Y., and Yao, M., Dielectric permittivity of room temperature ionic liquids: A relation to the polar and nonpolar domain structures, *J. Chem. Phys.* **132**, paper no. 164510 (2010).
- 30 Weingärtner, H., and Huang, M.-M., unpublished data.
- 31 Izgorodina, E. I., Forsyth, M., and MacFarlane, D. R., On the components of dielectric constants of ionic liquids: Ionic polarization? *Phys. Chem. Chem. Phys.* **11**, 2452–2458 (2009).
- 32 Stoppa, A., Hunger, J., Thoman, A., Helm, H., Hefter, G., and Buchner, R., Interactions and dynamics in ionic liquids, *J. Phys. Chem. B* **112**, 4854–4858 (2008).
- 33 Turton, D. A., Hunger, J., Stoppa, A., Hefter, G., Thoman, A., Walther, M., Buchner, R., and Wynne, K., Dynamics of imidazolium ionic liquids from a combined dielectric relaxation and optical Kerr effect study: Evidence for mesoscopic aggregation, *J. Amer. Chem. Soc.* **131**, 11140–11146 (2009).
- 34 Yamamoto, K., Tani, M., and Hangyo, M., Terahertz time domain spectroscopy of imidazolium ionic liquids, *J. Phys. Chem. B* **111**, 4854–4859 (2007).
- 35 Krüger, M., Funkner, S., Bründermann, E., Weingärtner, H., and Havenith, M., Polarity fluctuations of the protic ionic liquid ethylammonium nitrate in the terahertz regime, *J. Chem. Phys.* **132**, paper No. 101101 (2010).
- 36 Fumino, H., Wulf, A., and Ludwig, R., The cation-anion interaction in ionic liquids probed by far-infrared spectroscopy, *Angew. Chem. Int. Ed.* **47**, 3830–3834 (2008).
- 37 Fumino, K., Wulf, A., and Ludwig, R., Hydrogen bonding in protic ionic liquids: Reminiscent of water, *Angew. Chem. Int. Ed.* **48**, 3184–3186 (2009).
- 38 Schröder, C., and Steinhäuser, O., Using fit functions in computational dielectric spectroscopy, *J. Chem. Phys.* **132**, paper No. 244109 (2010).
- 39 Schmuttenmaer, C. A., Exploring dynamics in the far infrared with terahertz spectroscopy, *Chem. Rev.* **104**, 1759–1779 (2004).
- 40 Wulf, A., Ludwig, R., Sasisanker, P., and Weingärtner, H., Molecular reorientation in ionic liquids: A comparative dielectric and magnetic relaxation study, *Chem. Phys. Lett.* **439**, 323–326 (2007).
- 41 Huang, M.-M., Bulut, S., Krossing, I., and Weingärtner, H., Are hydrodynamic models suitable for describing the reorientational dynamics of ions in ionic liquids? A case study of methylimidazolium tetra(hexafluoroisopropoxy) aluminates, *J. Chem. Phys.* **133**, 101101 (2010).
- 42 Tokuda, H., Hayamizu, K., Ishii, K., Susan, M. A. B. H., and Watanabe, M., Physical properties of room temperature ionic liquids. 1. Variation of anionic species, *J. Phys. Chem. B* **108**, 16593–16600 (2004).

- 43 Tokuda, H., Hayamizu, K., Ishii, K., Susan, M. A. B. H., and Watanabe, M., Physical properties of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation, *J. Phys. Chem. B* **109**, 6103–6110 (2005).
- 44 Bulut, S., Klose, P., Huang, M.-M., Weingärtner, H., Dyson, P., Lawrenczy, G., Friedrich, C., Kümmerer, K., and Krossing, I., Synthesis of room temperature ionic liquids with the weakly coordinating $[\text{Al}(\text{ORF})_4]^-$ anion ($\text{RF} = \text{CH}(\text{CF}_3)_2$) and the determination of their principal physical properties, *Chem. Eur. J.* **16**, 13139–13154 (2010).
- 45 Dote, J. C., Kivelson, D., and Schwartz, R. N., A molecular, quasi-hydrodynamic free-space model for molecular rotational relaxation in liquids, *J. Phys. Chem.* **85**, 2169–2180 (1981).
- 46 Hunger, J., Stoppa, A., Buchner, R., and Hefter, G., Dipole correlations in the ionic liquid 1-N-ethyl-3-N-methylimidazolium ethylsulfate and its binary mixtures with dichloromethane, *J. Phys. Chem. B* **113**, 9527–9537 (2009).
- 47 Weingärtner, H., Nadolny, H.G., and Käshammer, S., Dielectric properties of an electrolyte solution at low reduced temperature, *J. Phys. Chem. B* **103**, 4738–4743 (1999).
- 48 Huang, M.-M., Schneiders, K., Schulz P., Wasserscheid, P., and Weingärtner, H., Ion speciation driving chirality transfer in imidazolium-based camphorsulfonate ionic liquid solutions, *Phys. Chem. Chem. Phys.* **13**, 4126–4131 (2011).
- 49 Debye, P., and Falkenhagen, H., The dispersion of conductivity and dielectric constant of strong electrolytes, *Phys. Z.* **29**, 121–132 (1928).
- 50 Chandra, A., and Bagchi, B., Frequency dependence of ionic conductivity of electrolyte solutions, *J. Chem. Phys.* **112**, 1876–1886 (2000).
- 51 Chandra, A., Wei, D. Q., and Patey, G. N., The frequency-dependent conductivity of electrolyte solutions, *J. Chem. Phys.* **99**, 2083–2094 (1993).
- 52 Bordi, F., Cametti, C., and Colby, R. H., Dielectric spectroscopy and conductivity of polyelectrolyte solutions, *J. Phys.: Condens. Matter* **16**, R1423–R1463 (2004).
- 53 Madel, M., and Odijk, T. Dielectric properties of polyelectrolyte solutions, *Annu. Rev. Phys. Chem.* **35**, 75–108 (1984).
- 54 Buchner, R., Baar, C., Fernandez, P., Schrödle, S., and Kunz, W., Dielectric spectroscopy of micelle hydration and dynamics in aqueous ionic surfactant solutions, *J. Mol. Liquids* **118**, 179–187 (2005).
- 55 Grosse, C., Permittivity of a suspension of charged particles in electrolyte solution, *J. Phys. Chem.* **92**, 3905–3910 (1988).
- 56 J. E. Anderson, The Debye-Falkenhagen effect: Experimental fact or fiction?, *J. Non-Cryst. Solids* **172–174**, 1190–1194 (1994).
- 57 Van Beek, W. M., and Mandel, M., Static relative permittivity of some electrolyte solutions in water and methanol, *J. Chem. Soc., Faraday Trans. 1* **74**, 2339–2351 (1978).
- 58 Ghowsi, K., and Gale, R. J., Some aspects of the high frequency conductance of electrolytes, *J. Electrochem. Soc.* **136**, 2806–2811 (1989).
- 59 Funke, K., and Riess, I. Debye-Hückel-type relaxation processes in solid ionic conductors. 1. The model, *Z. Phys. Chem. Neue Folge* **140**, 217–232 (1984).
- 60 Funke, K. Debye-Hückel-type relaxation processes in solid ionic conductors. 2. Experimental evidence, *Z. Phys. Chem. Neue Folge* **154**, 251–295 (1987).

- 61 Samanta, A., Dynamic Stokes shift and excitation wavelength dependent fluorescence of dipolar molecules in ionic liquids, *J. Phys. Chem. B* **110**, 13704–13716 (2006).
- 62 Arzhantsev, S., Jin, H., Baker, G. A., and Maroncelli, M., Measurement of the complete solvation response of ionic liquids, *J. Phys. Chem. B* **111**, 4978–4989 (2007).
- 63 Hasted, J., *Aqueous Dielectrics* (Chapman & Hall, London, 1973).
- 64 Gollei, A., Vass, A., Pallai, E., Gerzson, M., Ludanyi, L., and Mink, J., Apparatus and method to measure dielectric properties of ionic liquids, *Rev. Sci. Instr.* **80**, 044703 (2009).
- 65 Wu, J., and Stark, J. P. W., Measurement of low-frequency relative permittivity of room temperature molten salts by triangular wave form voltage, *Meas. Sci. Techn.* **17**, 781–788 (2006).
- 66 Kosmulski, M., Marczewska-Boczkowska, K., Zukowski, P., Subocz, J., and San-eluta, C., Permittivities of 1-alkyl-3-methyl tetrafluoroborates and hexafluorophosphates, *Croat. Chem. Acta* **80**, 461–466 (2007).
- 67 Huang, M.-M., Jiang, Y., Sasisanker, P., Driver, G., and Weingärtner, H., Static dielectric constants of forty ionic liquids at 298.25 K, *J. Chem. Eng. Data* **56**, 1494–1499 (2011).
- 68 Huang, M.-M., and Weingärtner, H., Protic ionic liquids with unusually high dielectric permittivities, *Chem. Phys. Chem.* **9**, 2172–2173 (2008).
- 69 Reichardt, C., and Welton, T., *Solvents and Solvent Effects in Organic Chemistry*, 4th ed. (Wiley-VCH, Weinheim, 2011).
- 70 Hallet, J. P., and Welton, T., How polar are ionic liquids? *ECS Trans.* **16**, 33–38 (2009).
- 71 Wangsness, K., *Electromagnetic Fields*, 2nd ed. (John Wiley & Sons, New York, 1986).
- 72 Kamlet, M. J., Abboud, J. L., and Taft, R. W., The solvatochromic comparison method 6: the π^* scale of solvent polarities, *J. Amer. Chem. Soc.* **99**, 8325–8327 (1977).
- 73 Jin, H., Baker, G. A., Arzhantsev, S., Dong, J., and Maroncelli, M., Solvation and rotational dynamics of coumarin 153 in ionic liquids: Comparisons to conventional solvents, *J. Phys. Chem B* **111**, 7291–7302 (2007).