

## Charge transport and mass transport in imidazolium-based ionic liquids

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The mechanism of charge transport in the imidazolium-based ionic liquid 1,3-dimethylimidazolium dimethylphosphate is analyzed by combining broadband dielectric spectroscopy (BDS) and pulsed field gradient nuclear magnetic resonance (PFG NMR). The dielectric spectra are dominated—on the low-frequency side—by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. Using the Einstein and Einstein-Smoluchowski equations enables one to determine—in excellent agreement with direct measurements by PFG NMR—the diffusion coefficient of the charge carriers. By that, it becomes possible to extract from the dielectric spectra separately the number density and the mobilities of the charge carriers and the type of their thermal activation. It is shown that the observed Vogel-Fulcher-Tammann (VFT) dependence of the dc conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found. Extrapolating the latter to room temperature indicates that nearly all charge carriers are participating in the conduction process.

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Charge transport and electrode polarization in disordered systems [1–4] are topics of special technological importance in contemporary science. Ionic liquids, a class of materials undergoing a rapid development in recent years, have attracted a strong interest in this field, due to their numerous applications [5–12]. For practical purposes, the transport mechanism of charge carriers needs to be understood over a possibly broadest range of frequencies and temperatures. Due to its ability to measure the complex dielectric function (and hence the complex conductivity) over many orders of magnitude in frequency and in a wide temperature interval, broadband dielectric spectroscopy turns out to be an ideal experimental tool in this field [13–21].

Usual conductivity spectra consist essentially of two regions, apparently related to two different phenomena. At high frequencies (and low temperatures) the conductive properties are governed by the transport of the charge carriers in the bulk. The underlying mechanism of this contribution represents the (translational) diffusion of ions and is theoretically well understood [22,23]. This part of the spectra can be used to extract important molecular parameters characterizing the hopping mechanism of the charge carriers. At lower frequencies (and higher temperatures) pronounced changes in the complex conductivity function are detected due to presence of solid electrodes, acting on the charge carriers as (nearly) blocking interfaces [24–27]. This part, exhibiting a peculiar dependence on the geometry of the measurement cell (e.g., the cell length) and on the material used for the electrodes, was considered a long time to be a parasitic effect (“electrode polarization”) and usually cut off from the bulk contribution of the spectra. An alternative approach to describing electrode polarization has been presented by Macdonald [28].

In the current paper the charge transport and the mass transport of an imidazolium-based ionic liquid is investigated by combining broadband dielectric spectroscopy and pulsed field gradient nuclear magnetic resonance (PFG NMR). It is shown that the Vogel-Fulcher-Tammann (VFT) character of

the conductivity originates from a similar temperature dependence of the mobility, while an Arrhenius-type thermal activation is found for the number density of charge carriers.

Pulsed field gradient (PFG) NMR self-diffusion measurements are based on NMR pulse sequences which generate the spin echo of the magnetization of resonant nuclei. Applying magnetic field gradient pulses, the spin echo becomes sensitive to the translational motion of the molecules which carry the nuclear spin under study. Assuming that the PFG is applied along the  $z$  axis on the laboratory frame of reference, the diffusive motion of the molecules leads to an attenuation of the spin echo intensity dependent on the field gradient strength, pulse duration, observation time, and the self-diffusion coefficient  $D_z$ . The slope of the semilogarithmic presentation of the spin echo attenuation is determined by  $D_z$ . Readers are referred to a recent review of PFG NMR spectroscopy presented by Stallmach and Galvosas [29].

The ionic liquid used in this study (1,3-dimethylimidazolium dimethylphosphate—MMIM Me<sub>2</sub>PO<sub>4</sub> [with MMIM<sup>+</sup> cation and (Me<sub>2</sub>PO<sub>4</sub>)<sup>-</sup> anion], density 1.26 g/cm<sup>3</sup>, molecular weight 222 g/mol, viscosity 363 mPa s) was purchased from Solvent Innovation GmbH. The dielectric measurements were performed between 0.1 Hz and 1 GHz using a high resolution alpha dielectric analyzer (for measurements up to 10 MHz) and a HP impedance analyzer (for high frequency investigations). Both analyzers were assisted by Quatro temperature controllers, using pure nitrogen as a heating agent and assuring a temperature stability better than 0.2 K. All measurements are carried out using brass electrodes, if not specified otherwise. This was an arbitrary choice and does not in any way compromise the validity of the analysis reported in this paper since we use only the high frequency (or low temperature) dielectric response to extract number densities and mobilities. We experimentally prove that the hopping frequency is a bulk property and does not depend on the nature of electrode used.

Typical dielectric spectra of MMIM-Me<sub>2</sub>PO<sub>4</sub> measured between 0.1 Hz and 1 GHz are shown in Fig. 1 in plots of  $\epsilon'$ ,

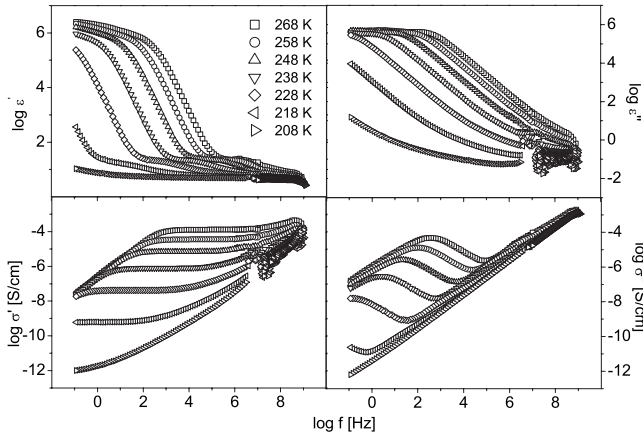


FIG. 1. Complex dielectric function and complex conductivity of MMIM-Me2PO4 as a function of frequency at different temperatures, as indicated. The error bars are comparable to the size of the symbols, if not specified otherwise. Log is used to refer to logarithm to base 10.

$\epsilon''$ ,  $\sigma'$ , and  $\sigma''$  vs frequency at different temperatures. The relation between the complex conductivity and complex dielectric function is given by  $\sigma^*(\omega, T) = i\epsilon_0\omega\epsilon^*(\omega, T)$ , which can be expressed as  $\sigma' = \epsilon_0\omega\epsilon''$  and  $\sigma'' = \epsilon_0\omega\epsilon'$  ( $\epsilon_0$  being the vacuum permittivity constant). We note at this point the equivalence between the complex conductivity and complex permittivity in the dielectric investigations.

The experimental curves presented in Fig. 1 are normalized with respect to the characteristic frequency at which the real part of the conductivity begins to increase with frequency. The result is that coinciding dependencies are obtained (Fig. 2). This indicates that the two spectral regions, apparently relating to different phenomena, are governed by the same underlying mechanism. Therefore, time-temperature superposition principle holds for the measured ionic liquid [30,31].

The dielectric spectra at high frequencies are well described by a recent theoretical approach developed by Dyre [30,32] and also discussed in [22,23]. The most important

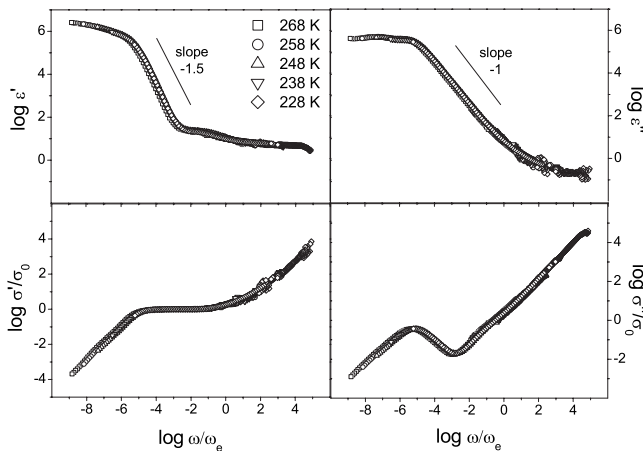


FIG. 2. Scaling with respect to temperature shown in normalized plots of complex permittivity and conductivity. Log is used to refer to logarithm to base 10.

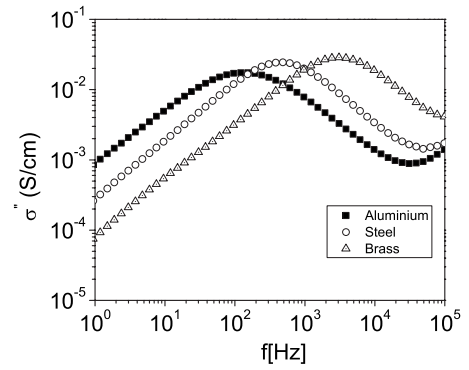


FIG. 3. Shifts in the position of the peak experimentally measured in  $\sigma''$  by employing different materials as electrodes (the geometry of the sample is kept identical).

feature in this spectral region is the plateau in  $\sigma'$  (corresponding to a linear dependence of slope 1 in the plots of  $\epsilon''$  vs frequency and giving  $\sigma_0$ , the value of conductivity in the dc limit), which at higher frequencies exhibits a pronounced increase. The turning point between this increase and the plateau of  $\sigma_0$  (corresponding to the position of the step detected in plots of  $\epsilon'$  vs frequency or of the peak in modulus  $M''$  vs frequency, not shown here) gives another important parameter extracted from the Dyre theory: the attempt rate  $\omega_e = 1/\tau_e = 2\pi f_e$  of the charge carriers to overcome the highest energy barrier (limiting the dc conductivity). This parameter is usually considered to give an estimate of the hopping rate of the ions and defines, on the frequency axis, the transition between diffusion and subdiffusion. The equivalence of frequency of the peak in  $M''$  and the characteristic frequency at which the real part of conductivity begins to increase with increasing frequency for disordered materials has been pointed out by a number of researchers [13,33]. However, the reason for the equivalence is not yet clear [33].

The analytical form of the Dyre formula describing the conductivity contribution in the bulk reads

$$\sigma(\omega) = \sigma_0 \left( \frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)} \right). \quad (1)$$

The low-frequency part of the spectra is dominated by electrode polarization effects and shows peculiar dependencies on the sample length [25,26] and on the material of the electrodes. The latter is exemplified in Fig. 3, where the imaginary part of the complex conductivity is represented as a function of temperature for different materials of the electrodes. The dependence on the material of the electrodes is summarized in Fig. 4, where  $\omega_{EP} = 1/\tau_{EP} = 2\pi f_{EP}$  and  $\omega_e = 1/\tau_e = 2\pi f_e$  [as determined both from the frequency position of the maxima in the  $M''$  spectra, Fig. 4(b)], and the frequency position of the peaks in  $\sigma''$  are analyzed in dependence on the inverse temperature.

In respect to the temperature variation, a Vogel-Fulcher-Tammann (VFT) dependence is detected for  $\tau_e$ , as well as for the dc conductivity contribution (Fig. 5). It should be noted that  $\tau_e$  is obtained from fits by the Dyre approach that yields identical values as the time corresponding to the peak in  $M''$ . These two VFT dependencies (namely, of  $\tau_e$  and  $\sigma_0$ ) run

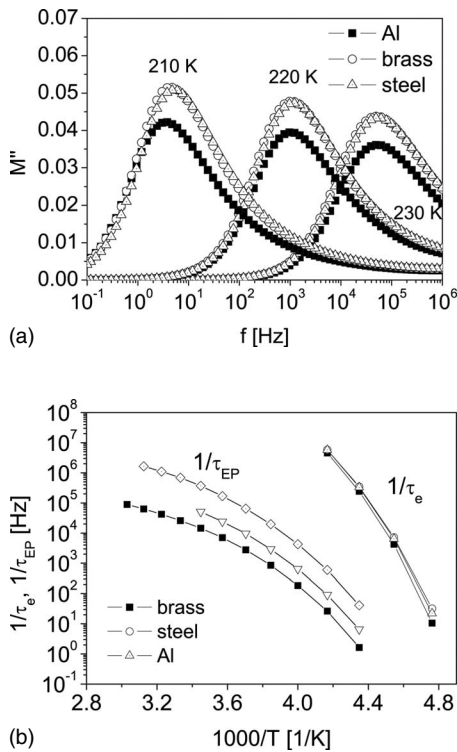


FIG. 4. (a) Imaginary part of the complex dielectric modulus vs frequency at different temperatures and for different materials of the electrodes (b) radial frequency position of the peak in  $\sigma''$  ( $1/\tau_{EP}$ ) and  $1/\tau_e$  as a function of inverse temperature for different materials of the electrodes (the geometry of the sample is kept identical). It is clear that the temperature dependence of the bulk response denoted  $1/\tau_e$  is practically independent of the material of the electrode used as opposed to ( $1/\tau_{EP}$ ), which shows a pronounced dependence on the material of the electrode.

parallel and can be easily overlapped if the same number of decades are allowed on the y axes of the activation plots. This expresses an empirical scaling law relating the dc conductivity to the value of  $\tau_e$ , known as the Barton-Nakajima-Namikawa (BNN) relation:  $\sigma_0 \sim 1/\tau_e$  (inset of Fig. 5). The relation can also be stated as  $\sigma_0 = p \epsilon_0 \Delta \epsilon \omega_h$ , where  $p$  is a constant of order 1,  $\Delta \epsilon$  is the dielectric strength, and  $\epsilon_0$  is the

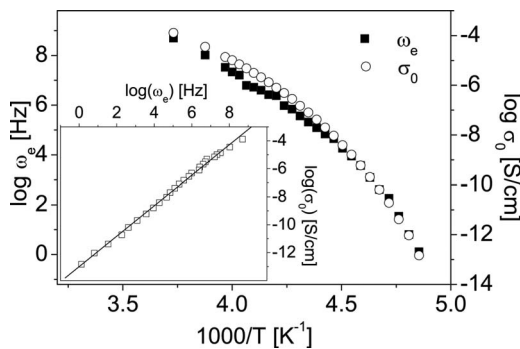


FIG. 5. Radial frequency  $\omega_e$  and dc conductivity  $\sigma_0$  as a function of inverse temperature. Inset:  $\sigma_0$  vs  $\omega_e$  (BNN plot). Log is used to refer to logarithm to base 10.

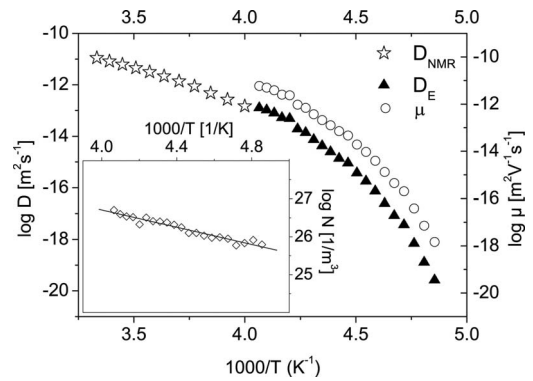


FIG. 6. Diffusion coefficient determined by the Einstein-Smolukowski equation (using  $\omega_e$  as hopping rate and  $\lambda=0.2$  nm as hopping length) compared with the diffusion coefficient measured by PFG NMR. Additionally, the mobility of the charge carriers is determined. Inset: effective number of charge carriers as a function of inverse temperature. Log is used to refer to logarithm to base 10.

permittivity of free space [13,23,34]. Its physical reason can be readily understood if we consider the Einstein and Einstein-Smoluchowski equation [35]

$$\sigma_0 = nq\mu = nq \frac{qD}{kT} = \frac{nq^2}{kT} D = \frac{nq^2 \lambda^2}{kT 2\tau_h}, \quad (2)$$

where  $n$  is the effective number density of the ions,  $\lambda$  represents the hopping length, and  $\tau_h$  is the hopping time. Taking into consideration that  $\tau_h \sim \tau_e = 1/\omega_e$ , leads, according to Eq. (2), directly to the BNN relation:  $\sigma_0 \sim \tau_e$ . The success rate of the hopping mechanism (the proportional factor between  $1/\tau_h$ , the hopping rate, and  $1/\tau_e$  defined as the attempt rate to overcome the energy barrier) as well as the hopping length  $\lambda$  are supposed to exhibit a negligible temperature dependence in comparison to the huge temperature variations (i.e., ten orders of magnitude) in the conductivity.

Estimative determinations of the diffusion coefficient can be extracted by setting  $\tau_h \cong \tau_e$  and by taking for the hopping length values comparable to the Pauling diameter [36], i.e.,  $\lambda=0.2$  nm. Excellent agreement with the diffusion coefficient of MMIM-Me2PO4 as directly measured by pulsed field gradient nuclear magnetic resonance [29,37,38] is found (Fig. 6). These calculations allow one to separate [using Eq. (2)] the contribution of  $n$ , the ion number density, from that of  $\mu$ , the electrical mobility. It turns out that the VFT character of the conductivity originates solely from the diffusion whereas, over a broad temperature range, the number density of ions follows an Arrhenius dependence (inset of Fig. 6). Extrapolating the latter to room temperature, gives a value of  $\sim 2.9 \times 10^{27}/\text{m}^3$  for the number density of effective charge carriers, close to  $3.4 \times 10^{27}/\text{m}^3$ , which represents the total number of ions in the system (determined from the density and the molecular weight). This implies that approximately 85% of the charge carriers participate in charge transport at room temperature. This finding is consistent with reports that not all the charge carriers participate in the conduction process [39,40].

In conclusion, separation between the number density  $n$  and the mobility  $\mu$  from the dc conductivity contribution enables one to unravel the origin of the VFT character of  $\sigma_0$ , proven to arise from the VFT dependence of the diffusion. The number density of charge carriers exhibit an Arrhenius dependence which, extrapolated to room temperature, indi-

cates that nearly all ions participate in the conduction process.

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