UNIVERSITÄT LEIPZIG

The dielectric properties of glassy ion-conducting materials

F.Kremer

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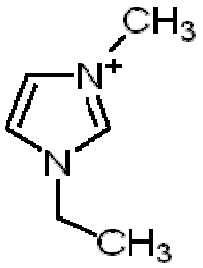
C. Iacob, S. Naumov, J. Kärger

Example for ion-conducting glassy materials: Ionic Liquids (ILs)

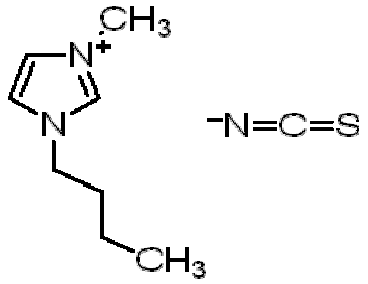
Ionic liquids are salts between an organic cation and a „simple“ anion:



BMIM BF4

BF_4^-

1-butyl-3-methylimidazolium tetrafluoroborate



BMIM SCN

1-n-butyl-3-methylimidazolium thiocyanate

Properties of ILs:

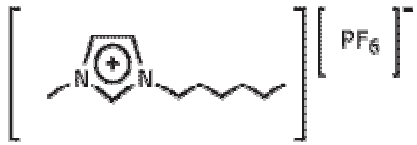
- Low glass transition temperature (220 K)
- High conductivity at room temperature
- Low viscosity even at low temperature (200 K)
- Novel solvent

Applications of ILs:

- Medium in fuel cells, super-capacitors, batteries and solar cells
- Catalysis, extraction and separation processes
- Lubricants and fuels

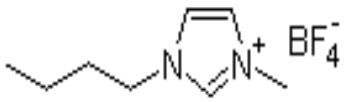
Structures of some of the ILs studied:

HMIM Cl

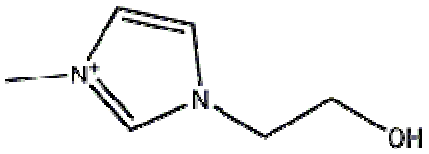


HMIM PF6

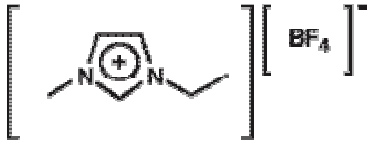
HMIM BF4



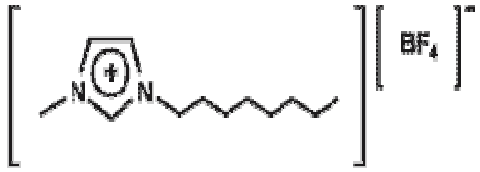
BMIM BF4



HEMIM BF4

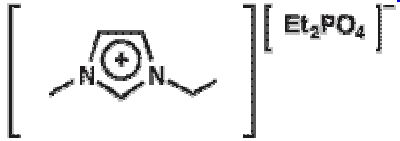


EMIM BF4

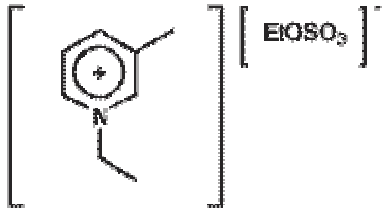


MOIM BF4

MMIM Me2PO4



MMIM Et2PO4



3-MEP EtSO3

Basic relations between the complex dielectric function ε* and the complex conductivity σ*

The *linear* interaction of electromagnetic fields with matter is described by Maxwell's equations

$$curl \quad H = j + \frac{\partial D}{\partial t}$$

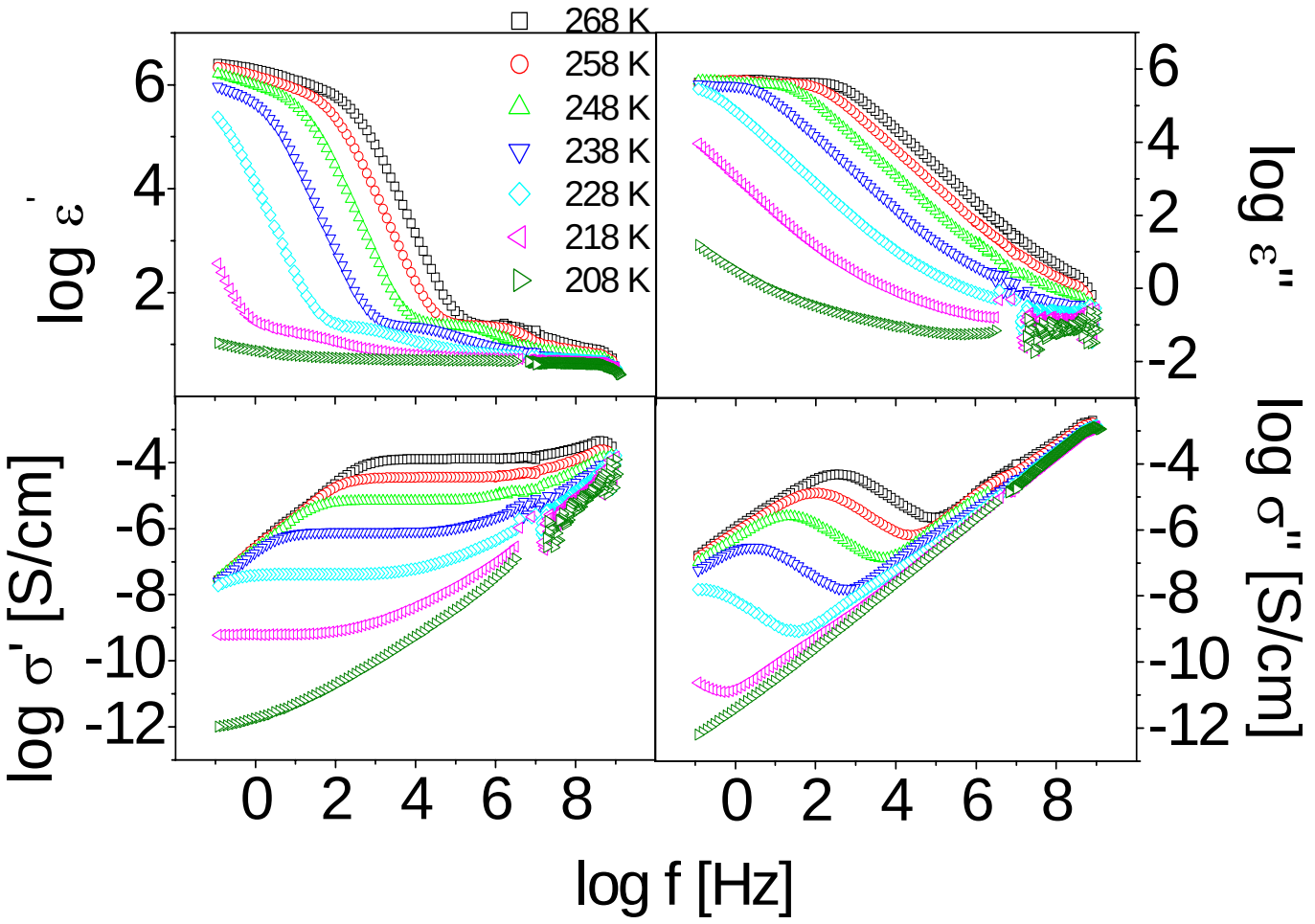
$$D = \varepsilon^* \varepsilon_0 \quad E \qquad\qquad j = \sigma^* E \qquad \text{(Ohm's law)}$$

(Current-density and the time derivative of D are equivalent)

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \qquad \sigma^*(\omega) = \sigma' + i\sigma''$$

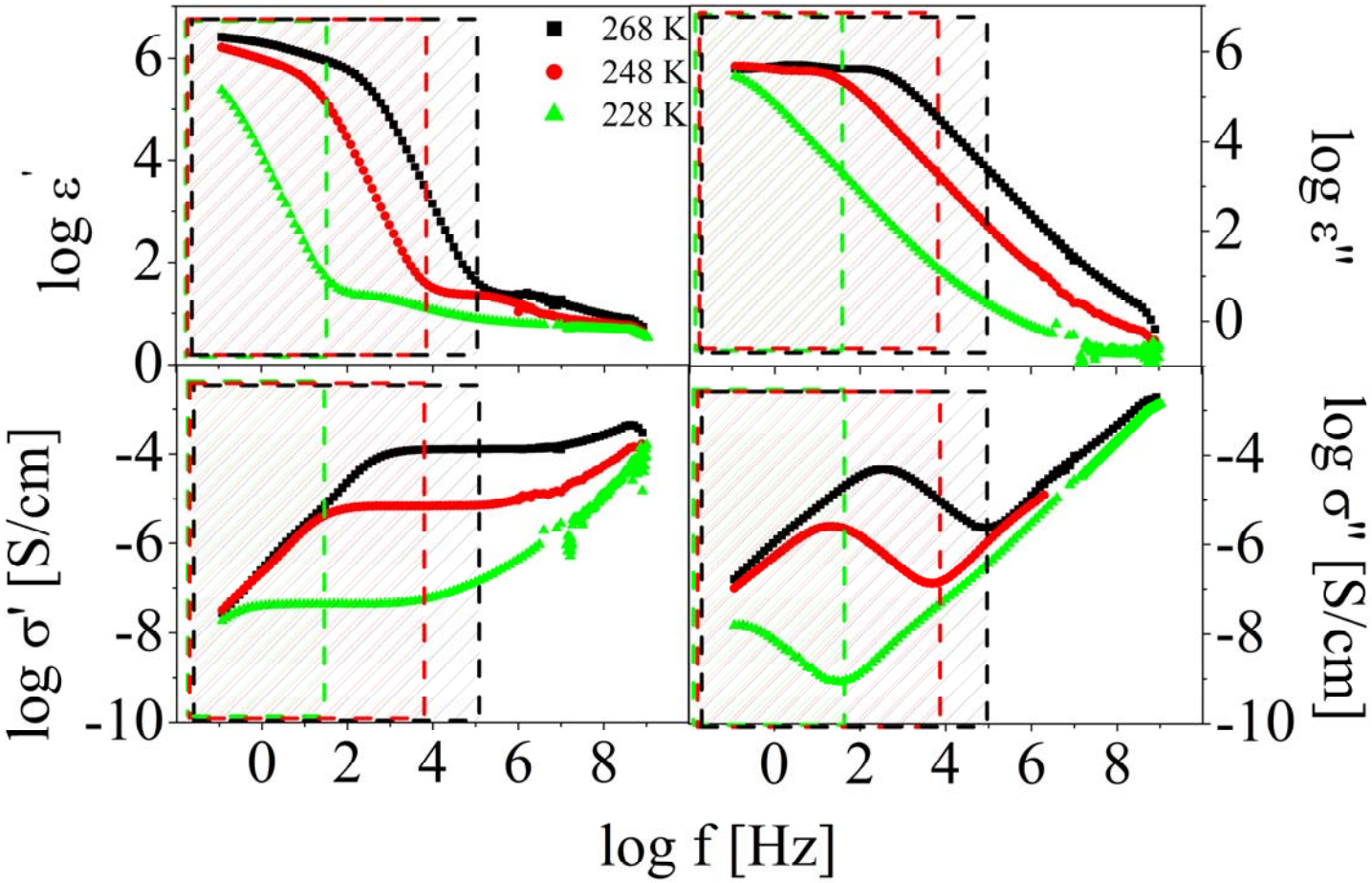
$$\boxed{\sigma^* = i\omega\varepsilon_0\varepsilon^*}$$

Broadband dielectric spectra of an ionic liquid (MMIM) Me2PO4



Strong temperature dependence of the charge transport processes and electrode polarisation

Two temperature dependent regimes: Electrode polarisation and bulk charge transport



The spectral range where electrode polarisation dominates depends strongly on temperature

Basic relations between rotational and translational diffusion

Stokes-Einstein relation:

$$D = kT/\zeta$$

D: diffusion coefficient, ζ ($=6\pi\,\eta\,a$) : frictional coefficient,T: temperature, k: Boltzmann constant, a: radius of molecule

Maxwell‘s relation:

$$\eta = \tau_\eta\, G\infty$$

G_∞: instantaneous shear modulus (~ 10^8 - 10^{10} Pa)

η: viscosity, τ_η: structural relaxation time

Einstein-Smoluchowski relation:

$$D = \frac{\lambda^2 \omega_c}{2}$$

λ : characteristic (diffusion) length

ω_c: characteristic (diffusion) rate

Basic electrodynamics and Einstein relation:

$$\sigma_0 = q\mu n = n\frac{q^2 D}{kT} \quad \Rightarrow \quad \sigma_0 \propto \omega_c$$

σ_0: : dc conductivity, μ: mobility ; q: elementary charge, n: effective number density of charge carriers

Predictions to be checked experimentally:

1.: $\omega_c = P\ \omega_\eta$

2.: $P = \dfrac{kT}{2\pi^2 G_\infty \lambda^2 a_s}$

3.: $D = \dfrac{\lambda^2 \omega_c}{2}$

4.: $\sigma_0 \sim \omega_c$

ω_c: characteristic (diffusion or hopping) rate

ω_η: structural relaxation rate

G_∞: instantaneous shear modulus (~ 10^8 Pa for ILs),

a_s : Stokes‘ hydrodynamic radius ~λ,

k: Boltzmann constant,

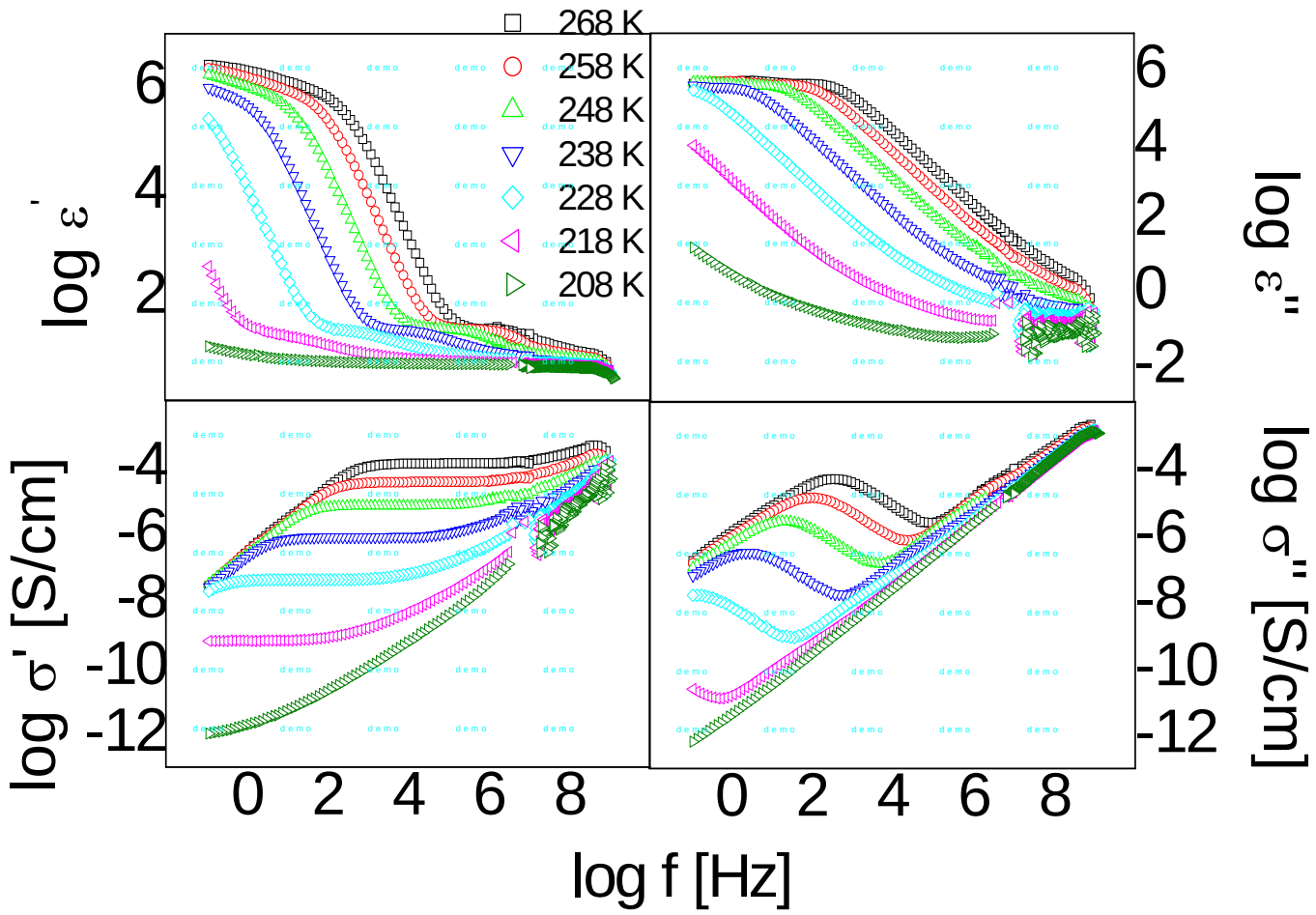
λ: characteristic diffusion length ~ .2 nm

D : molecular diffusion coefficient

(Barton-Nakajima-Namikawa (BNN) relation)

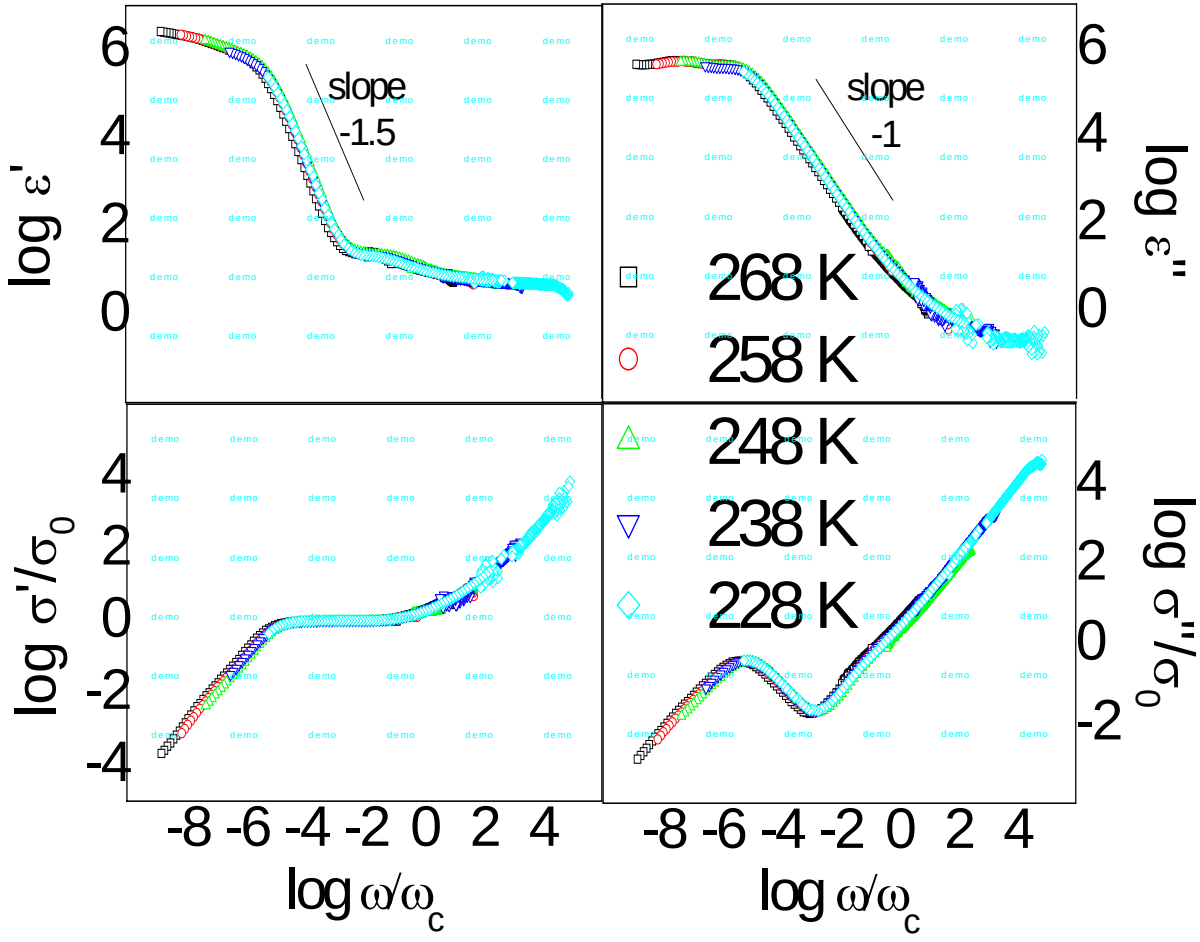
Measurement techniques required: Broadband Dielectric Spectroscopy (BDS); Pulsed Field Gradient (PFG)-NMR; viscosity measurements;

Dielectric spectra of MMIM Me2PO4 ionic liquid



Strong temperature dependence of the charge transport processes and electrode polarisation

Scaling of dielectric spectra with characteristic rate ω_c



All charts collapse into one if scaled with respect to ω_c. Identical thermal activation of charge transport and electrode polarisation

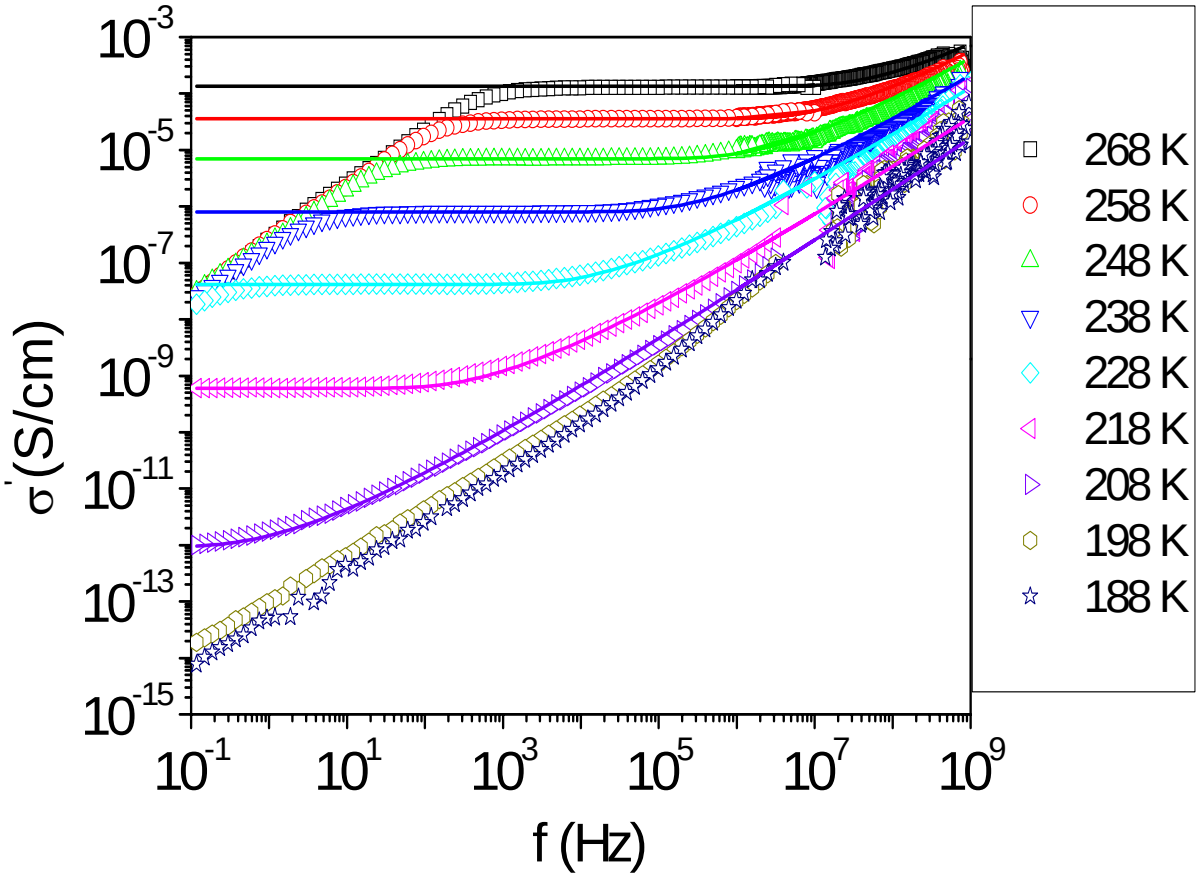
Description of the data: Random Barrier Model (Jeppe Dyre et al.)

- Hopping conduction in a spatially randomly varying energy landscape
- Analytic solution obtained within Continuous-Time-Random Walk (CTRW) approximation
- The largest energy barrier determines Dc conduction
- The complex conductivity is described by:

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

τ_e is the characteristic time related to attempt frequency to overcome the largest barrier determining the Dc conductivity

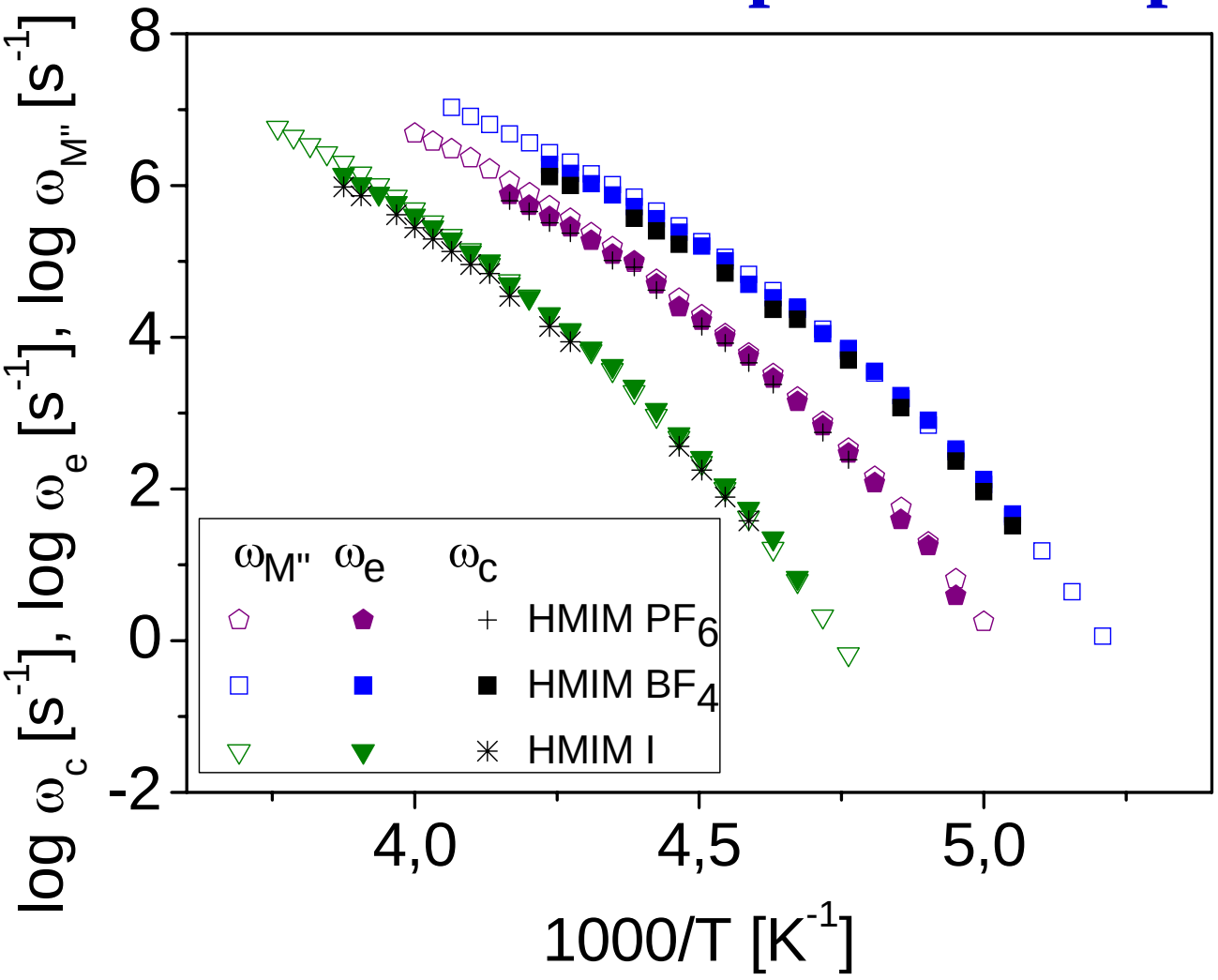
Random Barrier Model (RBM) used to fit the conductivity spectra of ionic liquid (MMIM Me2PO4)



Lines represent fits by RBM

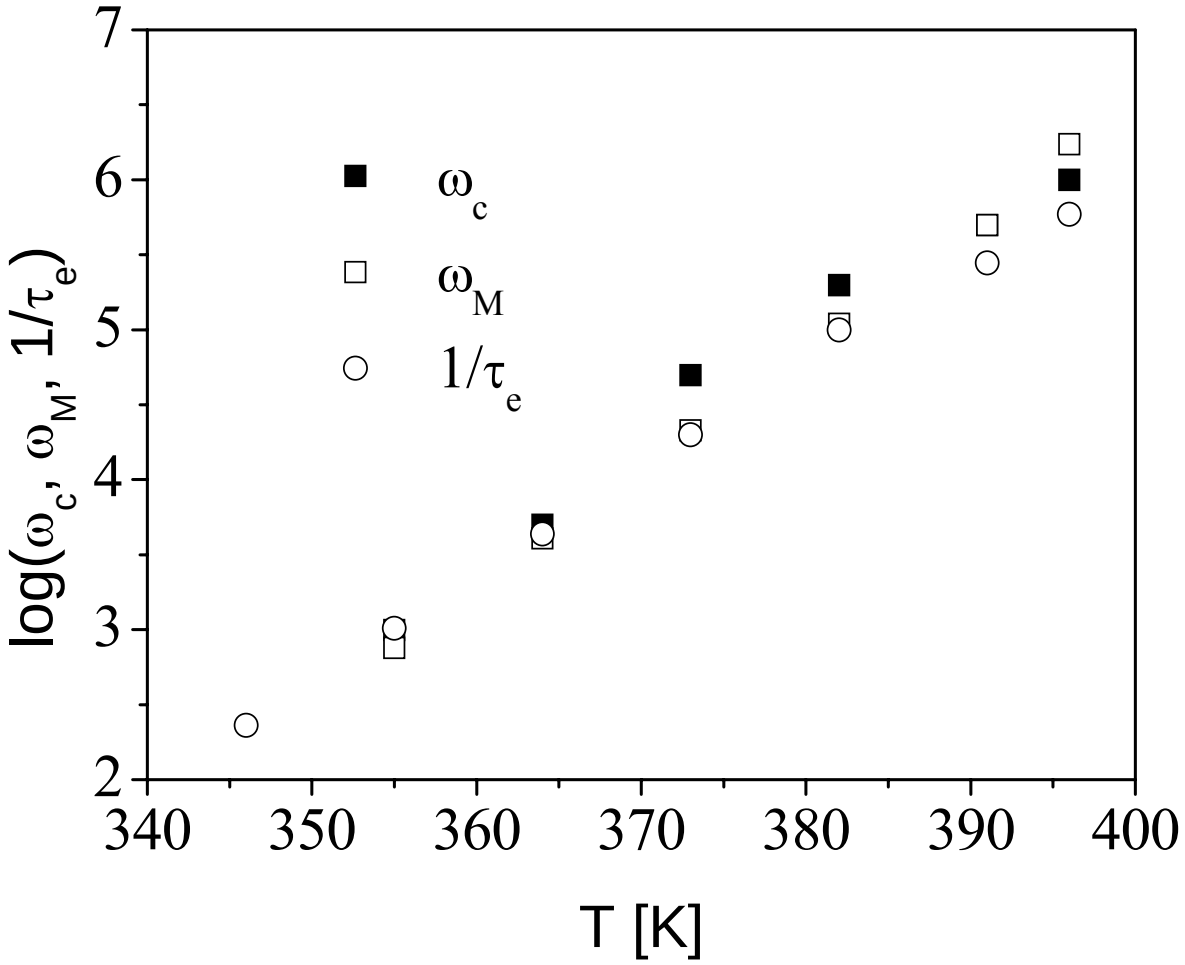
The random barrier model quantitatively describes the measured dielectric spectra describing charge transport

The rates ω_c, ω_M and $1/\tau_e$ coincide and have - over 6 decades - a similar temperature dependence



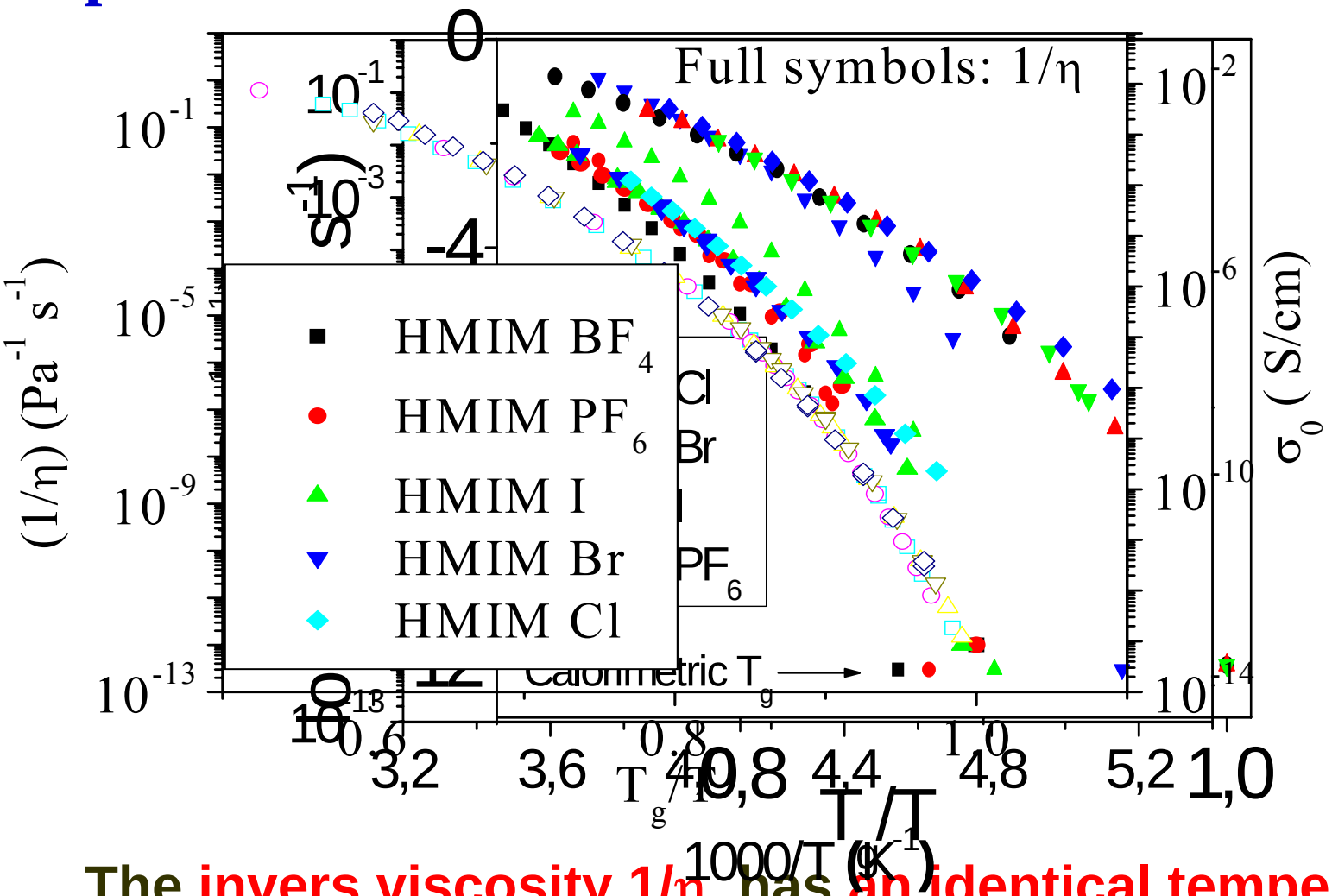
The different rates ω_c, ω_M and $1/\tau_e$ describe the same mechanism of charge transport

The rates ω_c, ω_M and $1/\tau_e$ nearly coincide and have - over 5 decades - a similar temperature dependence



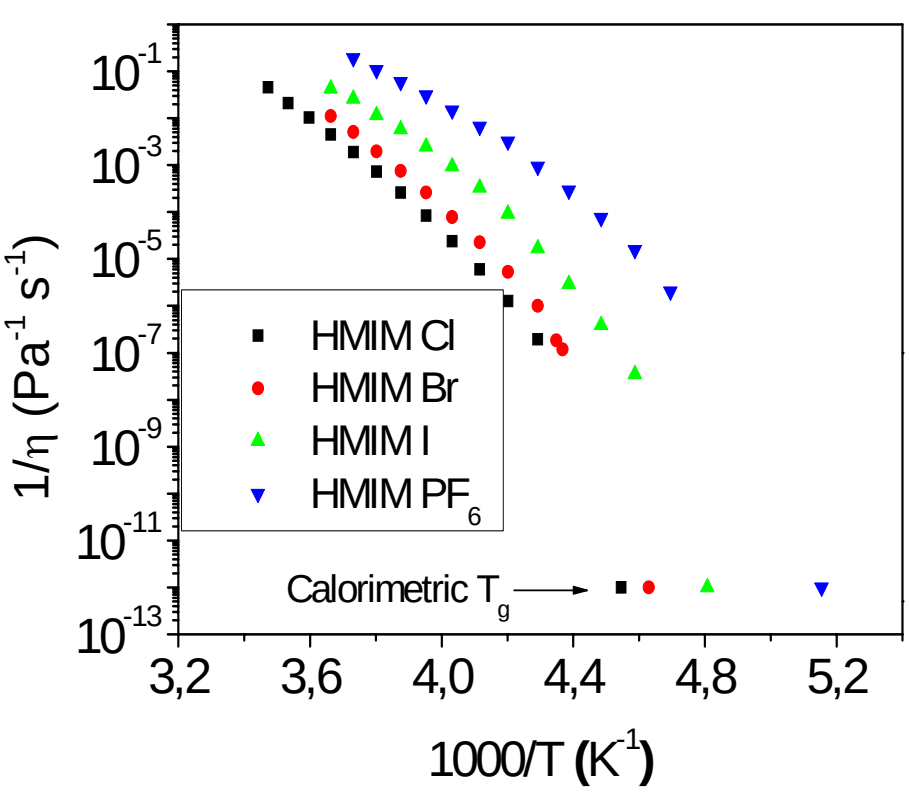
F. Kremer and A. Schönhals (2003), *Broadband Dielectric Spectroscopy*

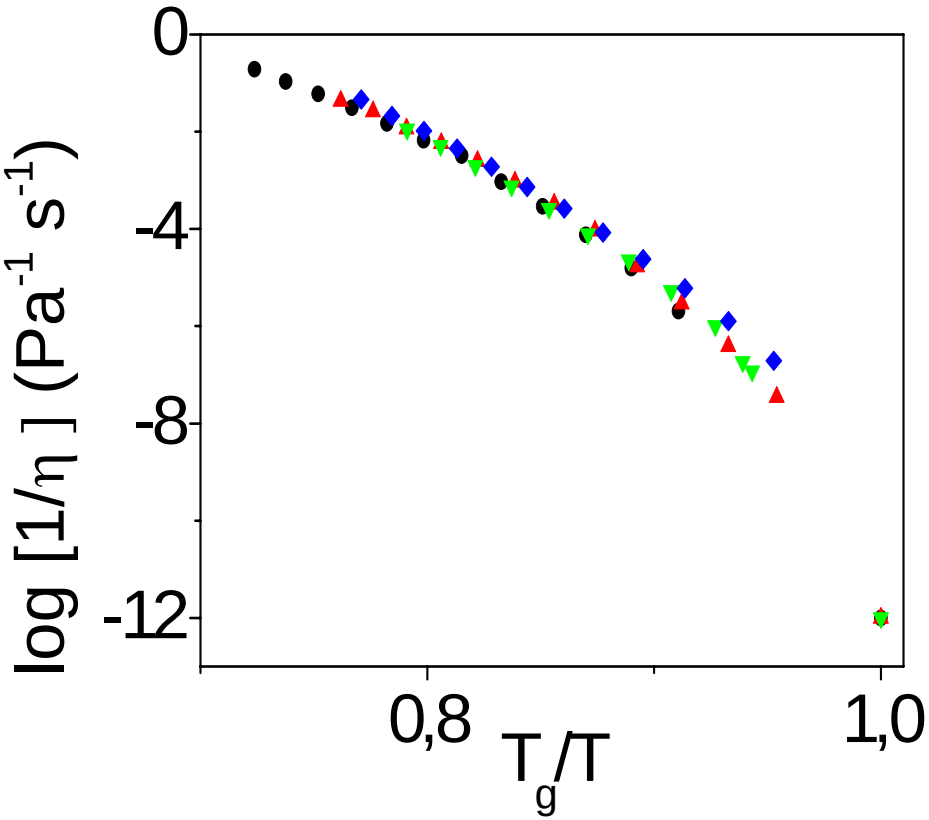
Scaling of invers viscosity $1/\eta$ and conductivity σ_0 with temperature



The invers viscosity $1/\eta$ has an identical temperature dependence as σ_0 and scales with T_g.

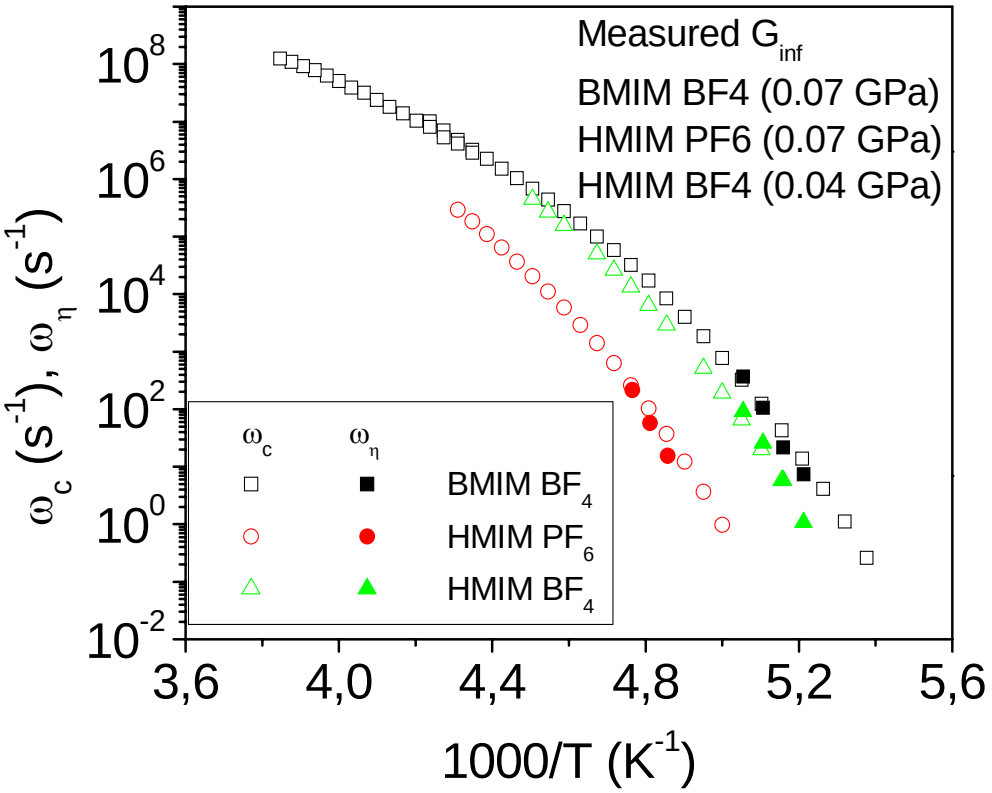
Effect of structural variation on viscosity





Fluidity (1/η) *strongly depends on the* anion (PF6 < I < Br < Cl)

Correlation between translational and rotational diffusion



Stokes-Einstein, Einstein-Smoluchowski and Maxwell relations:

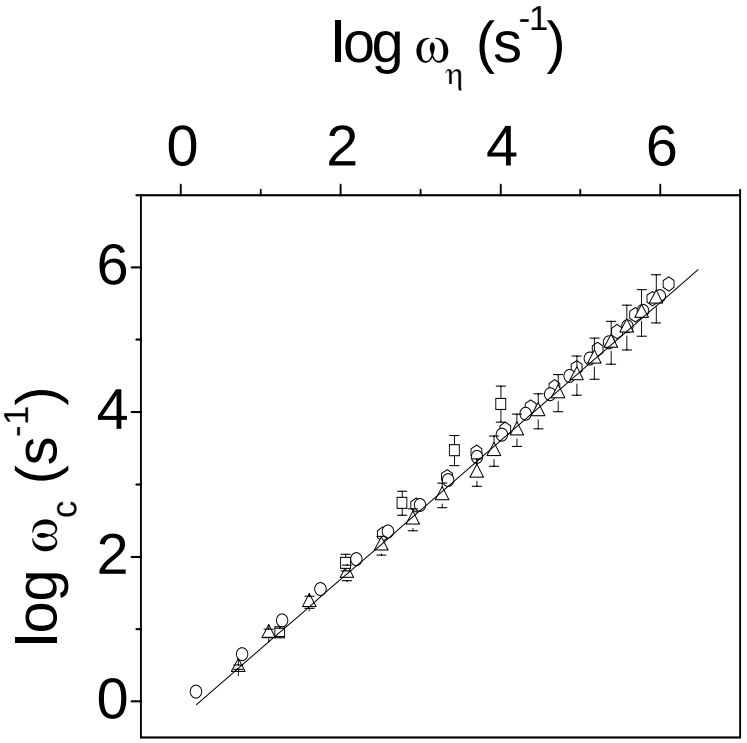
$$\omega_c = P\,\omega_\eta$$

$$P = \frac{kT}{2\pi^2 G_\infty \lambda^2 a_s} \quad 1$$

Typically: $G_\infty \cong 0.1$ Gpa; $\lambda \cong .2$ nm; $a_s \cong .1$ nm;

J. R. Sangoro et al. Phys. Chem. Chem. Phys, DOI: 0.1039/b816106b,(2009) .

Correlation between translational and rotational diffusion



Stokes-Einstein, Einstein-Smoluchowski and Maxwell relations:

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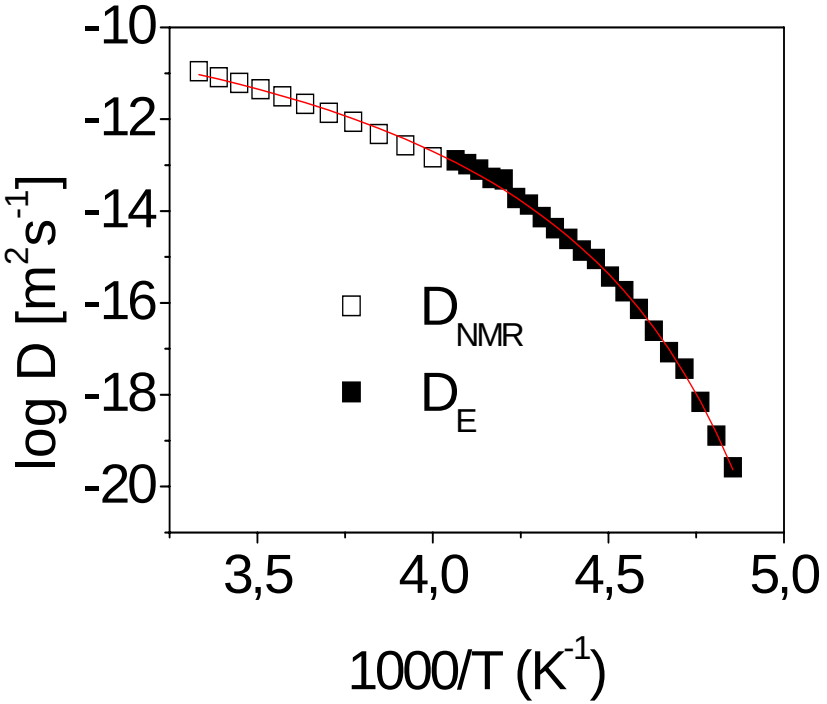
J. R. Sangoro et al. Phys. Chem. Chem. Phys, DOI: 0.1039/b816106b,(2009) .

Comparison with Pulsed-Field-Gradient NMR and deter - mination of diffusion coefficients from dielectric spectra

From Einstein and Einstein-Smoluchowski relations and assuming the root mean square diffusion distance similar to the order of Pauling diameters, i.e $\lambda \sim 0.2$ nm follows (idea: Joshua Rume Sangoro):

$$\sigma_0(T) = n(T)q\mu(T) = n(T)q\frac{qD(T)}{kT} = \frac{n(T)q^2}{kT}\frac{\lambda^2}{2\tau_h(T)} \sim \omega_e$$

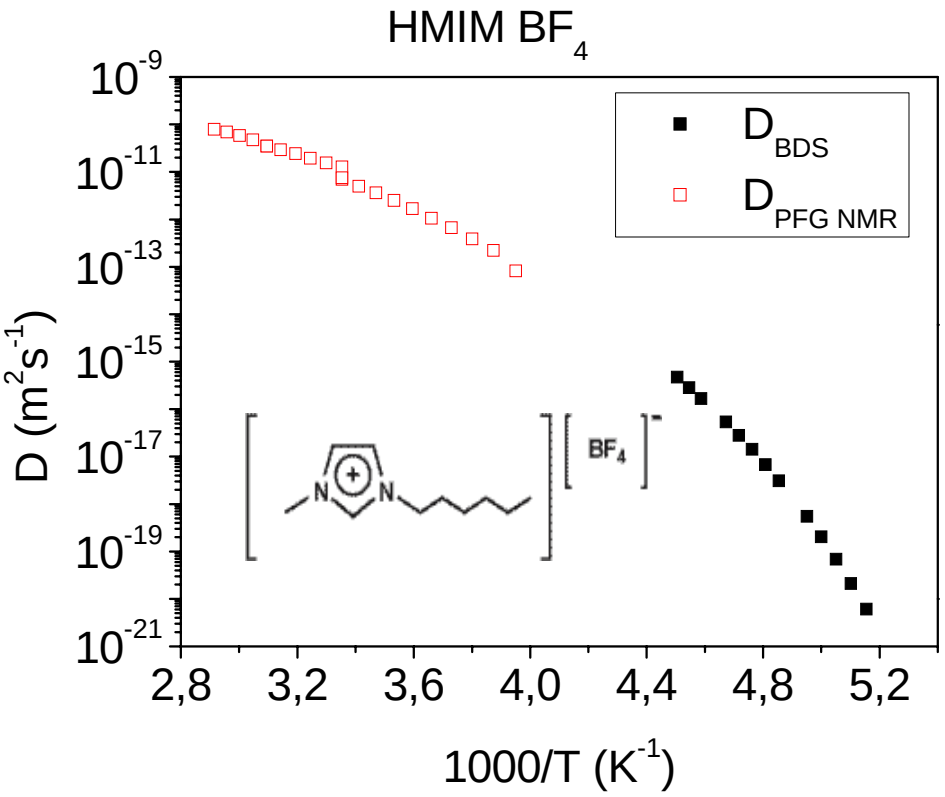


1. Quantitative agreement between PFG-NMR measurements and the dielectric determination of the diffusion coefficients.

2. In ILs mass diffusion (as measured by PFG-NMR) equals charge transport as measured by BDS but in a much wider spectral range.

3. The empirical BNN-relation is an immediate consequence.

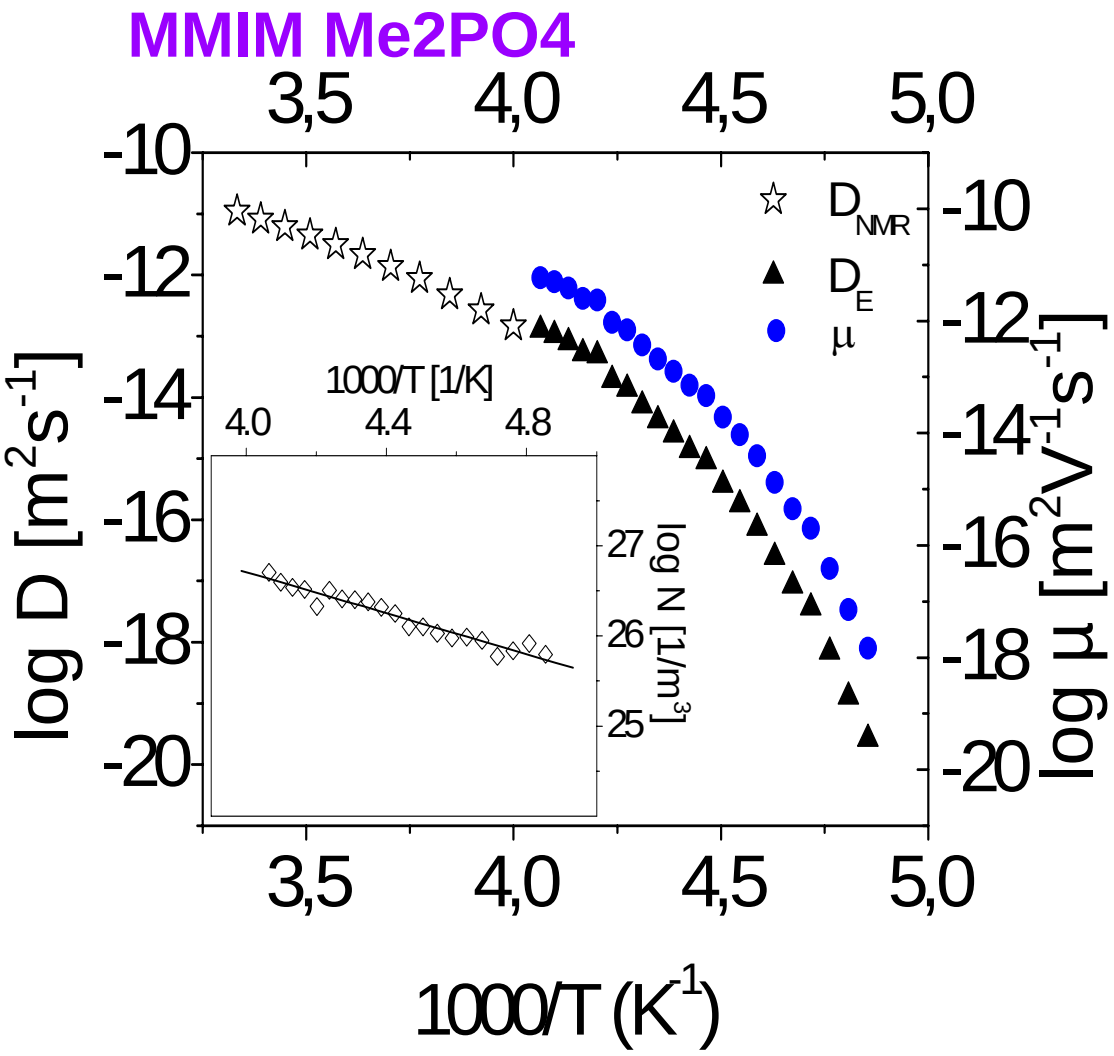
Further diffusion coefficients from dielectric spectra



Charge transport is mass transport in ionic liquids. Probing Flouride and Hydrogen yield practically the same diffusion coefficient!

PFG NMR measurements performed by Sergej Naumov

Separation of n(T) and μ(T) from σ_0 (T)



1. μ(T) shows a VFT-type temperature dependence

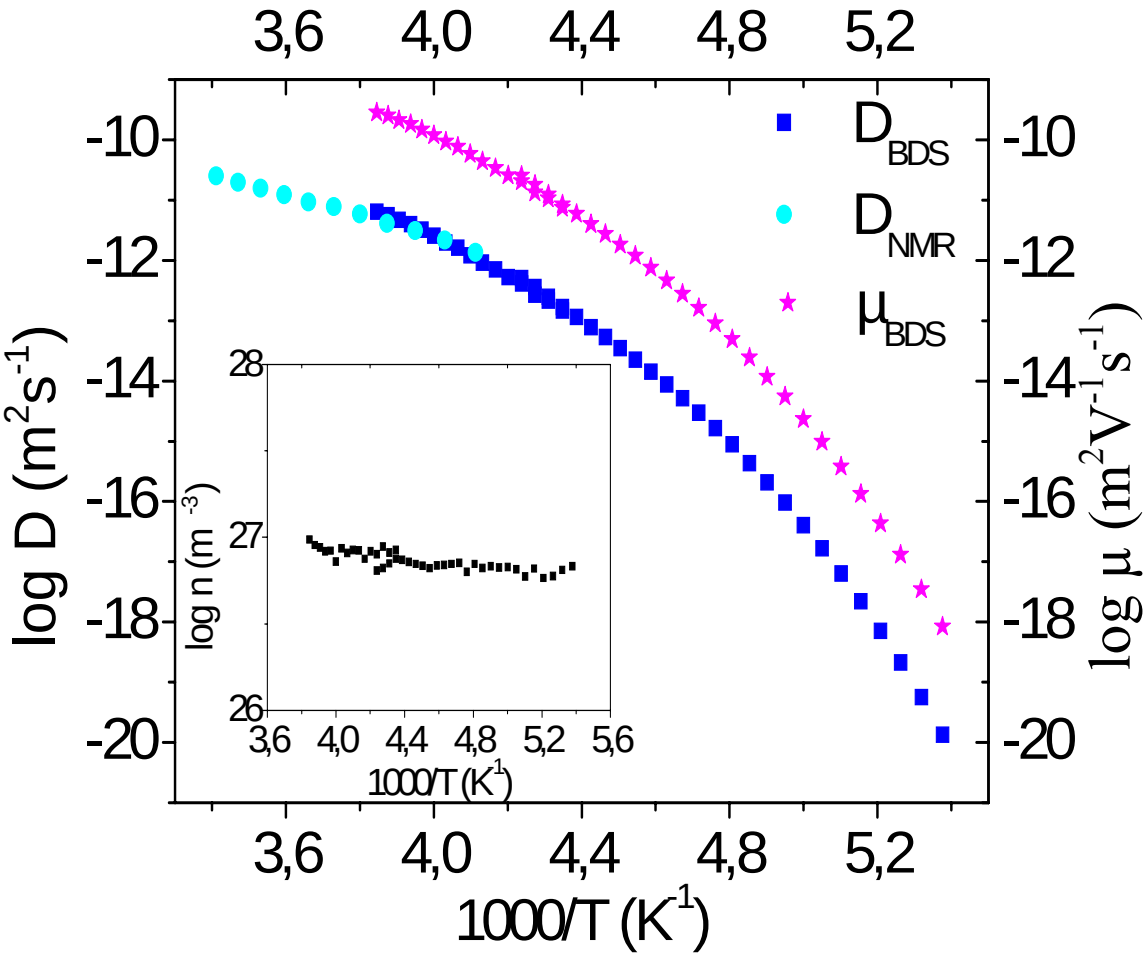
2. n(T) shows an Arrhenius-type temperature dependence

3. σ_0 (T) derives its dependence from μ(T)

J. Sangoro, *et al*., Phys. Rev. E 77, 051202 (2008)

Separation technique applied to BMIM BF4

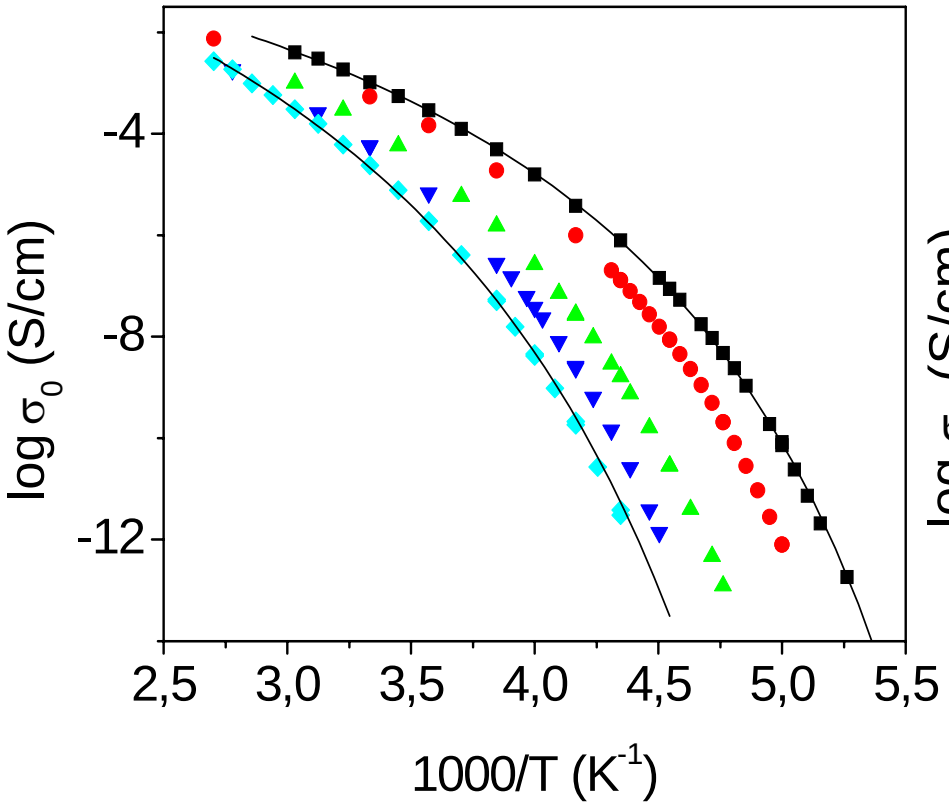
BMIM BF4

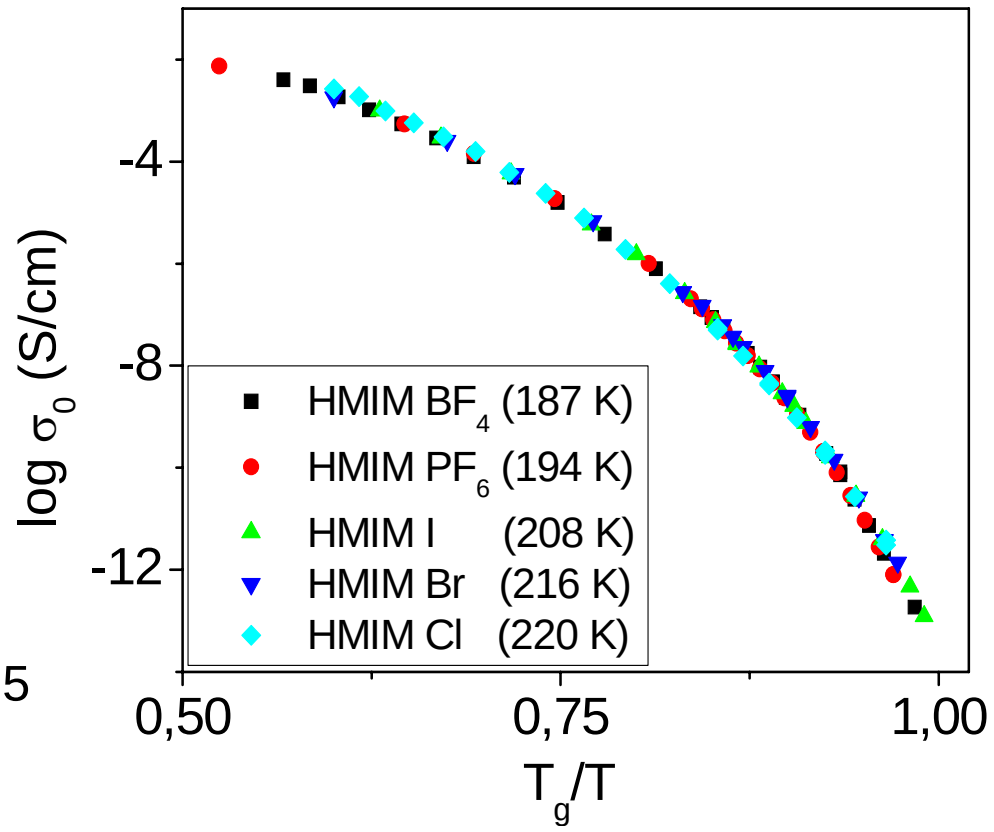


Agreement between dielectric and PFG NMR diffusion coefficients

J. R. Sangoro,...S. Naumov, J. Kärger,..., J. Chem. Phys. 128, 212509 (2008)

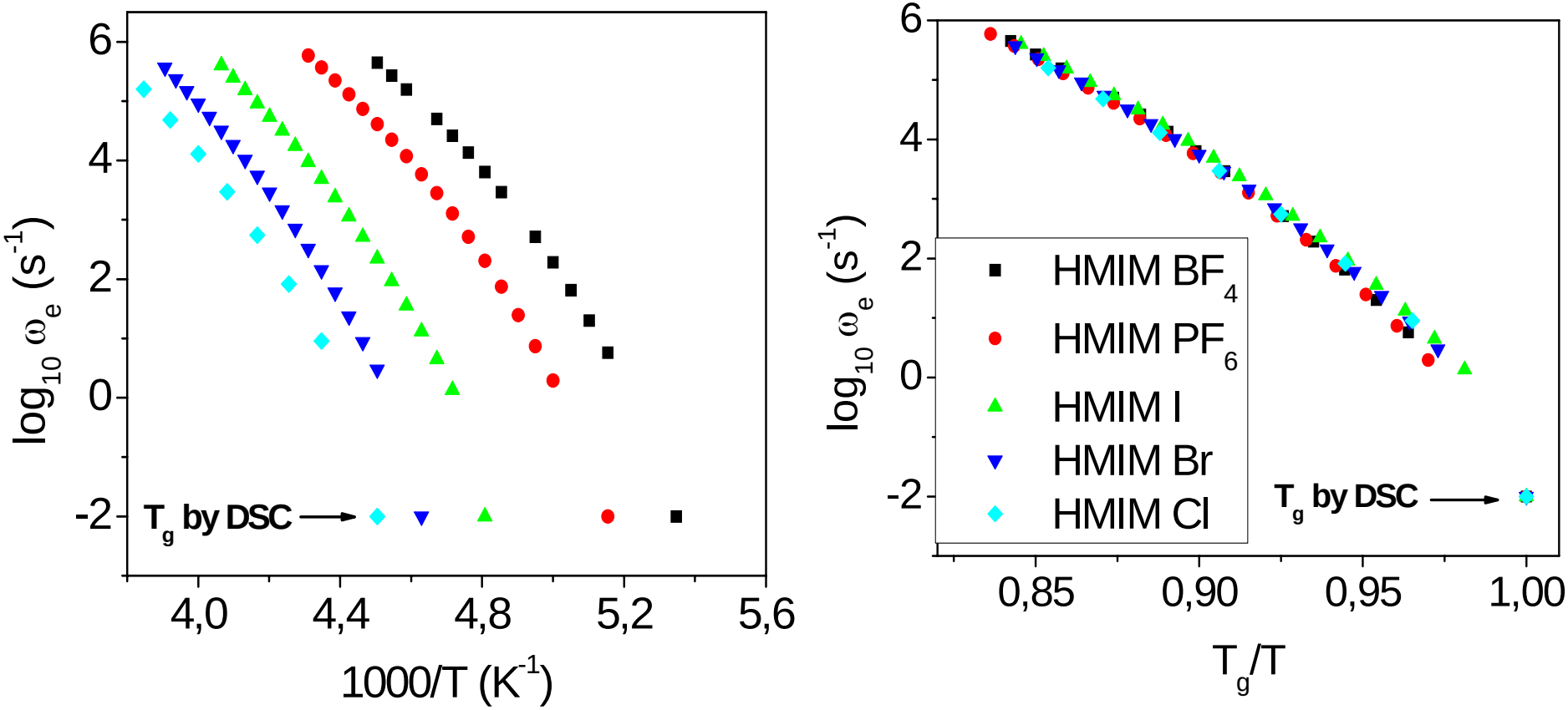
Temperature dependence of Dc conductivity of ILs





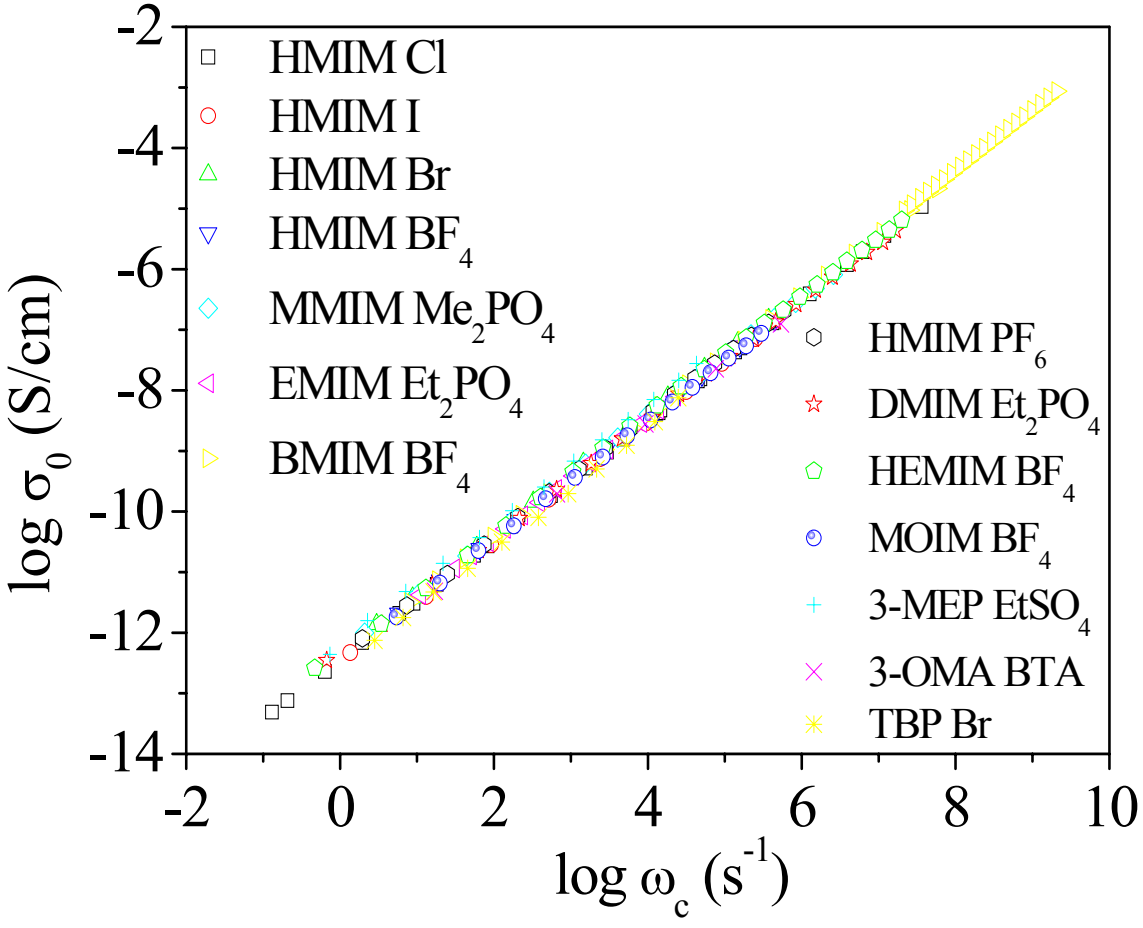
Excellent scaling with calorimetric glass transition temperature

Temperature dependence of characteristic diffusion rate



Characteristic diffusion rate shows a strong dependence on the anion (BF4 < PF6 < I < Br < Cl)

Universality of charge transport in ionic liquids



1. Universality despite significant structural variation (imidazolium-, ammonium-, pyridinium and phosphonium-based ionic liquids)

2. BNN relation holds

J. R. Sangoro et al. PCCP
DOI: 0.1039/b816106b,(2009)
.

Despite the structural variation, universal response is observed over 11 decades.

Predictions checked experimentally:

1.: $\omega_c = P\ \omega_\eta$

2.: $P = \frac{kT}{2\pi^2 G_\infty \lambda^2 a_s} \leq 1$

3.: $D = \frac{\lambda^2 \omega_c}{2}$

4.: $\sigma_0 \sim \omega_c$ (Barton-Nishijima-Namikawa (BNN) relation)

ω_c: characteristic (diffusion) rate

ω_η: structural relaxation rate

G_∞: instantaneous shear modulus (~ 10^8 Pa for ILs),

a_s : Stokes' hydrodynamic radius ~λ,

k: Boltzmann constant,

λ: characteristic diffusion length ~ .2 nm

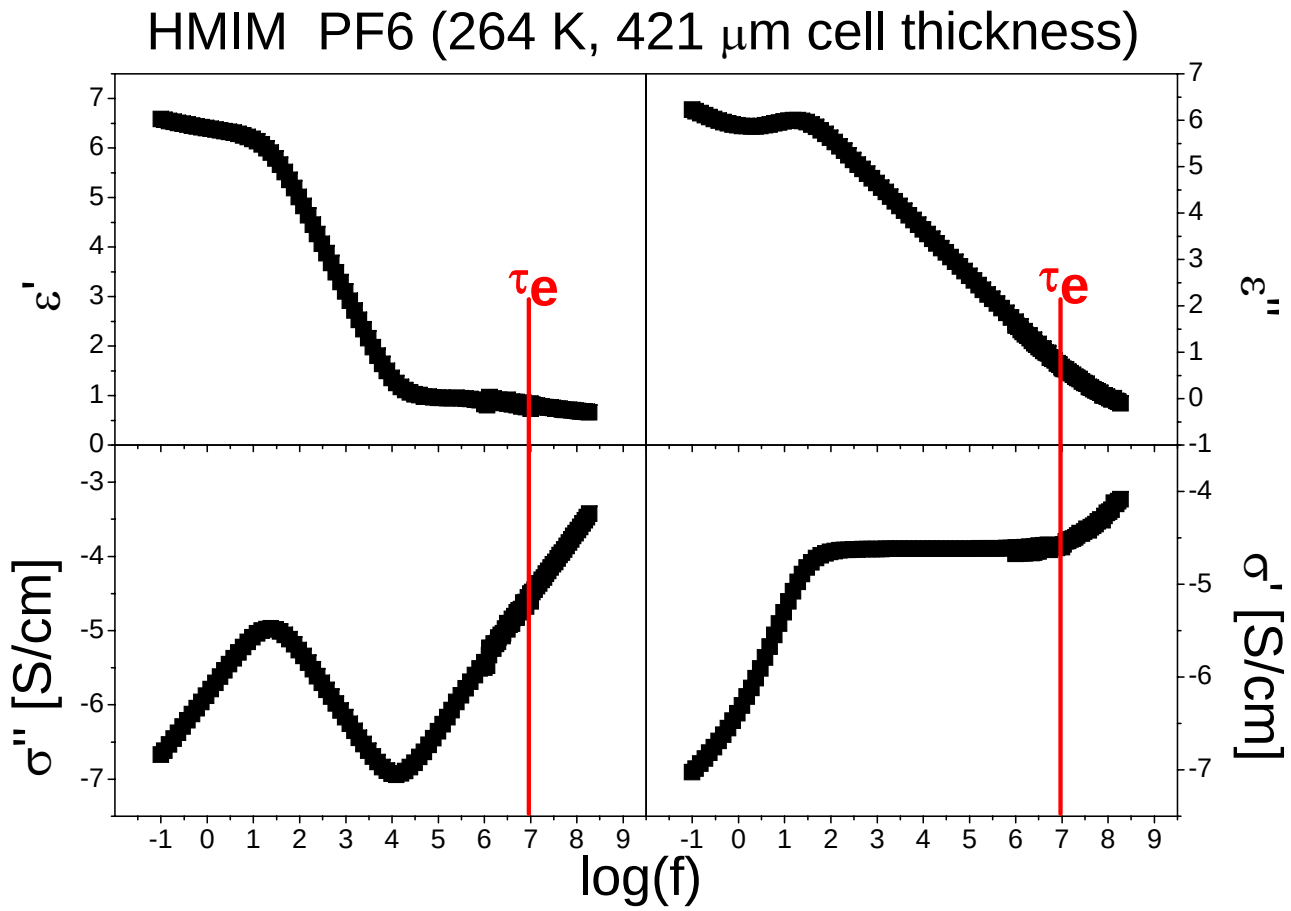
D : molecular diffusion coefficient

Electrode polarization (EP) in Ionic Liquids (ILs) experimental features and *quantitative* description

Questions to be adressed:

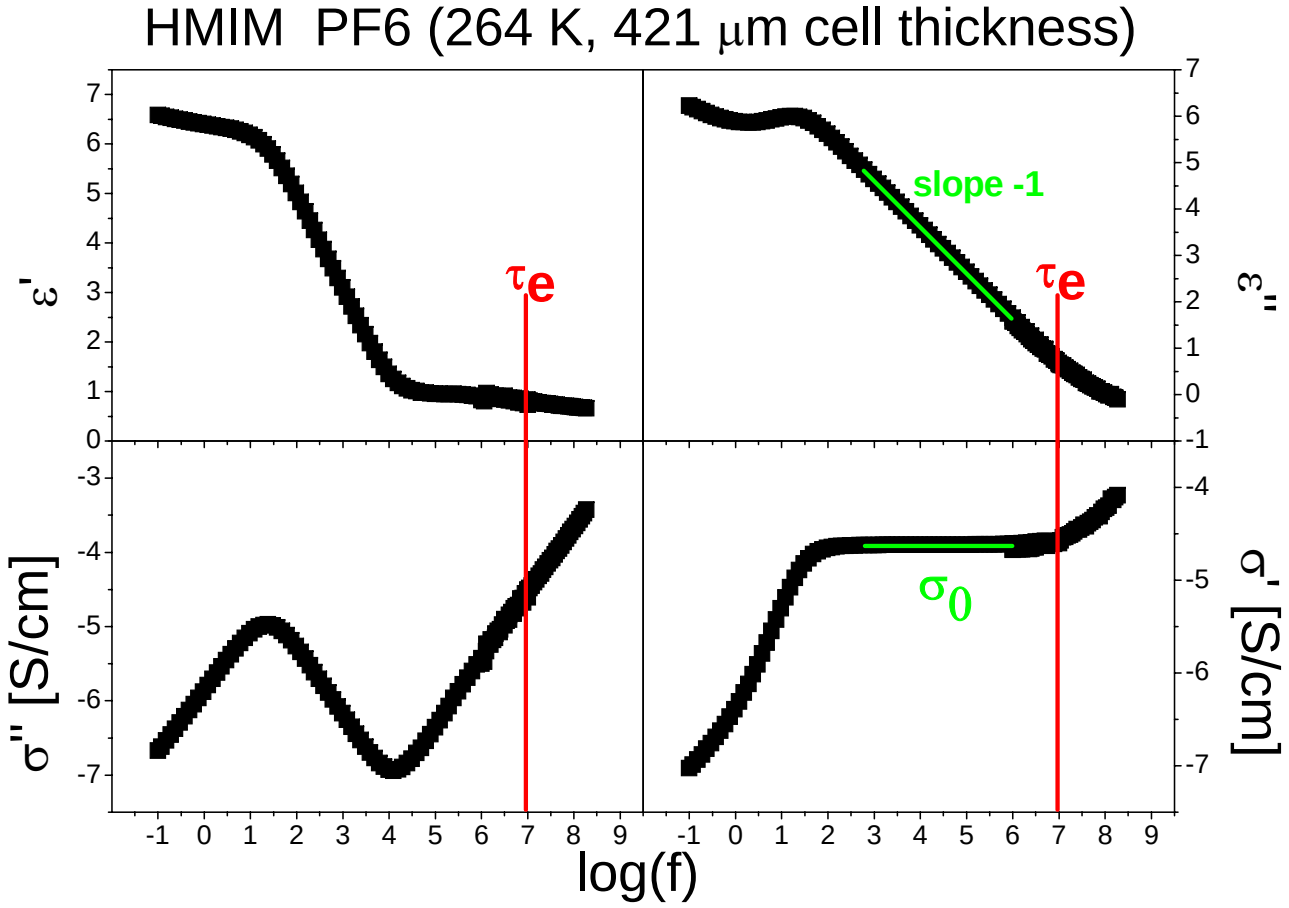
1. What is the *signature* of electrode polarisation (EP) and how can it be analysed *quantitatively*?
2. What *quantitative* information can be deduced from fits of the EP?
3. What is the *quantitative* model to describe EP?
4. What information can be deduced from EP?

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

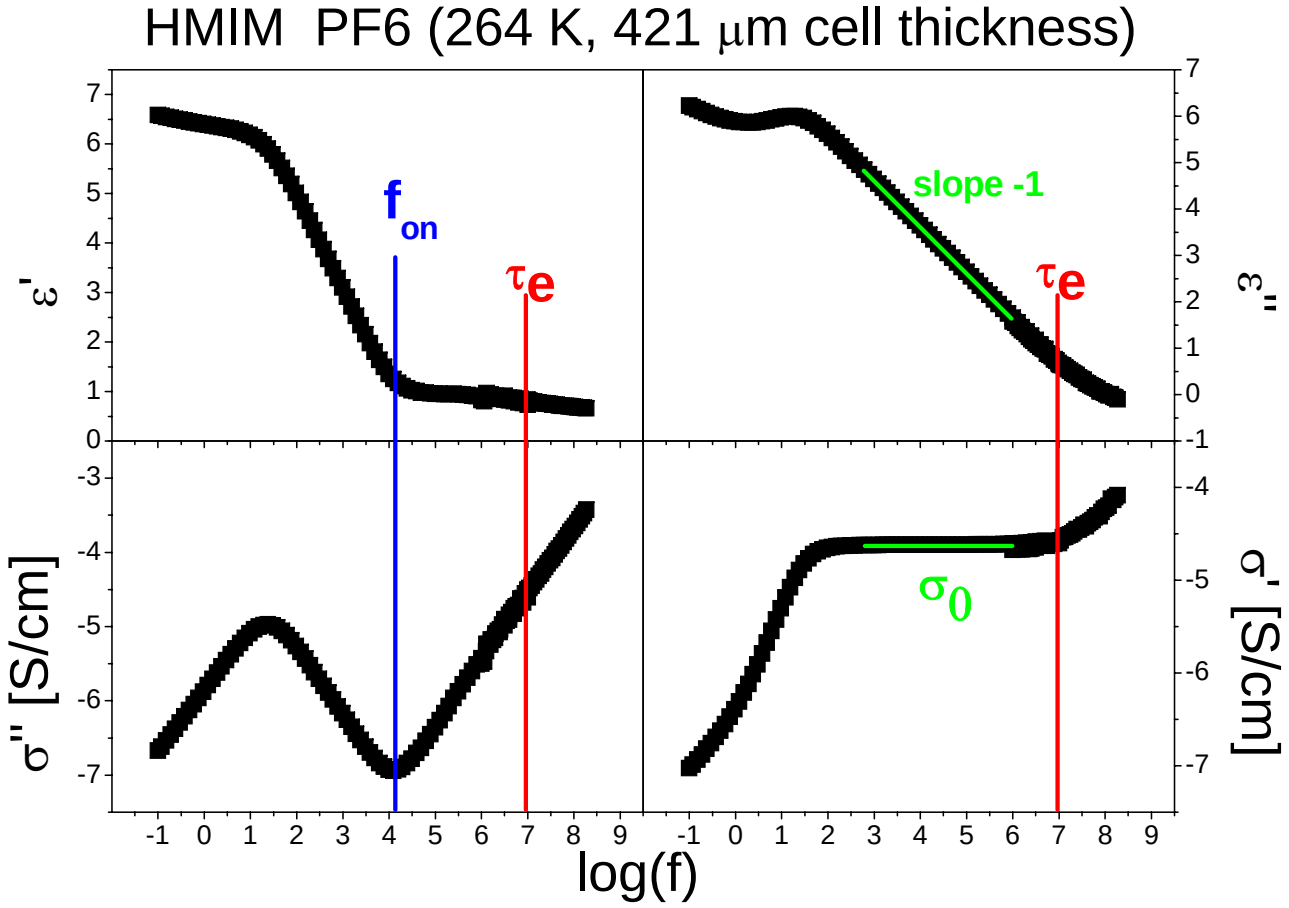
Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

Experimental features of EP in ILs - frequency dependence

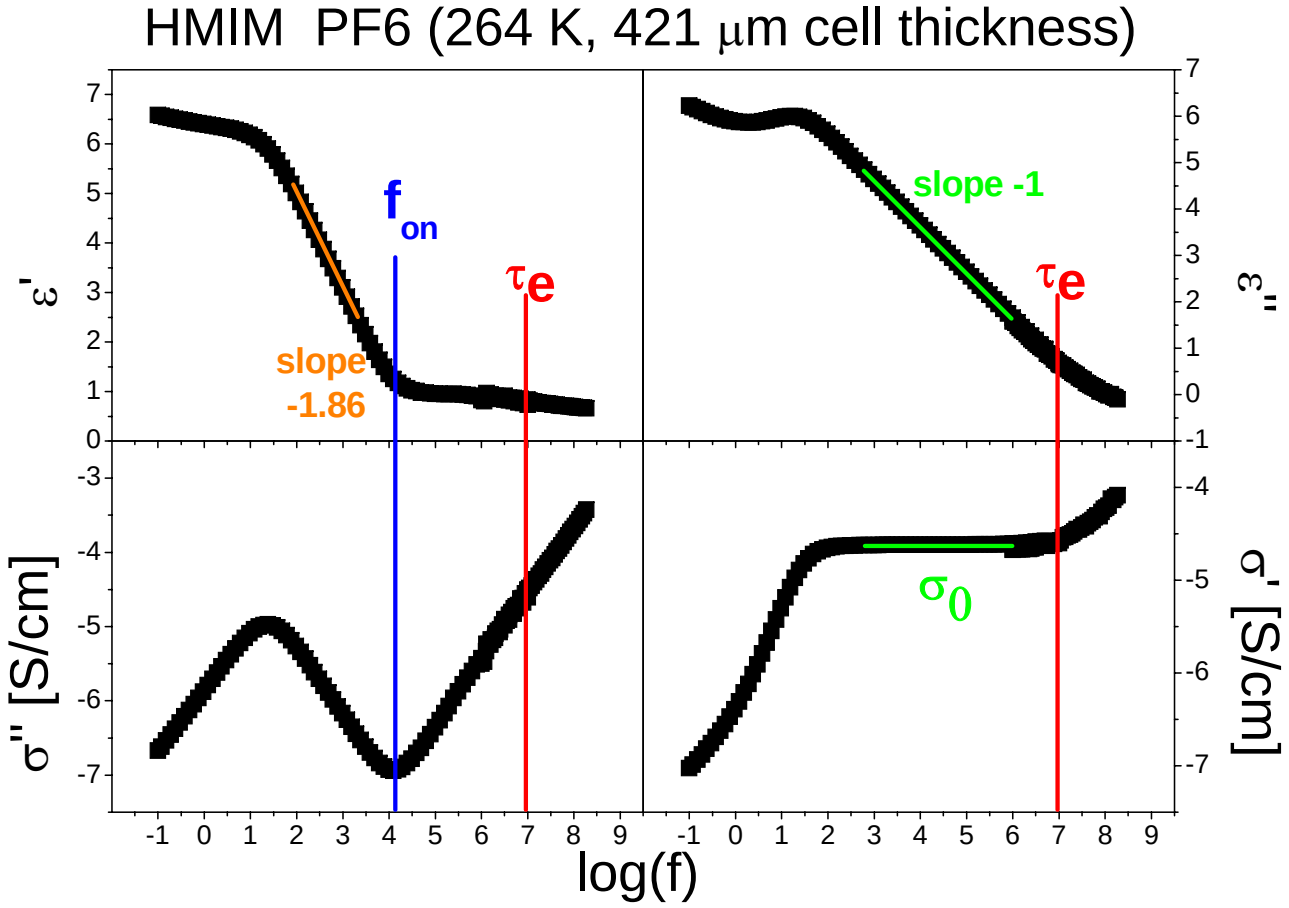


τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

Experimental features of EP in ILs - frequency dependence



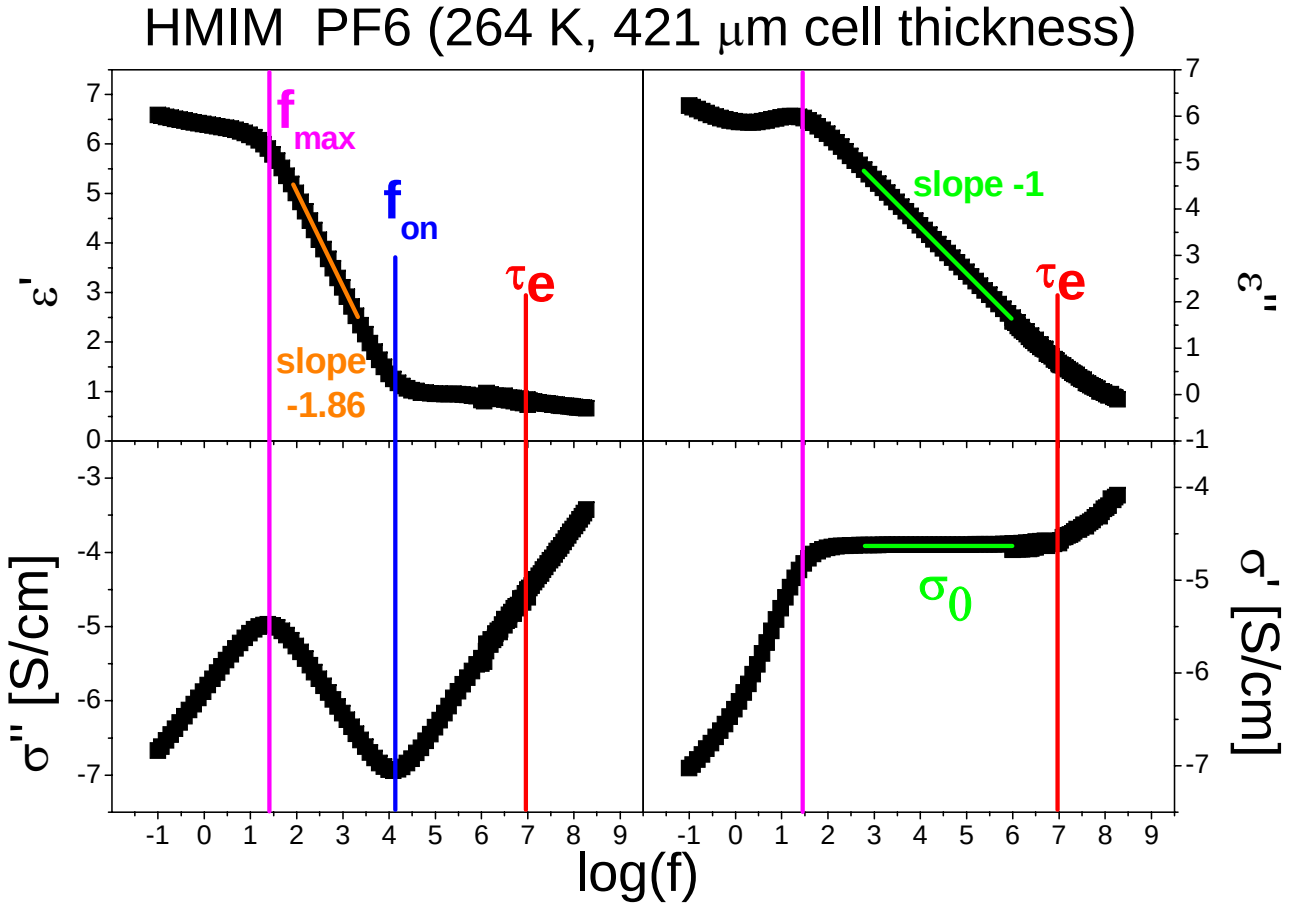
τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

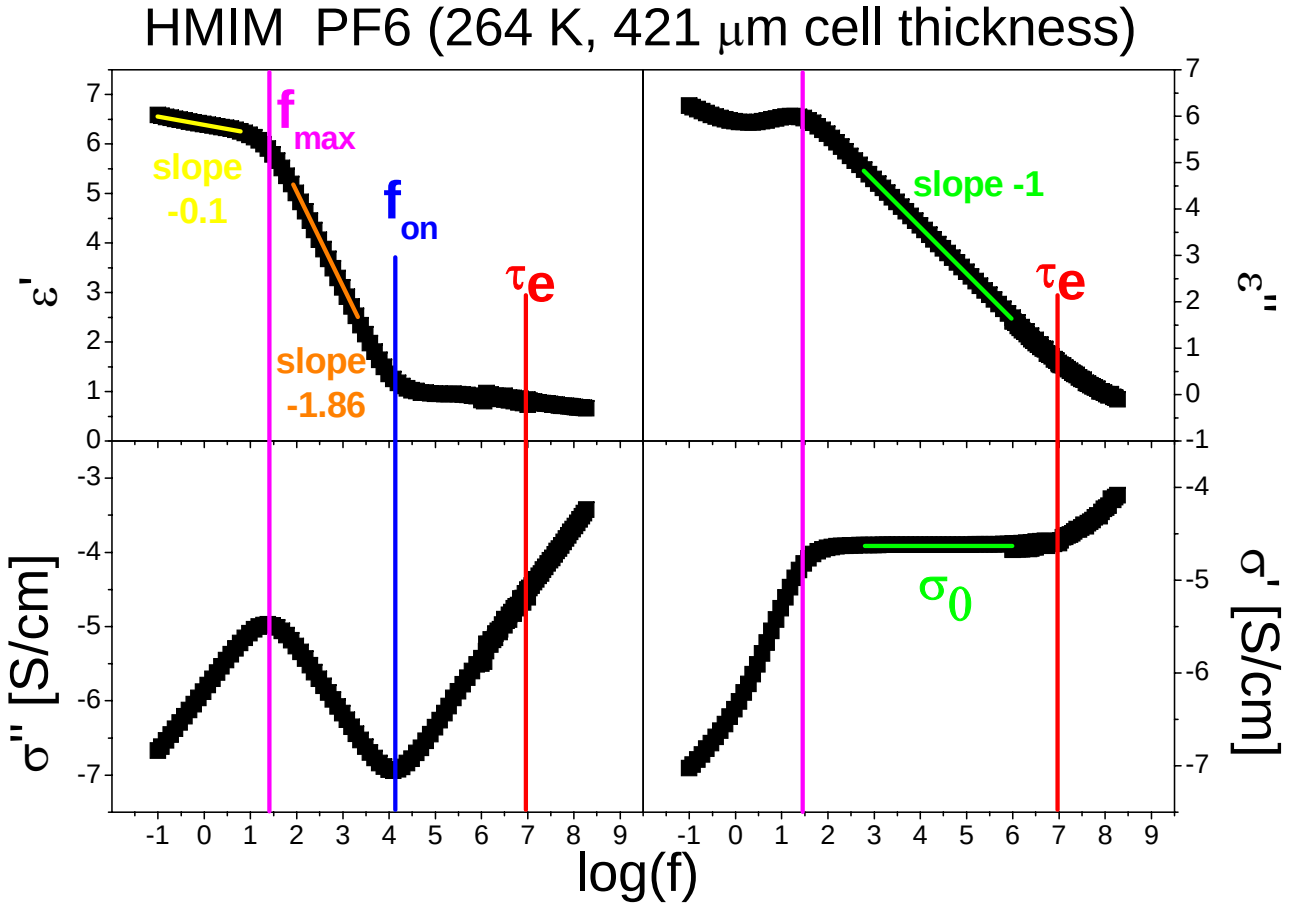
σ_0: DC conductivity

f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

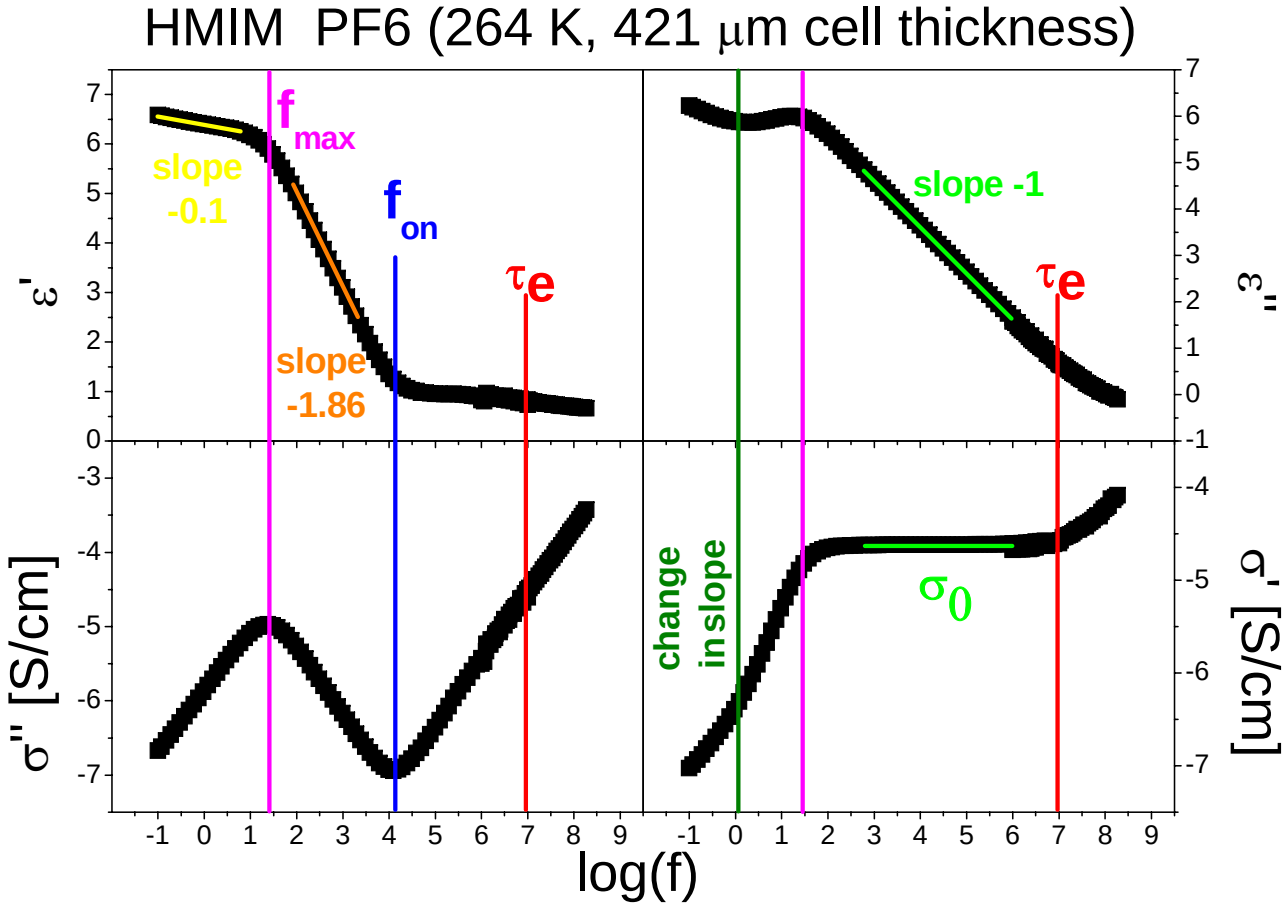
f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

slope of –0.1 in ε´ for $f < f_{max}$

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

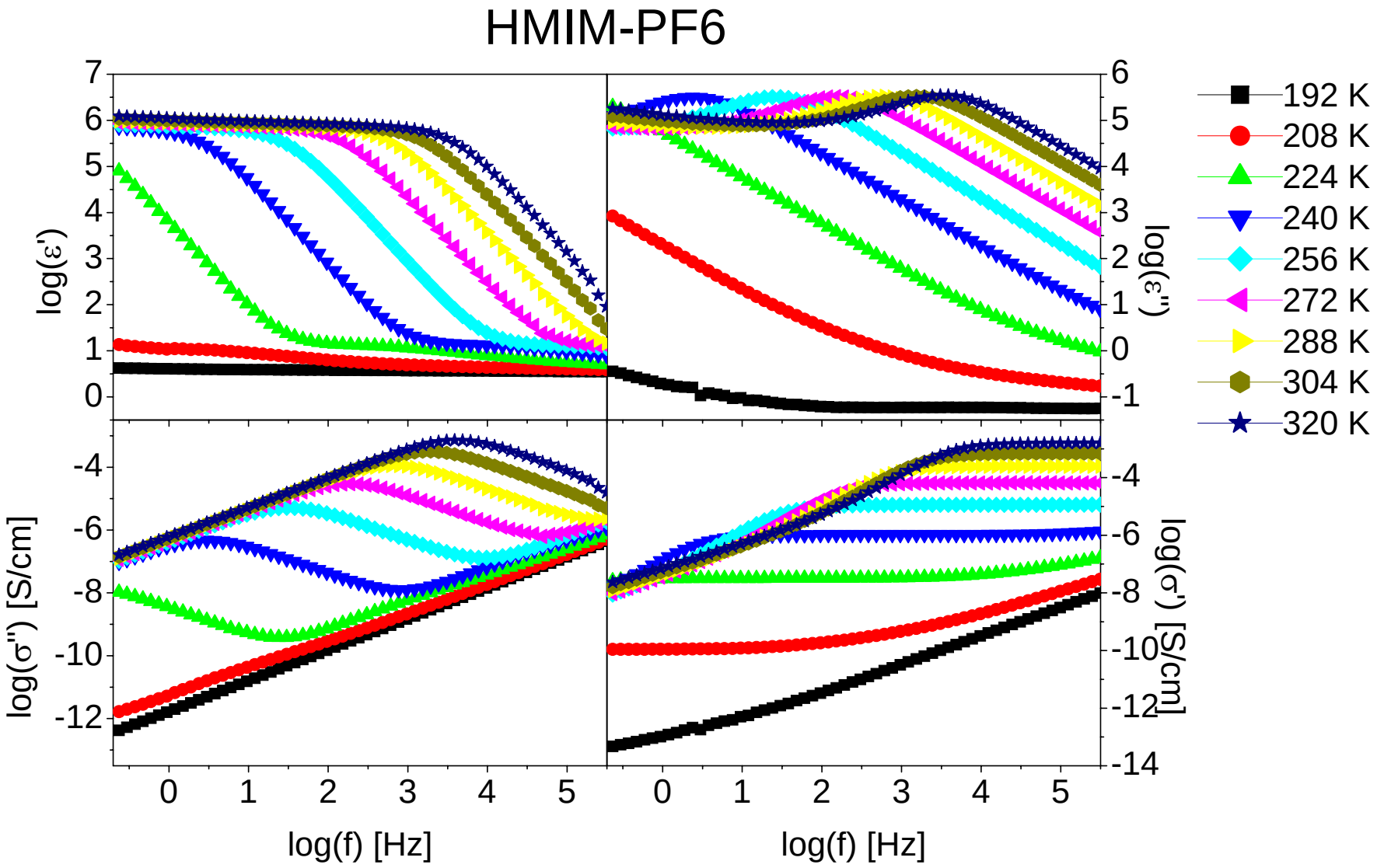
slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

slope of –0.1 in ε´ for $f < f_{max}$

change in slope of σ´ for $f < f_{max}$

Dielectric spectra of ionic liquids
- temperature dependence (experiment) -



Dielectric spectra of ionic liquids
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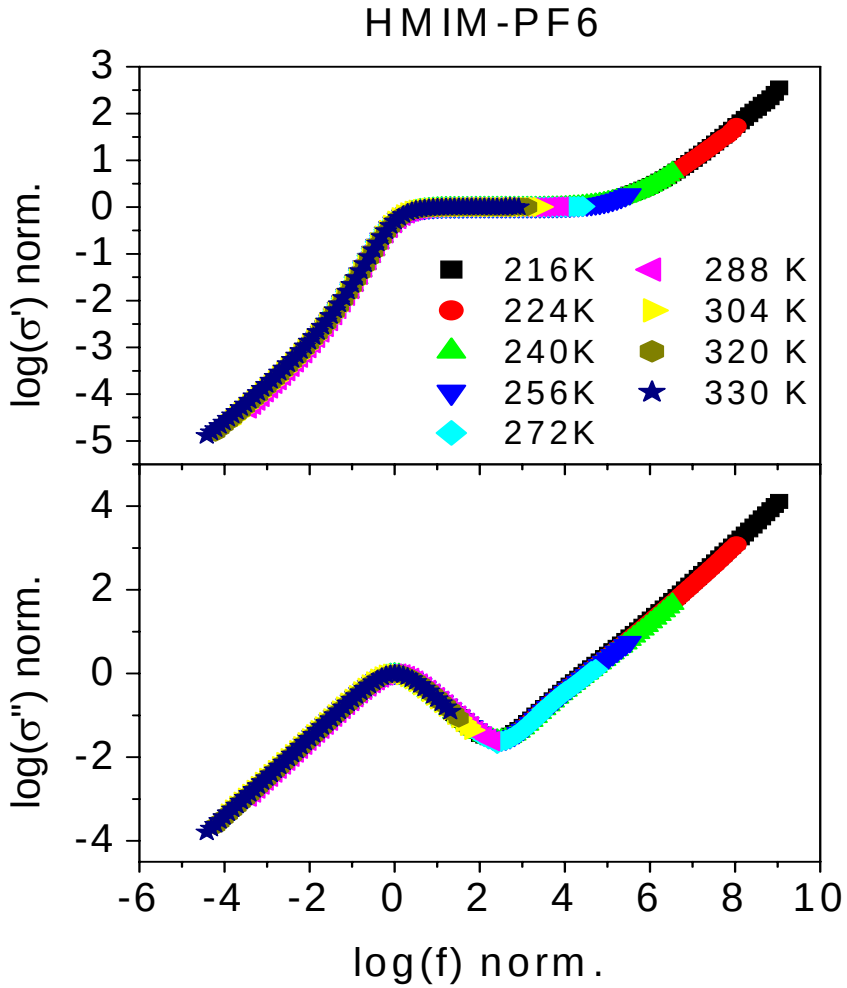
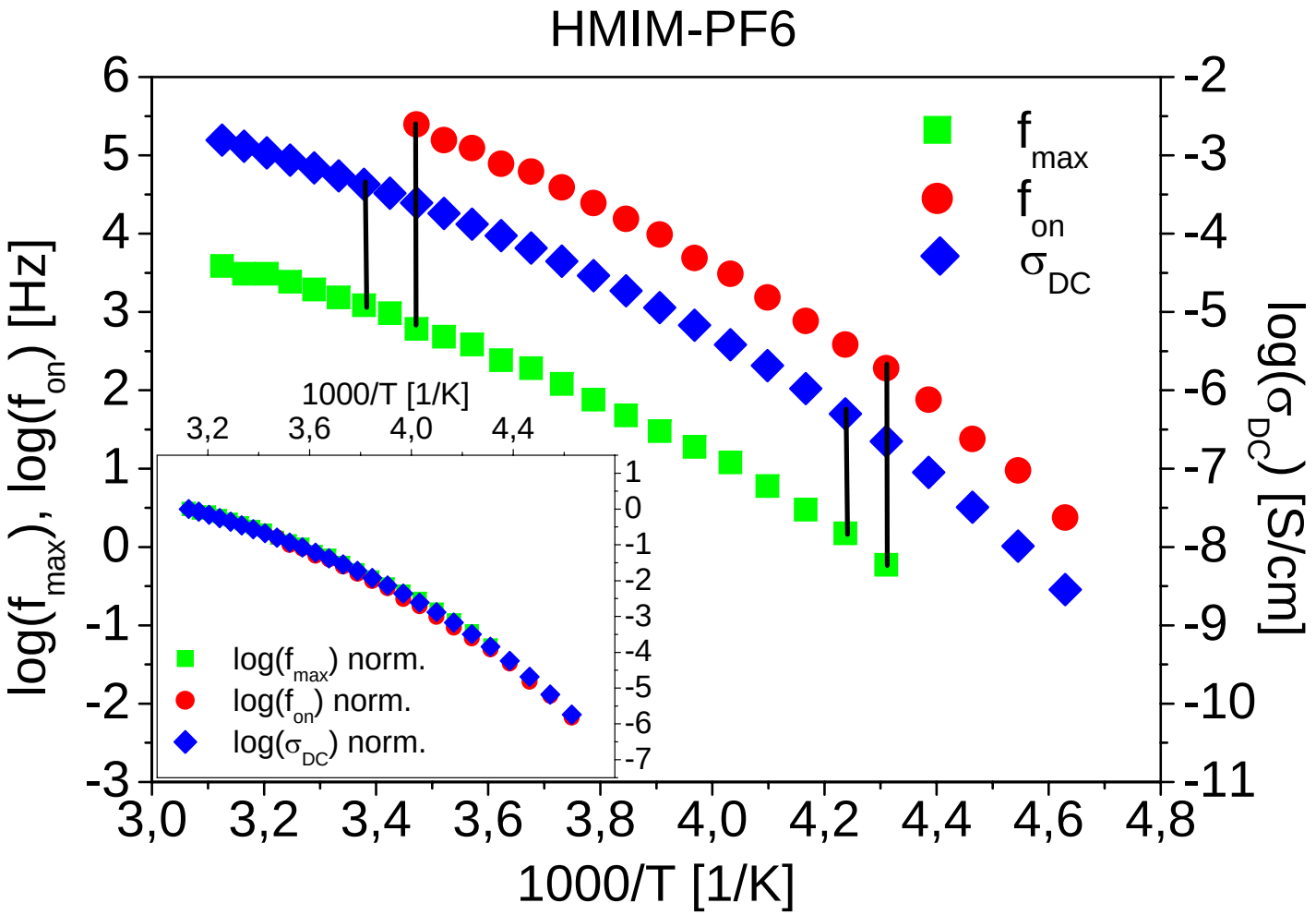


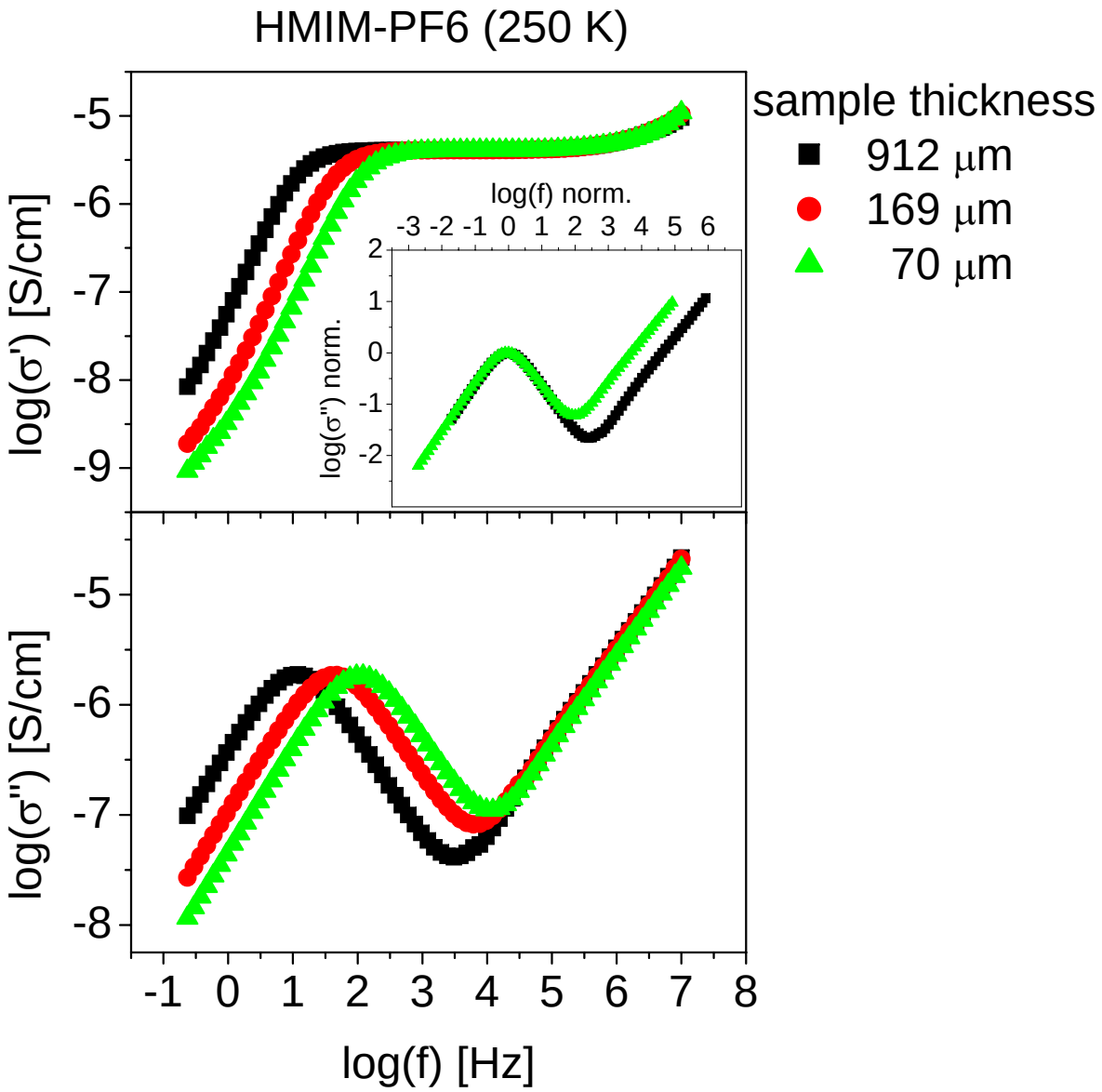
perfect scaling with temperature over many orders of magnitude in time

Dielectric spectra of ionic liquids
- temperature dependence (experiment) -

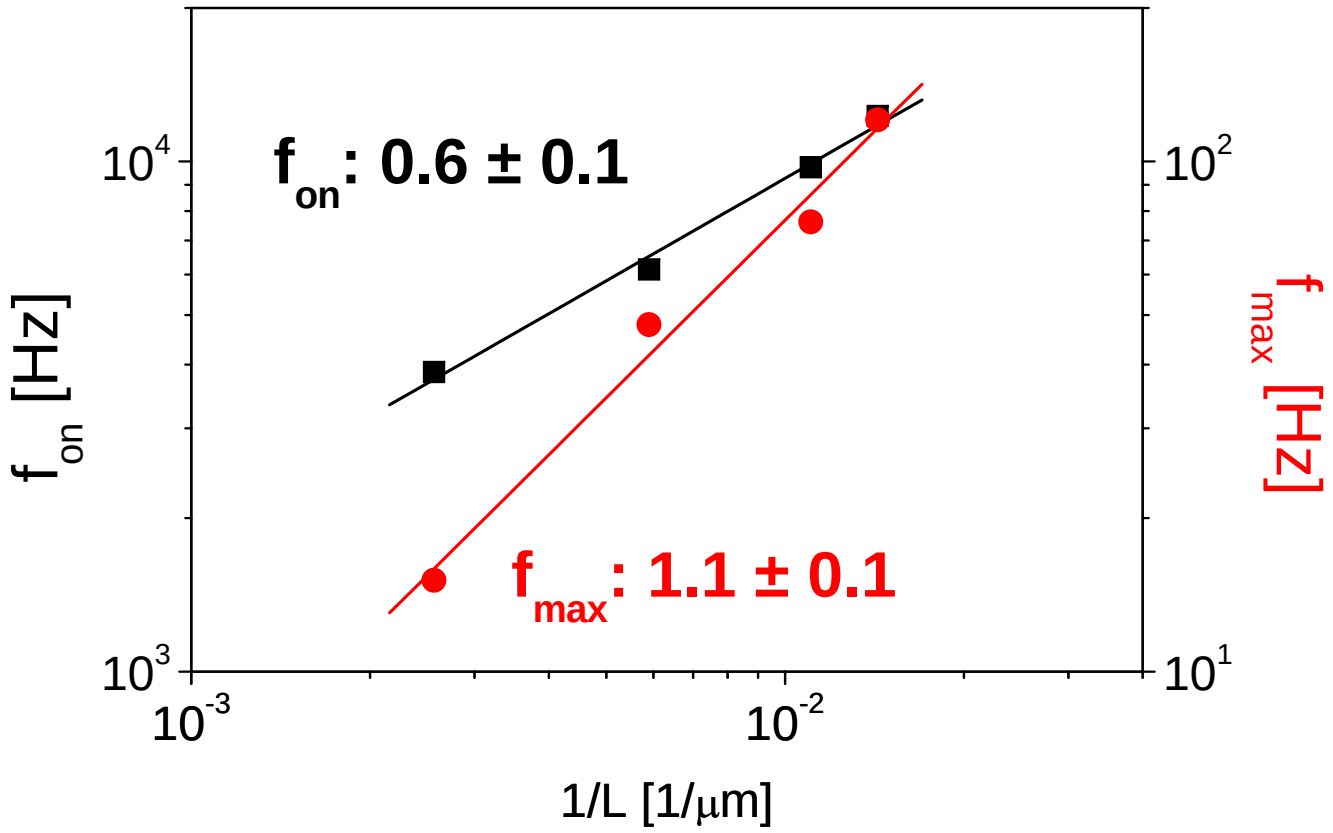


f_{max}, f_{on} and σ_{DC} scale similarly with temperature

Dielectric spectra of ionic liquids- dependence on the length of the sample cell (experiment) -

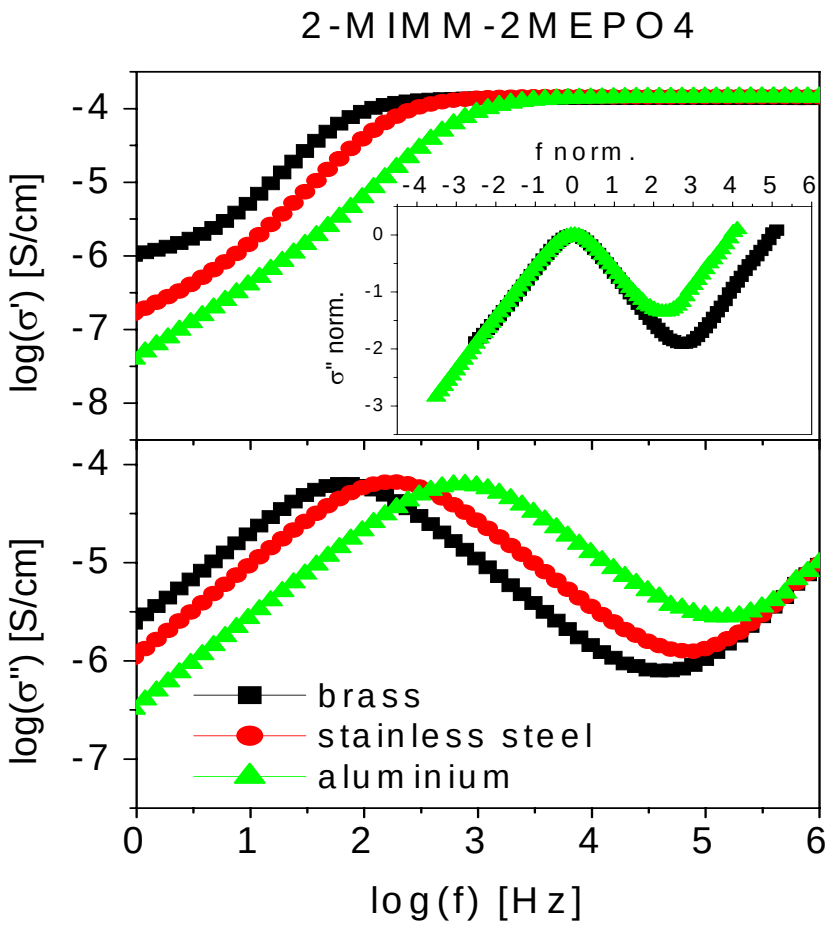


Dielectric spectra of ionic liquids- dependence on the length of the sample cell (experiment) -



No scaling of f_{on} and f_{max} with respect to 1/L !

Dielectric spectra of ionic liquids – effect of the electrode material (experiment) -



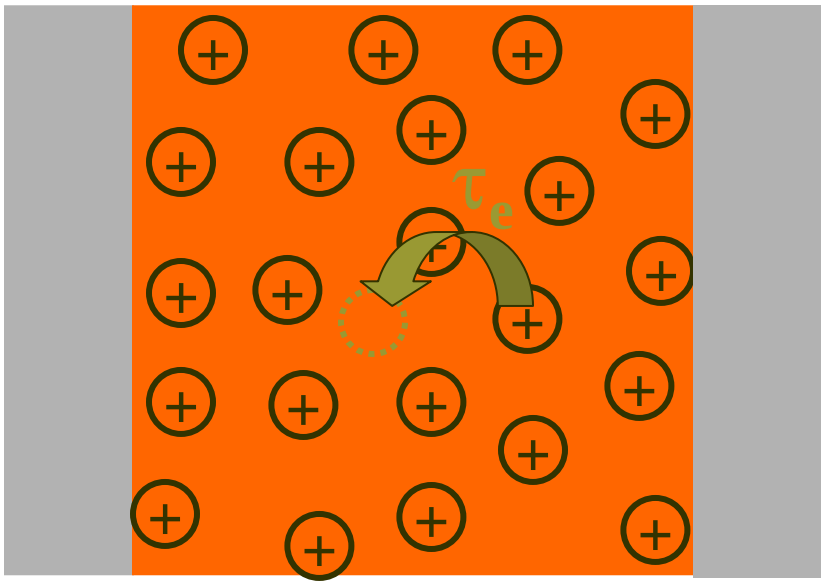
Pronounced effect of electrode material !

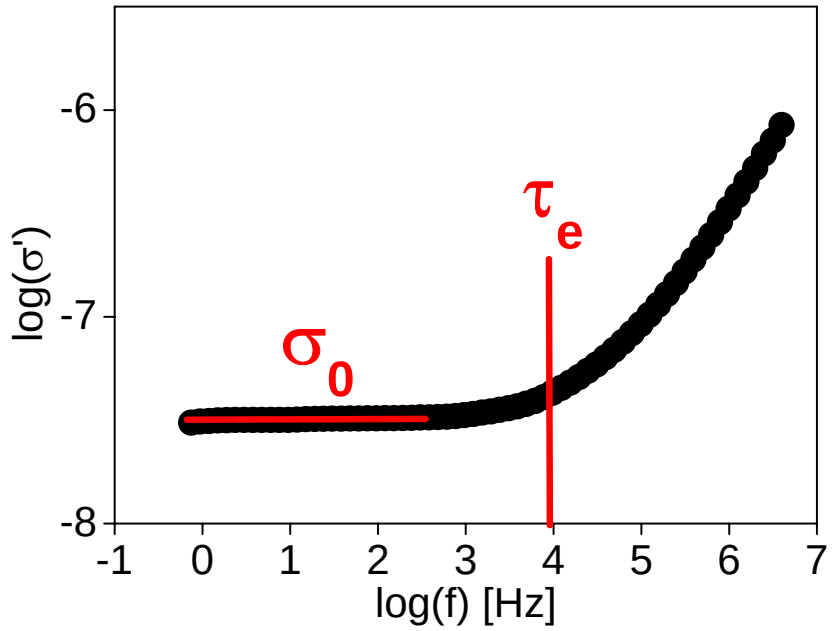
Experimental features of EP in ILs:

1. EP shows a complex dependence on frequency, temperature, concentration, sample length, material of the electrodes.
2. EP does *not* depend – below a certain (low) treshold, i.e. 10 V/cm – on the applied electric field.
3. EP does *not* depend on the roughness of the electrodes, as long as: roughness << sample thickness
4. Over many decades in frequency, scaling with respect to variation of temperature and concentration
5. *No* scaling with respect to variation of the length of the sample cell and material of the electrodes.

What is the microscopic mechanism of EP ?

Charge transport in the bulk



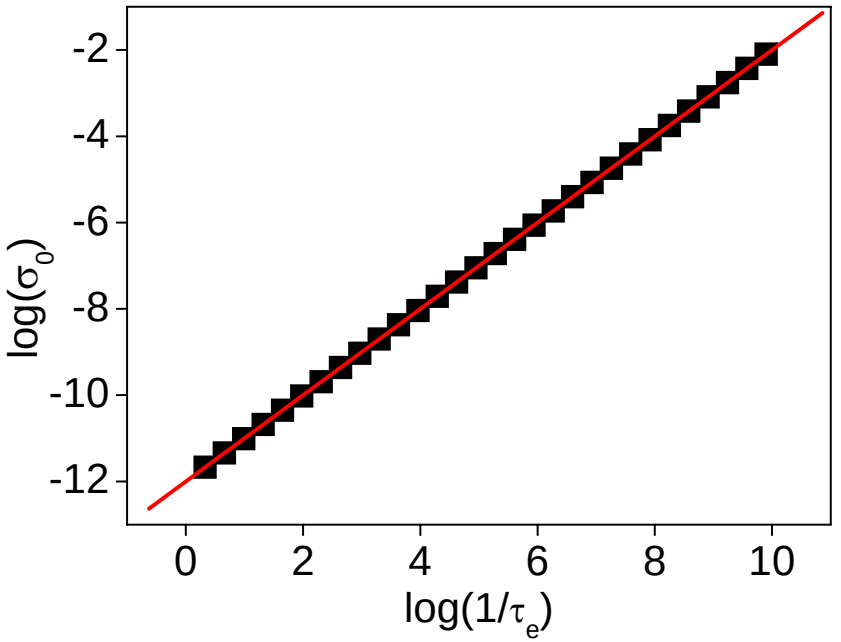


1. hoping time in bulk:

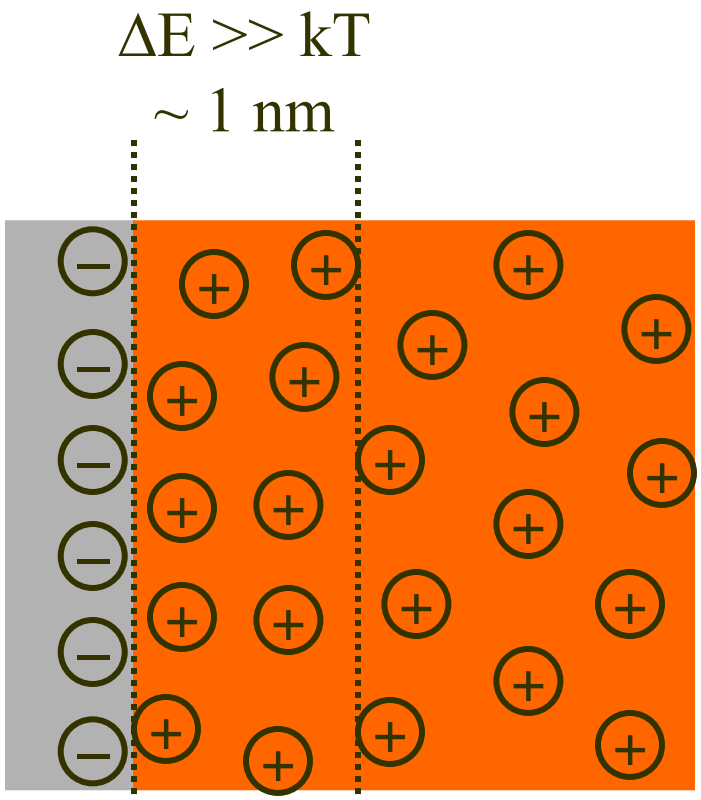
$$\tau_e = \tau_0 \exp\left(\frac{E}{kT}\right)$$

2. BNN-relation:

$$\sigma_0 \sim \frac{1}{\tau_e}$$



Charge transport at interfaces



Due to the coulombic interactions increase by many orders of magnitude in the hoping time at the interface.

hoping time at the interface:

$$E_i \cong E_b + \Delta E$$

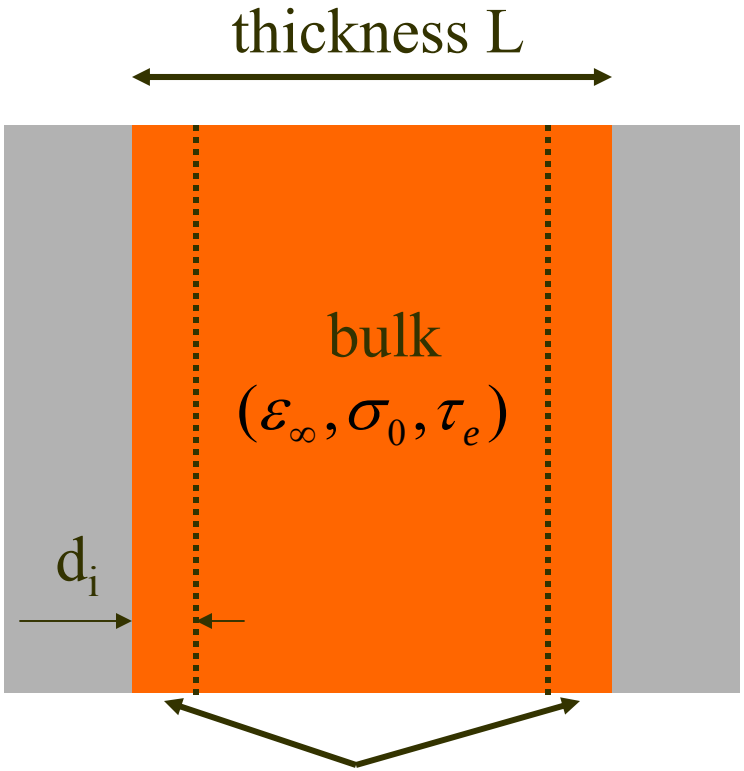
$$\frac{\tau_e(\text{interface})}{\tau_e(\text{bulk})} \approx \exp\left(\frac{\Delta E}{kT}\right) >> 1$$

Since: $\sigma_0 \sim \frac{1}{\tau_e}$ **(BNN relation)**

this implies:

$$\sigma_0(\text{interface}) << \sigma_0(\text{bulk})$$

Microscopic model of sample cell



$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_i}{\varepsilon^*_i} + \frac{L-2d_i}{\varepsilon^*_b}$$

$$\varepsilon^*_b = f\left(\varepsilon_\infty, \sigma_0^{bulk}, \tau_0^{bulk}\right)$$

$$\varepsilon^*_i = f\left(\varepsilon_\infty, \sigma_0^{i}, \tau_0^{i}\right)$$

$$\frac{\tau_e(\text{interface})}{\tau_e(\text{bulk})} \approx \frac{\sigma_0(\text{bulk})}{\sigma_0(\text{interface})} >> 1$$

Electrode polarization

$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_i}{\varepsilon^*_i} + \frac{L-2d_i}{\varepsilon^*_b}$$

$$\varepsilon'_{meas} = (x+1)\left(\left(\varepsilon'_b\right)^2 + \left(\varepsilon''_b\right)^2\right)\frac{x\varepsilon'_b + y\varepsilon'_i}{\left(x\varepsilon'_b + y\varepsilon'_i\right)^2 + \left(x\varepsilon''_b + y\varepsilon''_i\right)^2}$$

$$\varepsilon''_{meas} = (x+1)\left(\left(\varepsilon'_b\right)^2 + \left(\varepsilon''_b\right)^2\right)\frac{x\varepsilon''_b + y\varepsilon''_i}{\left(x\varepsilon'_b + y\varepsilon'_i\right)^2 + \left(x\varepsilon''_b + y\varepsilon''_i\right)^2}$$

where: $x = \dfrac{L-2d_i}{2d_i}$ $y = \dfrac{\left(\varepsilon'_b\right)^2 + \left(\varepsilon''_b\right)^2}{\left(\varepsilon'_i\right)^2 + \left(\varepsilon''_i\right)^2}$

with

$\varepsilon^* = \dfrac{\sigma^*}{i\varepsilon_0\omega}$ and $\sigma^*(\omega) = \sigma_0\left[\dfrac{i\omega\tau_e}{\ln(1+i\omega\tau_e)}\right]$ Dyre functions

EP - consequences of the model

$$\frac{d}{d\omega}\left(\sigma''_{meas}\right)=0 \quad \Rightarrow \qquad f_{on}\cong\frac{\sigma_0}{\varepsilon_0}\frac{1}{\sqrt{\varepsilon'_b\varepsilon'_i}}\sqrt{\frac{2d_i}{L}}$$

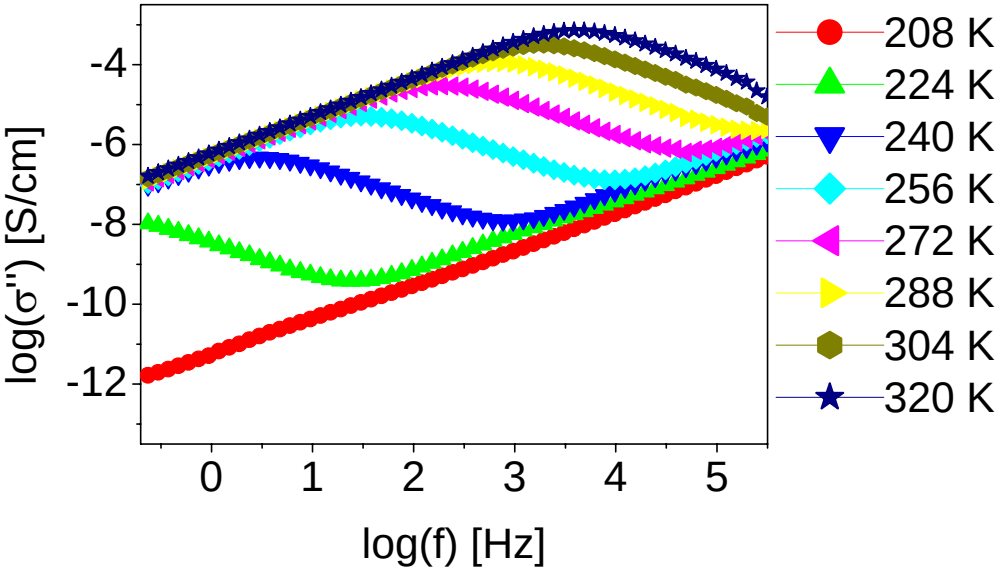
$$f_{max}\cong\frac{\sigma_0}{\varepsilon_0}\frac{1}{2\pi\varepsilon'_i}\frac{2d_i}{L}$$

Consequences:

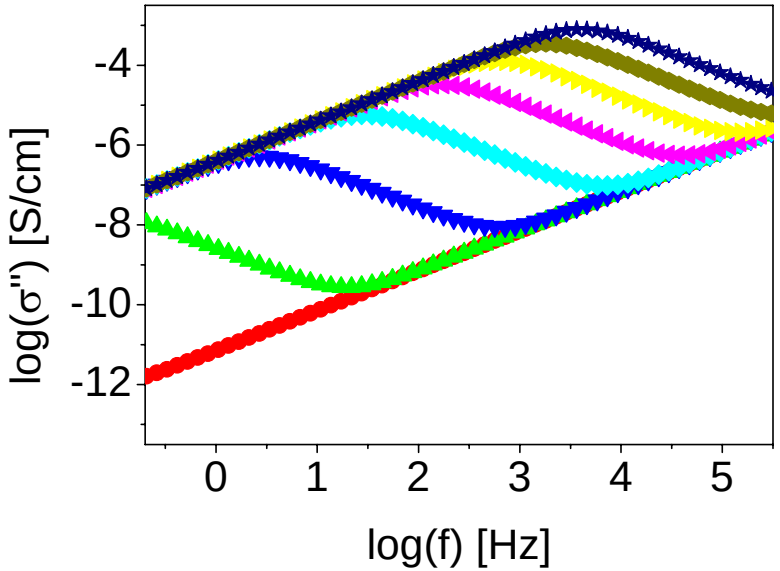
1. $f_{on}\sim f_{max}\sim\sigma_0$
2. $f_{on}\sim\frac{1}{\sqrt{L}}$, while $f_{max}\sim\frac{1}{L}$
3. $f_{on}\sim\sqrt{d_i}$, while $f_{max}\sim d_i$
4. $f=f_{max}$ solution for both $\frac{d\left(\sigma''_{meas}\right)}{d\omega}=0$ and $\frac{d\left(\varepsilon''_{meas}\right)}{d\omega}=0$
5. $\sigma_0=2\pi\varepsilon_0\varepsilon_S\frac{\left(f_{on}\right)^2}{f_{max}}$

Comparison of experiment and calculations - dielectric spectra of ionic liquids

experiment

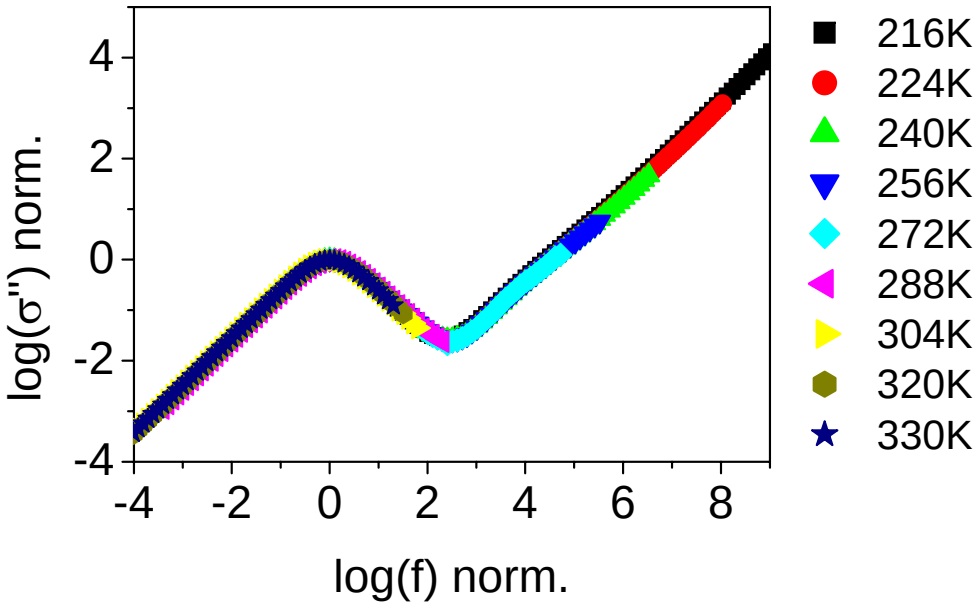


calculations

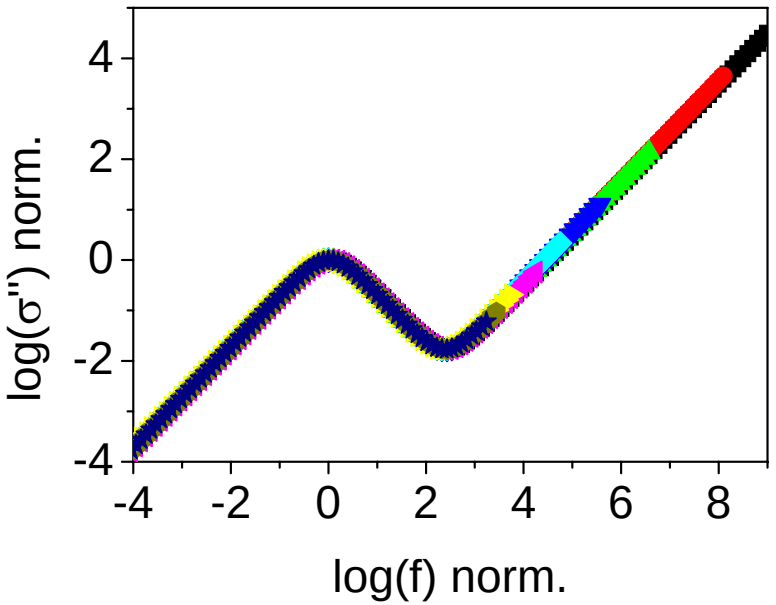


Comparison of experiment and calculations - dielectric spectra of ionic liquids

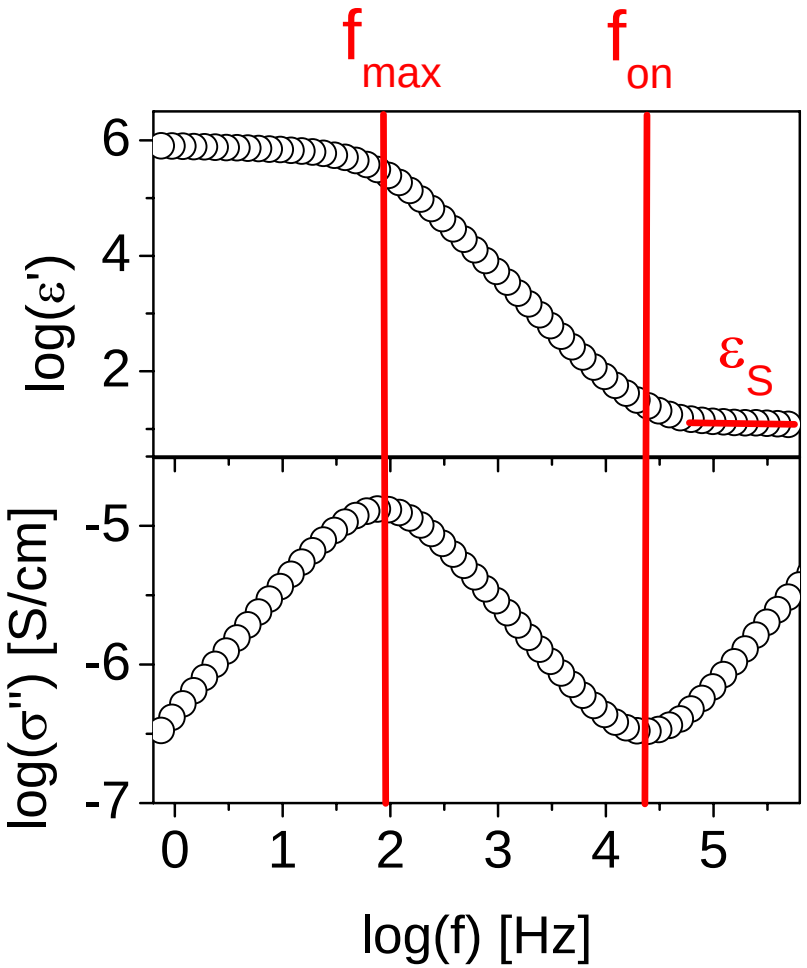
experiment



calculations



What information can be deduced from EP – a novel formula.



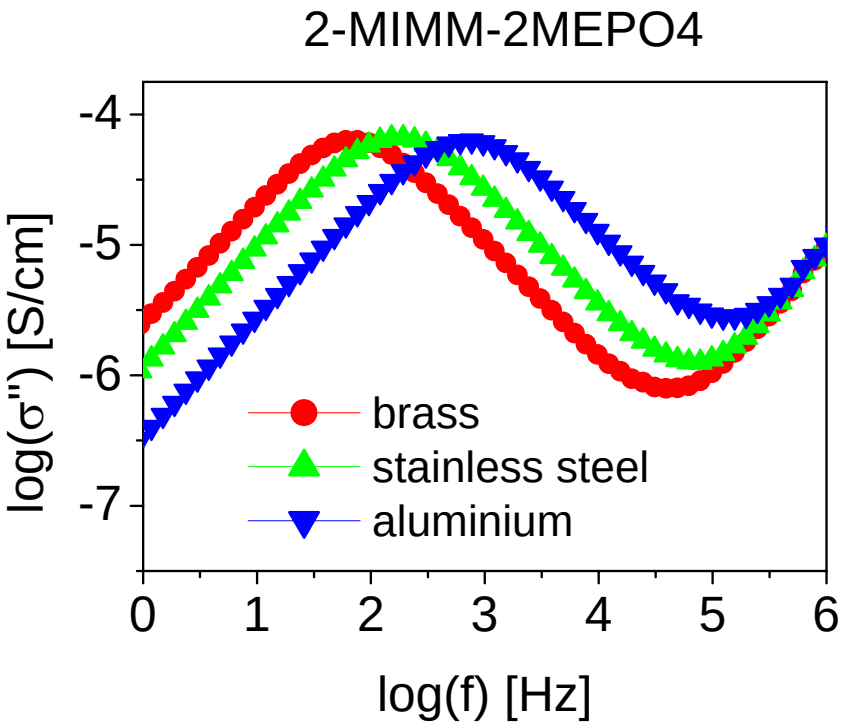
$$\sigma_0 = ?$$

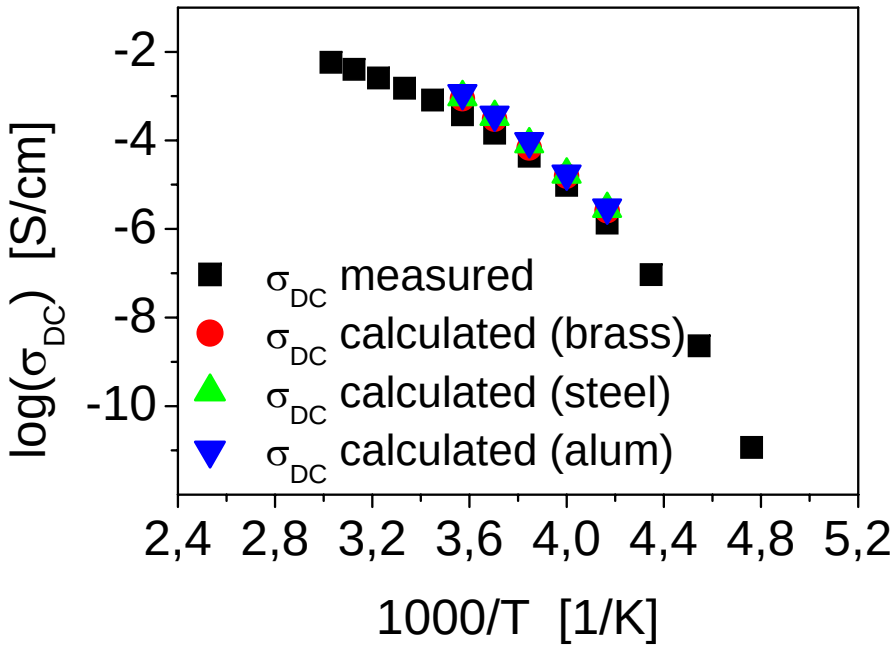
$$\sigma_0 = 2\pi\varepsilon_0\varepsilon_S \frac{(f_{on})^2}{f_{max}}$$

discovered by Anatoli Serghei et al.

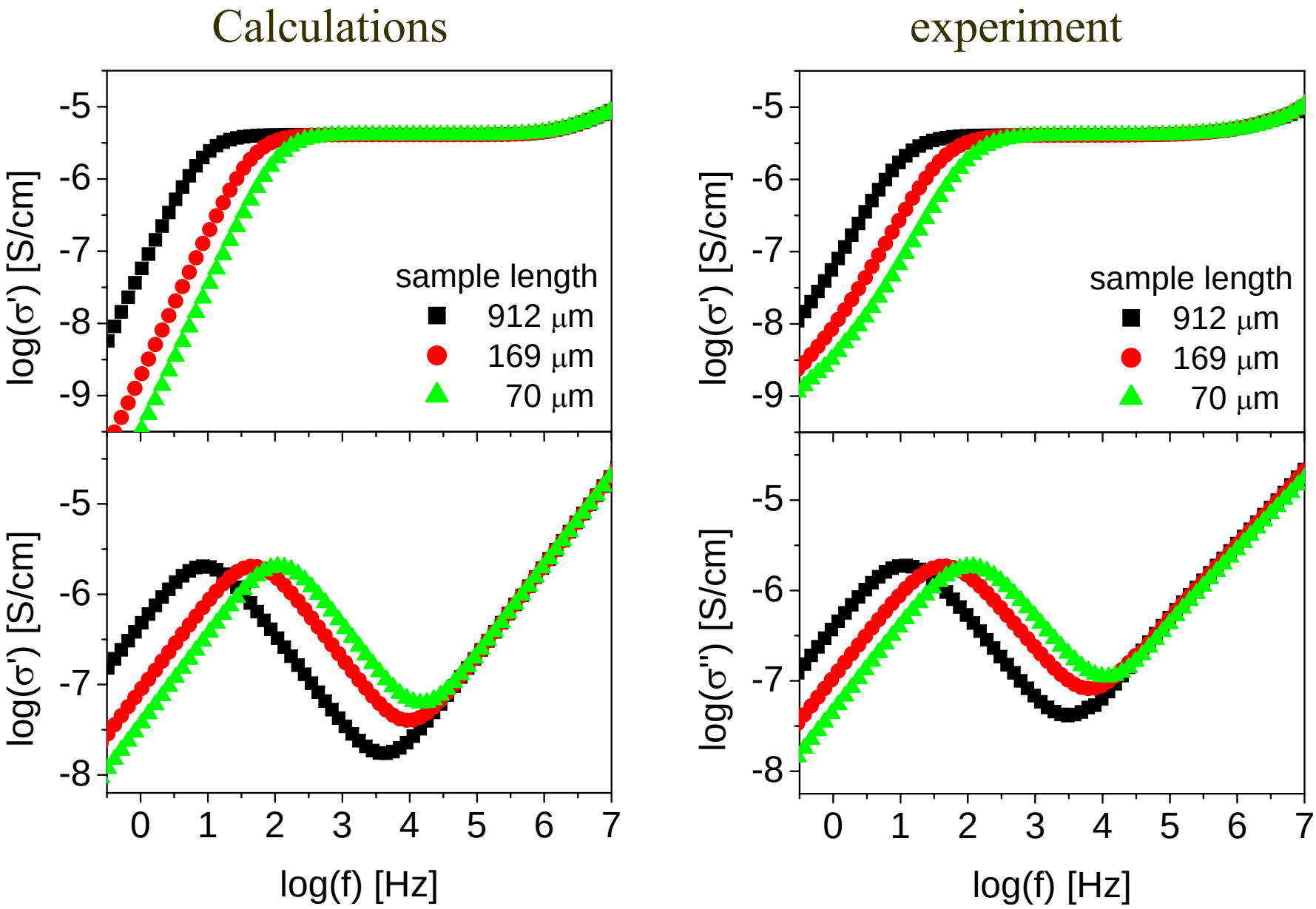
Test of the validity of the novel formula

$$\sigma_0 = 2\pi\varepsilon_0\varepsilon_S \frac{(f_{on})^2}{f_{max}}$$



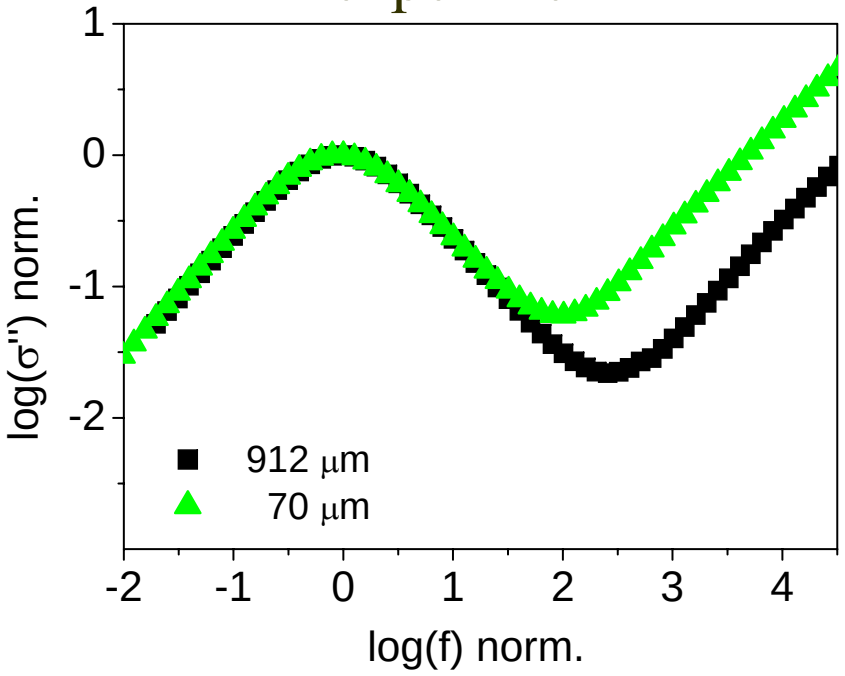


Dielectric spectra of ionic liquids - length dependence (2MIMM-2MePO4, experiment and calculations) -

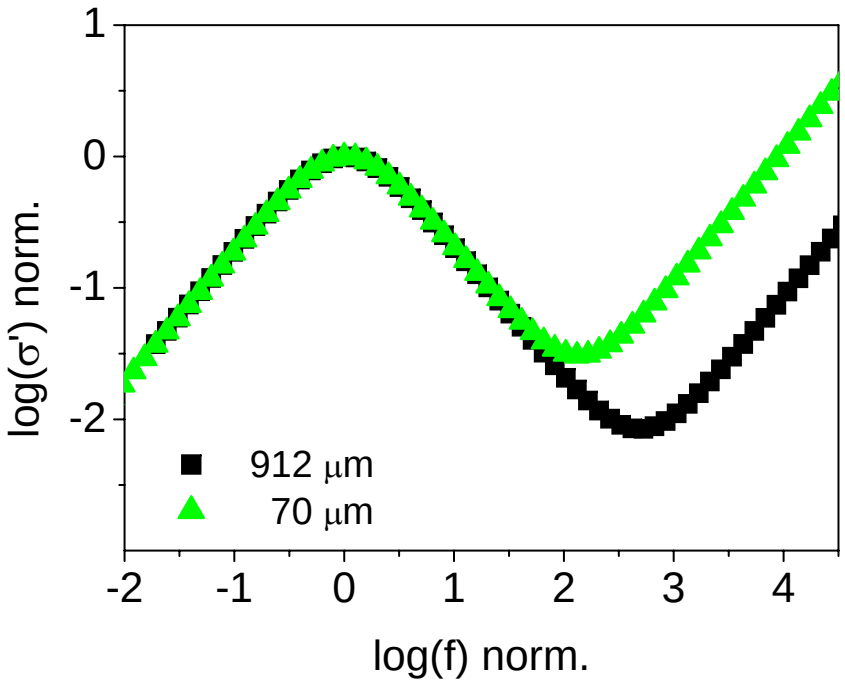


Dielectric spectra of ionic liquids
- length dependence, scaling -

experiment



calculations

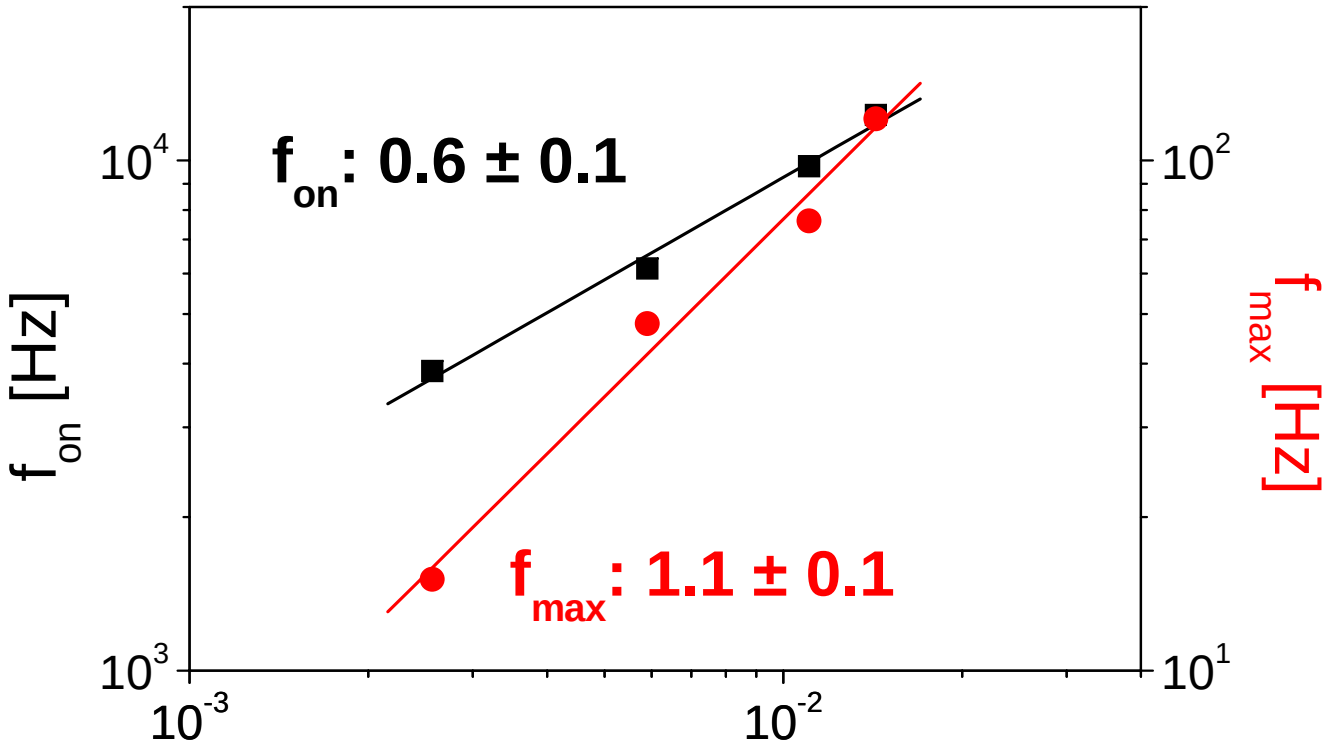


$$\frac{d}{d\omega}\left(\sigma''_{meas}\right)=0 \Rightarrow f_{on} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{\sqrt{\varepsilon'_b \varepsilon'_i}}\sqrt{\frac{2d_i}{L}} \text{ and } f_{max} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{2\pi\varepsilon'_i}\frac{2d_i}{L}$$

$$f_{on} \sim \frac{1}{\sqrt{L}}, \text{ while } f_{max} \sim \frac{1}{L}$$

Dielectric spectra of ionic liquids
- length dependence, scaling -

experiment



$$f_{on} \sim \frac{1}{\sqrt{L}} \Rightarrow \text{slope of } 0.5$$

$$f_{max} \sim \frac{1}{L} \Rightarrow \text{slope of } 1.0$$

Summary for EP

1. What is the *signature* of electrode polarisation (EP) and how can it be analysed *quantitatively*?
   EP has a peculiar signature in the complex dielectric function and conductivity but as well the length of the sample cell.
2. What *quantitative* information can be deduced from fits of the EP?
   With a novel formula discovered by A. Serghei σ_0 can be deduced from f_{min} and f_{max} of $\sigma''(f)$.
3. What is the *quantitative* model to describe EP?
   A model adding the complex impedances at the interface and in the bulk.
4. What information can be deduced from EP?
   A detailed understanding of the geometry and the complex dielectric function of the interphase is in reach.

Thanks to

...DFG for finacial support and to you for attention