

# STUDY OF THE ION DYNAMICS IN IONIC LIQUIDS BY FLUIDITY SPECTROSCOPY

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## Introduction

Ionic liquids (ILs) are purely ionic, salt-like materials, which are by definition liquids below 100 °C [1]. Their unique properties, such as non-volatility, non-flammability, chemical and thermal stability and high ionic conductivity, make them promising materials for electrochemical devices and as solvents in “green” chemistry.

Generally, ILs show a non-Arrhenius temperature dependence of the viscosity,  $\eta$ , and the DC conductivity,  $\sigma_{DC}$ , characteristic for fragile glass-forming liquids [2]. Recent investigations on the ionic liquid BMIm-BF<sub>4</sub> [3] have revealed that curves of  $\sigma_{DC}$  and fluidity  $f$  (inverse viscosity,  $1/\eta$ ), have the same shape and when suitably shifted, can be exactly superimposed. To describe the non-Arrhenius  $f$  and  $\sigma_{DC}$ , the most popular approach is the empirical Vogel-Tammann-Fulcher (VTF) relation. However, when using equations derived for the modeling of conductivity spectra with the MIGRATION concept [3, 4], we obtain an activation energy  $E^*$  for an elementary displacive step of an ion, which is the same for both fluidity and conductivity. This strongly suggests that the electrical and mechanical properties can be traced back to the same elementary steps and, consequently, these properties should show similar frequency dependence.

Based on this premise, we have measured the fluidity spectra,  $f(\nu)$  of two ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF<sub>4</sub>), and 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIm-BF<sub>4</sub>), and compared them with their conductivity spectra  $\sigma(\nu)$  [3, 4] in order to obtain a deeper insight into the motions of ions that determine their electrical and mechanical properties.

## Experimental

The complex shear viscosities of BMIm-BF<sub>4</sub> and HMIm-BF<sub>4</sub> have been measured at different temperatures above the glass transition ( $T_g \approx 188$  K) in a frequency range from 0.01 Hz to 2 kHz. The experimental setup used is based on a Bohlin Gemini 150 rheometer equipped with a high frequency extension (Piezo Rotary Vibrator).

## Results and Discussion

Both BMIm-BF<sub>4</sub> and HMIm-BF<sub>4</sub> display strikingly similar shifts for superimposing their respective non-Arrhenius  $f_{DC}$  and  $\sigma_{DC}$ .

When we consider their fluidity spectra, in both ILs the dispersive regime is observed only in a small temperature range above  $T_g$ . Remarkably, in both ILs, the fluidity and conductivity isotherms show similar shape, with the onset frequencies for fluidity shifted by less than one decade to lower frequencies as compared to the conductivity onset, cf. Fig. 1.

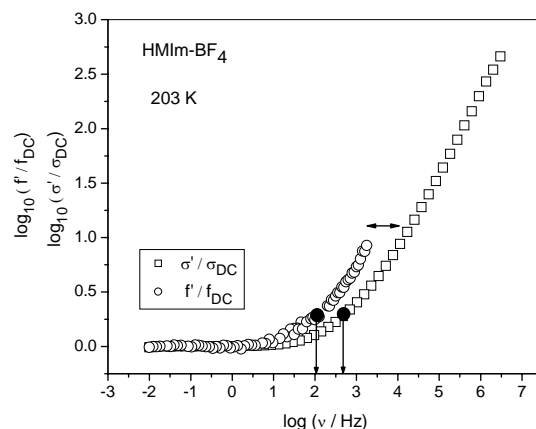


Fig. 1. Scaled fluidity and conductivity spectra of HMIm-BF<sub>4</sub> at 203 K.

These results demonstrate clearly that i) the underlying processes for shear flow and flow of charge are very similar and ii) slower dynamics are involved in the shear flow. This has led us to attempt a model treatment for fluidity spectra using the MIGRATION concept. The details of such a modeling are presented and discussed. In particular, we suggest that the time correlation function related to fluidity must share features with the current density autocorrelation function.

## References

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