

# Multiply Charged Ionic Liquid Nanodroplets as Mobility Standards for Tandem Ion Mobility – Mass Spectrometry

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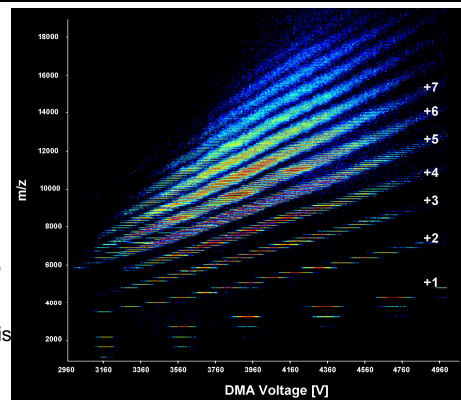
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## Introduction

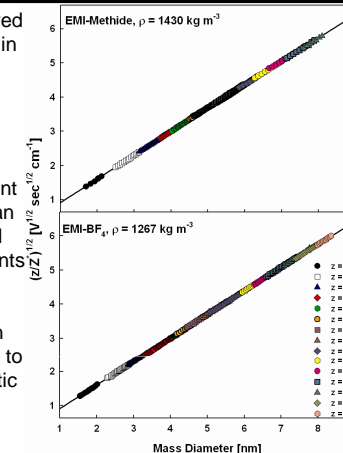
- Comparison of molecular models to ion mobility measurements (e.g to determine protein quaternary structure) requires quantitative mobility measurement.
- Quantitative mobility measurement requires:
  - Calibration of IMS-MS instruments with ions of known mobility.
  - Precise knowledge of the relation between ion mobility and ion size.
- Current IMS-MS calibration procedures typically utilize proteins electro sprayed under denaturing conditions and measured in He.
  - Highly charged proteins not spherical in gas phase → Coulombic Stretching
  - Hard-Sphere approximation acceptable in He, but in N<sub>2</sub> and air, polarization potential becomes important.

**Figure 2.** Differential mobility analyzer (DMA)-mass spectrometer spectrum of nanodrops of the ionic liquid 1-ethyl-3-methyl-imidazolium<sup>+</sup> tris(trifluoromethylsulfonyl)methide<sup>-</sup> (EMI-Methide). DMA Voltage is directly proportional to ion mobility, Z<sub>p</sub>. Each group of line segments has a fixed charge state. Ion mobility is determined by DMA calibration.



## Results & Conclusions

**Figure 3.** Comparison of measured mobilities (normalized as (zZ<sub>p</sub>)<sup>1/2</sup> in N<sub>2</sub> at atmospheric pressure to predicted mobilities using the Stokes-Millikan equation and the bulk densities of the ionic liquids. For both ionic liquids, measured nanodrop mobilities are in excellent agreement with the Stokes-Millikan equation, showing that ionic liquid nanodrops are suitable as calibrants for IMS-MS instruments. Small deviations (not visible) from the Stokes-Millikan equation are seen for small ions with z = 1, likely due to an increase in the fraction of elastic collisions.



## Goals

- Measure the mobility of electro sprayed ionic liquid nanodrops by differential mobility-mass spectrometry (DMA-MS, see left panel) and compare measured mobilities to predicted mobilities.
  - Ionic liquid nanodrops highly spherical (liquids!).
  - Multiply ionic liquid nanodrop charge states are reduced by ion evaporation<sup>1</sup>, reducing the effect of polarization (i.e. unlike proteins, ionic liquids act as hard spheres in most bath gases).
- With an appropriate mobility-size relationship, ion mobility spectrometers can be calibrated by measuring a single IMS-MS spectrum of electro sprayed ionic liquid nanodrops.

## Mobility Equation

• Stokes-Millikan equation shown valid in air, and N<sub>2</sub> at atmospheric pressure for singly charged aerosol nanoparticles<sup>2,3</sup>.

• Semi-empirical, assumes 91% inelastic collisions.

$$Z_p \left( 1 + \frac{m_g}{m_i} \right)^{-1/2} = \frac{zeC}{3\pi\mu(d_i + d_g)}$$

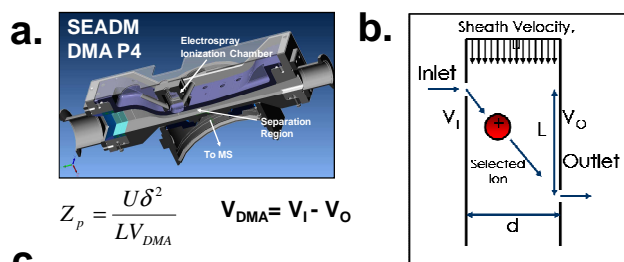
$Z_p$ : ion mobility,  $z$ : charge state,  
 $d_i$ : ion mass diameter,  $d_g$ : gas diameter,  
 $m_g$ : gas molecules mass,  $m_i$  ion mass,  
 $C = 1 + \frac{2\lambda}{d_i + d_g} \left( 1.257 + 0.4 \exp\left( \frac{-0.55[d_i + d_g]}{\lambda} \right) \right)$   $\mu$ : gas viscosity,  $e$ : electron charge,  
 $\lambda$ : mean free path

- Using nanodrop mass diameters and the Stokes-Millikan equation, nanodrop mobilities can be predicted if < 1% error from measured values.
  - Excellent candidates as calibrant ions.
  - Agreement with Stokes-Millikan shows that in N<sub>2</sub> collisions are largely inelastic for charged particles > 2.0 nm in diameter.
  - With an IMS of sufficient resolving power, measurement of ionic liquid nanodrops generates hundreds of calibrant data points.

## Acknowledgements & References

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## DMA-MS Operation



**Figure 1.** a. CAD image of parallel plate DMA P4 (SEADM). b. The DMA operating principle. c. Schematic of the DMA P4 mounted on a QSTAR mass spectrometer (Sciex).

$$Z_p = \frac{U\delta^2}{LV_{DMA}} \quad V_{DMA} = V_1 - V_0$$