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

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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.

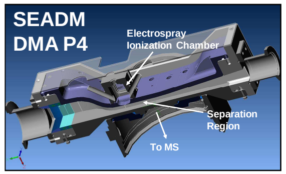
•Current IMS-MS calibration procedures typically utilize proteins electrosprayed under denaturing conditions and measured in He.

•Highly charged proteins not spherical in gas phase→ Coulombic Stretching

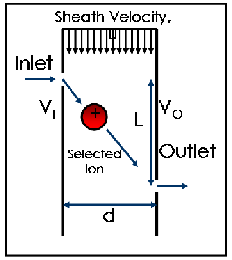
•Hard-Sphere approximation acceptable in He, but in N_2 and air, polarization potential becomes important.

DMA-MS Operation

a.



b.



$$Z_p = \frac{U\delta^2}{LV_{DMA}}$$

$V_{DMA} = V_I - V_O$

c.

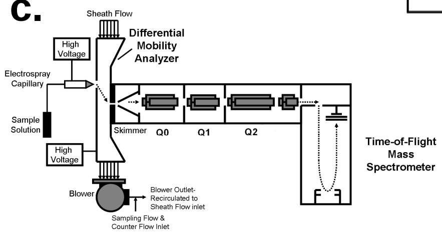
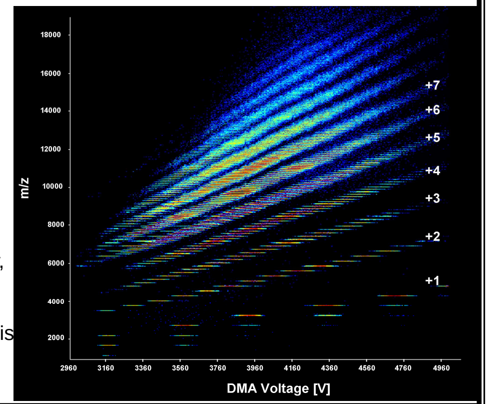


Figure 1. a. CAD image of parallel plate DMA P4 (SEADM). **b.** The DMA operating principle. **c.** Schematic of the DMA P4 mounted on a QSTAR mass spectrometer (Sciex).

Figure 2. Differential mobility analyzer (DMA)-mass spectrometer spectrum of nanodrops of the ionic liquid 1-ethyl-3-methyl-imidazolium$^+$ tris(trifluoro-methylsulfonyl)methide$^-$ (EMI-Methide). DMA Voltage is directly proportional to ion mobility, Z_p. Each group of line segments has a fixed charge state. Ion mobility is determined by DMA calibration.



Goals

•Measure the mobility of electrosprayed 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[1], 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 electrosprayed ionic liquid nanodrops.

Mobility Equation

•Stokes-Millikan equation shown valid in air, and N_2 at atmospheric pressure for singly charged aerosol nanoparticles[2,3].

•Semi-empirical, assumes 91% inelastic collisions.

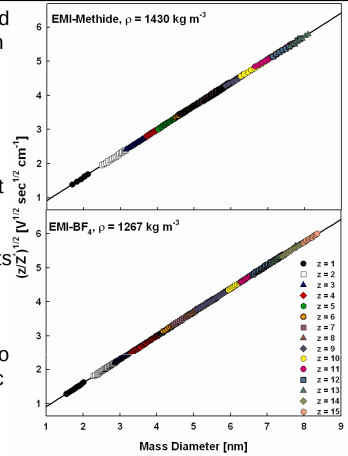
$$Z_p\left(1+\frac{m_g}{m_i}\right)^{-1/2} = \frac{zeC}{3\pi\mu(d_i+d_g)}$$

$$C = 1+\frac{2\lambda}{d_i+d_g}\left(1.257+0.4\exp\left(\frac{-0.55[d_i+d_g]}{\lambda}\right)\right)$$

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, μ: gas viscosity, e: electron charge, λ: mean free path

Results & Conclusions

Figure 3. Comparison of measured mobilities (normalized as $(z/Z_p)^{1/2}$ in N_2 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.



•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_2 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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