Tandem Ion Mobility-Mass Spectrometry (IMS-MS) Study of Ion Evaporation from Ionic Liquid-Acetonitrile Nanodrops

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Physical Chemistry Chemical Physics
Supporting Information

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Information Available

-Calculation of ion mobilities from DMA voltages.

-Estimation of standard ion mobility in N_2.

-Figures S1 and S2.

Calculation of Mobility

For conversion from V_{DMA} to Z_p, the applied potential difference in the DMA, V_{ref}, necessary to isolate an ion of known mobility, Z_{ref}, was determined while also measuring pump rotation frequency, f_{ref}. The reference ion was tetraheptylammonium$^+$, which has a known mobility of 0.971 $cm^2 \ V^{-1} \ sec^{-1}$ in air at standard temperature and pressure[1]. Tetraheptylammonium ions were introduced into the DMA-MS by electrospraying a 1 mM solution of tetraheptylammonium bromide in methanol similarly as the ionic liquid-acetonitrile samples. Since our measurements were made in N_2 rather than air, Z_{ref} was approximated as 0.978 $cm^{-2} \ V^{-1} \ sec^{-1}$, using a mobility adjustment procedure described in next section. The pump frequency was controlled by assigning an input voltage to the pump, V_{pump}, but there was no feedback control loop to prevent slight frequency variations. For all experiments with ionic liquids, $V_{pump} = 4V$. To correct for small drift in pump frequency f during the experiments, f was measured once at each of the DMA voltages, and the locally linear response between the mobility shift and the frequency shift was determined by calibration of V_{ref} with tetraheptylammonium ions while controlling f with V_{pump} in the range of pump voltages 3.5 - 4.5 V. From these measurements, the slope, S, of the V_{ref} versus f_{ref} curve was calculated near the pump frequency measured for $V_{pump} = 4$ V. A given experimentally determined V_{DMA} and pump frequency f were then converted to a mobility, Z_p, by the equation:

$$Z_p = \frac{Z_{ref}\left(V_{ref} + S\left(f - f_{ref}\right)\right)}{V} \tag{1}$$

where V_{ref} and f_{ref} are the applied potential difference in the DMA necessary to select an ion of mobility Z_{ref} and f_{ref} is the pump frequency when $V_{pump} = 4V$ during the calibration measurement. Using the tetraheptylammonium ion, the calibration values were $V_{ref} = 1765$ V, $f_{ref} = 8144$ revolutions per minute (rpm), and $S = 0.2169$ V/rpm.

Tetraheptyl Ammonium[+] Mobility

In the absence of polarization effects (i.e. for hard-sphere collisions) in the free-molecular limit[2], the mobility of an ion in N_2 can be calculated as $(MW_{air}/MW_{N2})^{1/2} * Z_{air}$, where MW_{air} and MW_{N2} are the molecular weights of air and N_2, respectively, and Z_{air} is the mobility of the ion in air. For the tetraheptylammonium ion, the mobility in N_2 as expected by the hard-sphere limit is $(28.8 \text{ Da} /28 \text{ Da})^{1/2}$ x 0.971 cm^2 V^{-1} $sec^{-1} = 0.984$ cm^2 V^{-1} sec^{-1}. Conversely, in the polarization limit, the mobility of ions in N_2 can be calculated as[3] $(\alpha_{air} \mu_{air} / \alpha_{N2} \mu_{N2})^{1/2} * Z_{air}$, where α_{air} and α_{N2} are the polarizabilities of air and N_2, respectively. μ_{air} and μ_{N2} are the reduced masses of clusters in air and N_2, respectively, which (because of the large tetraheptylammonium molecular mass) are only slightly reduced from the mass of air and N_2. Using the polarizabilities of air an N_2, the mobility of tetraheptylammonium ions in the polarizability limit is $([1.678$ x 10^{-30} $m^3 *$ 27.2 Da$] / [1.71$ x 10^{-30} $m^3 * 26.5$ Da$])^{1/2} * 0.971$ cm^2 V^{-1} $sec^{-1} = 0.973$ cm^2 V^{-1} sec^{-1}. Neither the hard-sphere nor polarizability limits hold strictly for the tetraheptylammonium ion. However, given the similarity in estimated mobilities with both limits, an approximate value of 0.978 cm^2 V^{-1} sec^{-1} was used for tetraheptylammonium ion mobility here, introducing errors in mobility of less than 1% at most, which would have a negligible impact on presented results.
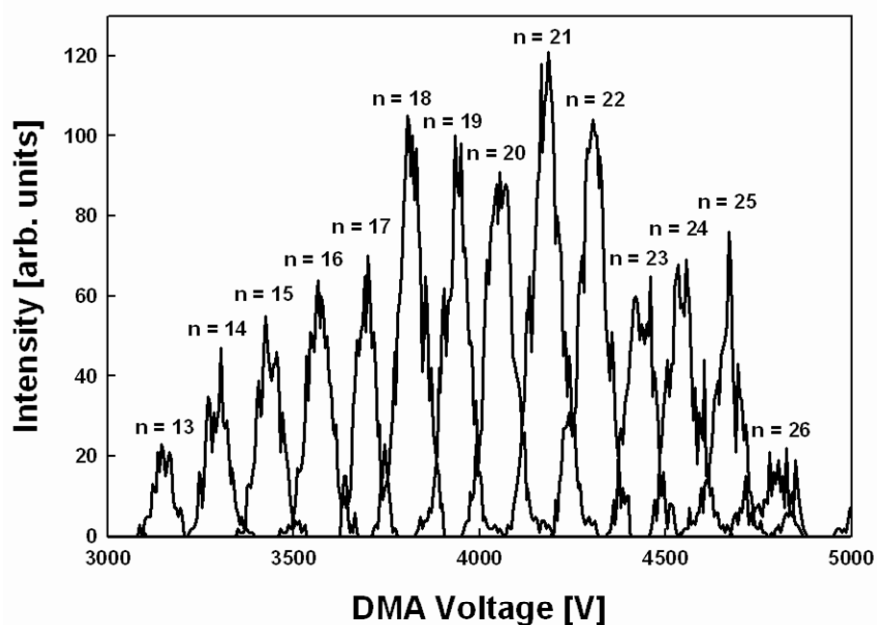
Figure S1. Mass selected mobility distributions (full isotopic envelope) for positively charged EMI-Methide nanodrops for $z = 2$ (with mobility expressed as DMA Voltage, which is proportional to inverse mobility). The number of neutral ion pairs in each cluster, n, is indicated.
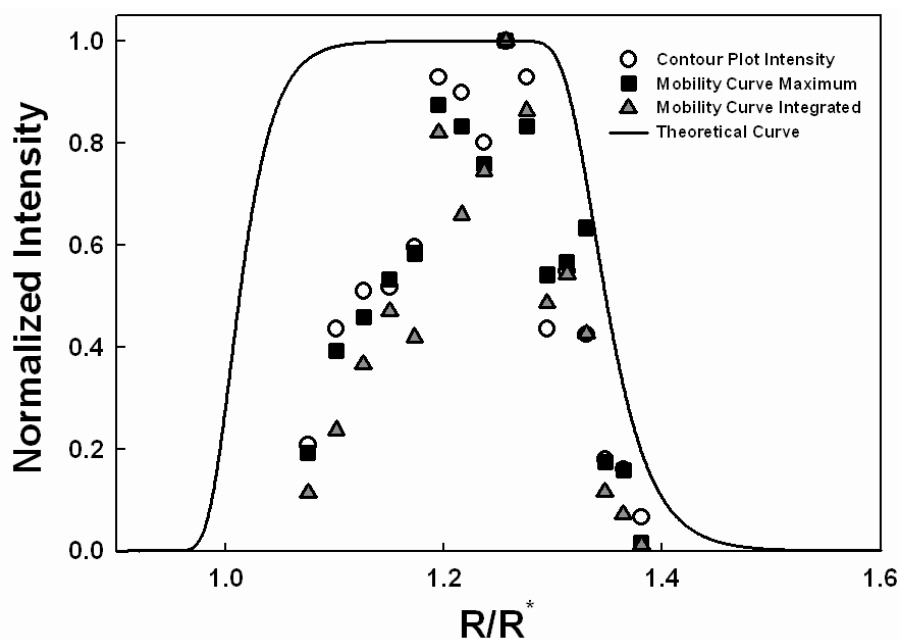
Figure S2. EMI-Methide nanodrop signal intensities with $z = +2$ measured by three different schemes: (i) directly from the maximum signal in each line segment in contour plots (white circles); (ii) peak intensity in mobility curves in Figure S2 (black squares); (iii) integrated peak area in the mobility curves (gray triangles). Also shown is the theoretically predicted curve (Equation 8b) for the doubly charged nanodrop size distribution, which is much wider in all cases than measured values. Secondary ion evaporation was not accounted for in thse measurements.

References

(1)   S. Ude, J. Fernandez de la Mora. *Journal of Aerosol Science* 2005, **36**, 1224.
(2)   S. K. Friedlander *Smoke, Dust, and Haze*; Oxford University Press: New York, 2000.
(3)   E. W. McDaniel, E. A. Mason *The Mobility and Diffusion of Ions in Gases*, 1973.