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

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Information Available

- Calculation of ion mobilities from DMA voltages.
- Estimation of standard ion mobility in N₂.
- 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 $0.971 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ in air at standard temperature and pressure¹. 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 N₂ rather than air, $Z_{ref}$ was approximated as $0.978 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$, 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, $V_{pump} = 4 \text{ V}$. 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 $V_{pump} = 4 \text{ V}$. A given experimentally determined $V_{DMA}$ and pump frequency $f$ were then converted to a mobility, $Z_p$, by the equation:
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\[ Z_p = \frac{Z_{ref}(V_{ref} + S(f - f_{ref}))}{V} \]  

(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 \( (MW_{air}/MW_{N2})^{1/2} \times Z_{air} \), 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 \((28.8 \text{ Da} / 28 \text{ Da})^{1/2} \times 0.971 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} = 0.984 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \). Conversely, in the polarization limit, the mobility of ions in \( N_2 \) can be calculated as \( (\alpha_{air} \mu_{air} / \alpha_{N2} \mu_{N2})^{1/2} \times Z_{air} \), where \( \alpha_{air} \) and \( \alpha_{N2} \) are the polarizabilities of air and \( N_2 \), respectively. \( \mu_{air} \) and \( \mu_{N2} \) 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 polarization limit is \( ([1.678 \times 10^{-30} \text{ m}^3 \times 27.2 \text{ Da}] / [1.71 \times 10^{-30} \text{ m}^3 \times 26.5 \text{ Da}])^{1/2} \times 0.971 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} = 0.973 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \). 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 \( 0.978 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \) 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 these measurements.

References