The Mobility-Volume Relationship below 3.0 nm examined by Tandem Mobility-Mass Measurement

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ABSTRACT

The validity of the Stokes-Millikan equation is examined in light of mass and mobility measurements of clusters of the ionic liquid 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMI-BF_4) in ambient air. The mobility diameter d_Z based on the measured mobility and the Stokes-Millikan law is compared with the volume diameter d_v, which generalizes the mass diameter for binary substances such as salts. d_v is based on the sum of anion and cation volumes in the cluster corrected for the void fraction of the bulk ionic liquid. For $d_v > 1.5$ nm, d_Z is within 1.4% of d_v+0.3 nm. For smaller clusters 3.84 and 14.3% deviations are observed at $d_v = 1.21$ nm and 0.68 nm, respectively. These differences are smaller than expected due to a cancellation of competing effects. The increasing difference seen for $d_v<1.5$ nm is due primarily to the interaction between the cluster and the dipole it induces in the gas molecules. Other potential sources of disagreement are non-globular cluster geometries, and departures of the cluster void fraction from the bulk value. These two effects are examined via molecular dynamics simulations, which confirm that the volume diameter concept is accurate for EMI-BF_4 nanodrops with d_v as small as 1.6 nm.