Scanning Activity Gravimetric Analysis (SAGA)

Adam P. Olsen, Richard C. Flagan, and Julia A. Kornfield
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Supporting Information

The relative humidity, or activity of water ($a_w$), inside the particle levitation chamber is controlled by modulating the pressure of a nitrogen stream that contains a fixed mole fraction of water vapor such that:

$$a_w = a_{w,o}(p/p_o)$$  \hfill (S1)

where $a_{w,o}$ is the activity of water in the nitrogen stream recorded at atmospheric pressure ($p_o$) by a humidity sensor, and $p$ is the absolute pressure inside the chamber recorded by a pressure transducer. Accuracy of eq S1 requires that the mole fraction of water vapor inside the chamber is identical to that at the humidity sensor. As humidity increases, however, there is an increasing likelihood that water is sorbed by surfaces within the apparatus, introducing capacitance that prevents very rapid changes in $a_w$. The actual instrument response to imposed changes in $a_w$ was measured during continuous (Figure S1) and stepwise (Figure S2) scans with an aqueous sodium chloride droplet, which maintains equilibrium with the surrounding atmosphere. Discrepancy in the measured mass between continuous scans up and down in $a_w$ was used to quantify the lag and derive a correction that was applied to the PEO data in the main text. The difference in water activity between that recorded during the up scan ($a_{w,up}$) and down scan ($a_{w,dn}$) at a given $m/m_o$ for $4 < m/m_o < 11$ was determined from the data in Figure S1. Since the equilibration time exhibited in Figure S2 is symmetric with respect to a steps up and down in activity, we assume that the actual activity is $a_w = (a_{w,up} + a_{w,dn})/2$, and, therefore, the data requires a lag correction of $\Delta a_w = (a_{w,up} - a_{w,dn})/2$; $\Delta a_w$ increases with increasing $a_w$ for $a_w > 0.79$ (Figure S3). A linear fit to the data in Figure S3 was used to correct for the hysteresis exhibited in the continuous scan at high activity (Figure S4). The corrected data displays no hysteresis and agrees well with the 4 equilibrium data points determined from the stepwise scan.
Figure S1. Response of a sodium chloride particle to a continuous triangular scan in water activity between 0.45 and 0.93 @ 0.04 hr⁻¹. T = 21.1 ±0.05 °C.

Figure S2. Response of a sodium chloride particle to a stepwise scan in water activity between 0.850 and 0.925. T = 21.1 ±0.05 °C.

Figure S3. Estimation of the lag in activity as a function of nominal activity during a linear scan rate of 0.04 hr⁻¹.

Figure S4. Data from Figure S1 corrected for lag. Open circles denote equilibrium measurements from Figure S2.