# Analysis of Heterogeneous Uptake by Nanoparticles via Differential Mobility Analysis-Drift Tube Ion Mobility Spectrometry

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## Supplementary Information

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## INFORMATION AVAILABLE

- Calculation of the collision kernel enhancement factors for the ion-dipole potential
- Description of the approach used to determine the water activity of particles
- A list of parameters used in theoretical growth factor predictions
- Plots comparing measured growth factors to theoretical predictions based upon constant $\Delta E$.

## Collision Kernel Enhancement Factors

We evaluate both $\eta_C$ and $\eta_{FM}$ as functions of $\Psi_D$, the characteristic ion-dipole potential energy to thermal energy ratio, which is defined as:

$$\Psi_D = \frac{ze\mu_D}{\pi\varepsilon_0 k_b T \left(d_g + d_v\right)^2}$$ (S1)

where $z$ is the integer number of charges on the particle (absolute value), $\mu_D$ is the vapor molecule dipole moment (1.85 D for water), $\varepsilon_0$ is the permittivity of free space, and the remaining parameters are defined in the main text. Assuming that the dipole remains "locked" during migration to the particle surface (an approximation which simplifies analysis but is known to not rigorously apply[1]), the continuum regime enhancement factor can be calculated using Fuchs's[2] integral expression as:

$$\eta_C = \left(\int_1^\infty \frac{1}{r^2}\exp\left(\frac{-\Psi_D}{r^2}\right)dr\right)^{-1} = \frac{2\Psi_D^{1/2}}{\pi^{1/2}\mathrm{erf}\left(\Psi_D^{1/2}\right)}$$ (S2)

where "erf" denotes the error function evaluated for the interval $(0, \Psi_D^{1/2})$. In the free molecular regime, through a combination of conservation of energy and angular momentum, a given vapor molecule's dimensionless initial impact parameter ($b^* = 2b/(d_g+d_v)$), dimensionless distance of closest approach to a particle ($r_m^* = 2r_m/(d_g+d_v)$), $\Psi_D$, and dimensionless initial speed ( $v^* = v\left(\frac{m_v}{2kT}\right)^{1/2}$ ), can be related to one another as:

$$r_m^* = \left(b^{*2} - \frac{\Psi_D}{v^{*2}}\right)^{1/2}$$ (S3)

If the value of $r_m^*$ either does not exist (condition 1) or is less than unity (condition 2), then the vapor molecule in question, with the prescribed initial speed and impact parameter, will collide

with the particle. Condition (1) leads to the criteria for collision that $b^* \leq (\Psi_D/v^{*2})^{1/2}$, while condition (2) leads to $b^* \leq (1+\Psi_D/v^{*2})^{1/2}$. As the latter of these is more inclusive for all possible values of $\Psi_D$ and $v_*$, the minimum dimensionless impact parameter ($b_m^*$) for a given $v^*$ is:

$$b_m^* = \left(1+\frac{\Psi_D}{v^{*2}}\right)^{1/2} \tag{S4}$$

From $b_m^*$, following Ouyang et al[3] the free molecular enhancement factor can be calculated as:

$$\eta_{FM} = 2\int_0^\infty b_m^{*2}v^{*3}\exp\left(-v^{*2}\right)dv^* = 2\int_0^\infty \left(v^{*3}+\Psi_D v^*\right)\exp\left(-v^{*2}\right)dv^* = 1+\Psi_D \tag{S5}$$

The development of equation S5, again, a "locked" dipole has been assumed. Table S1 displays values of $\eta_C$ and $\eta_{FM}$ for selected $\Psi_D$ values. As with is encountered with many other attractive potential functions, $\eta_{FM} > \eta_C$, and strong potential interactions serve to decrease the diffusive Knudsen number.

**Table S1.** A list of continuum and free molecular enhancement factors for the ion-dipole potential as a function of the dimensionless ion-dipole potential energy to thermal energy ratio.

| $\Psi_D$ | $\eta_C$ | $\eta_{FM}$ | $\Psi_D$ | $\eta_C$ | $\eta_{FM}$ |
|---|---|---|---|---|---|
| 0.01 | 1.003 | 1.010 | 1 | 1.339 | 2.000 |
| 0.02 | 1.007 | 1.020 | 2 | 1.672 | 3.000 |
| 0.03 | 1.010 | 1.030 | 3 | 1.983 | 4.000 |
| 0.04 | 1.013 | 1.040 | 4 | 2.267 | 5.000 |
| 0.05 | 1.017 | 1.050 | 5 | 2.527 | 6.000 |
| 0.06 | 1.020 | 1.060 | 6 | 2.765 | 7.000 |
| 0.07 | 1.023 | 1.070 | 7 | 2.986 | 8.000 |
| 0.08 | 1.027 | 1.080 | 8 | 3.192 | 9.000 |
| 0.09 | 1.030 | 1.090 | 9 | 3.385 | 10.000 |
| 0.10 | 1.033 | 1.100 | 10 | 3.568 | 11.000 |
| 0.20 | 1.067 | 1.200 | 15 | 4.370 | 16.000 |
| 0.30 | 1.101 | 1.300 | 20 | 5.046 | 21.000 |
| 0.40 | 1.135 | 1.400 | 25 | 5.642 | 26.000 |
| 0.50 | 1.169 | 1.500 | 30 | 6.180 | 31.000 |
| 0.60 | 1.203 | 1.600 | 35 | 6.676 | 36.000 |
| 0.70 | 1.237 | 1.700 | 40 | 7.136 | 41.000 |
| 0.80 | 1.271 | 1.800 | 45 | 7.569 | 46.000 |
| 0.90 | 1.305 | 1.900 | 50 | 7.979 | 51.000 |

**Activity of Water on Particles**

The activity of water on a particle, $a_w$, is determined for particles of known dry diameter, $d_0$ and number of sorbed vapor molecules, $g$. First, the combined number of cations and anions, $n_{ca}$ in each dry particle is calculated as:

$$n_{ca} = 2 \frac{\rho_{ca} \frac{\pi}{6} d_0^3}{m_{ca}} \tag{S6}$$

where $\rho_{ca}$ is the bulk density of the cation-anion pair, and $m_{ca}$ is the cation-anion pair mass. With $g$ number of vapor molecules sorbed, the number of cations and anions dissolved in a saturated solution $n_{d,ca}$ is calculated as:

$$n_{d,ca} = 2 \frac{g m_{H_2O}}{m_{ca}} X_{sat} \tag{S7}$$

where $X_{sat}$ is the mass ratio of the cation-anion pair to water in a saturation solution (which is a function of temperature). If $n_{d,ca} < n_{ca}$, then the activity of water on the particle surface is taken to be equal to the saturated solution activity ($a_w = a_{w,sat}$) for the cation-anion pair under examination. Otherwise, the activity is equated with the mole fraction of water in solution, i.e. $a_w$ is calculated with the equation:

$$a_w = \frac{g}{g + n_{ca}} \tag{S8}$$

**Parameters used in Growth Factor Predictions**

| | Lithium Iodide | Sodium Iodide |
|---|---|---|
| $d_0$, dry diameters (nm) | 3.54, 4.91, 7.59 | 2.85, 4.24, 5.61 |
| Saturation Ratio Range | 0-0.32 | 0-0.38 |
| Bulk Density, $\rho_{ca}$ (kg m$^{-3}$) | 4080 | 3670 |
| Cation-anion pair mass, $m_{ca}$ (kg mol$^{-1}$) | 0.13385 | 0.14989 |
| $a_{w,sat}$ | 0.186 | 0.397 |
| Solubility Mass Ratio, $X_{ca}$ | 1.51 | 1.84 |
| Water molecule diameter (nm) | 0.385 | 0.385 |
| Water Diffusion Coefficient (m$^2$ s$^{-1}$) | 2.68 X 10$^{-5}$ | 2.68 X 10$^{-5}$ |

**Comparison of Growth Factor Measurements to Predictions with constant $\Delta E$**
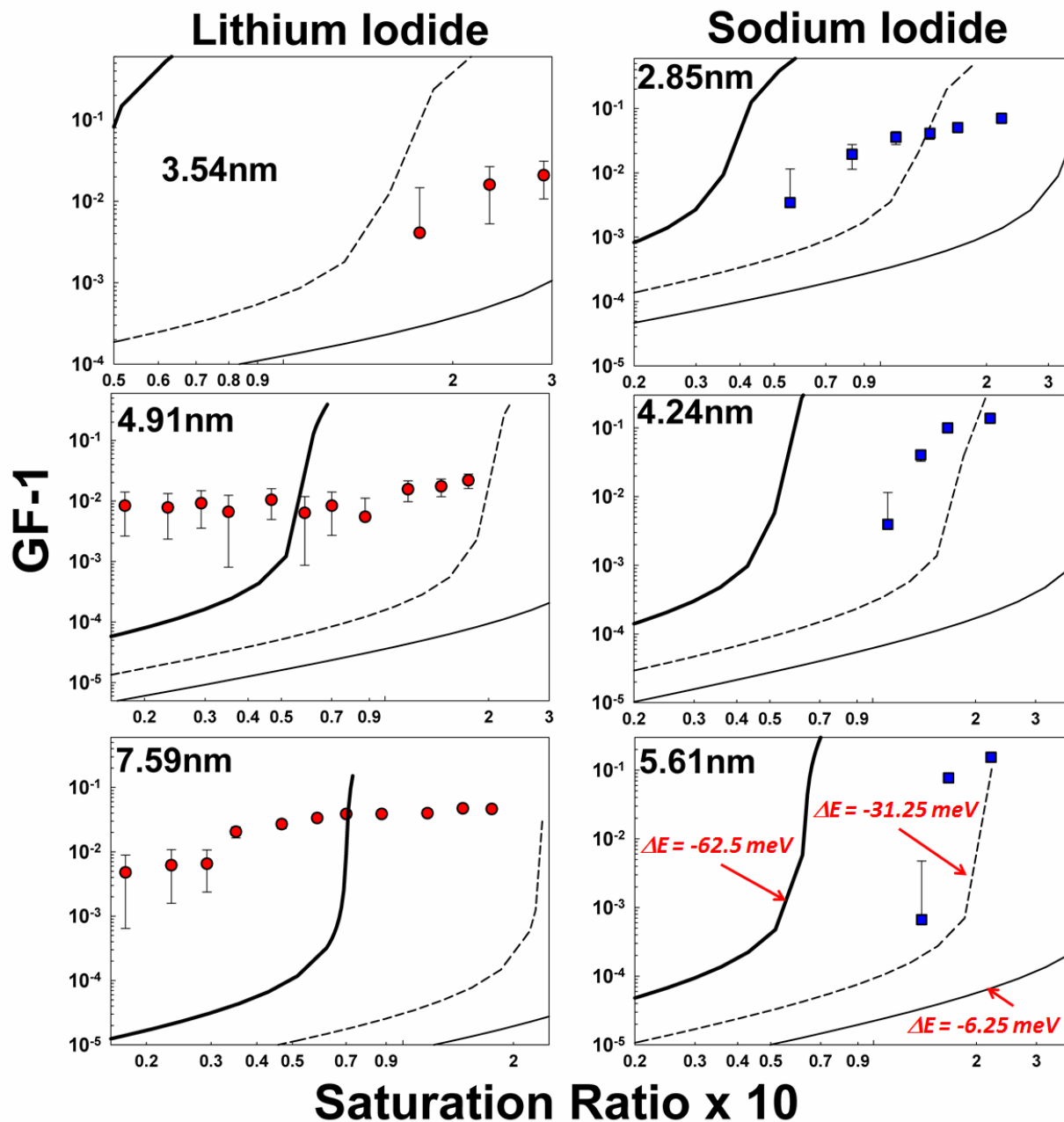


**Figure S1.** A comparison of measured growth factors (less unity) to predictions considering the ion-induced dipole potential but with constant values of $\Delta E$ = -6.25 meV, -31.25 meV, and -62.5 meV. Curves for each energy value are labelled in the sodium iodide 5.61 nm plot.

1.      T. Su, M. T. Bowers, *Journal of the American Chemical Society* 1973, *95*. 7609-7610
2.      N. A. Fuchs, *Geofis. Pura Appl.* 1963, *51*. 185-193
3.      H. Ouyang, R. Gopalakrishnan, C. J. Hogan, *The Journal of Chemical Physics* 2012, *137*. 064316