Hygroscopic Tandem DMA Measurements of Inorganic Nanoparticles

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Outline

- Introduction
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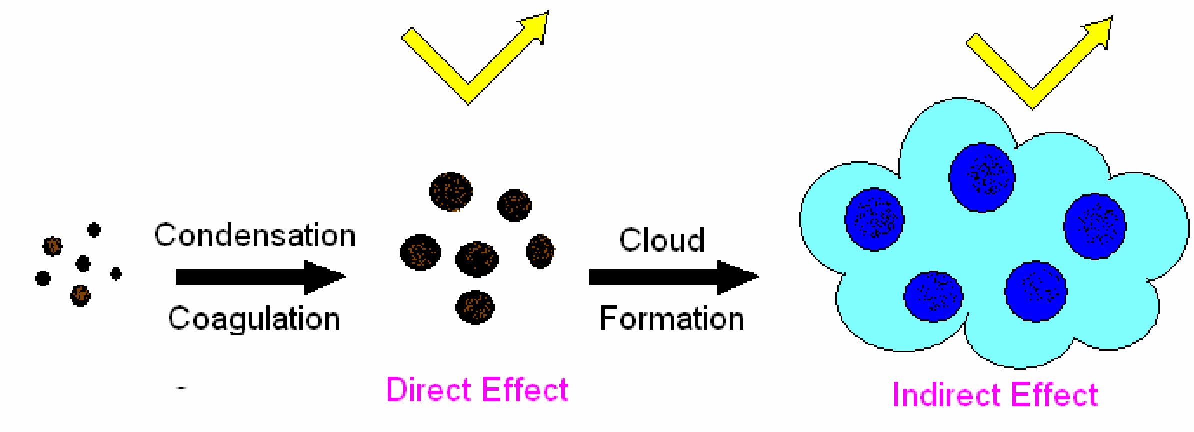
  - –Nanoparticles
- Experimental
  - –The Hygoscopic Tandem nano-Differential Mobility Analyzer
  - –General Procedure
- Results
  - –Potassium Bromide
  - –Potassium Iodide
  - –Sea Salt
- Conclusions
- Future Work

Why Study Aerosol Particles?

- How aerosols contribute to climate change:
  - –Directly by scattering and absorbing radiation
  - –Indirectly by acting as cloud condensation nuclei



- Nano-particles contribute by forming larger particles through condensation

- The hygroscopic properties of nano-particles influence the rates of the processes leading to larger particle formation (Biskos et al. 2006)

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., Martin, S. T. (2006). Prompt Deliquescence and Efflorescence of Aerosol Nanoparticles. *Atmos. Chem. Phys.*. 6:4633-4642.

Background: Aerosols

- Sea Salt Aerosols:
  - Composed primarily of NaCl (Tang et. al, 1997)
  - Produced by waves and bubble bursting
- Anthropogenic Aerosols:
  - Primary aerosols emitted as particles
  - Secondary aerosols generated from gas to particle conversion

Tang, L. N., Tridico, A. C., Fung, K. H. (1997). Thermodynamic and Optical Properties of Sea Salt Aerosols, *Journal of Geophys. Res.* 102:23,269-23275.

Background: Nanoparticles

- Inorganic nano-particles have been observed in…
  - The marine boundary layer (O'Dowd et al. 2001)
  - Laboratory simulations of sea salt aerosol production (Tyree et al. 2007)
  - Freshly nucleated sulfuric acid and ammonium sulfate particles observed (Biskos et al. 2006)

- Hygroscopic growth of nanoparticles
  - The DRH of a large aerosol particle (> 100 nm) can be calculated from the vapor pressure of water over a saturated salt solution

O'Dowd, C.D., Becker, E., Kulmala, M. (2001). Mid-latitude North-Atlantic Aerosol Characteristics in Clean and Polluted Air. *Atmos. Res.* 58:167-185.
Tyree, C.A., Hellion, V.M., Alexandrova, O.A., Allen, J.O. (2007). Foam Droplets Generated from Natural and Artificial Seawaters, *Journal of Geophys. Res.* 112.

Background: Nanoparticles

- Increased surface energy contribution relative to total particle free energy for nanoparticles compared to large particles

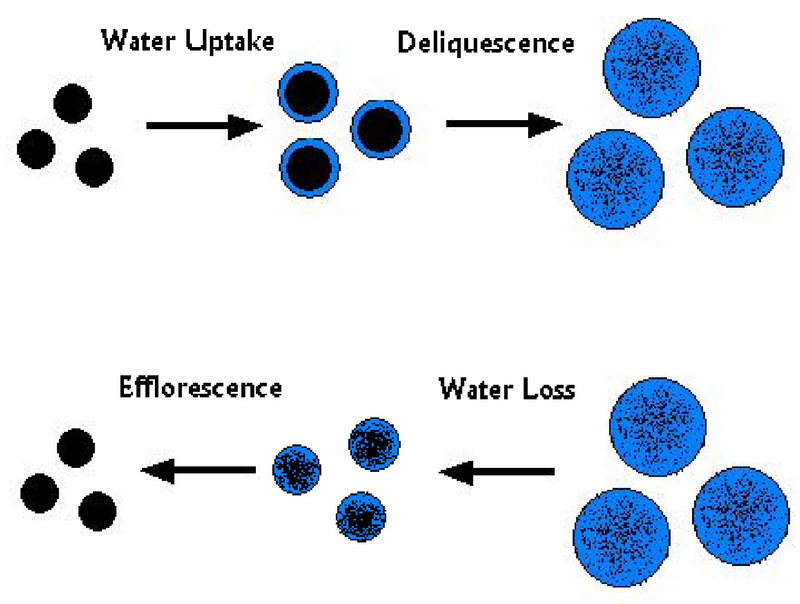
- Kelvin Effect
  - At small particle diameters (< 60 nm) the curvature of the aerosol particle becomes increasingly important
  - Predicts increased vapor pressure of water over the particle surface with increasing curvature

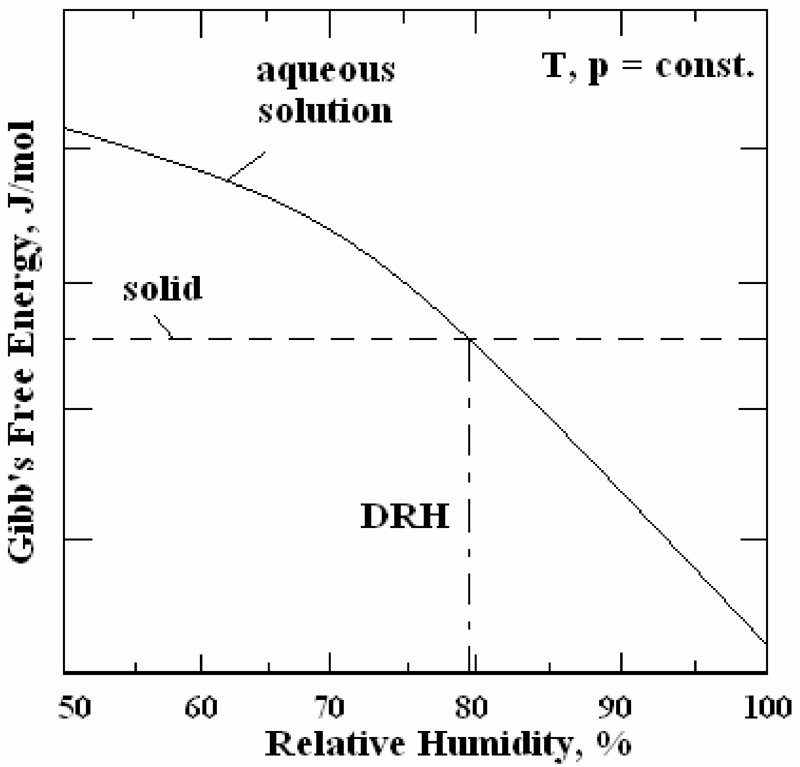
- Theory predictions of DRH can differ depending on the presence of adsorbed water mono-layers prior to deliquescence
  - Increase with decreasing particle size (Russell and Ming, 2002)
  - Decrease with decreasing particle size (Mirabel et. al, 2000)

Mirabel, P., Reiss, H., Bowles, R. K., (2000). A Theory for the Deliquescence of Small Particles. *J. Chem. Phys.* 113:8200-8205.
Russell, L. M., Ming, Y. (2002). Deliquescence of Small Particles, *J. Chem. Phys.* 116:311-321.

Efflorescence and Deliquescence

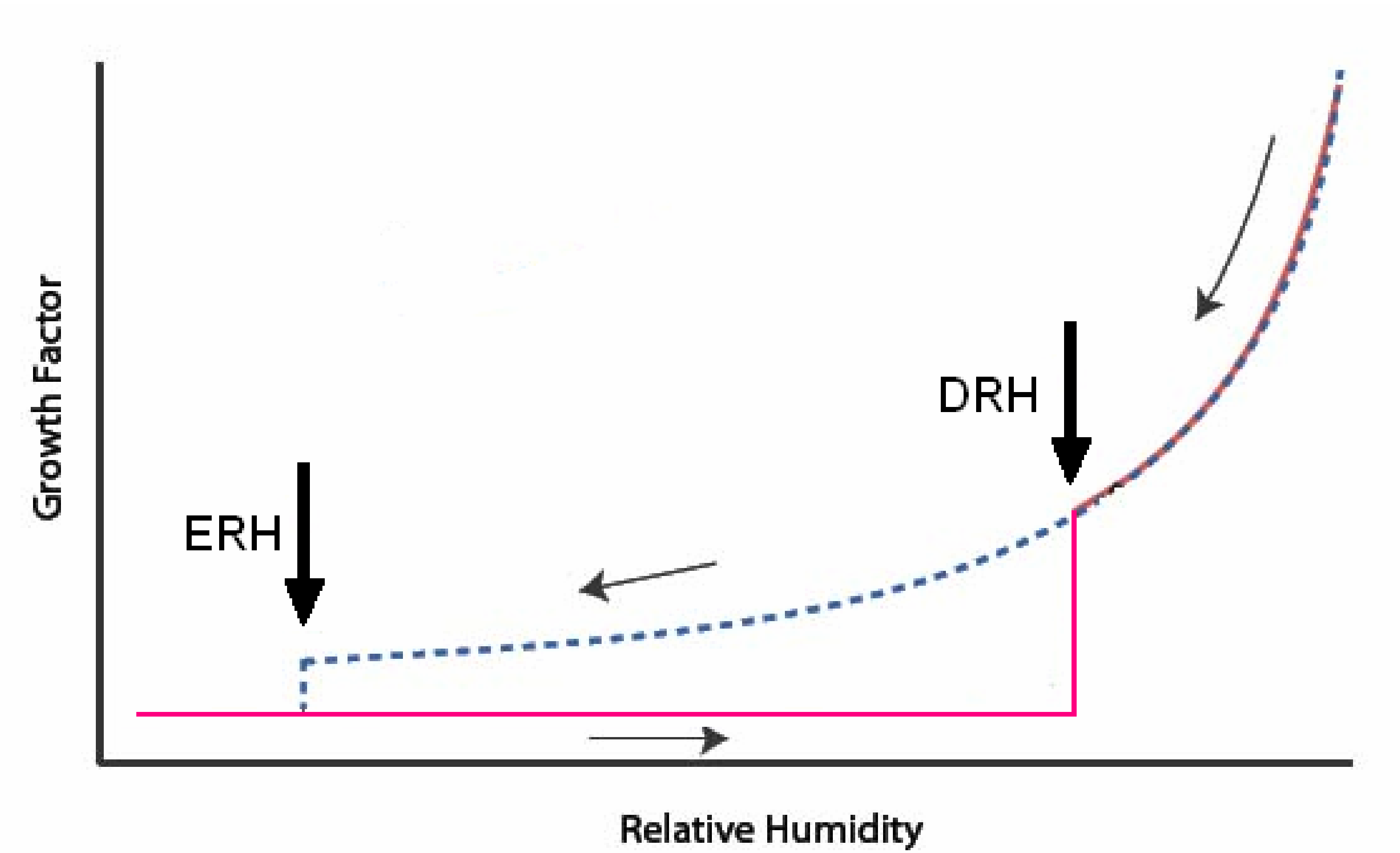
- Deliquescence refers to the phase transition of aerosol particles from solid crystals to aqueous droplets.
- The efflorescence relative humidity (ERH) is the point at which an aqueous particle crystallizes from a supersaturated solution.





Efflorescence and Deliquescence

- There is a hysteresis effect between the DRH and ERH, thus, particle phase is a path function



Research Goals

- Investigate nanosize effects on the DRH, ERH and growth factors of inorganic sodium, potassium and lithium salts
  - Sodium: NaF, NaBr, NaI
  - Potassium: KF, KCl, KBr, KI
  - Lithium: LiCl, LiBr, LiI

- Also look for nanosize effects on the hygroscopic growth of synthetic and natural sea salts

Experimental: How are DRH and ERH Measured?

- Generate a polydisperse aerosol
  - Vaporization-Condensation
  - Electrospray
- Select a monodisperse aerosol with a DMA
- Measure the particle diameter after exposing the aerosol stream to varying RH values
- Analyze the data with a plot of growth factors vs. RH

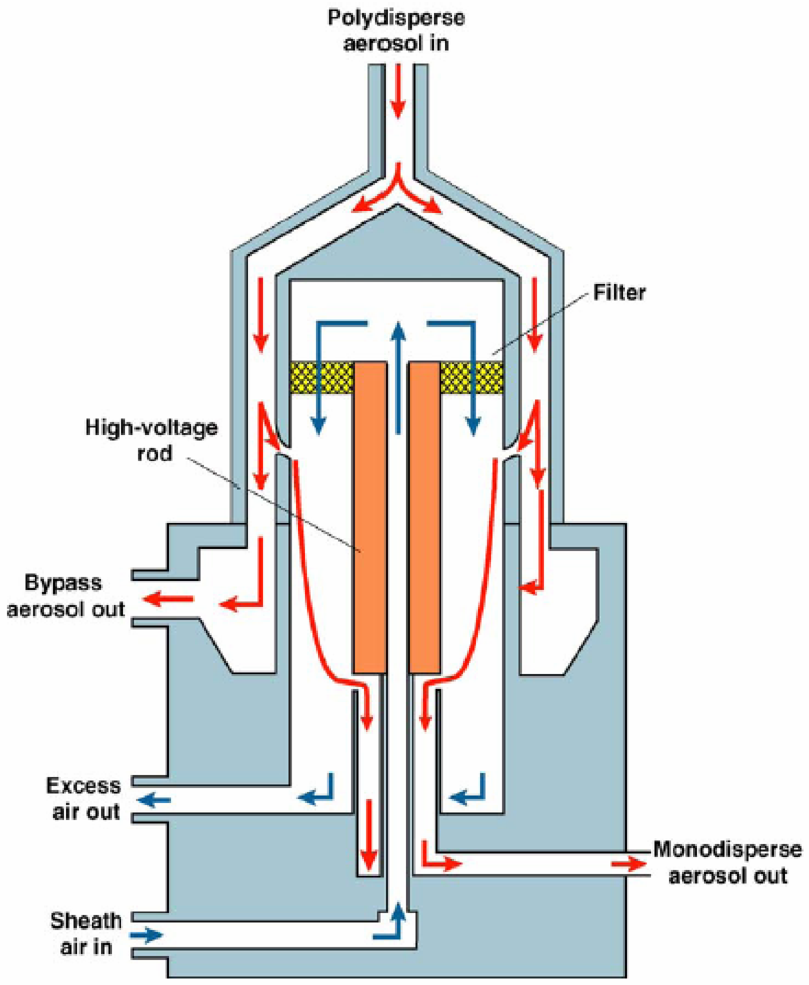
$$gf(RH) = \frac{d(RH)}{d_{dry}}$$

Experimental: The DMA

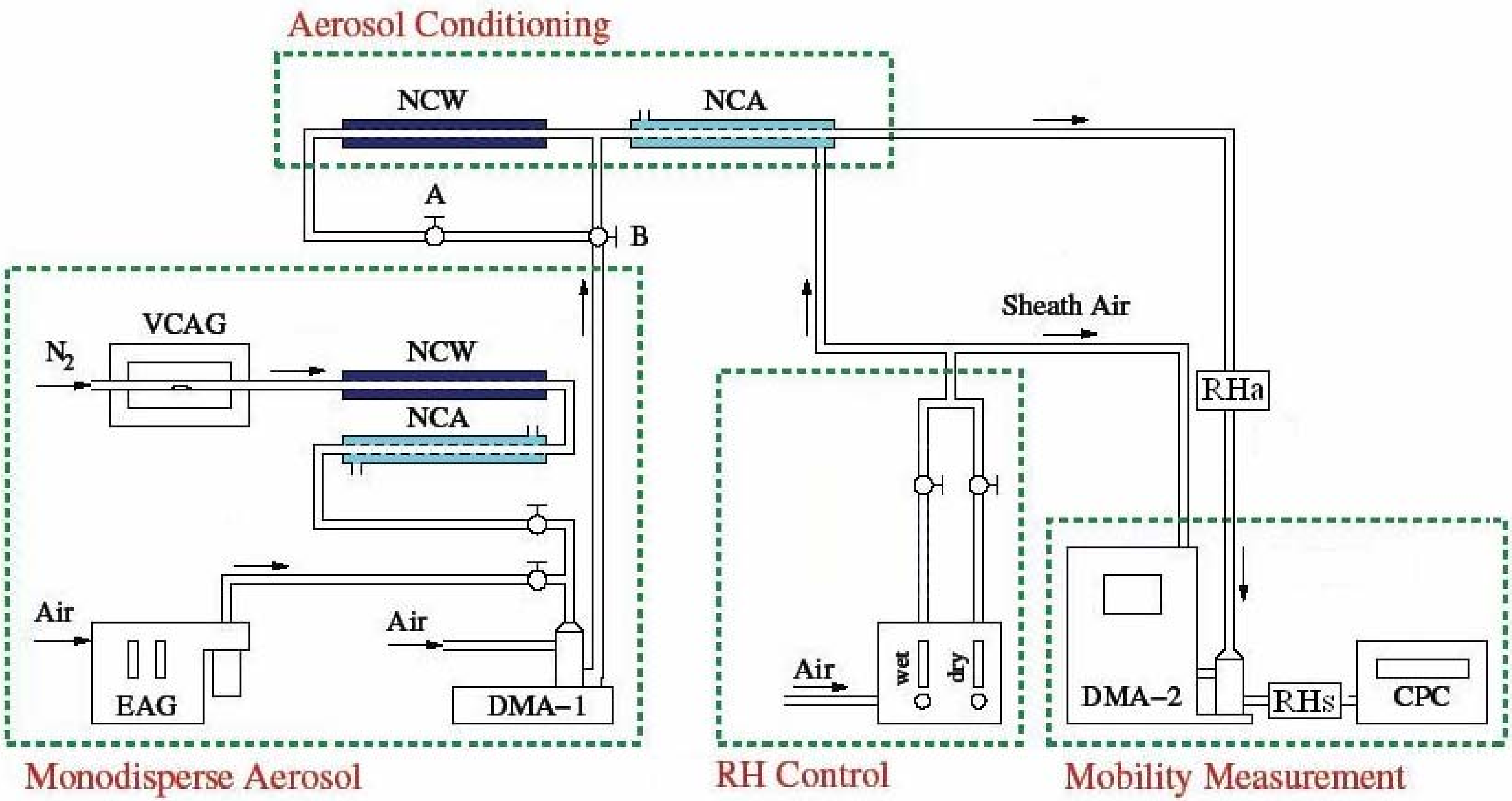
- Measures particle electrical mobility
  - Ability of a particle to move in an electric field

$$Z = \frac{V_T}{E} = \frac{neC_c}{3\pi\eta D}$$

  - Particle diameter calculated from electrical mobility and particle charge
- Can select a specific diameter or scan to determine the distribution of diameters

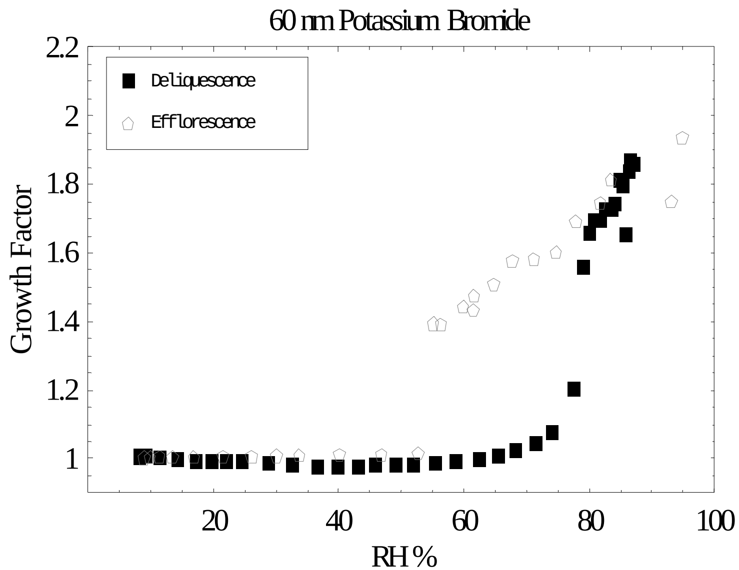


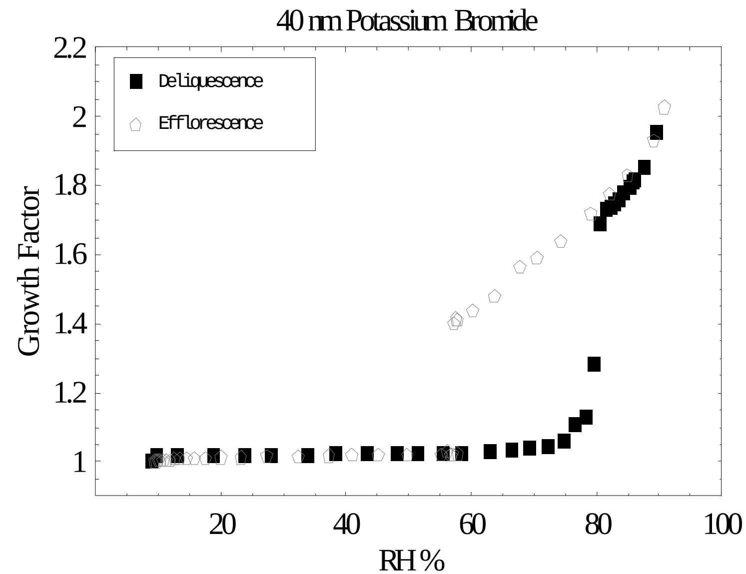
Experimental : The HTDMA Setup

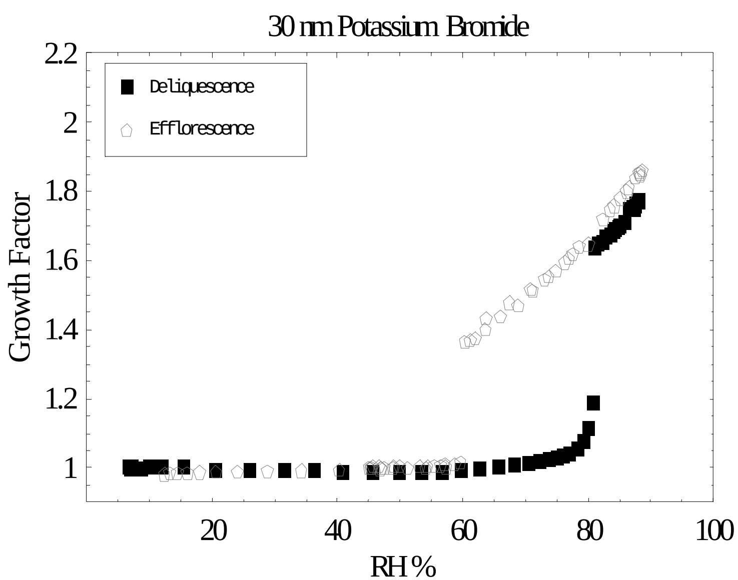


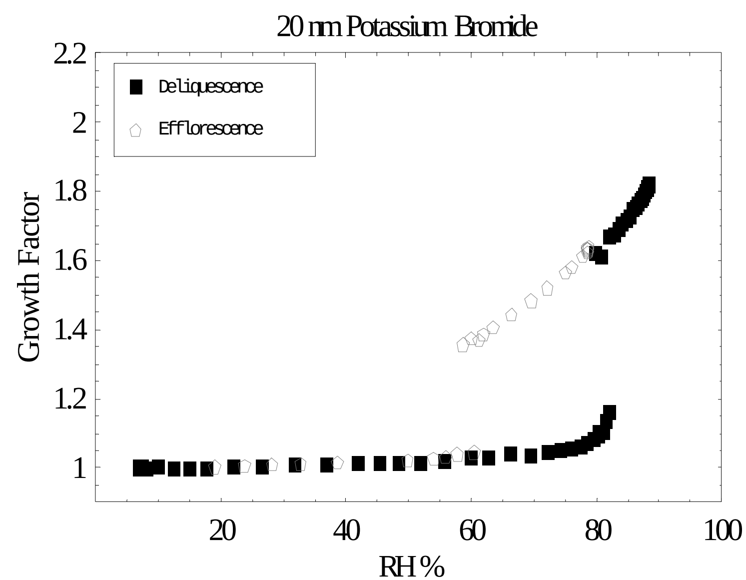
VCAG: Vaporization–Condensation Aerosol Generator
EAG: Electrospray Aerosol Generator
DMA: Differential Mobility Analyzer
NCW: Nafion tube Conditioner with Water
NCA: Nafion tube Conditioner with Air
CPC: Condensation Particle Counter

Results: Potassium Bromide

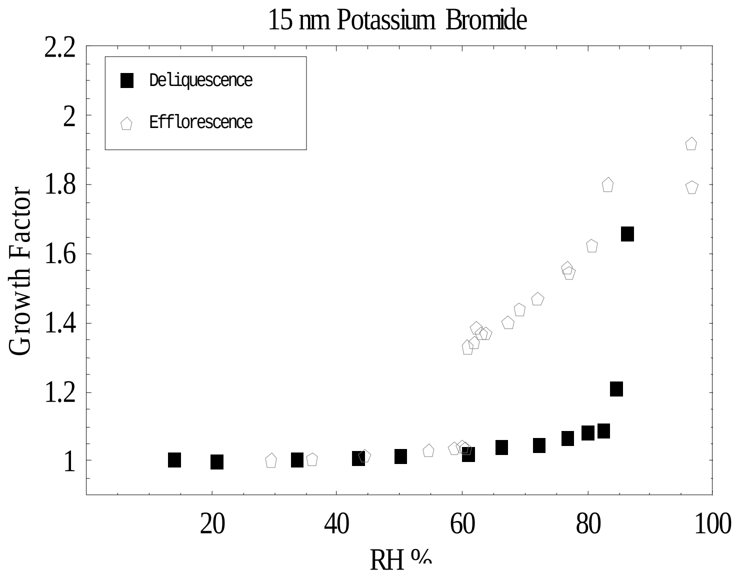


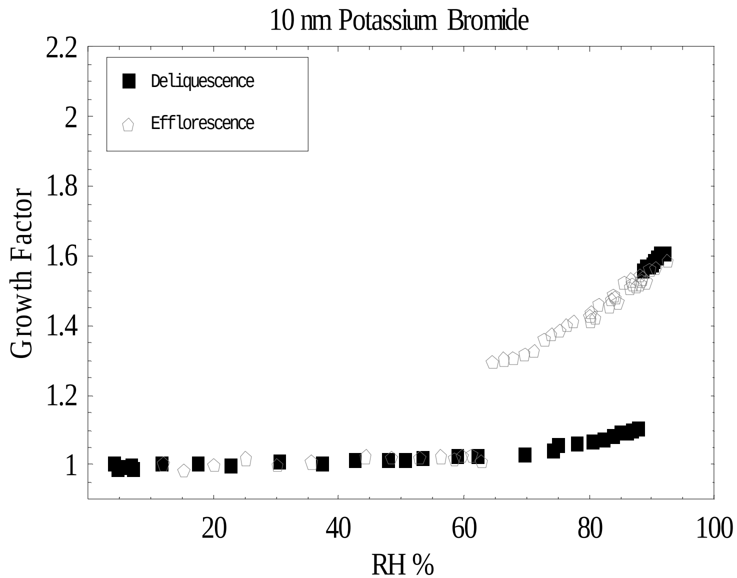


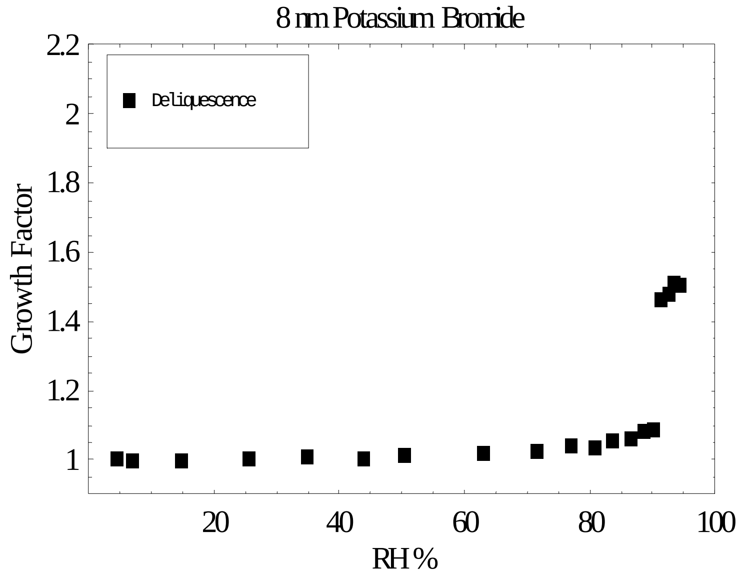




Results: Potassium Bromide

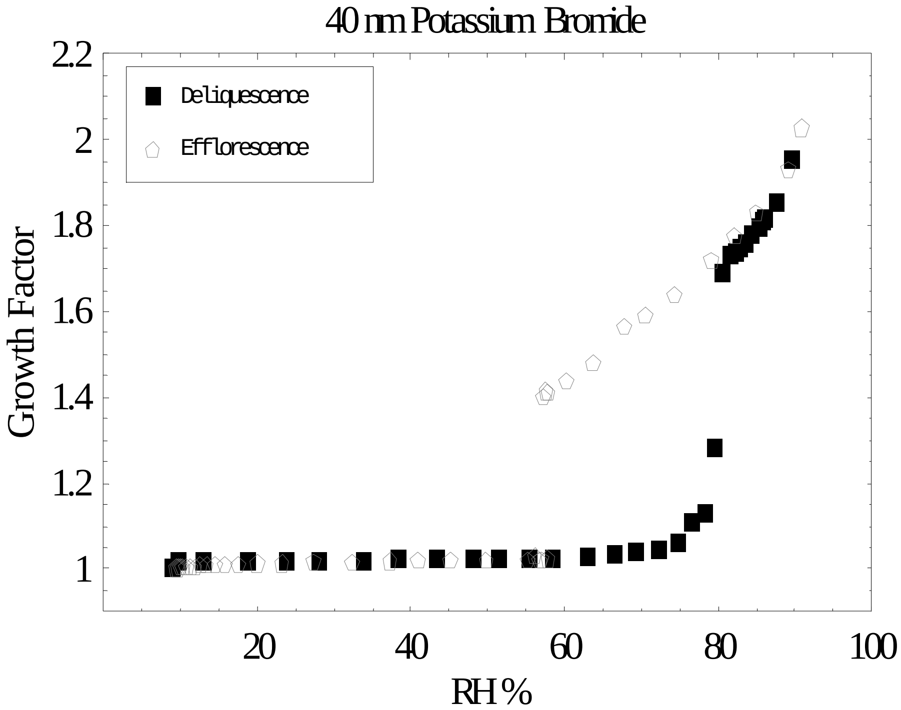


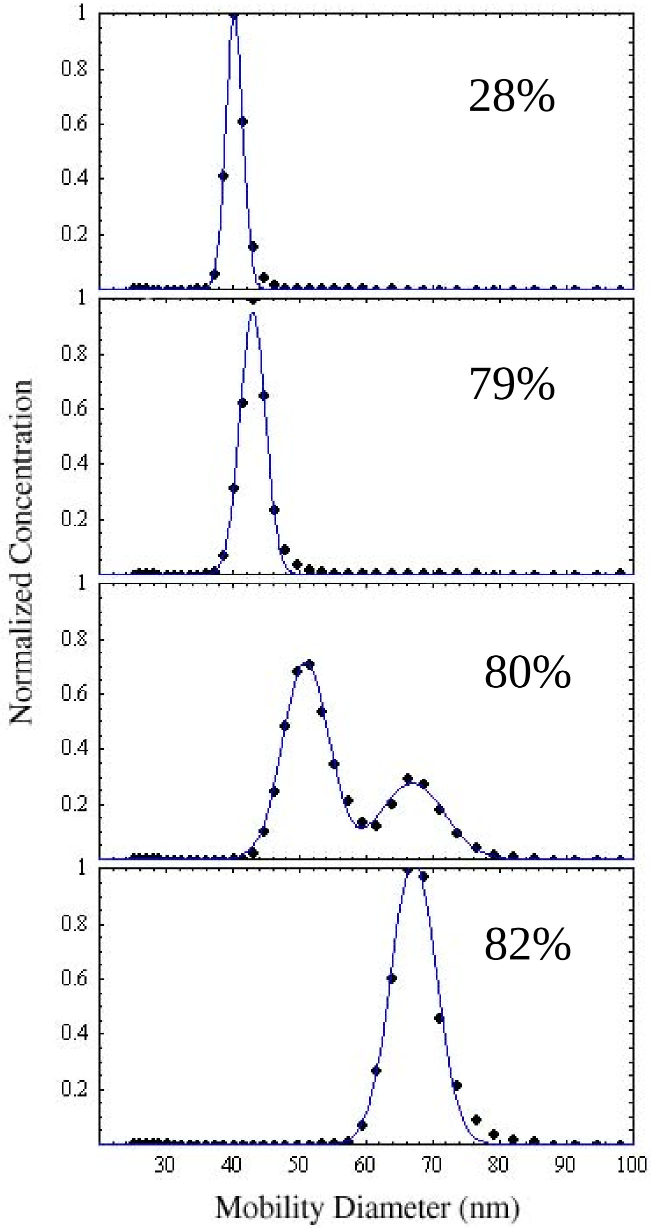




40 nm KBr Data

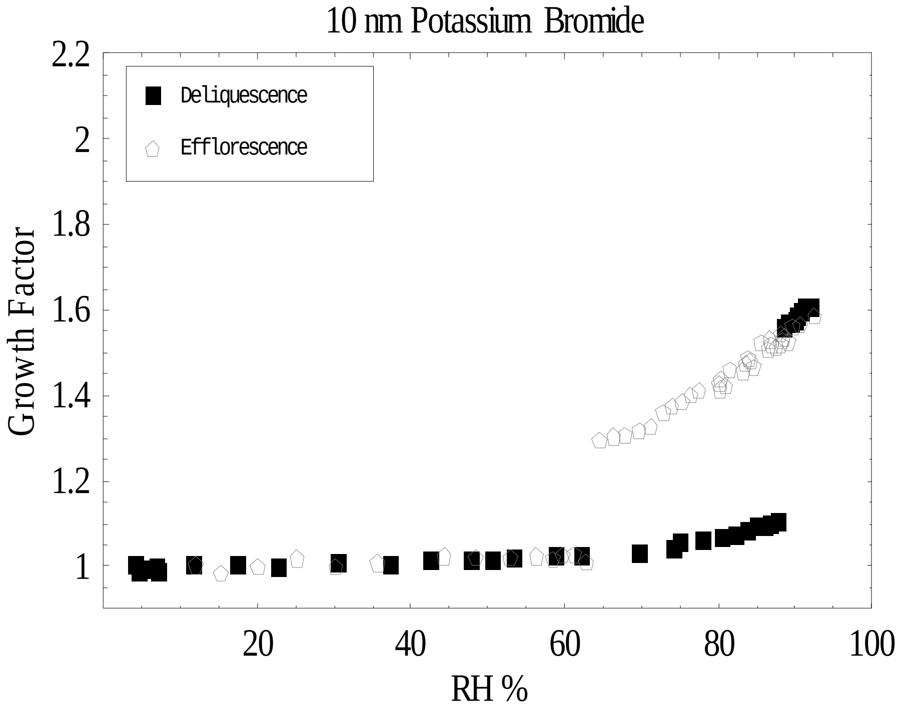
- The DRH is ~80-81%
- The ERH is ~57%

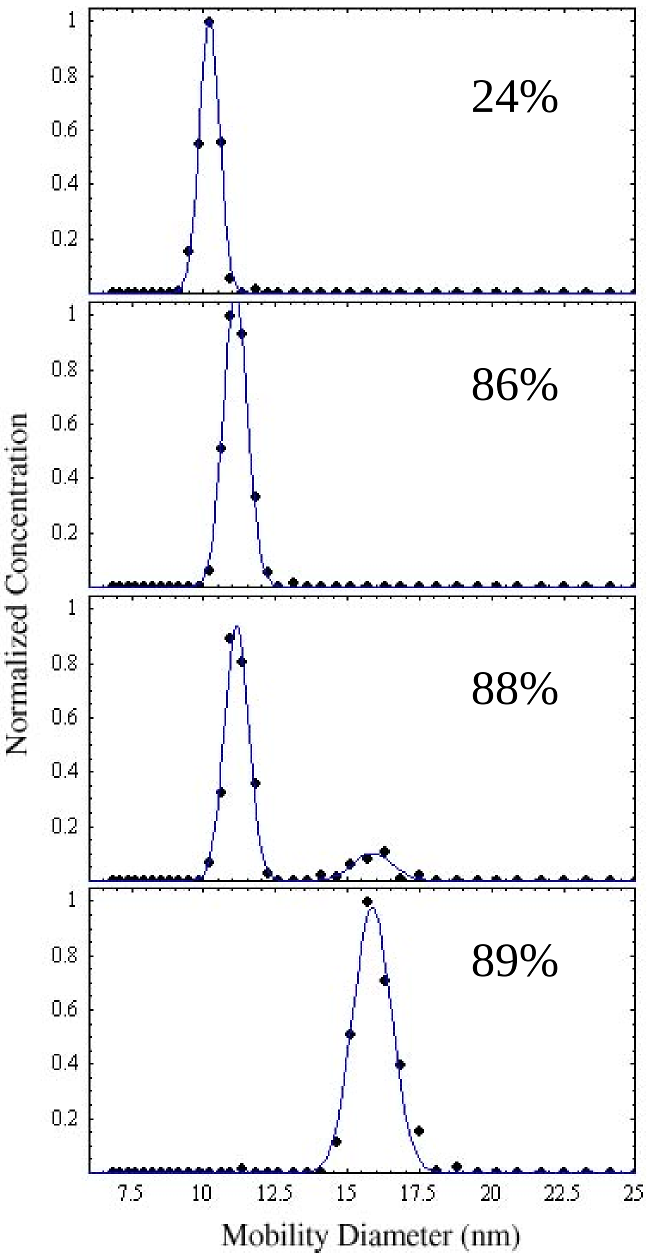




10 nm KBr Data

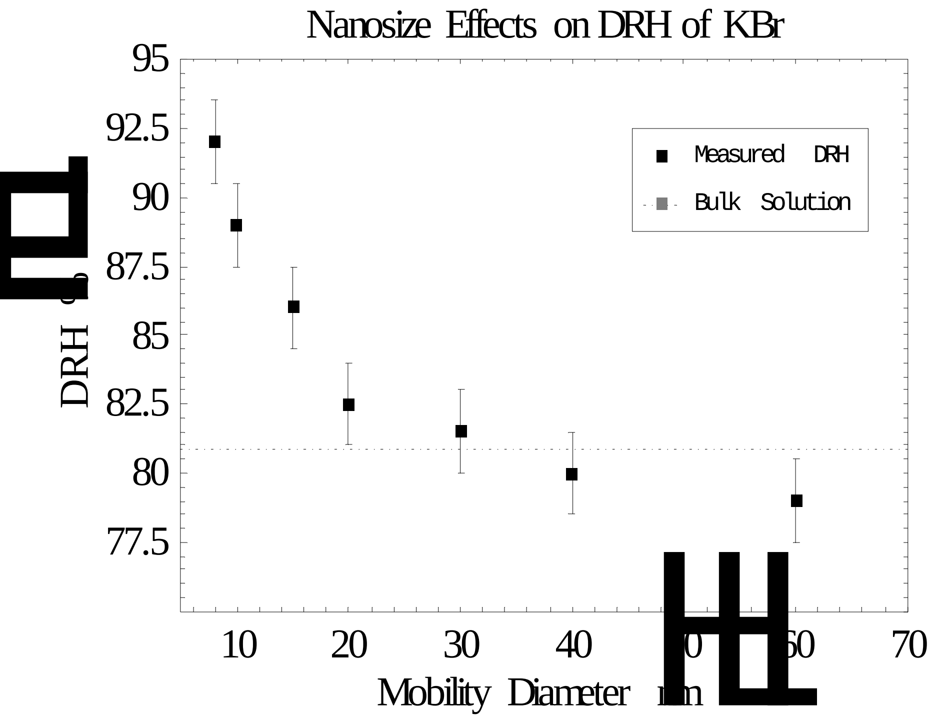
- The DRH is ~89%
- The ERH is ~65%

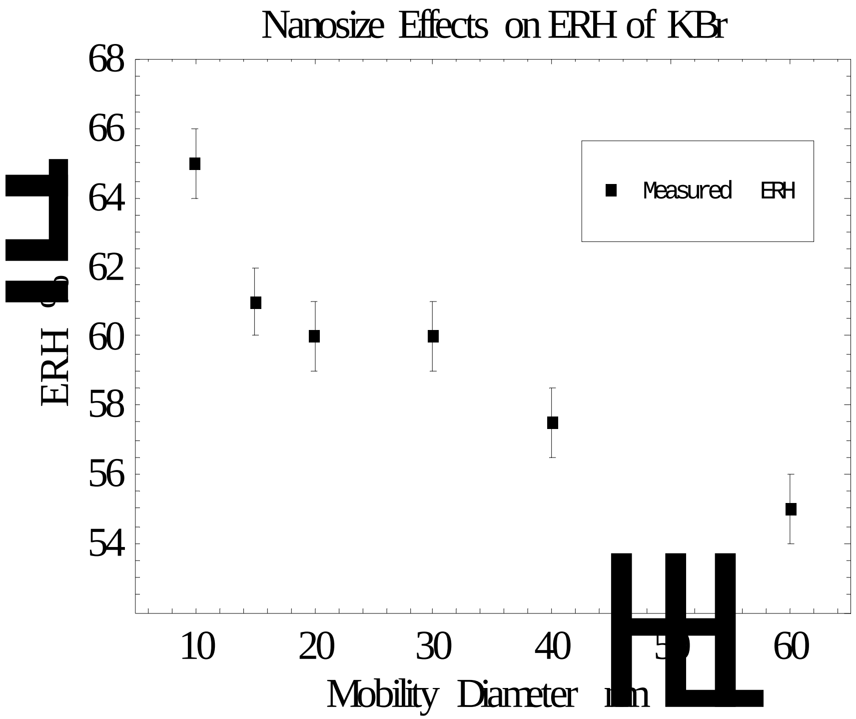




Results: Potassium Bromide

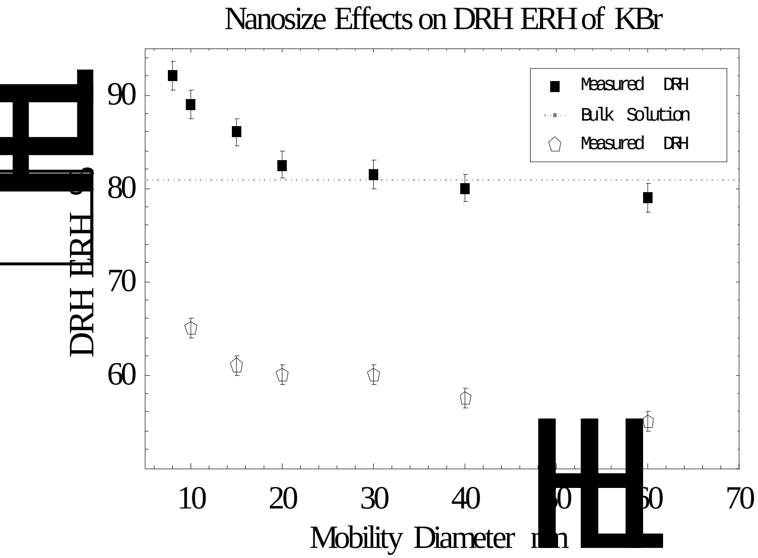
- KBr Results
  - Increase in DRH and ERH with decreasing particle size
  - Decrease in growth factor with decreasing particle size

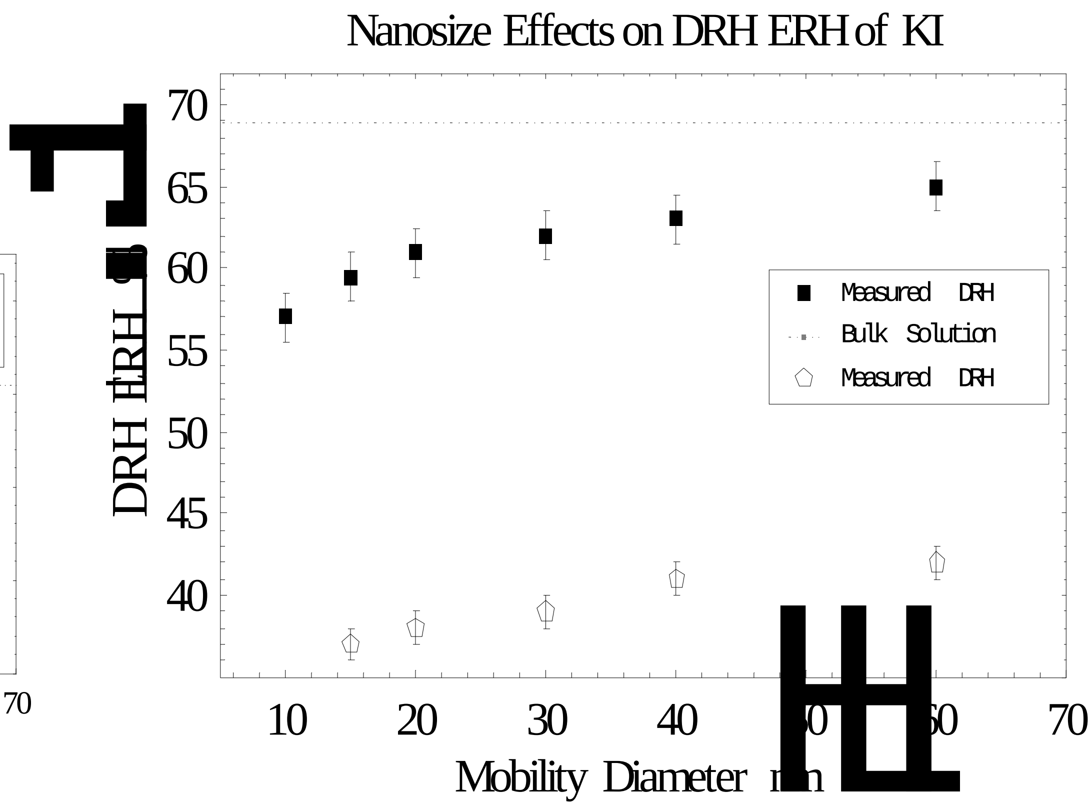




Results: Potassium Iodide

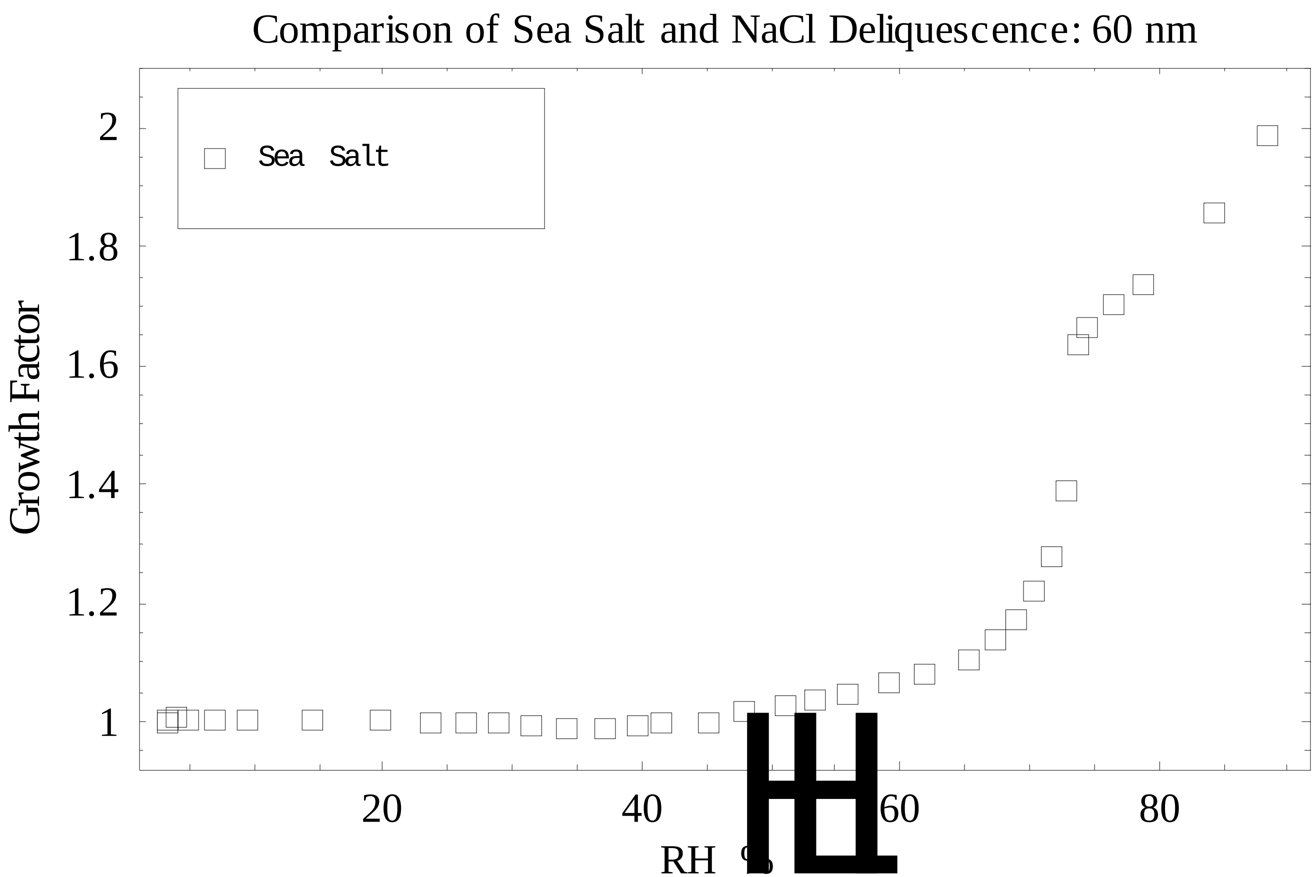
- KI
  - Differs from NaCl and KBr data
  - Decrease in DRH and ERH





Results: Sea Salt

- Typical sea salt composition: NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$ (Tang et. al, 1997)



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Results: Sea Salt

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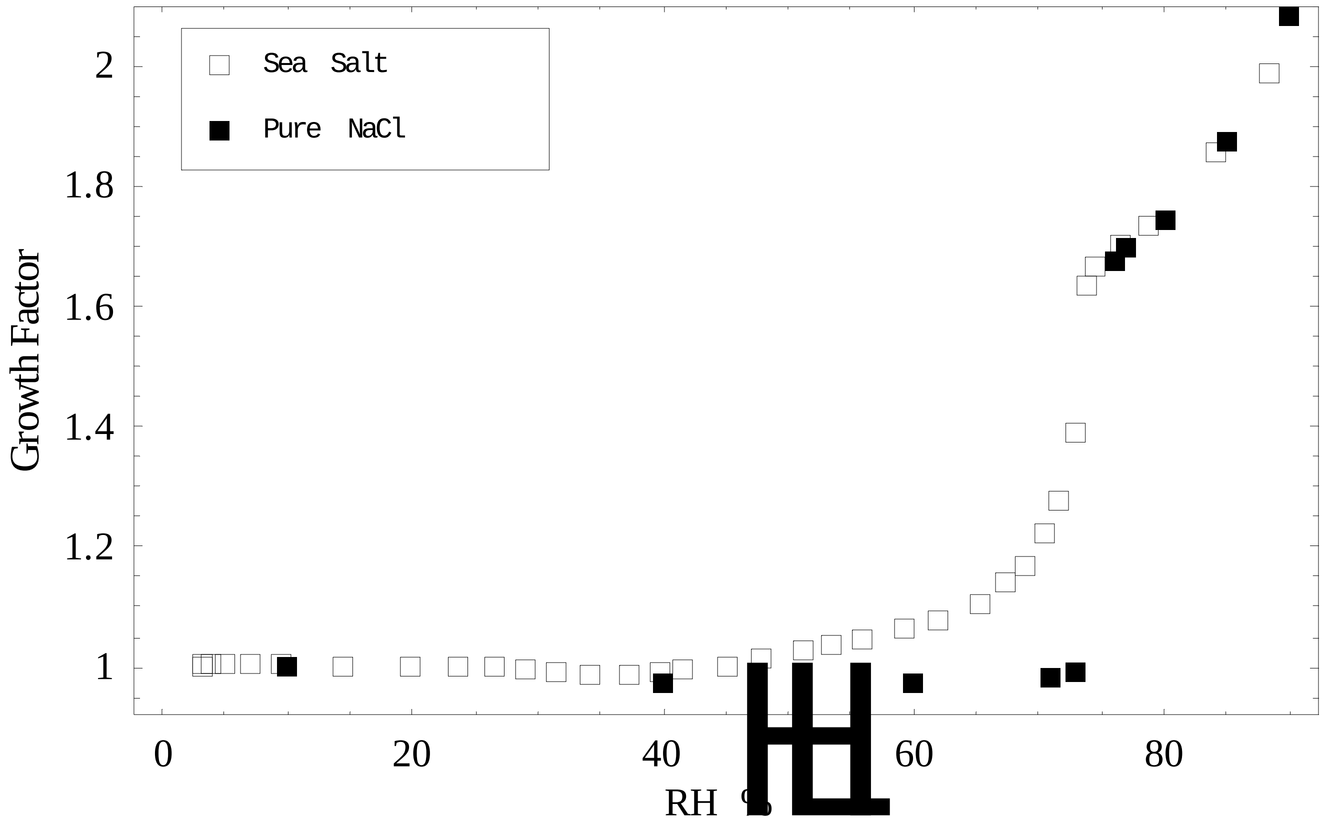
Comparison of Sea Salt and NaCl Deliquescence: 60 nm



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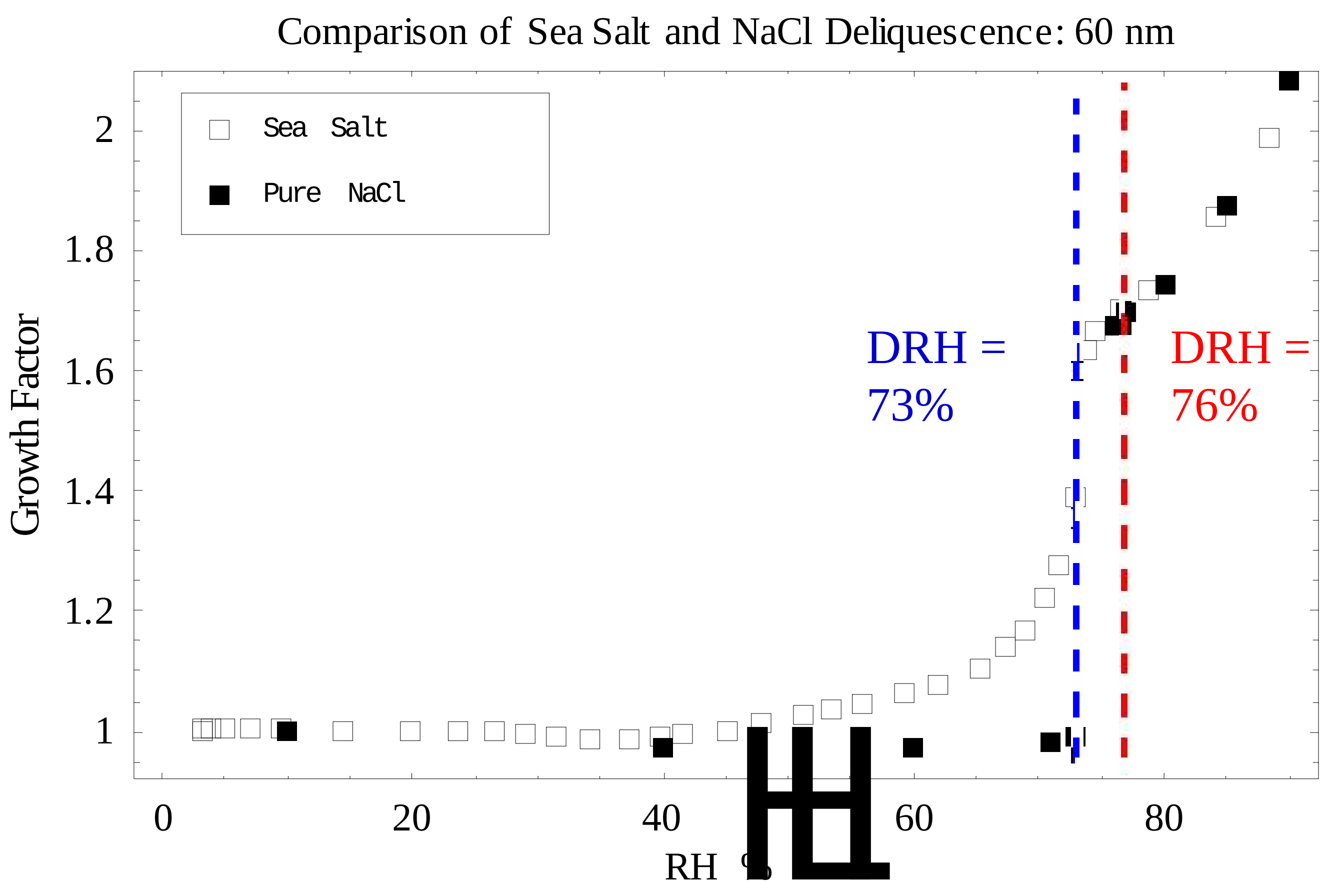
Results: Sea Salt

- Compare sea salt to NaCl: Impurities expected to lower the DRH
- DRH agrees well with the findings of Tang et. al for large sea salt particles (74%)



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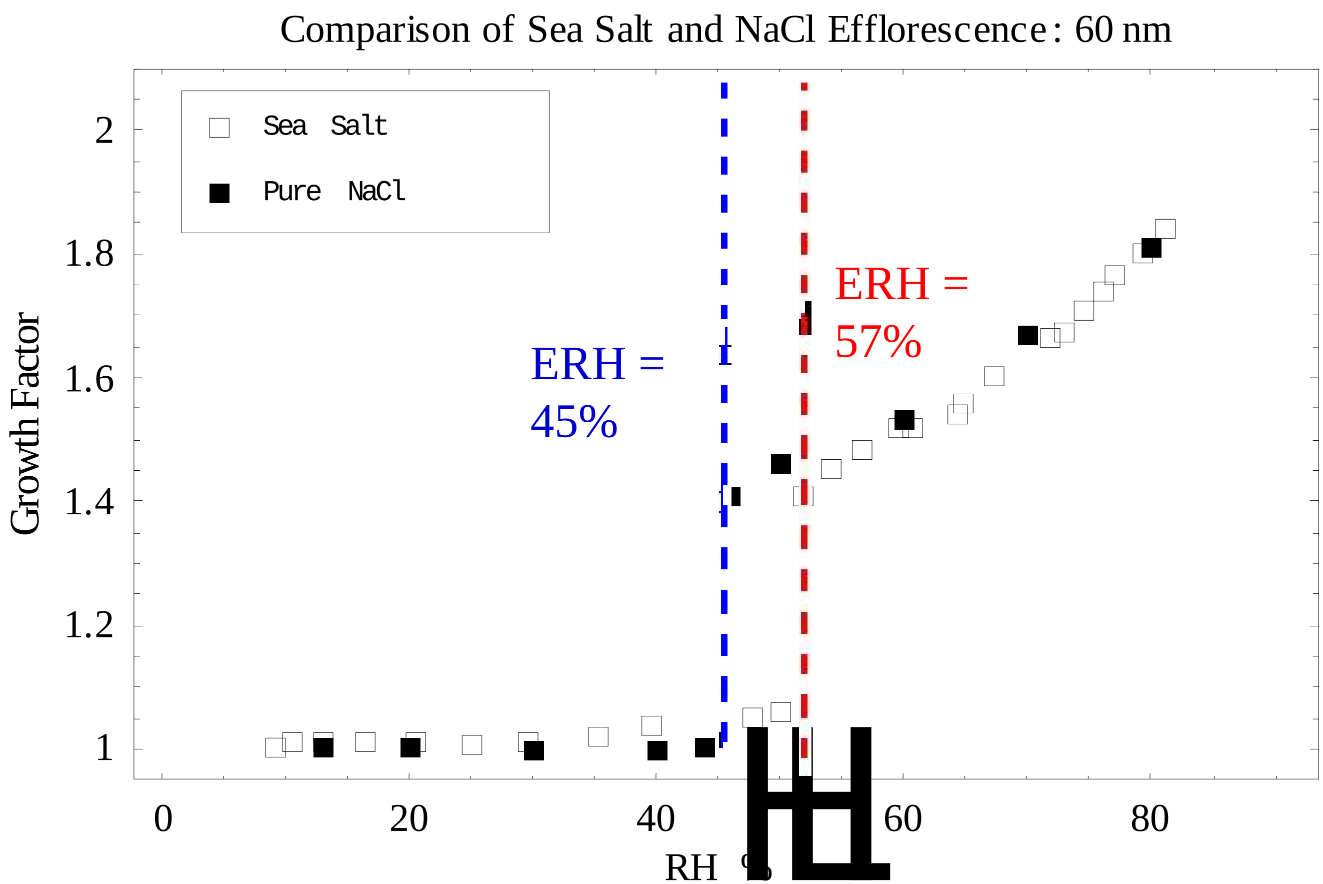
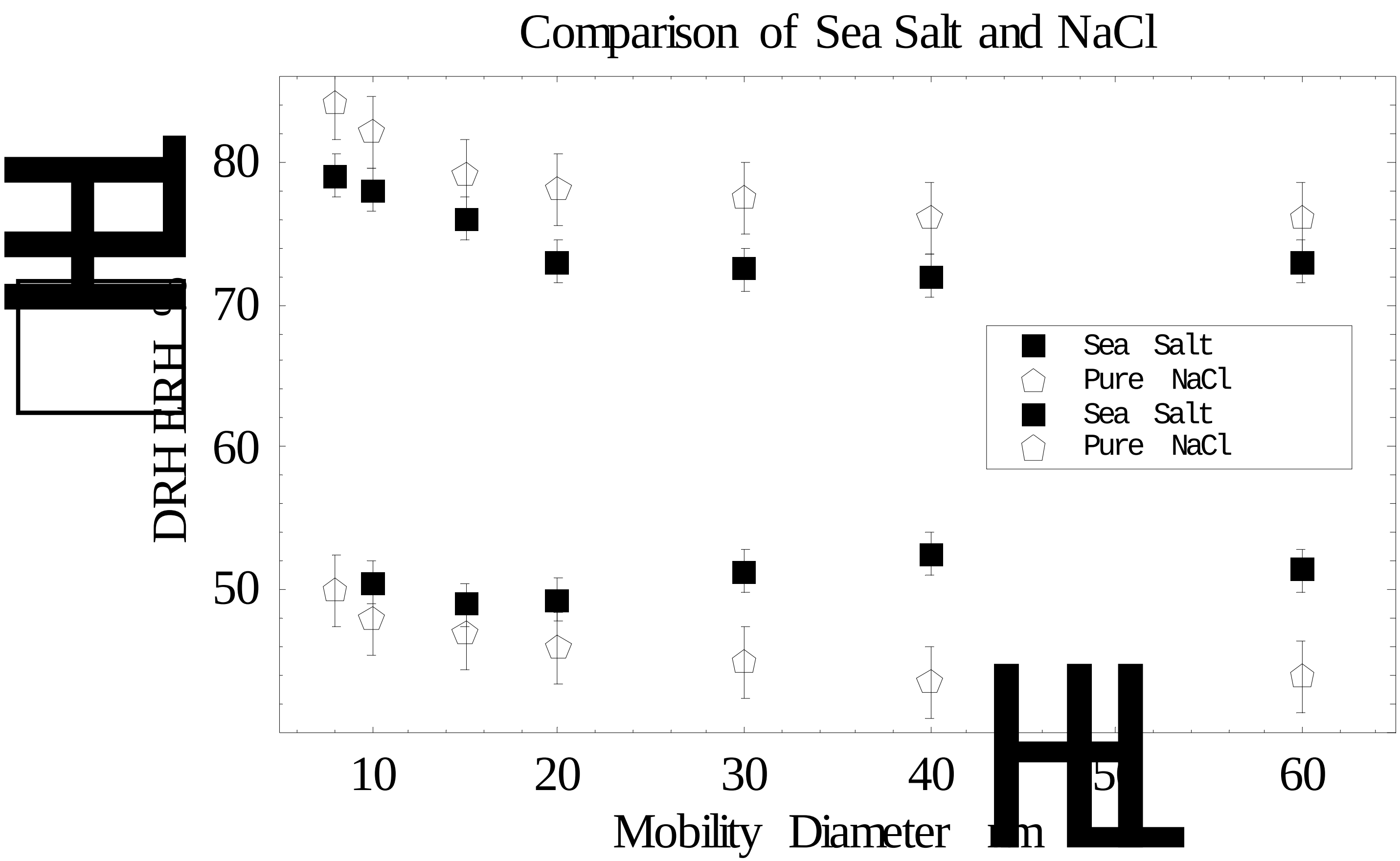
Results: Sea Salt

- Compare sea salt to NaCl



Results: Sea Salt

- Compare sea salt to NaCl
- DRH lower
- ERH higher



Conclusions

- Different nanosize effects were observed for potassium salts
  - Increase in DRH and ERH for Potassium Bromide
  - Decrease in DRH and ERH for Potassium Iodide

- Nanosize effects were observed for sea salt particles
  - Consistent with the major component of sea salt being NaCl

Future Work

- Continue inorganic salt experiments
  - Natural sea salts
  - Lithium salts

- Develop a better theoretical understanding/explanation of results

- Expand project beyond inorganic salts
  - Organic compounds have been identified in atmospheric nanoparticles as well

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