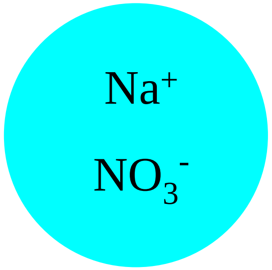
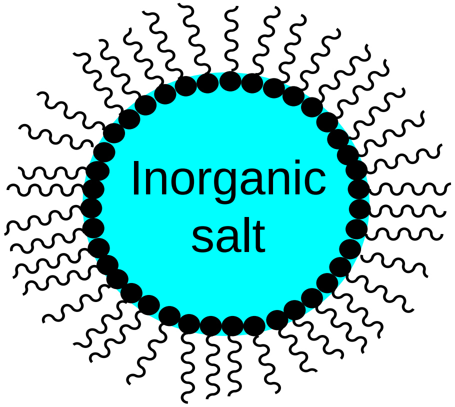
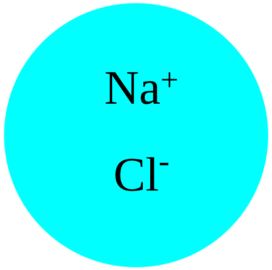
Effects of Soluble Surfactants on Density, Shape and Water Uptake of Common Hygroscopic Particles







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CGEP End-of-Summer

August 14th, 2007

Gracias

- GCEP-GREF (Milton, Jeff, Staff)
- B. Ellison and Ellison’s group
- Alla Zelenyuk (PNNL-EMSL)
- DOE-Basic Science

Inorganic Particles' Properties

- Physical and Chemical properties

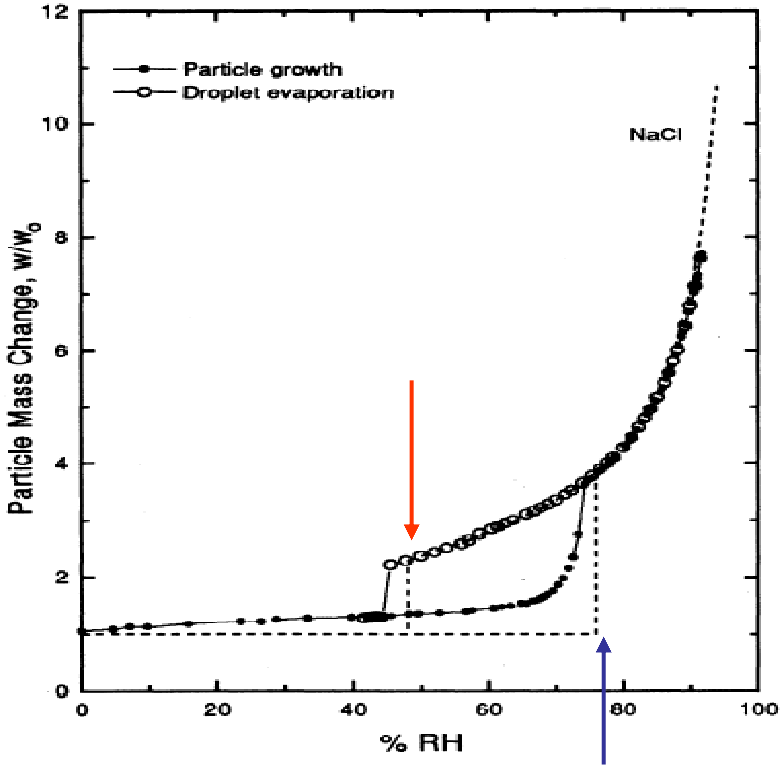
- Efflorescence → relative humidity at which particles lose all the water and crystallized. (liquid→solid)

- Deliquescence → relative humidity at which particles gain water and become a droplet. (solid→liquid)

- Growth Factors (GFs)

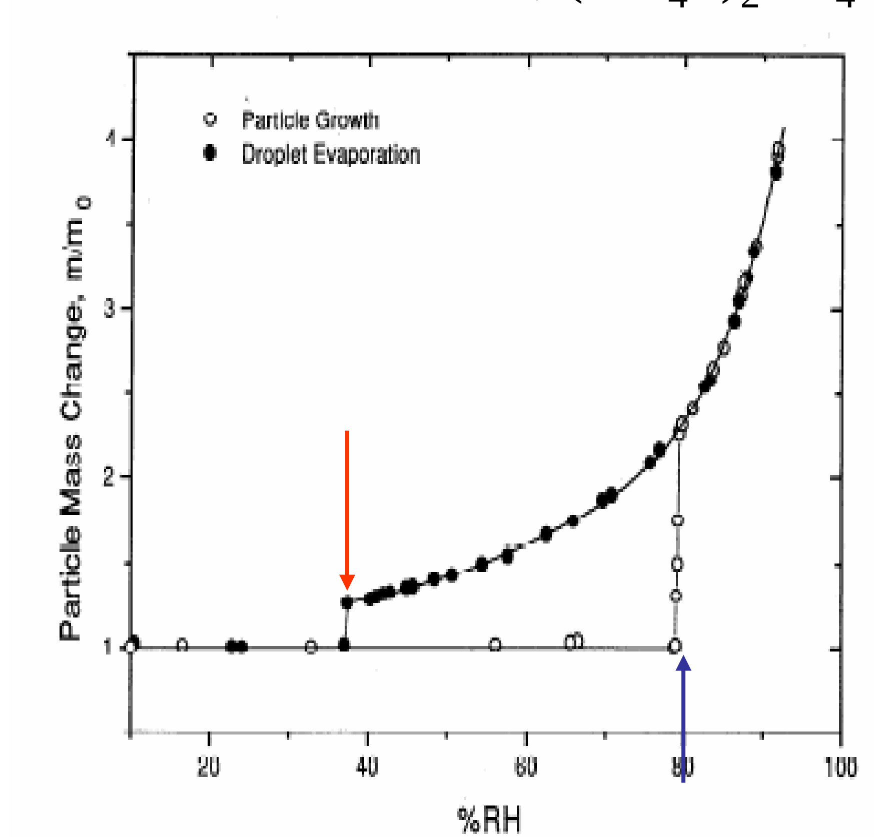
Sub-micron-size Particles Properties

Sodium Chloride, Na^+Cl^-



Efflorescence ~ 42% RH
Deliquescence ~78% RH

Ammonium Choride, $(NH_4^+)_2SO_4^{2-}$

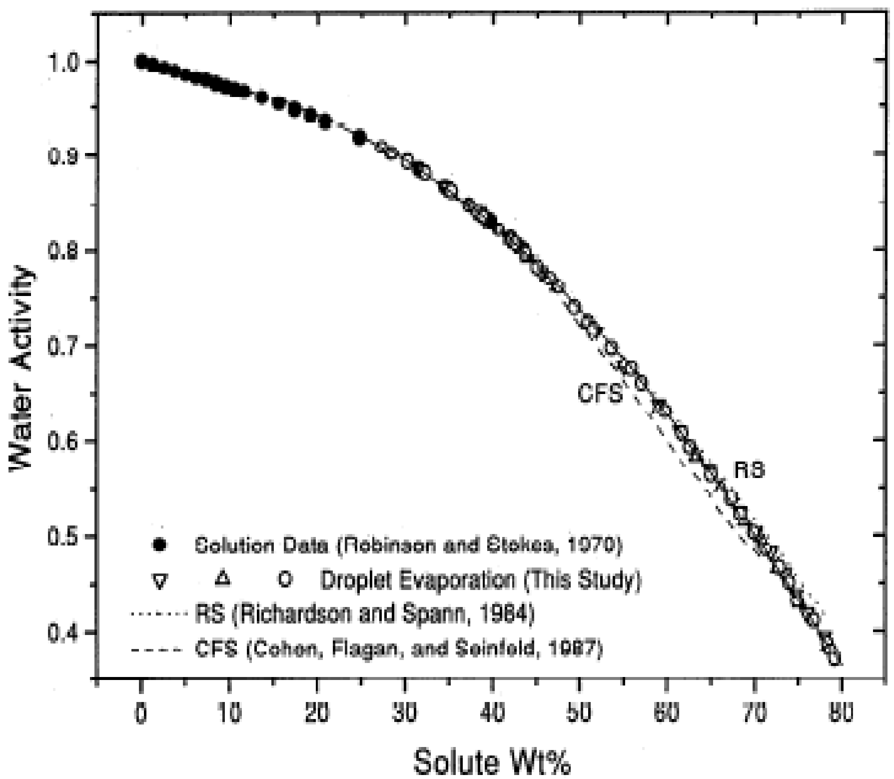


Efflorescence ~ 37-40% RH
Deliquescence ~80% RH

Tang,I.N.; Munkelwitz,H.R. *J Geophys. Res-Atmos* 1994, 99(D9): 18801-18808
Tang, I.N.; Tridico, A.C.; Fung, K.H. *J Geophys. Res-Atmos* 1994, 102(D19): 23269-23275

Micron-sized Particles Properties

$(NH_4^{+})_2SO_4^{2-}$



$$a_w = 1.00 + \sum C_i wf_i$$

$$RH = 100\, a_w$$

$$\rho = 1.00 + \sum A_i wf_i$$

$$d_{ve}^3 = \left(\frac{(wf\ )\rho_p}{\rho_{salt}} \right) d_m^3$$

$$d_{ve} = \sqrt[3]{\left(\frac{(wf\ )\rho_p}{\rho_{salt}} \right)}\, d_m$$

$$\frac{d_{ve}}{d_m} = \sqrt[3]{\left(\frac{(wf\ )\rho_p}{\rho_{salt}} \right)}$$

Tang,I.N.; Munkelwitz,H.R. *J Geophys. Res-Atmos* 1994, 99(D9): 18801-18808
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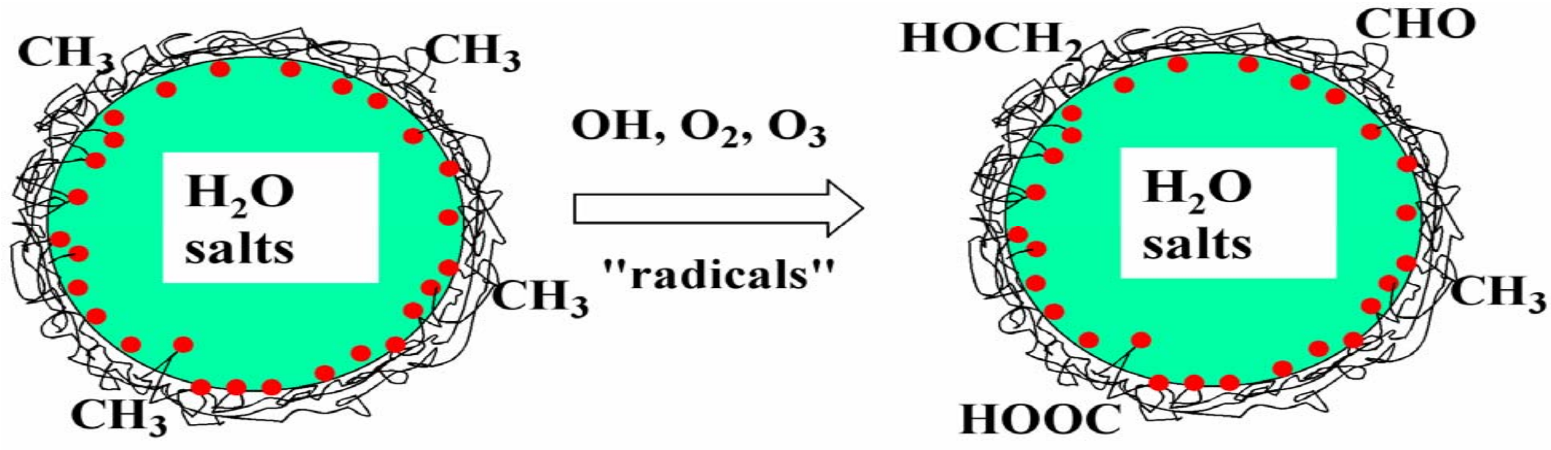


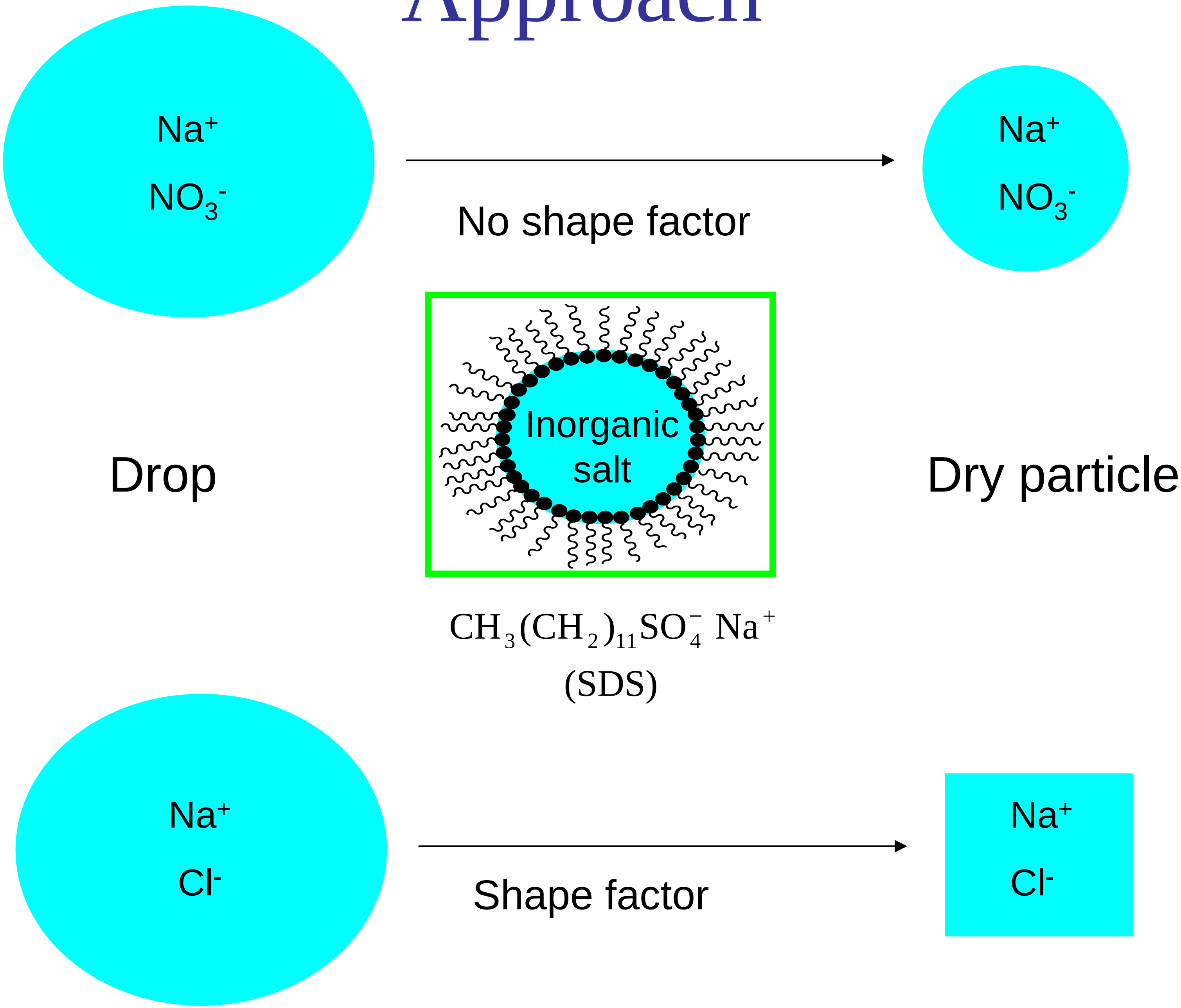
- A large fraction of atmospheric particles are composed of common hygroscopic inorganic salts (sulfates, nitrates, sea salts) that are mixed with a variety of organics.
- *Surfactants* – coat particle's surface, alter particles' interactions with the atmosphere (gas species, water vapor), CCN activity, change size and optical properties as a function of RH.
- It is important to quantitatively characterize these particles' behavior as a function of RH

Surfactant effects-Previous work

- *Growth Factors (GFs)* – HTDMA work showed that the addition of organics to inorganics does NOT prevent water uptake or loss but the amount gained or loss. (Hansson *et al*. (1999), Chen & Grace (1999 & 2001)
  - Larger organic fraction → lower GFs
  - Deliquescence points are lower compare to pure salt.

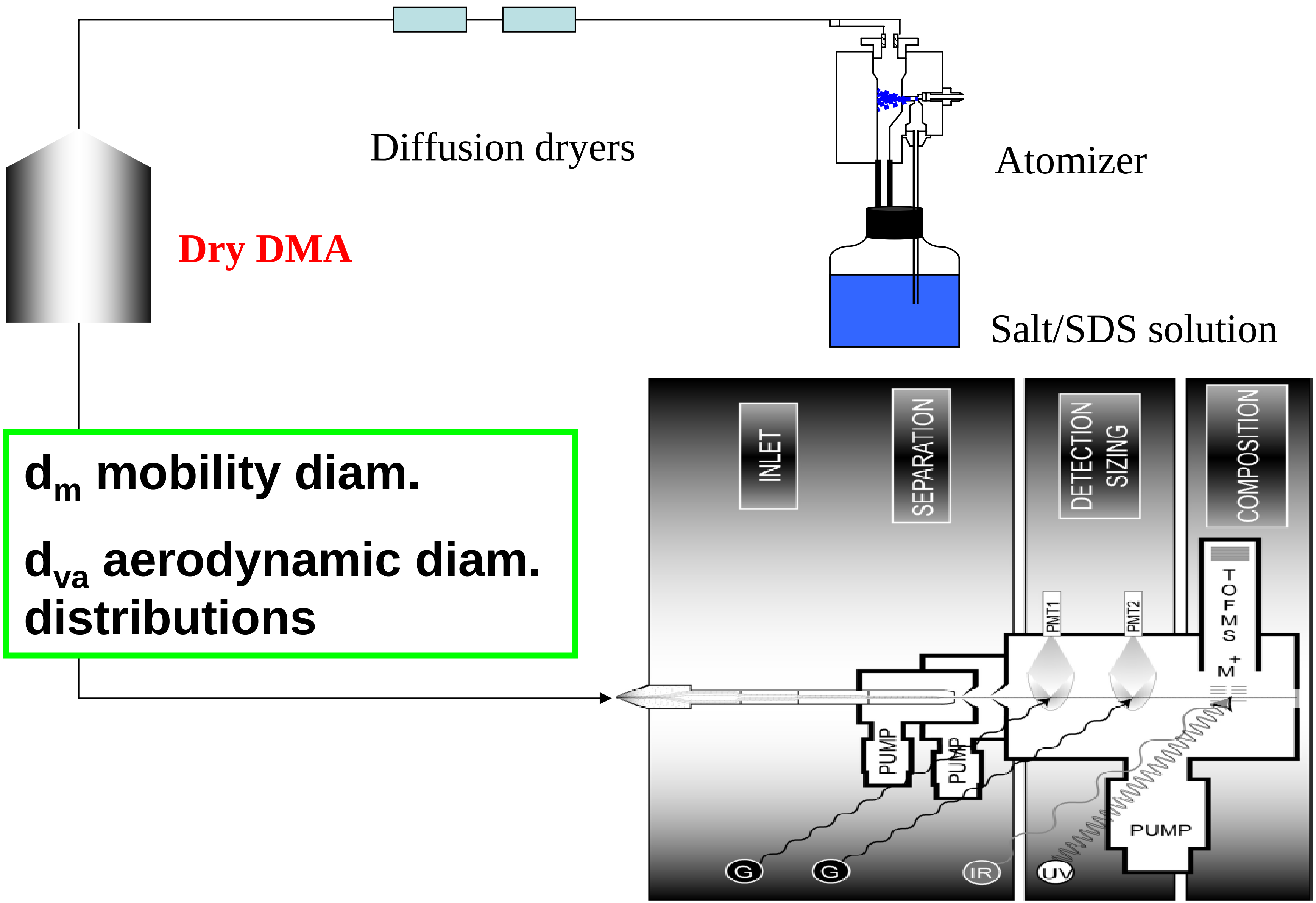
- CCN activity – surfactants did "alter" $(NH_4)_2SO_4$ particle activation, did NOT inhibit it, except for estearic acid.

Approach



Na+
NO3-
No shape factor
Na+
NO3-
Drop
Inorganic salt
Dry particle
CH3(CH2)11SO4- Na+
(SDS)
Na+
Cl-
Shape factor
Na+
Cl-

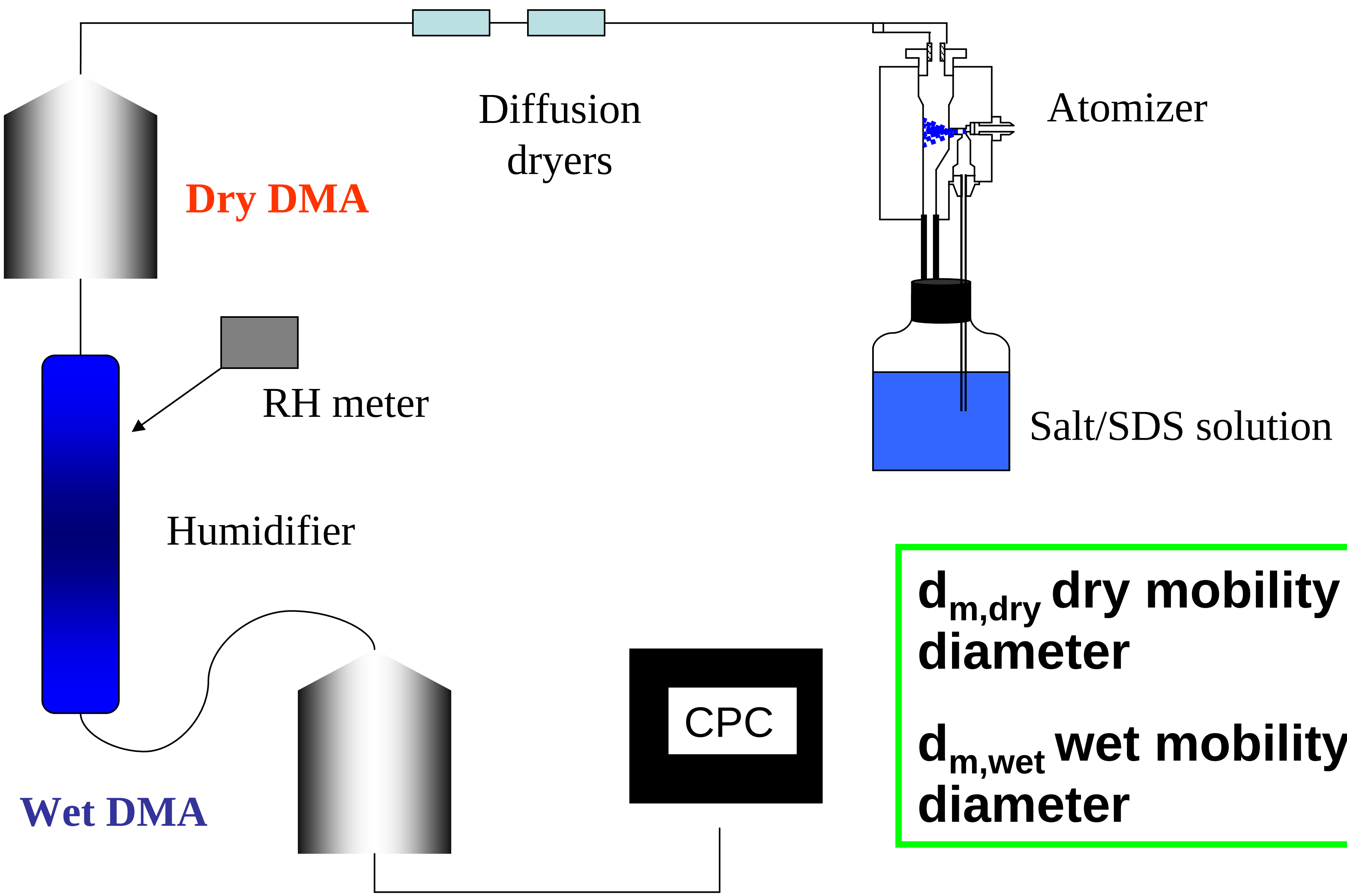
Experimental (Density)



d_m mobility diam.

d_{va} aerodynamic diam. distributions

Experimental (GFs)



$d_{m,dry}$ dry mobility diameter

$d_{m,wet}$ wet mobility diameter

Density

$$\rho_p = \rho_0 \frac{d_{va}}{d_m}$$

$$\rho_{eff} \equiv \frac{d_{va}}{d_m} = \frac{\rho_p}{\rho_0} \frac{1}{\bar{\chi}^2} \frac{C_c(d_{va}\bar{\chi}\rho_0/\rho_p)}{C_c(d_m)}$$

$$\frac{1}{\bar{\chi}^2} = 1.094 \frac{\rho_{eff}}{\rho_p} - 0.096$$

GFs

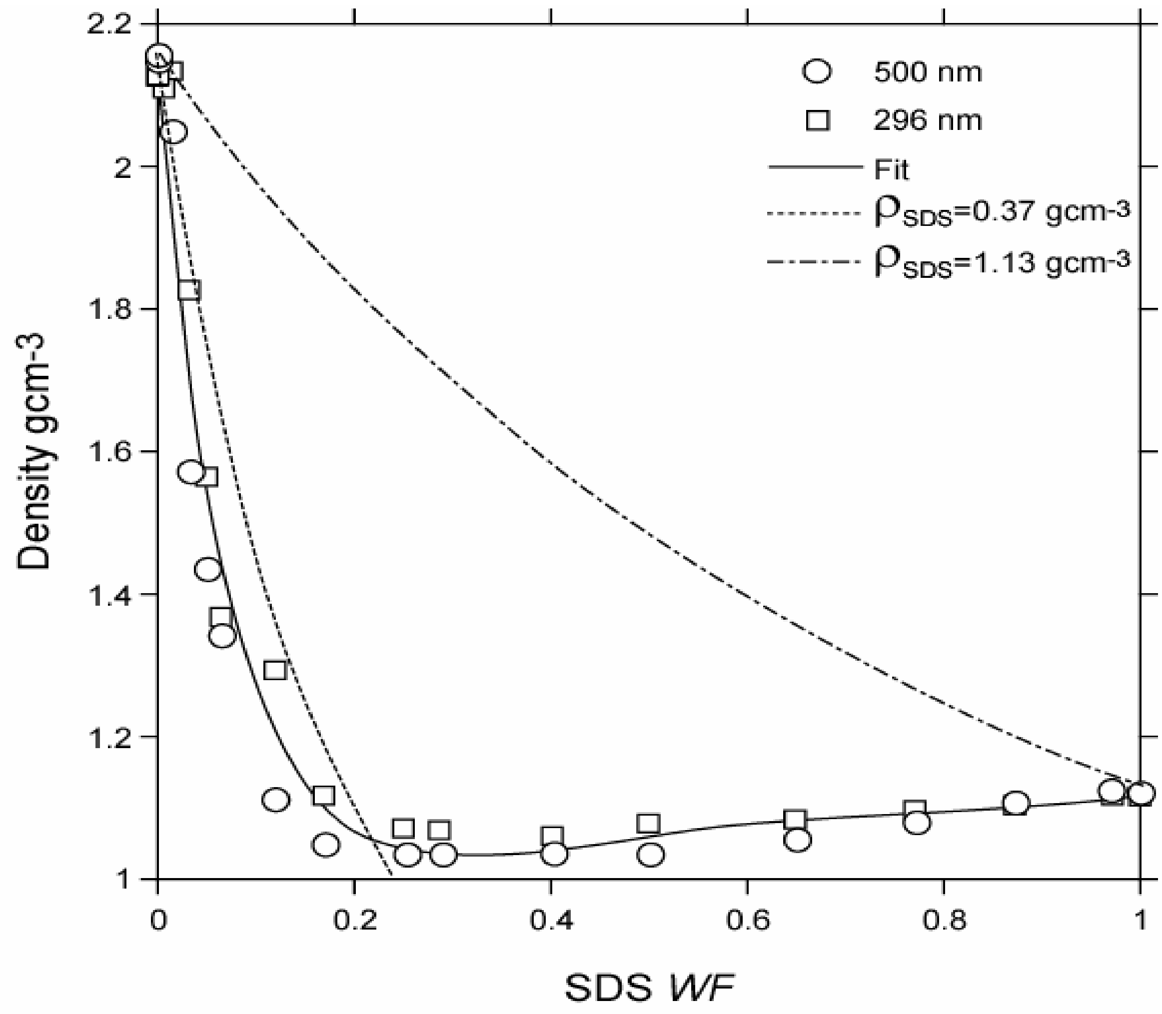
$$GF_m = \frac{d_{m,wet}}{d_{m,dry}}$$

$$GF_m = \frac{d_{m,wet}}{d_{m,dry}} = \frac{d_{ve,wet}}{d_{ve,dry}\chi_{DMA} C_c(d_{m,dry})/C_c(d_{ve,dry})}$$

$$GF = \left(\varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3\right)^{1/3}$$

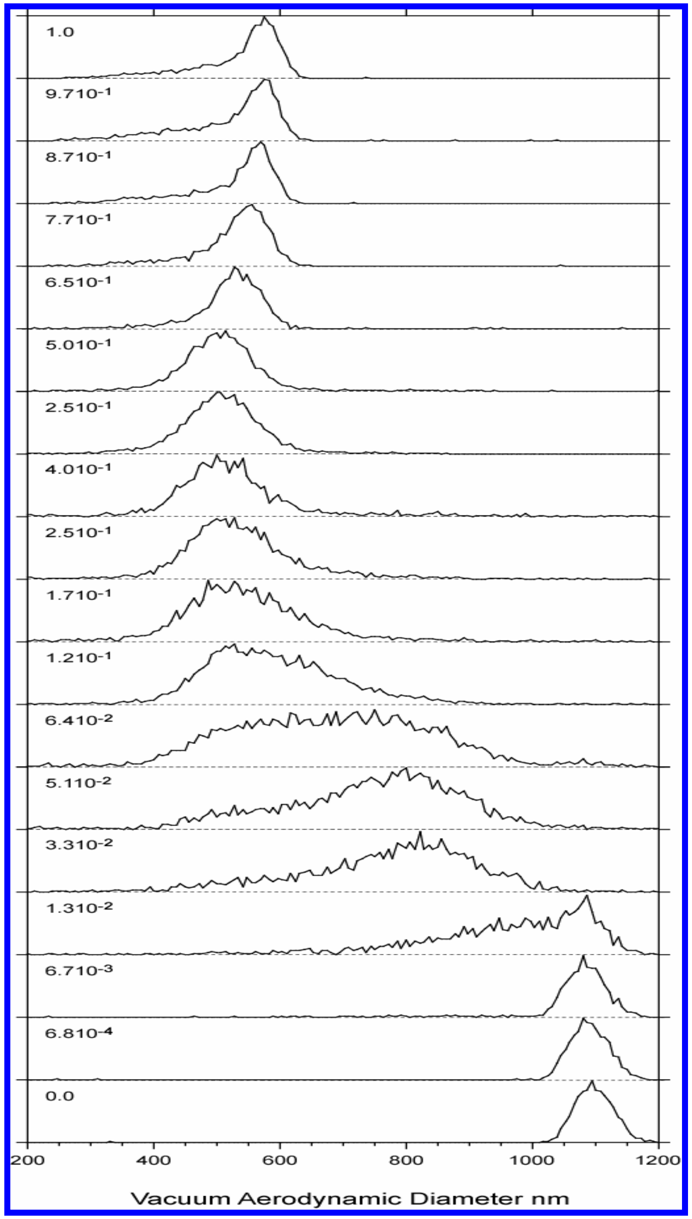
ZSR model

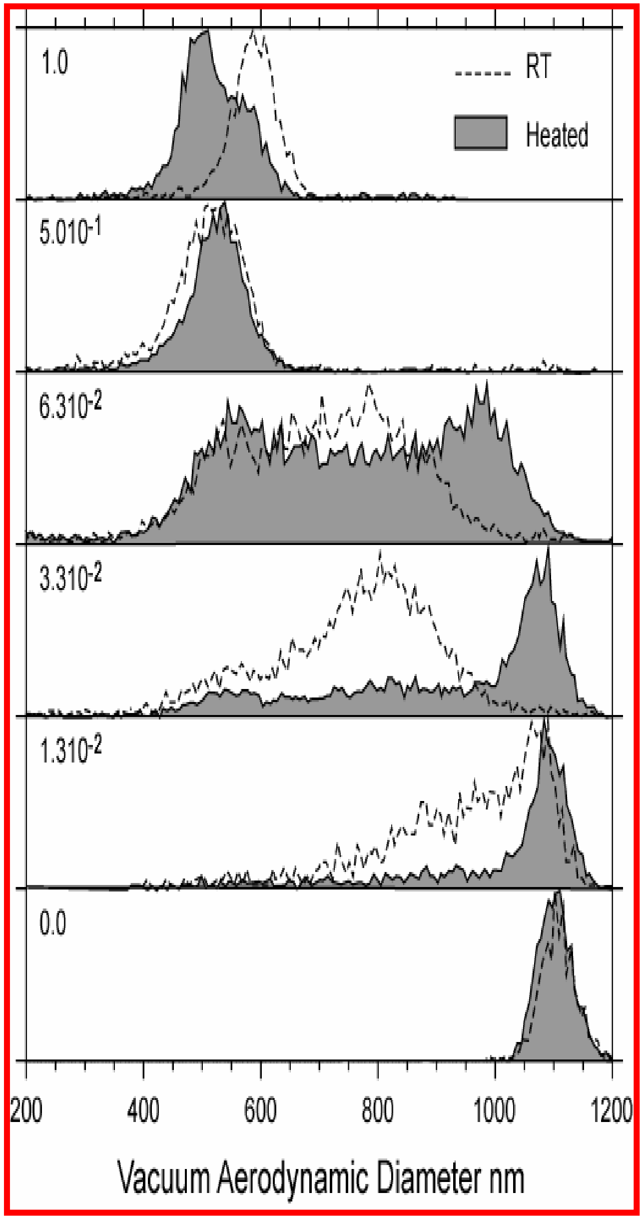
SN/SDS density



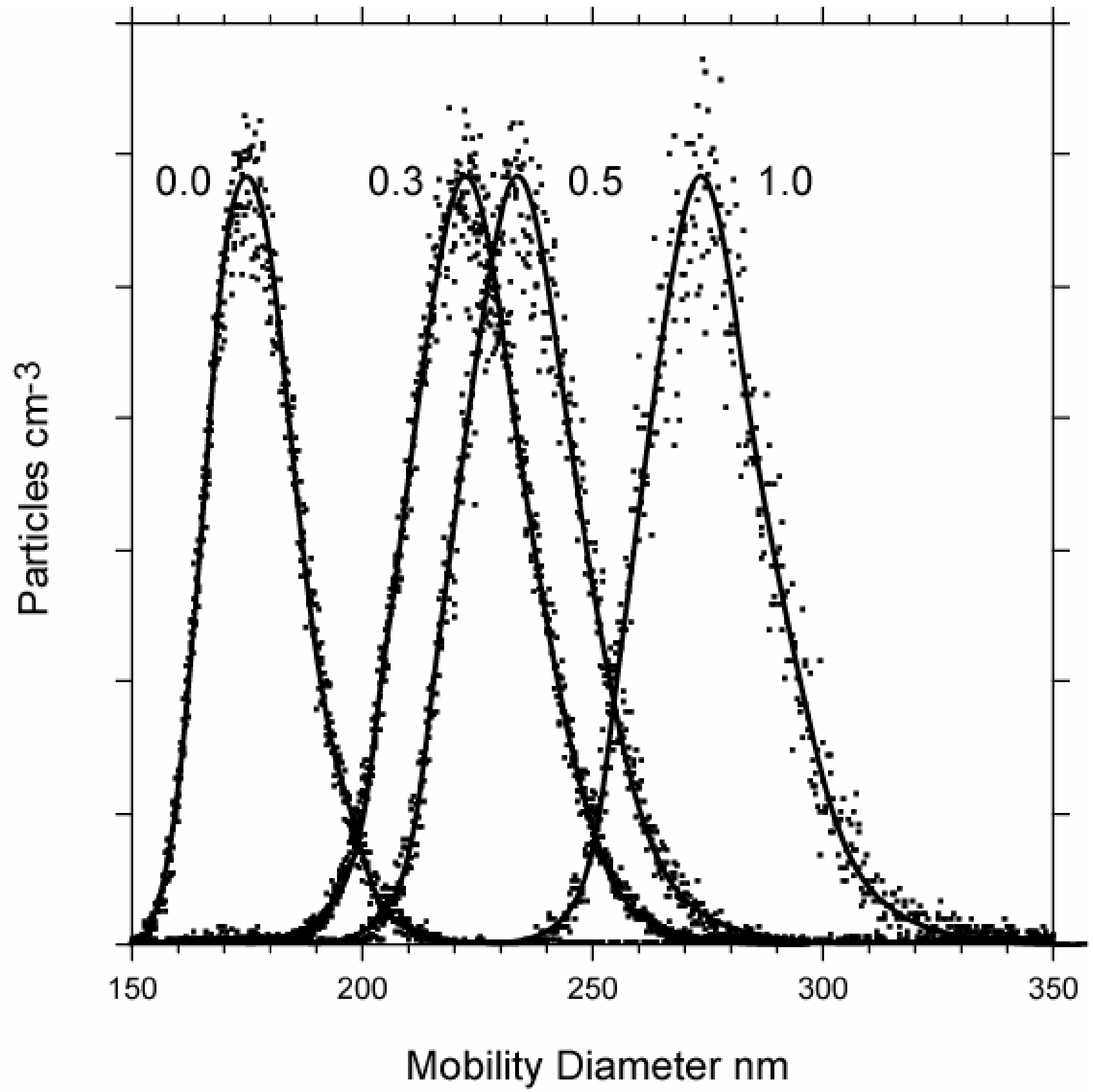
$$\rho_{SDS} = 0.24 - 3.61 \times 10^{-3} WF + 3.94 WF^{2} - 5.19 WF^{3} + 2.14 WF^{4}$$

SN/SDS d_{va} distributions



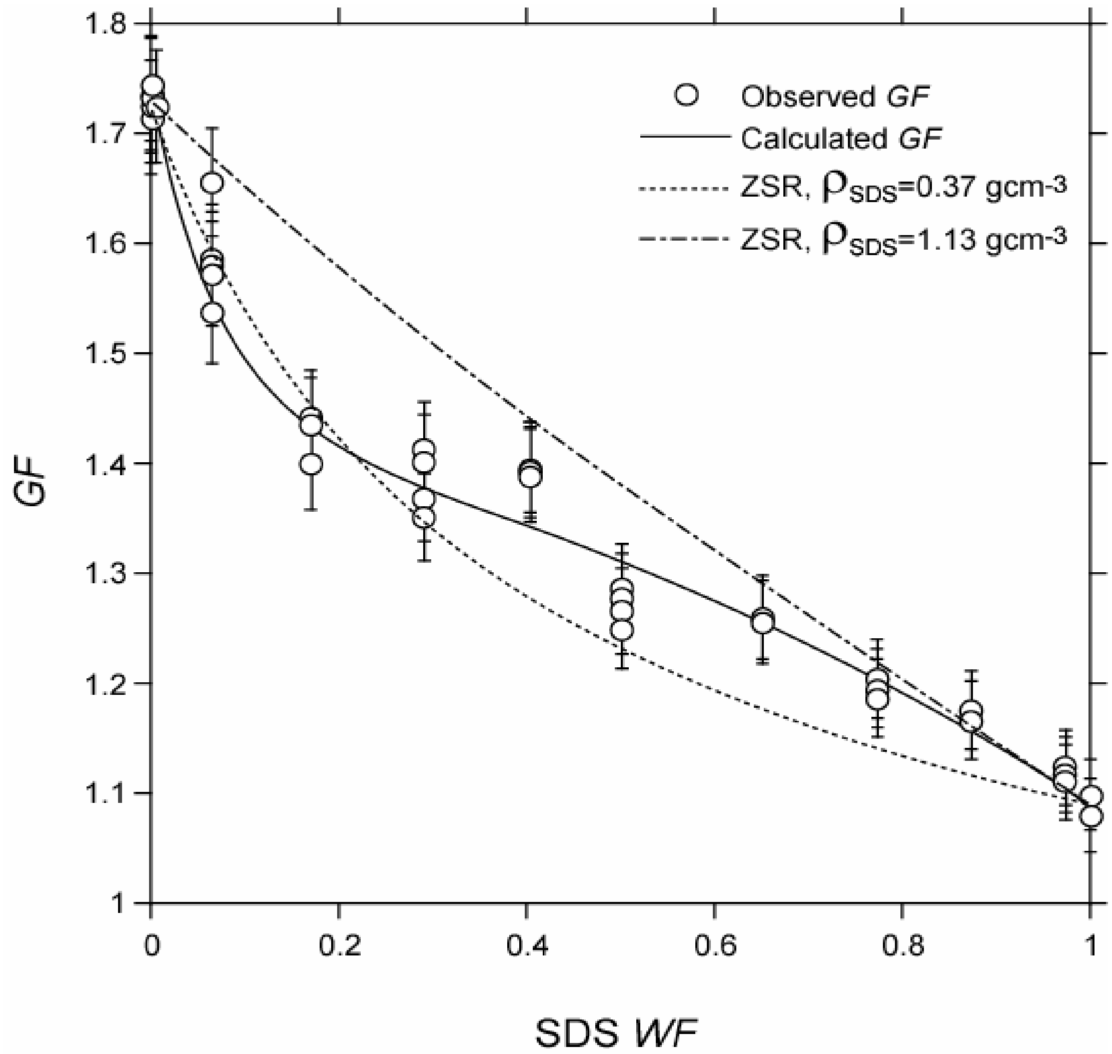


SN/SDS GFs



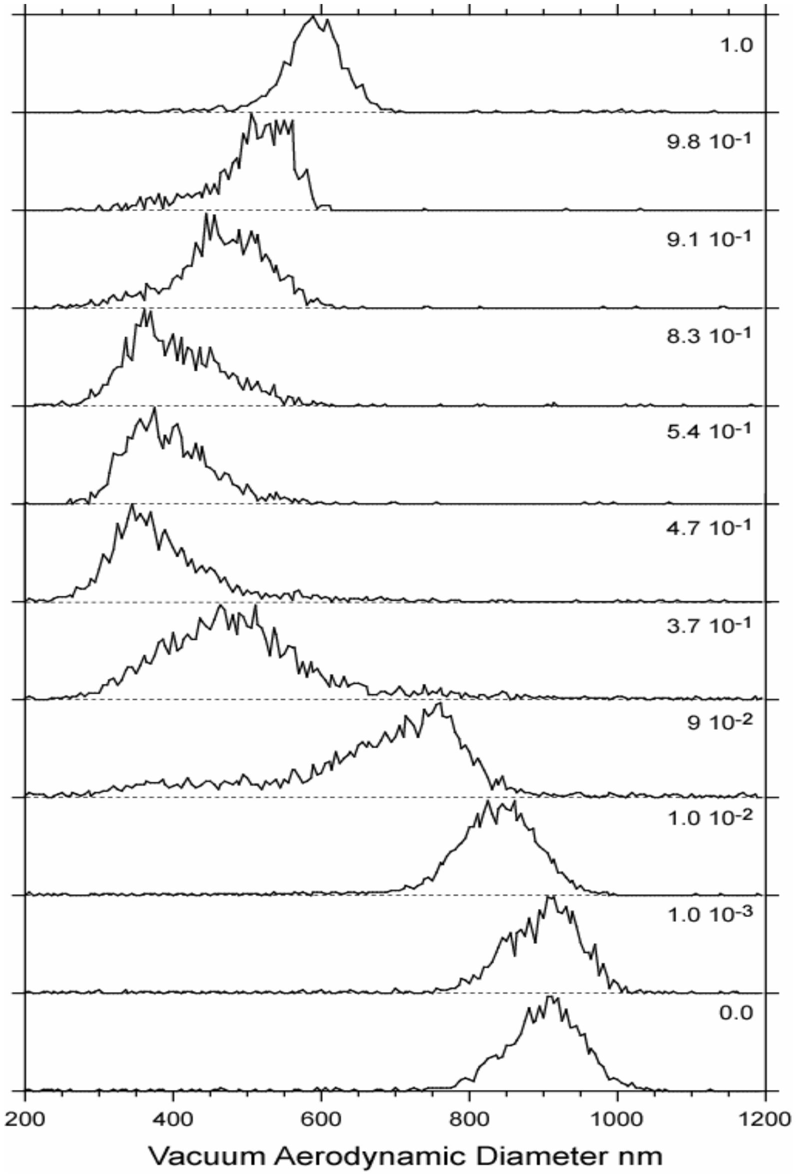
0.0
0.3
0.5
1.0
Particles cm-3
150
200
250
300
350
Mobility Diameter nm

SN/SDS GFs

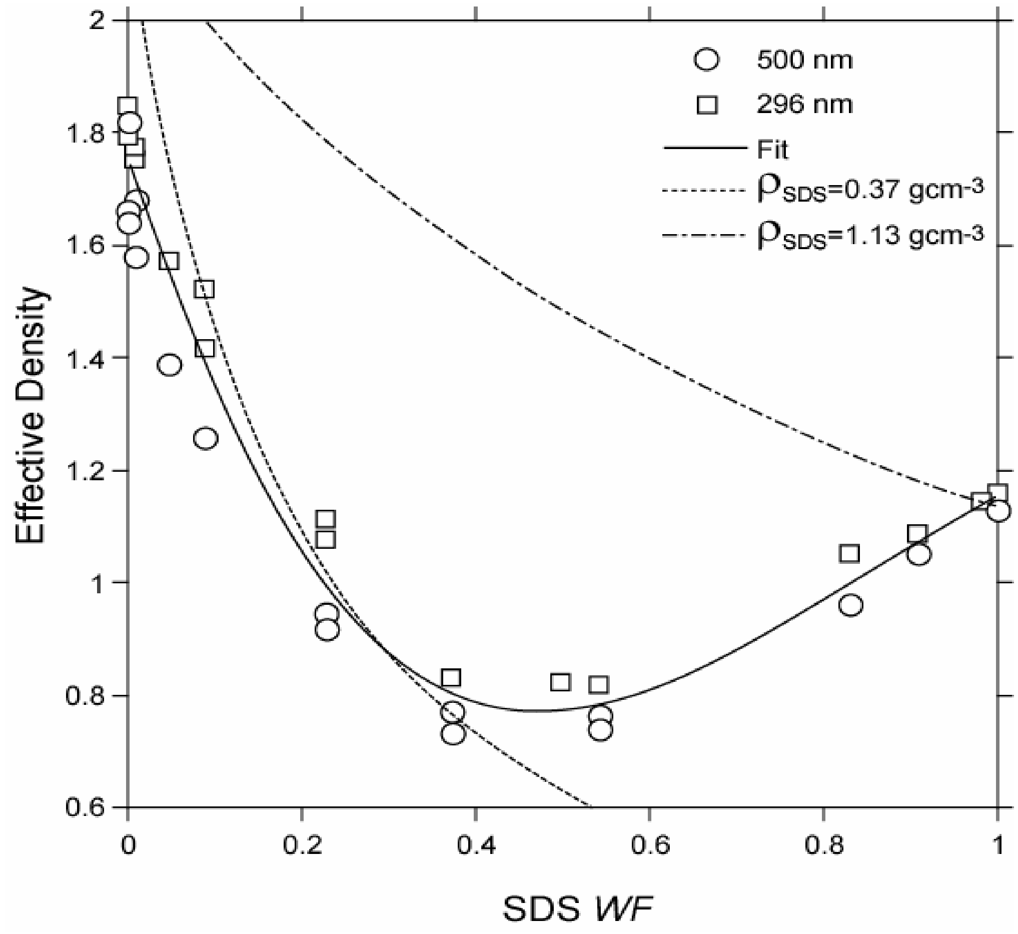


$$GF = \left(\varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3\right)^{1/3}$$

NaCl/SDS d_{va} distributions



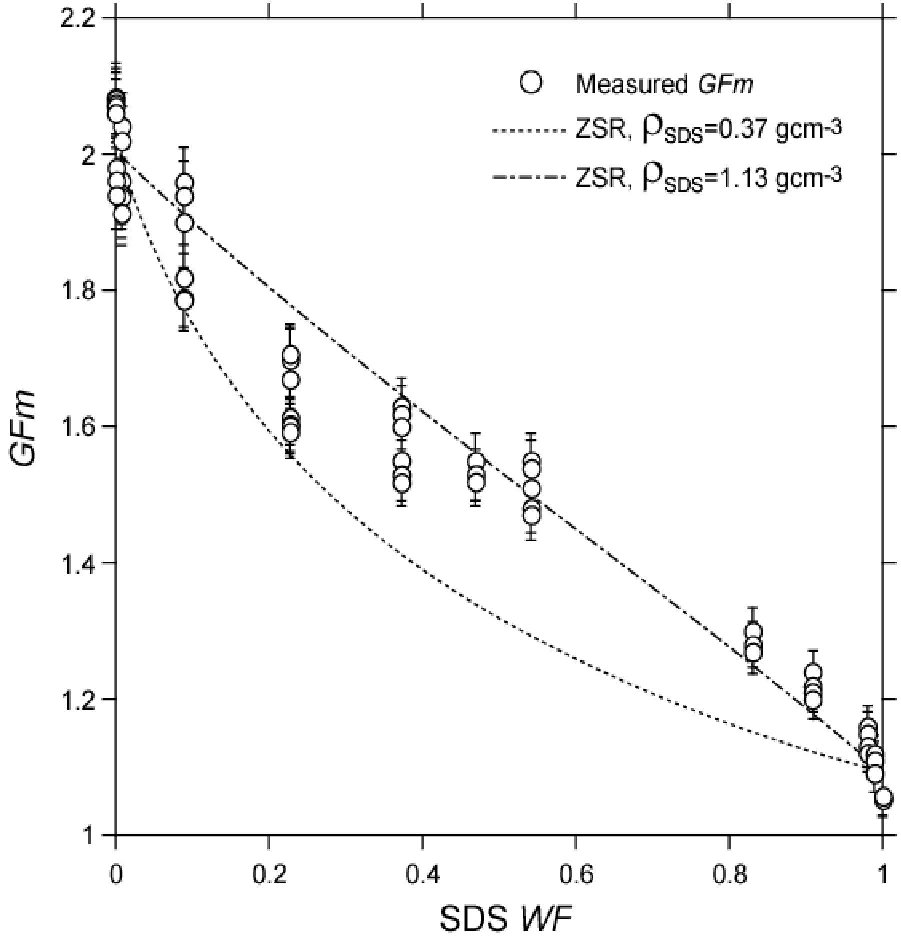
NaCl/SDS effective density

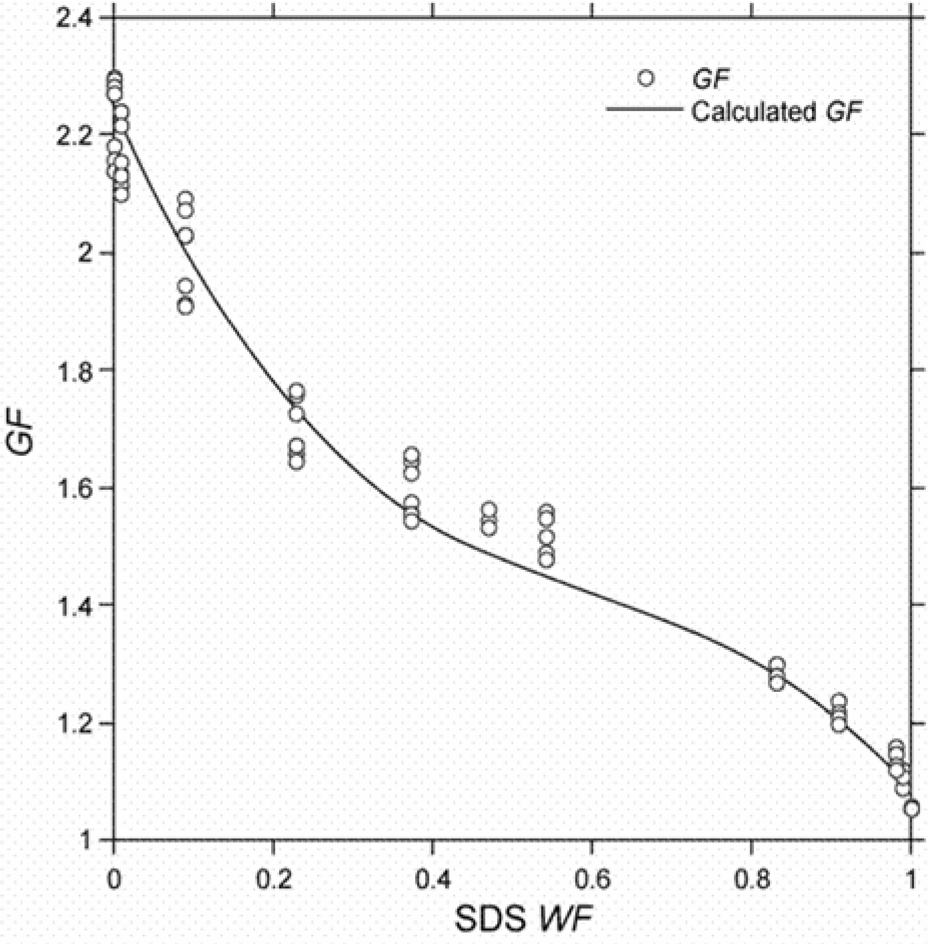


$$\rho_{SDS} = 0.381 + 0.226WF - 1.95WF^{2} + 5.01WF^{3} - 2.47WF^{4} - 0.0554WF^{5}$$

$$DSF = 1.10 - 0.467WF + 0.944WF^{2} - 1.09WF^{3} + 0.687WF^{4} - 0.181WF^{5}$$

NaCl/SDS GFs





$$GF_m = \frac{d_{m,wet}}{d_{m,dry}} = \frac{d_{ve,wet}}{d_{ve,dry}\chi_{DMA}C_c(d_{m,dry})/C_c(d_{ve,dry})}$$

Conclusions

- Quantitatively described the physical properties of SN and NaCl using multidimensional analysis where independent measurements are coupled and fit.
- Behavior is complex (composition, RH, shape).
- These data (or method) could be used in prediction models and ambient sampling of organic aerosols.