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

Luis A. Cuadra-Rodríguez
University of Colorado at Boulder
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 $\rightarrow$ relative humidity at which particles lose all the water and crystallized. (liquid $\rightarrow$ solid)

• Deliquesce $\rightarrow$ relative humidity at which particles gain water and become a droplet. (solid $\rightarrow$ liquid)

• Growth Factors (GFs)
Sub-micron-size Particles Properties

Sodium Chloride, $\text{Na}^+\text{Cl}^-$

Efflorescence $\sim 42\%$ RH
Deliquescent $\sim 78\%$ RH

Ammonium Chloride, $(\text{NH}_4^+)_2\text{SO}_4^{2-}$

Efflorescence $\sim 37-40\%$ RH
Deliquescent $\sim 80\%$ RH

Micron-sized Particles Properties

\((\text{NH}_4^+)_2\text{SO}_4^{2-}\)

\[ a_w = 1.00 + \sum C_i w_{fi} \]
\[ RH = 100 \ a_w \]

\[ \rho = 1.00 + \sum A_i w_{fi} \]

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


• 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” \((\text{NH}_4)_2\text{SO}_4\) particle activation, did NOT inhibit it, except for estearic acid.
Approach

Drop

\[ \text{Na}^+ \quad \text{NO}_3^- \]

No shape factor

\[ \text{Inorganic salt} \quad \text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \quad \text{Na}^+ \quad (\text{SDS}) \]

Dry particle

\[ \text{Na}^+ \quad \text{NO}_3^- \]

Shape factor

\[ \text{Na}^+ \quad \text{Cl}^- \]

\[ \text{Na}^+ \quad \text{Cl}^- \]
Experimental (Density)

- Dm mobility diam.
- dv aerodynamic diam.
- distributions

Diagram:
- Diffusion dryers
- Atomizer
- Dry DMA
- Salt/SDS solution
Experimental (GFs)

- Dry DMA
- RH meter
- Humidifier
- Diffusion dryers
- Atomizer
- Salt/SDS solution
- Wet DMA
- CPC

**dm,dry** dry mobility diameter

**dm,wet** wet mobility diameter
Density

\[ \rho_p = \rho_0 \frac{d_{va}}{d_m} \]

\[ \rho_{eff} = \frac{d_{va}}{d_m} \rho_p \frac{1}{\rho_0} \frac{\frac{C_c(d_{va}\chi \rho_0)}{\rho_p}}{\frac{d_m}{d_{va}}} \]

\[ \frac{1}{\chi} = 1.094 \frac{\rho_{eff}}{\rho_p} - 0.096 \]

GFs

\[ GF_m = \frac{d_{m,wet}}{d_{m,dry}} \]

\[ GF = \frac{d_{ve,wet}}{d_{ve,dry} C_{DMA} C_c(d_{m,dry})/C_c(d_{ve,dry})} \]

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

ZSR model
$\rho_{SDS} = 0.24 - 3.61 \times 10^{-3} WF + 3.94 WF^2 - 5.19 WF^3 + 2.14 WF^4$
SN/SDS $d_{va}$ distributions
SN/SDS GFs

[Graph showing distribution of particles as a function of mobility diameter in 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.