Effects of Soluble Surfactants on Particle Properties

Luis A. Cuadra-Rodríguez
Prof. G. Barney Ellison
University of Colorado at Boulder
GREF Fellow

Dr. Alla Zelenyuk
PNNL-EM SL

CGEP End-of-Summer
August 17th, 2010
OUTLINE

• Introduction to Marine Aerosol Model
  – Ongoing work and highlights
• Background on hygroscopic (Inorganic) particles
• Experimental Approach
• Results
• Conclusions
**Marine Aerosol Model**


- “Inverted” micelle
- Water core \((10^{10})\) surrounded by surfactants \((10^7)\) for a 1µm aerosol
- Poor CCN
- Atmospheric oxidants make them good CCN
- Accounts for C mass on atm
• Gill *et al.* proposed the same model 1983
  – Soluble vs Insoluble surfactants
  – Equilibrium vs surface partition
  – Photochemistry
  – Role of water
  – Transport
  – Chemistry
Marine Aerosol Model (cont…)

- Thorton group (University of Washington)
- Sodium Dodecyl Sulfate (SDS)
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, $\text{Na}^+\text{Cl}^-$

- Efflorescence ~ 42% RH
- Deliquescence ~ 78% RH

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

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


Micron-sized Particles Properties

\[(NH_4^+)_2SO_4^{2-}\]

\[a_w = 1.00 + \sum C_i w_f i\]

\[RH = 100a_w\]

\[\rho = 1.00 + \sum A_i w_f i\]

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

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

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


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.
Approach

Na\(^+\)  NO\(_3^-\) → Na\(^+\)  NO\(_3^-\)

No shape factor

Inorganic salt

CH\(_3\)(CH\(_2\))\(_{11}\)SO\(_4^-\)  Na\(^+\)
(SDS)

Na\(^+\)  Cl\(^-\) → Na\(^+\)  Cl\(^-\)

Shape factor
Experimental (Density)

Dry DMA

Diffusion dryers

Atomizer

Salt/SDS solution

$d_m$ mobility diam.

d$_{va}$ aerodynamic diam. distributions
Experimental (GFs)

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

$d_{m,dry}$ dry mobility diameter

$d_{m,wet}$ wet mobility diameter
Density

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

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

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

GFs

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

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

ZSR model
\[ \rho_{SDS} = 0.24 - 3.61 \times 10^{-3} WF + 3.94WF^2 - 5.19WF^3 + 2.14WF^4 \]
\[ GF = \left( \varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3 \right)^{1/3} \]
SN / SDS GFs

![Graph showing the relationship between GF and SDS WF]

\[ GF = \left( \varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3 \right)^{1/3} \]
NaCl/ SDS $d_{va}$ distributions
NaCl/ SDS effective density

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

\[ DSF = 1.10 - 0.467WF + 0.944WF^2 - 1.09WF^3 + 0.687WF^4 - 0.181WF^5 \]
\[
GF_m = \frac{d_{m,\text{wet}}}{d_{m,\text{dry}}} = \frac{d_{\text{ve, wet}}}{d_{\text{ve, dry}} \chi_{\text{DMA}} C_c(d_{m, \text{dry}})/C_c(d_{\text{ve, dry}})}
\]
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.
10-30 mJ/10 ns pulse
2.94 µm focused to 1 mm

50 mW 532 nm diodes

PM Ts for green scattered light

Drift Region

Capillary inlet
Ø = 0.5mm x 10 cm
Gracias

- GCEP-GREF (Milton Constantin, Jeff Gaffney, Nancy Marley, Rick Petty, Staff)
- Dr. Alla Zelenyuk (PNNL-EMSL)
- B. Ellison and Ellison’s group
- DOE-Basic Science
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.