Cloud Condensation Nuclei

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- Köhler theory
- Complications

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Assumptions

- Particles are composed of internal mixtures of salts and insoluble components.
- Bulk hygroscopicity = volume-weighted mean of hygroscopicity of all components.
- Supersaturation is small.
- Particle water dominates the dry volume.
- Aerosol can be described by multiple log-normal size distributions, each with uniform bulk hygroscopicity.
- CCN concentration is determined by the number with critical supersaturation less than the maximum supersaturation.

Köhler Theory: Droplet Growth and Supersaturation

$$r\frac{dr}{dt} = G(S - \frac{A}{r} + \frac{\kappa r_d^3}{r^3})$$

droplet water balance
Köhler (1938)

$$\frac{dS}{dt} = \underbrace{\alpha V}_{\text{cooling}} - \underbrace{\gamma \int \frac{dW}{dt}}_{\text{condensation}}$$

supersaturation balance

$$A = \frac{2\tau M_w}{\rho_w RT}$$

r : droplet radius

r_d : dry radius

G : diffusivity

S : supersaturation = RH-1

τ : surface tension

κ: hygroscopicity parameter

V : vertical velocity

Köhler Theory at Equilibrium

$$r\frac{dr}{dt} = G(S - \frac{A}{r} + \frac{\kappa r_d^3}{r^3})$$

At equilibrium,

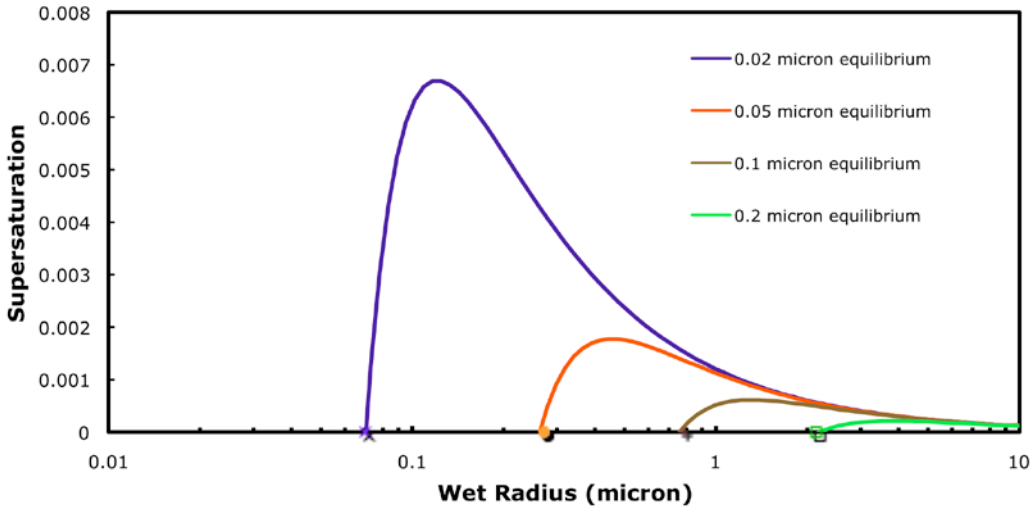
$$S_{eq} = \frac{A}{r} - \frac{\kappa r_d^3}{r^3}$$

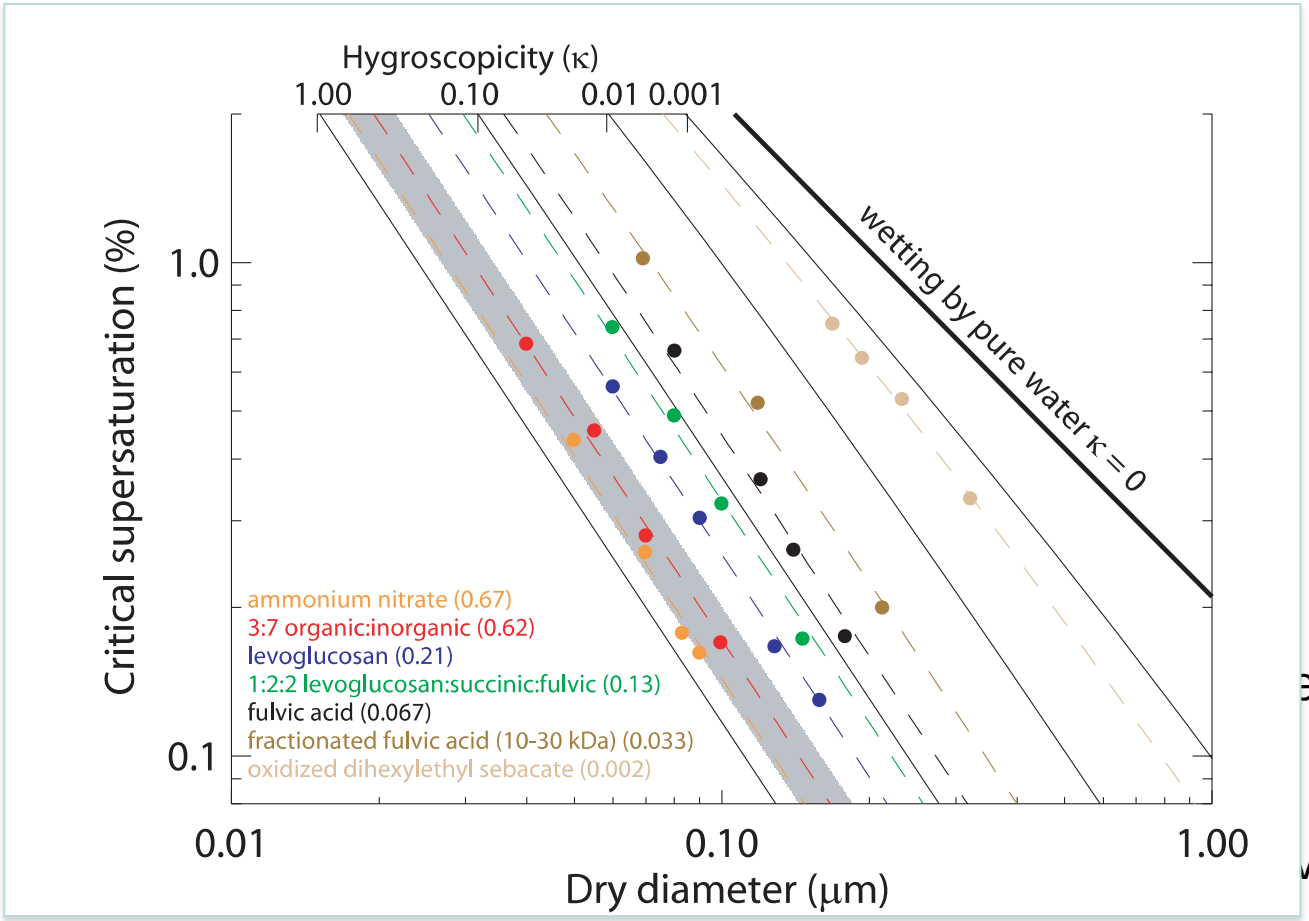
At the maximum of the Köhler curve, $r^4 \frac{dS_{eq}}{dr} = -Ar^2 + 3\kappa r_d^3 = 0$

$$\Rightarrow r_c^2 = \frac{3\kappa r_d^3}{A}$$

Then

$$S_c^2 = \frac{4A^3}{27\kappa r_d^3}$$





es of solute in particle

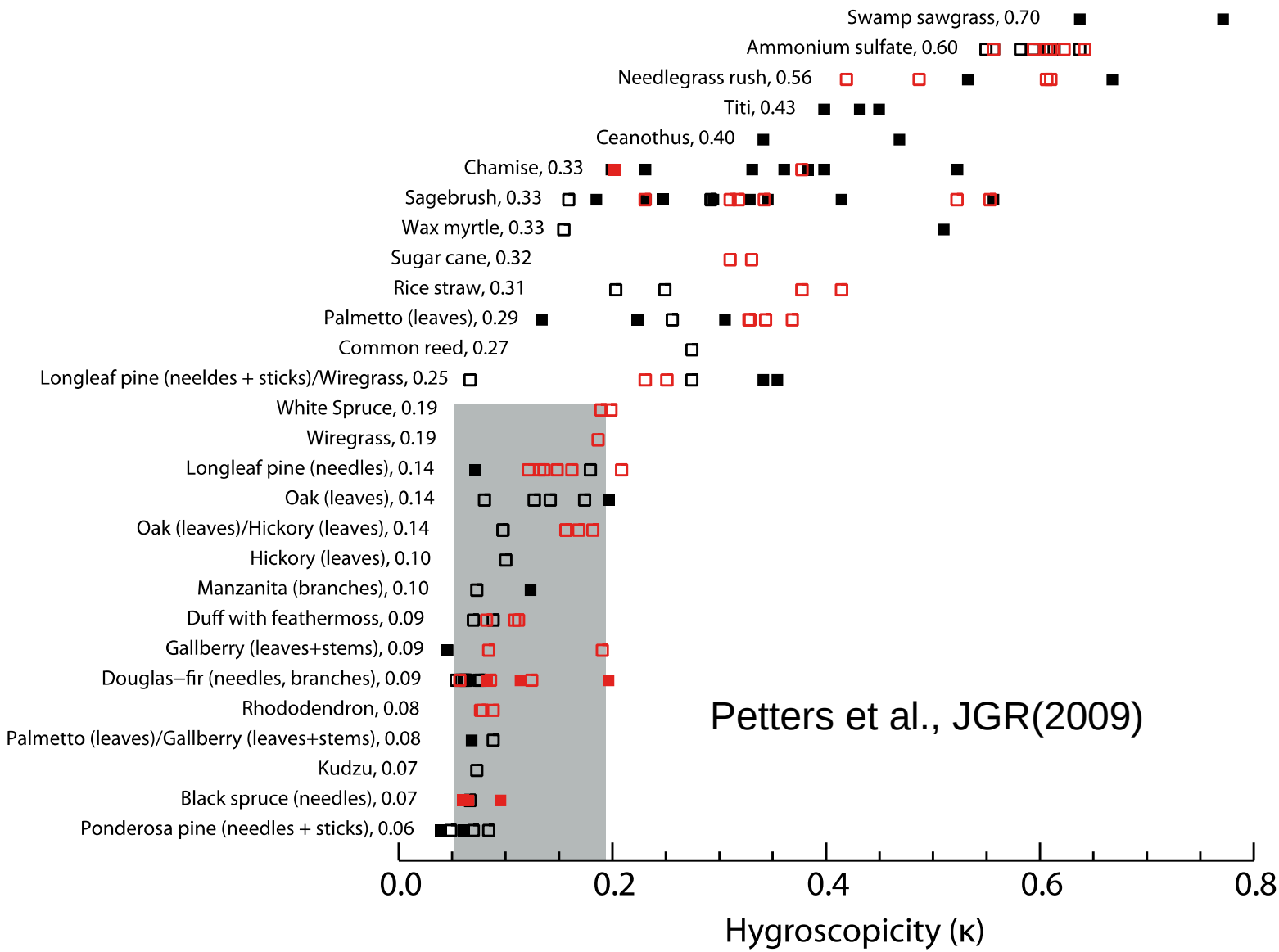
volume of particle

- Petters and Kreidenweis (2007) $\kappa = \frac{4A^3}{27S_c^2 r_d^3}$

| for different materials

NaCl	1.28	Petters and Kreideweis (2007)
$(NH_4)^2 SO_4$	0.61	Petters and Kreideweis (2007)
a–pinene/O_3/dark secondary organic aerosol	0.1	Petters and Kreideweis (2007)
dust	0.01-0.08	Kohler et al. (2009)
BC	0.00	
Biomass burning	0.05-0.5	Petters et al. (2009)

Biomass Burning Hygroscopicity



Mixtures of Components

$$\kappa = \sum \varepsilon_i \kappa_i$$

Petters and Kreidenweis, ACP (2007)

From size distribution to CCN concentration

$$\frac{dN}{d\ln r_d} = \sum_m \frac{N_m}{\sqrt{2\pi}\ln\sigma_m} \exp\left(-\frac{\ln^2(r_d/r_m)}{2\ln^2\sigma_m}\right)$$

Convert from size distribution of number to S_c distribution

$$\frac{dN}{d\ln S_c} = \frac{dN}{d\ln r_d}\frac{d\ln r_d}{d\ln S_c}$$

From $S_c^2 = \frac{4A^3}{27\kappa r_d^3}$ $\longrightarrow$ $\frac{d\ln r_d}{d\ln S_c} = -\frac{2}{3}$

$$\frac{dN}{d\ln S_c} = -\sum_m \frac{2N_m}{3\sqrt{2\pi}\ln\sigma_m} \exp\left(-\frac{\ln^2(S_m/S_c)^{2/3}}{2\ln^2\sigma_m}\right) \qquad S_m^2 = \frac{4A^3}{27\kappa r_m^3}$$

CCN is number with $S_c < S$. Assume all particles in mode have same composition.

$$CCN(S) = \frac{1}{2}\sum_m N_m\left[1 - \mathrm{erf}(z_m)\right]$$

where $z_m \equiv 2\ln(S_m/S)/(3\sqrt{2}\ln\sigma_m)$

How CCN concentration is used in models

- N_m and mass concentrations of each component in the mode are predicted.
- κis diagnosed from the volume mean ofκ for all components in the mode.
- CCN concentration is diagnosed from size distribution and κ at specific S
- S_{max} parameterized in terms of aerosol and updraft velocity
- The challenge is to determine the maximum supersaturation S_{max}

Complications

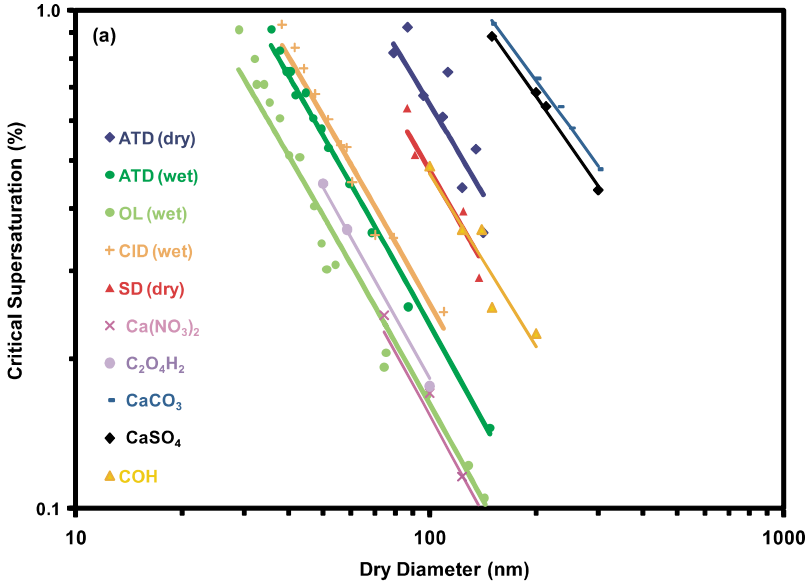
- Adsorption
- Surfactants
- Semi-volatile soluble components

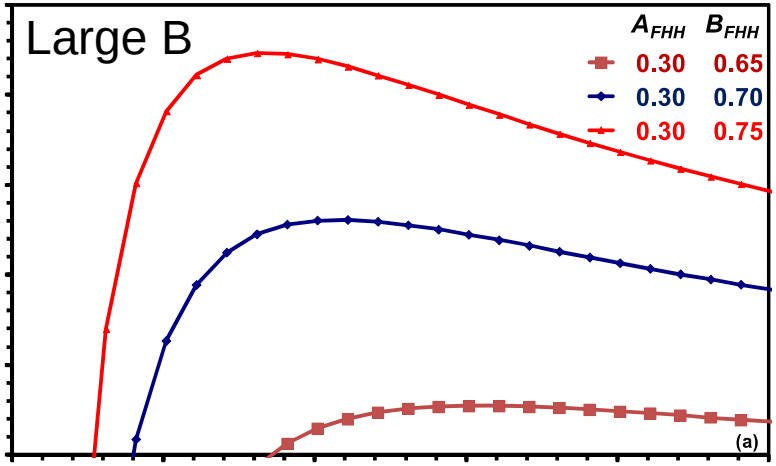
Adsorption by Dust

$$S_{eq} = \frac{A}{r} - C\left(\frac{r - r_d}{2r_w}\right)^{-B}$$

Kumar et al., ACP (2009a,b)

$$S_c = Cr_d^x \quad x \approx -0.9$$





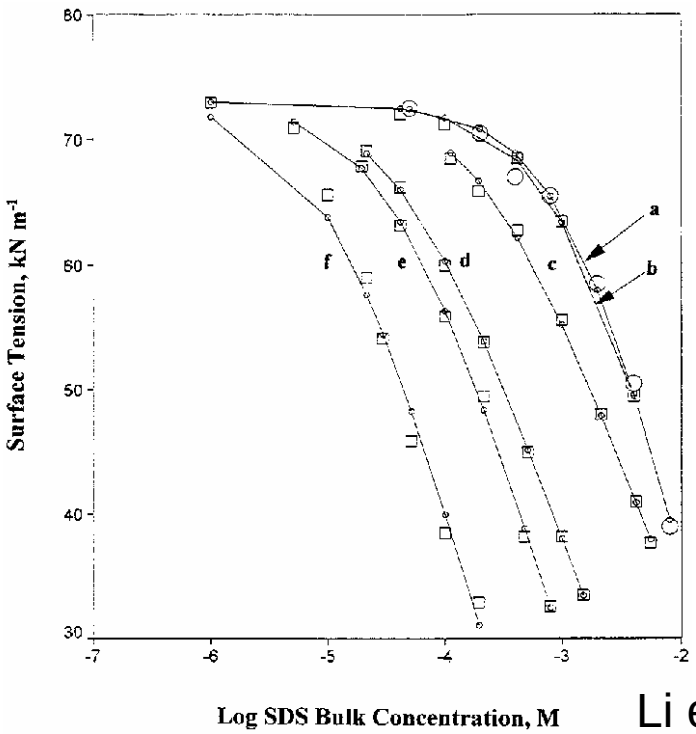
Small B

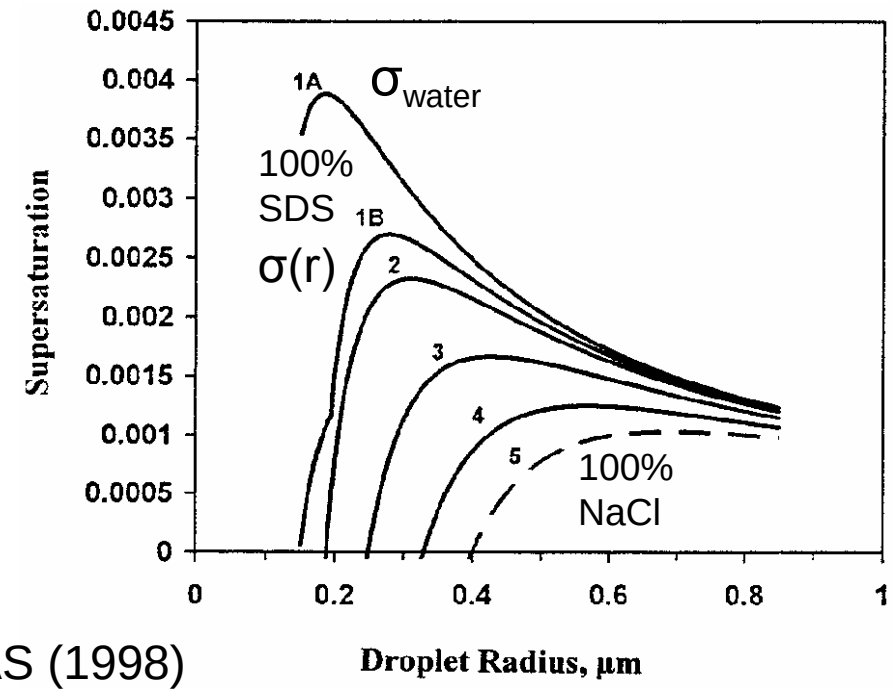
Surface Tension Effects

Abdul-Razzak and Ghan, JGR 2004

- Surfactants suppress surface tension, particularly at high concentrations.
- Suppression of surface tension decreases as droplets become diluted during condensation.
- For activation it is only the surface tension at activation that matters.
- The critical radius and supersaturation follow from solving for the maximum in the Köhler curve:

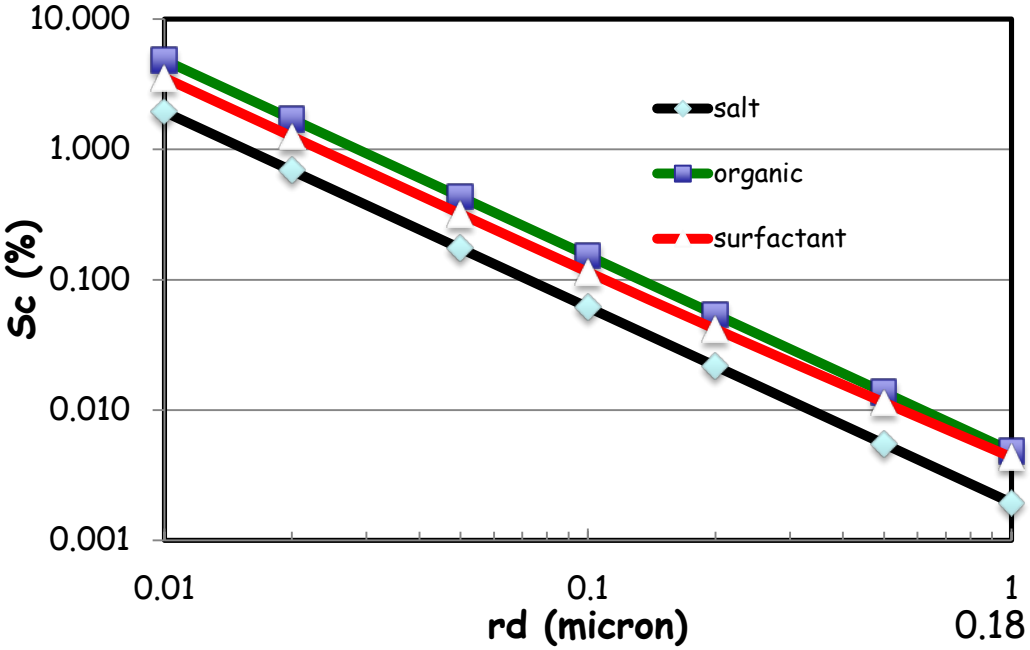
$$r_c^4 \frac{dS_{eq}}{dr_c} = -Ar_c^2 + 3\kappa r_d^3 + r_c^3 \frac{dA}{dr_c} = 0$$



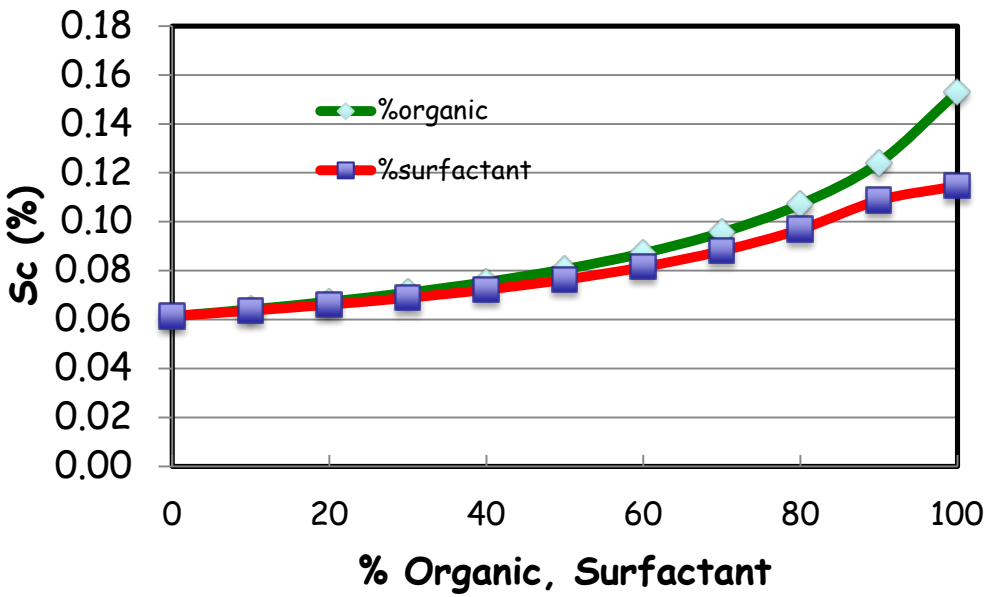


Li et al. JAS (1998)

Surfactant vs Hygroscopicity

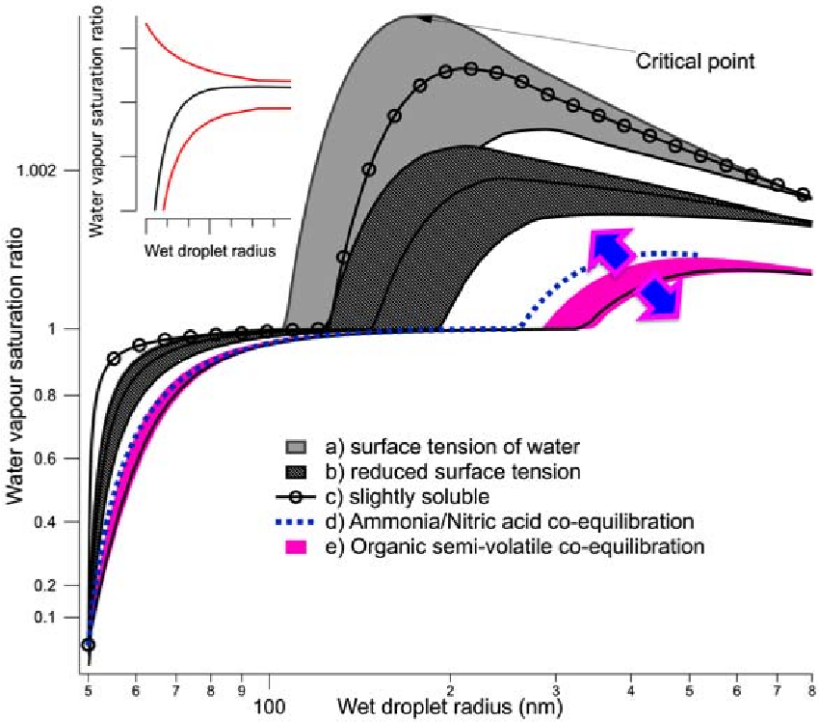


- hygroscopicity difference more important than surfactant effect



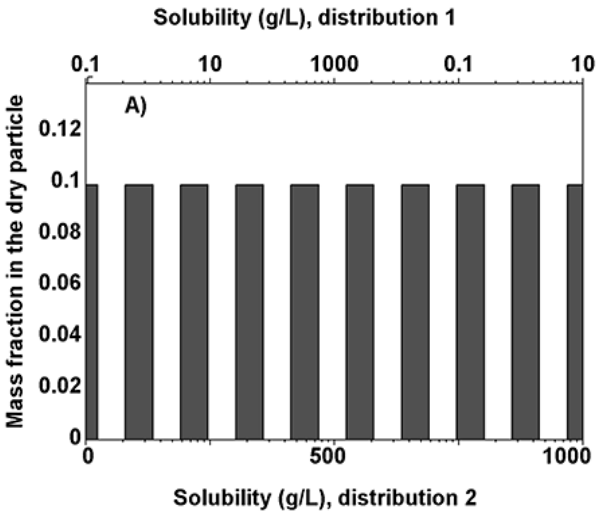
Co-Condensation of Semi-Volatile Soluble Components

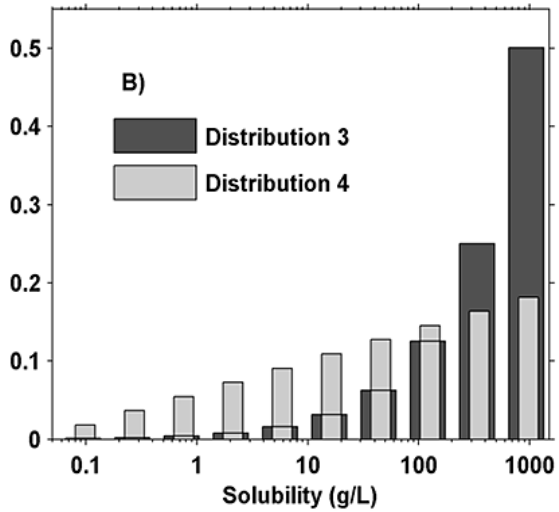
- Condensed and dissolved semi-volatile mass increases as droplet volume increases
- Increased size and solute reduces Sc $S_c^2 = \frac{4A^3}{27\kappa r_d^3}$
- This effect depends on aerosol number concentration too
- Hard to represent in models

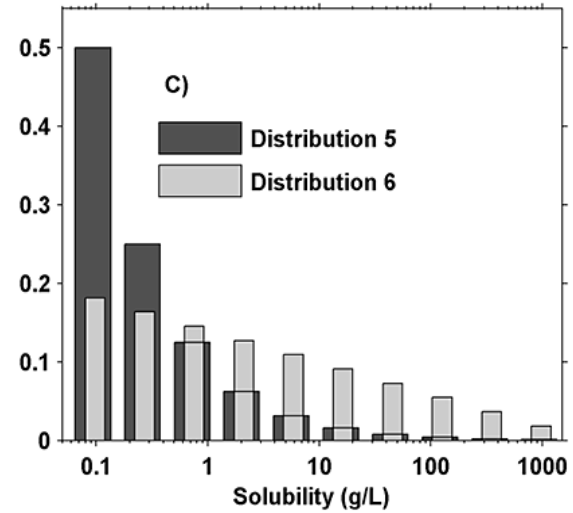


Topping and McFiggins, ACP (2012)

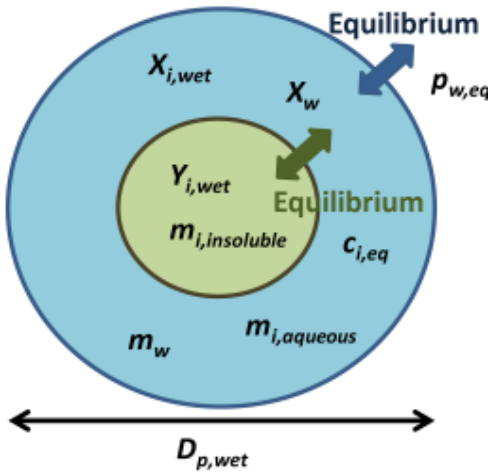
Solubility Basis Set



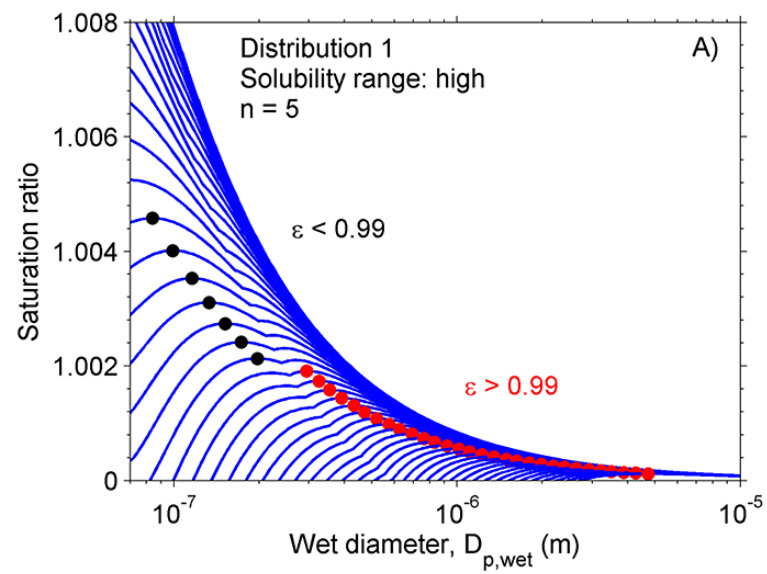




Riipinen et al., ACPD (2014)
3 simplifying assumptions :
(1) complete dissolution at the point of activation, (2) combining the aerosol solubility with molar mass and density into a single hygroscopicity parameter κ, (3) assuming a fixed water-soluble fraction ε_{eff}



Wet particle with organics and water in equilibrium



Conclusions

- Theory for salts is mature
- Hygroscopicity can be determined from size-resolved measurements of S_c
- Adsorption by dust can be represented
- Surfactant effects can be neglected
- Co-condensation of soluble components can be important but difficult to represent
- Solubility Basis Set and equivalent κ provide a path forward