What Impact do SOAs have on Light Extinction?

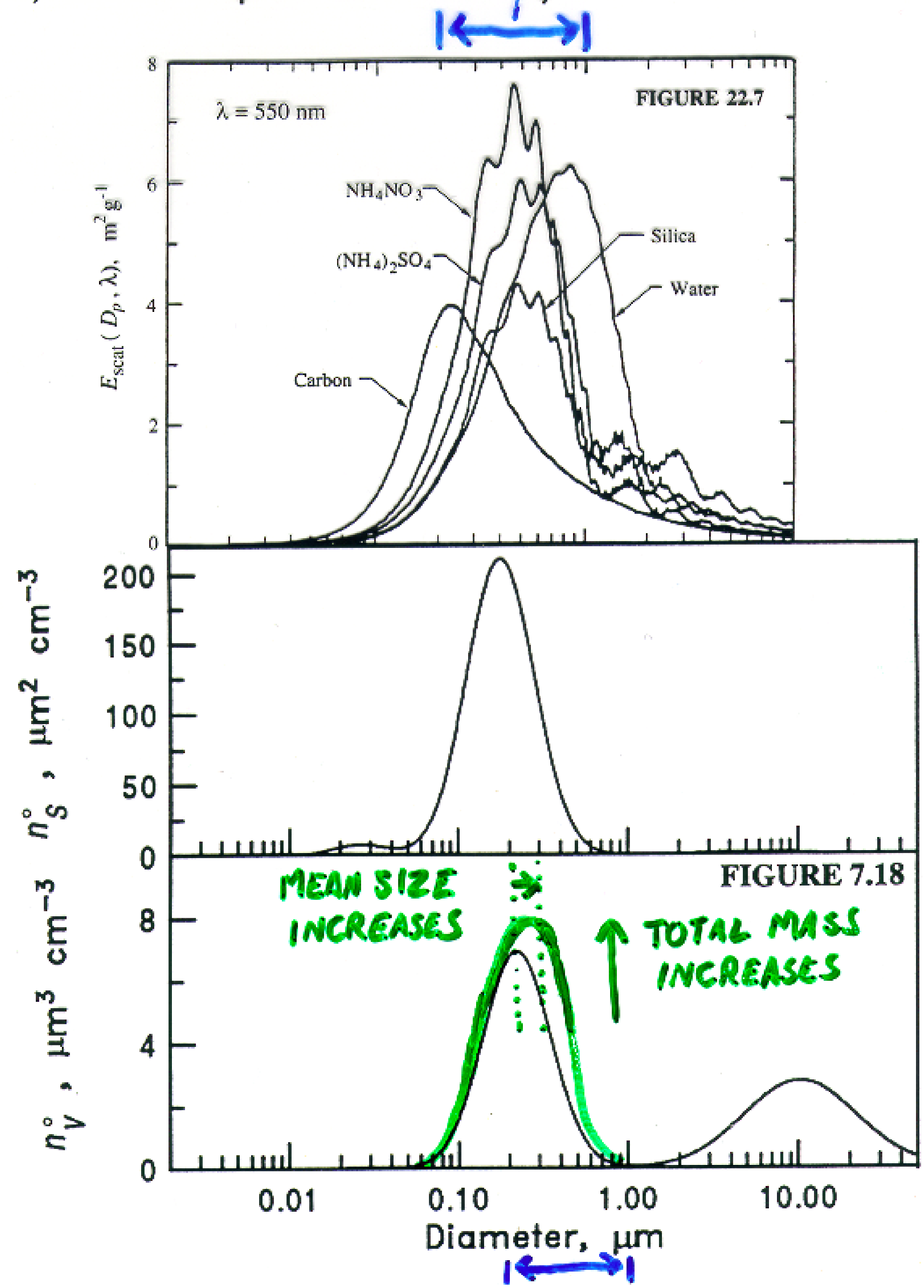
(1) Condense onto existing particulate matter, increasing airborne mass and altering the size distribution

(2) Condensed coating may add to or may inhibit water uptake by the core particles

On What Particle Sizes do you find SOAs?

Depends on ambient size distribution present:

Will tend to accumulate most significantly on 0.2–1.0 um particles, where impact on visibility will be substantial.



(from Seinfeld and Pandis, *Atmos.Chem.&Physics*, Wiley-Intersc., ©1997)

What is Hygroscopic Behavior?

Water-soluble species such as certain inorganic salts will take up water under elevated relative humidity conditions.

This water uptake degrades visibility by increasing the aerosol mass, and by shifting the aerosol size distribution towards 0.5-1.0 um particles.

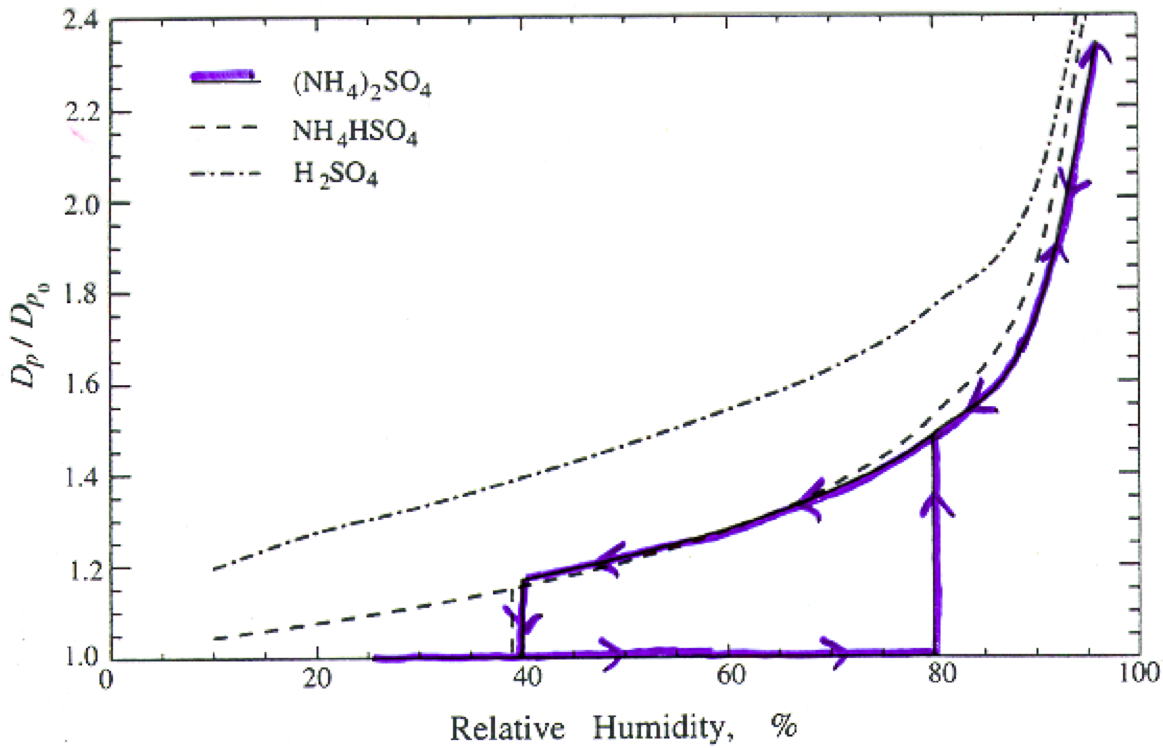


FIGURE 9.4 Diameter change of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 particles as a function of relative humidity. D_{p0} is the diameter of the particle at 0% RH.

(from Seinfeld and Pandis, *Atmos.Chem.&Physics*, Wiley-Intersc., ©1997)

This hygroscopic behavior is well-understood from a theoretical standpoint for most inorganic species. But much less is known about water uptake by organic species.

What Hygroscopic Behavior is seen for Organics?

Moderately–soluble organics like malic acid (solubility = 145 g/100 g water) exhibit deliquescence behavior.

Highly–soluble organics like acetic acid (solubility = ∞) take up water over a wide range of relative humidities.

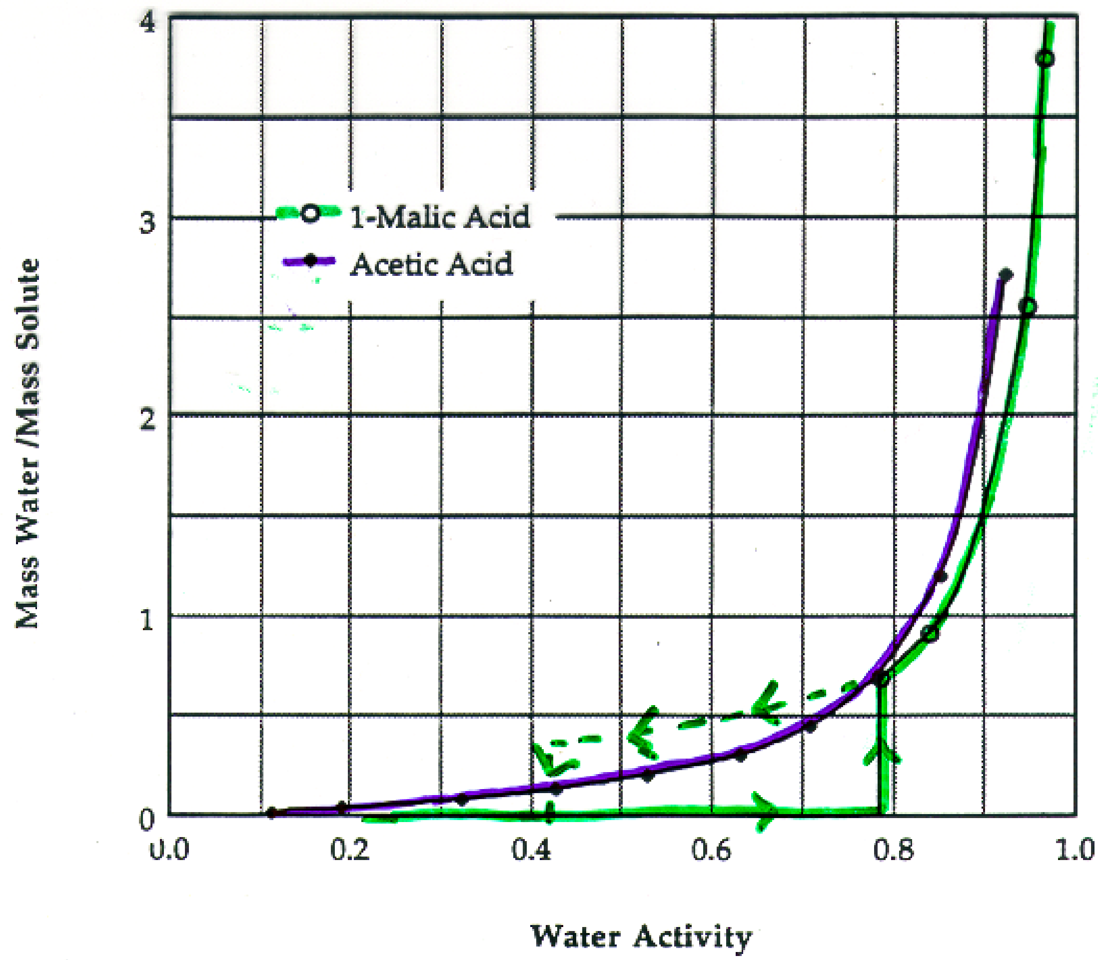


Figure 1. Growth curves (water mass/solute mass) for $T = 25°C$ as a function of water activity (aw) for acetic acid [*Sebastiani and Lacquaniti*, 1967] and 1-malic acid [*Carlo*, 1971]. At equilibrium, RH = aw for particles with Dp ≥ 0.1 μm.

(from Saxena et al., *JGR* 100:18755-70, 1995)

Which Organics will be Hygroscopic?

Organic species must have low volatility to exist in aerosol phase, and must be soluble in water (i.e., polar).

Singly-substituted organics become more nonpolar as they get larger: only alkanoic acids < C7 have an aqueous solubility > 1.0 g/100 g water.

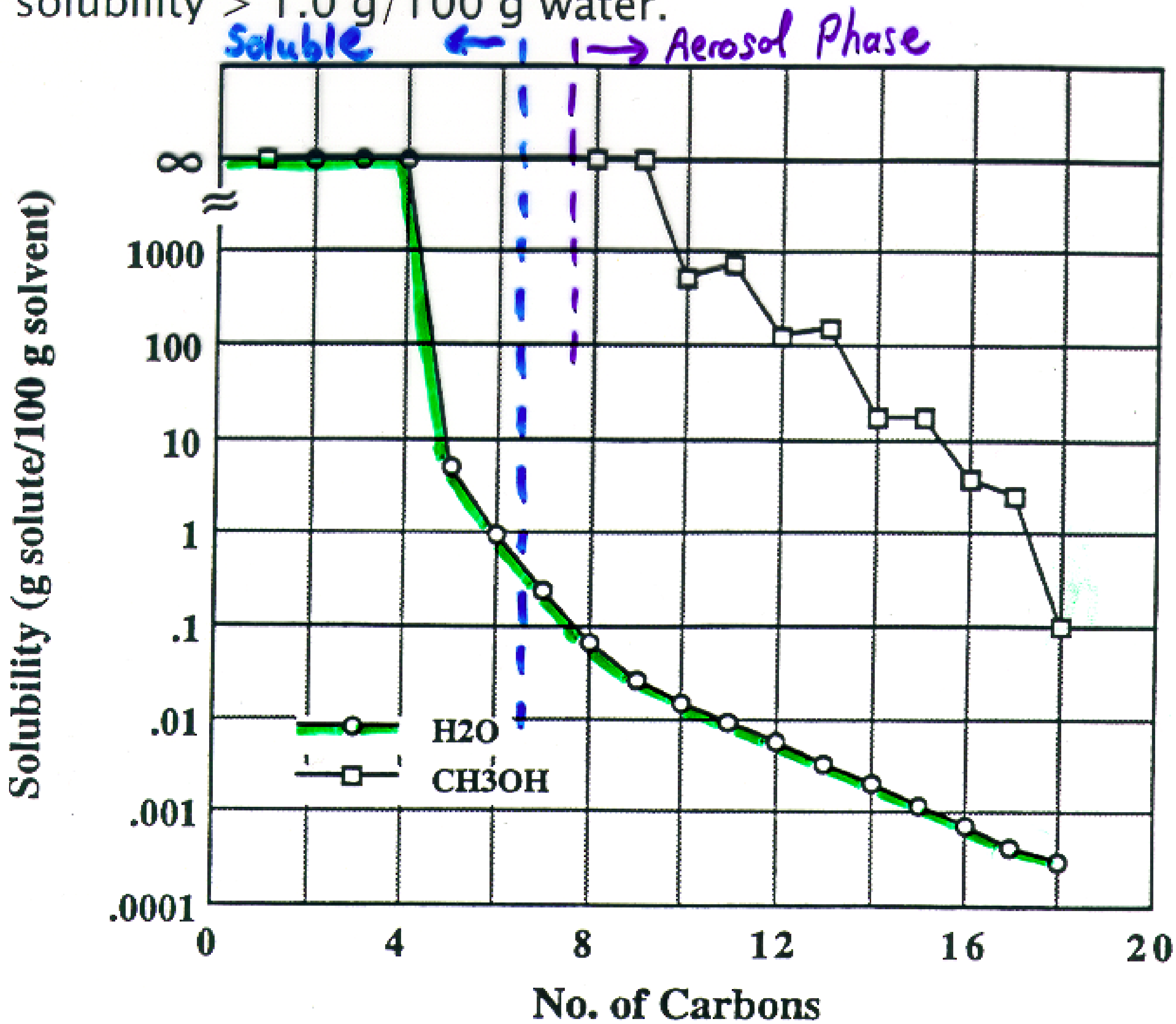


Figure 1a. (from Saxena and Hildemann, *J.Atmos.Chem.* 24:57-109, 1996)

But alkanoic acids < C8 exist almost entirely in the gas phase, due to their high vapor pressure.

Which Organics will be Hygroscopic?

Thus, only multi-substituted organics will have the potential to be both condensable and soluble in water.

Examples:

- Polyols (2 or more alcohol groups)
- Polyglycols (2 or more glycol groups)
- Keto-carboxylic acids (ketone & aldehyde groups)
- Dicarboxylic acids (2 aldehyde groups)

What are the Sources of Polar Organic Aerosols?

Main primary sources are inefficient combustion processes involving fuels that contain polar organics:

Table 1. Characteristics of Organic Aerosols in Combustion Emissions

Combustion source (no. of samples)	% of organics that eluted
Catalyst-equipped automobiles (1)	>100%
Noncatalyst automobiles (1)	>100%
Diesel trucks (1)	92%
Home appliances, nat'l. gas (1)	94%
Fireplace, pine wood (1)	51%
Fireplace, oak wood (1)	45%
Fireplace, synthetic log (1)	77%
Cigarette smoke (2)	81–87%
Hamburger charbroiling (2)	27–43%
Hamburger frying (1)	60%

(from Hildemann, and Yu, *Air Pollution VII*, WIT Press, pp.935-942, 1999)

Since photochemical reactions in the atmosphere tend to lead to more polar products, expect SOA to be a significant contributor.

Evidence for Hygroscopic Behavior of Organics:

(1) Analysis of Field Experimental Data:

In an urban location (Claremont CA), the TDMA data suggested that organics were inhibiting or retarding water uptake by the inorganics.

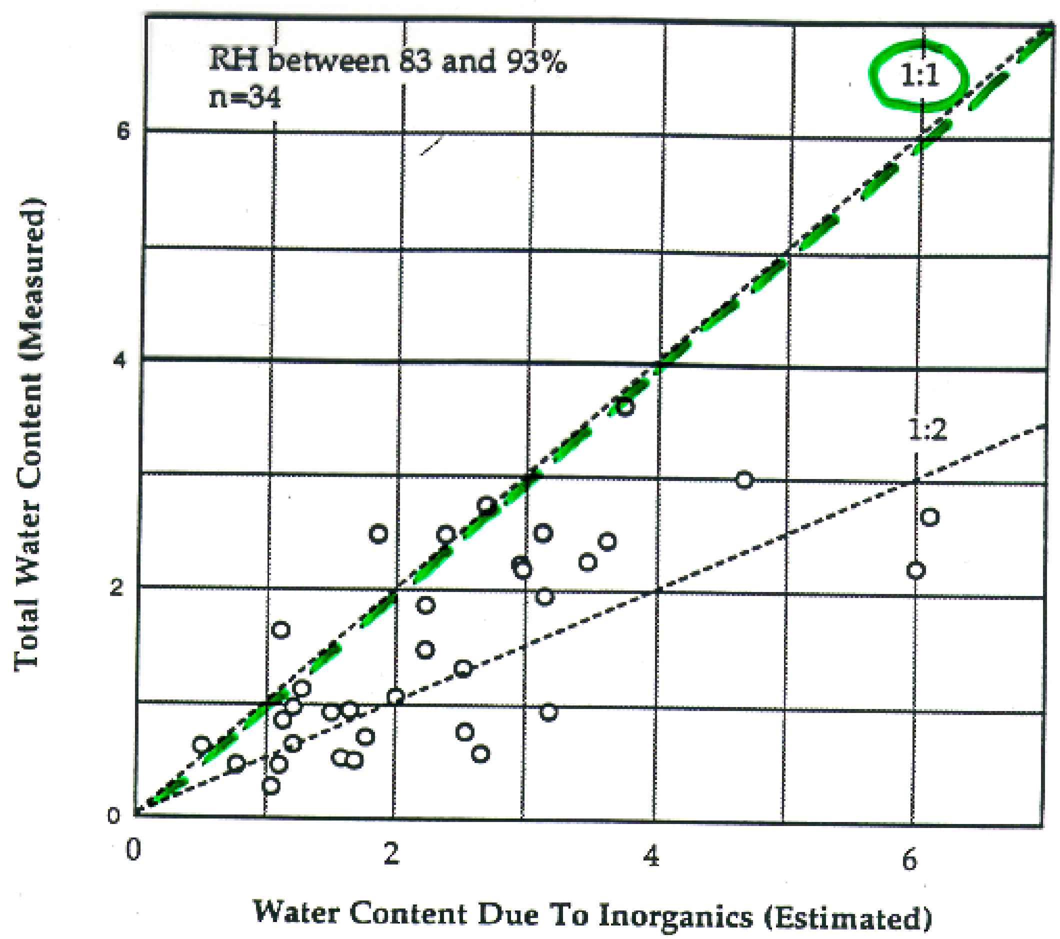


Figure 8. Measured (v_{wt}) versus estimated (v_{wi}) water volume per unit dry particle volume for Claremont, summer 1987.

(from Saxena et al., *JGR* 100:18755-70, 1995)

Evidence for Hygroscopic Behavior of Organics:

(1) Analysis of Field Experimental Data:

Evaluated whether water uptake observed via TDMA measurements could be explained solely by the hygroscopic properties of the inorganic species present.

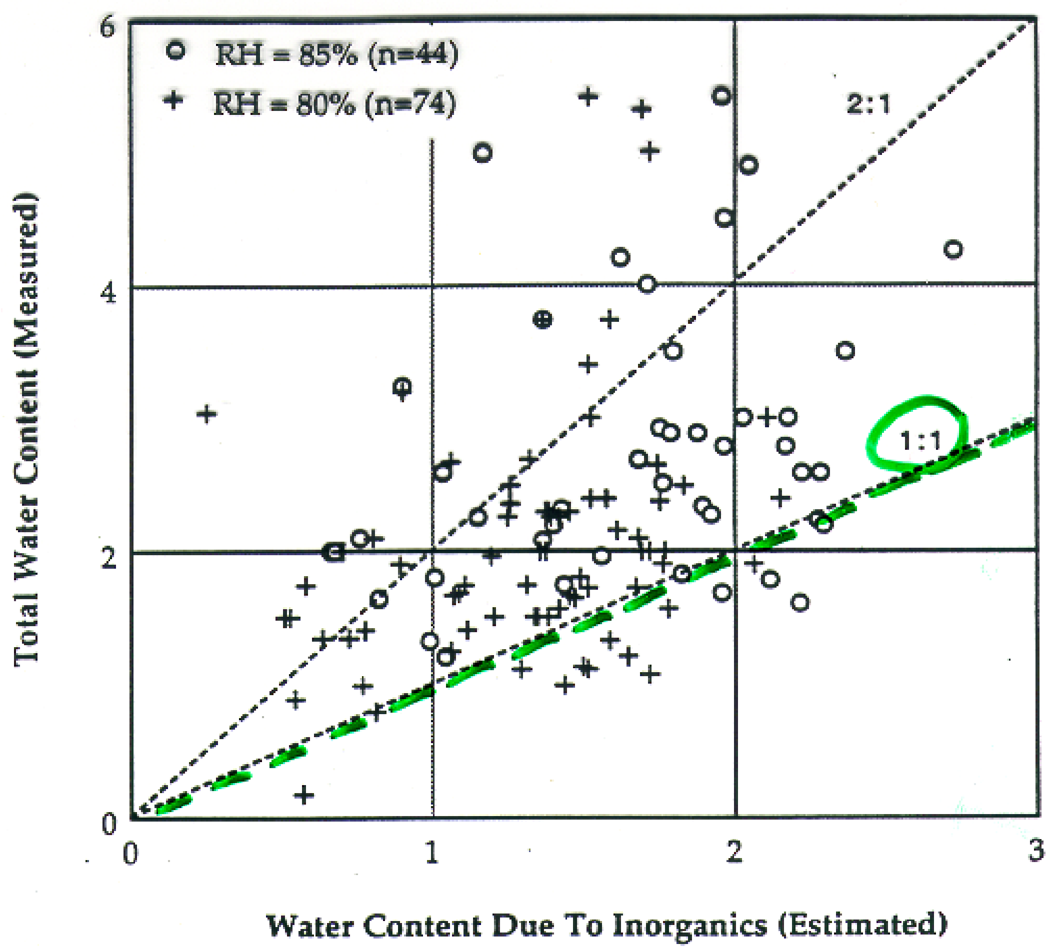


Figure 3. Measured (v_{wt}) versus estimated (v_{wi}) water volume per unit dry particle volume for Meadview, summer 1992.

(from Saxena et al., *JGR* 100:18755-70, 1995)

Evidence for Hygroscopic Behavior of Organics:

(1) Analysis of Field Experimental Data:

In 3 rural locations (Meadview AZ, Hopi Point AZ, and the Smoky Mountains), this approach suggested that organics were also contributing to water uptake.

However, analysis of light-scattering measurements taken at the same time in the Smoky Mountains found that the total light scattering observed could be adequately explained assuming no water uptake by organics.

Evidence for Hygroscopic Behavior of Organics:

(2) Laboratory experiments

A limited number of papers have examined the hygroscopic behavior of laboratory aerosols consisting of:

- Hygroscopic inorganics with hydrophobic organics
- Hygroscopic inorganics with hygroscopic organics
- Hydrophobic inorganics with hygroscopic organics

In some cases, aqueous mixtures were generated; in other cases, inorganic seed aerosols were "coated" with organics.

Evidence for Hygroscopic Behavior of Organics:

(2) Laboratory experiments

The answers to the following questions are not yet clear from the work done to date:

- Does the deliquescence point of a hygroscopic inorganic change when an organic is also present?
- How does the total amount of water uptake relate to the compounds present?
- Does the rate of water uptake change?
- Does particle size, chemical composition, or the amount of organic present influence the results?

Evidence for Hygroscopic Behavior of Organics:

(3) Theoretical Work

Aerosol-phase organics will be concentrated mixtures of many organic species. But very little data is available on the behavior of ~~aqueous mixtures of~~ single organics, and almost no data is available on aqueous organic mixtures.

- Thus, must estimate critical parameters like vapor pressure and activity coefficients.

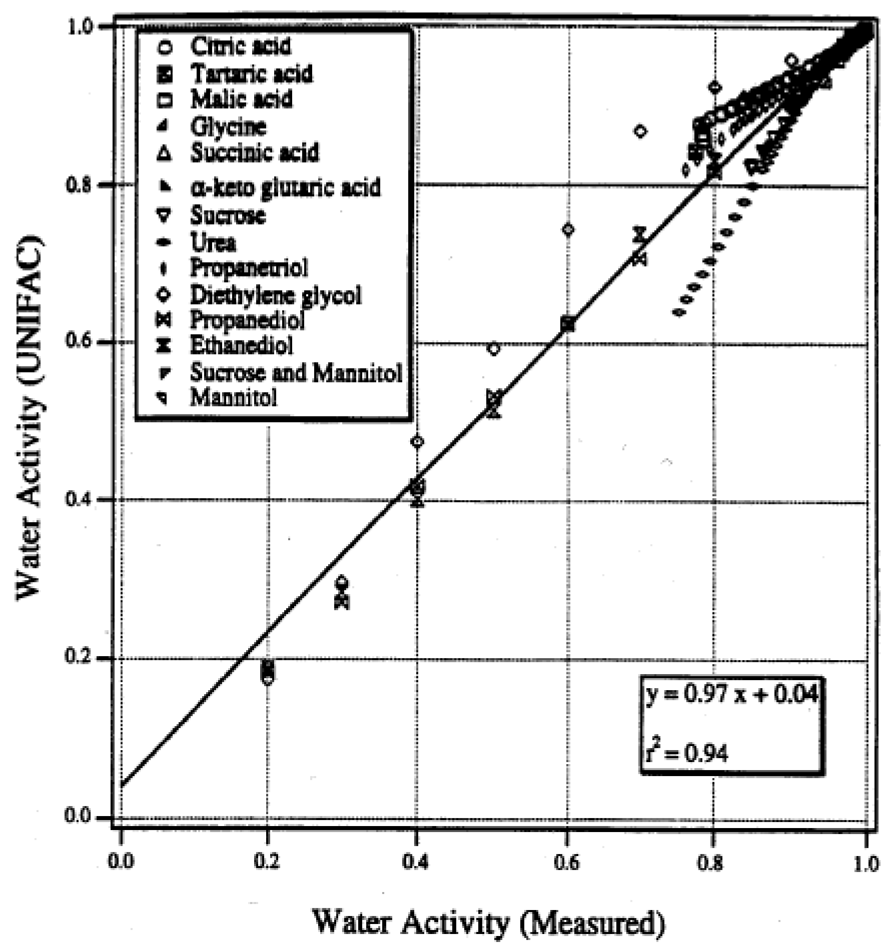


FIGURE 3. Correlation between observed and UNIFAC-estimated water activity.

(from Saxena and Hildemann, *ES&T* 31:3318-24, 1997)

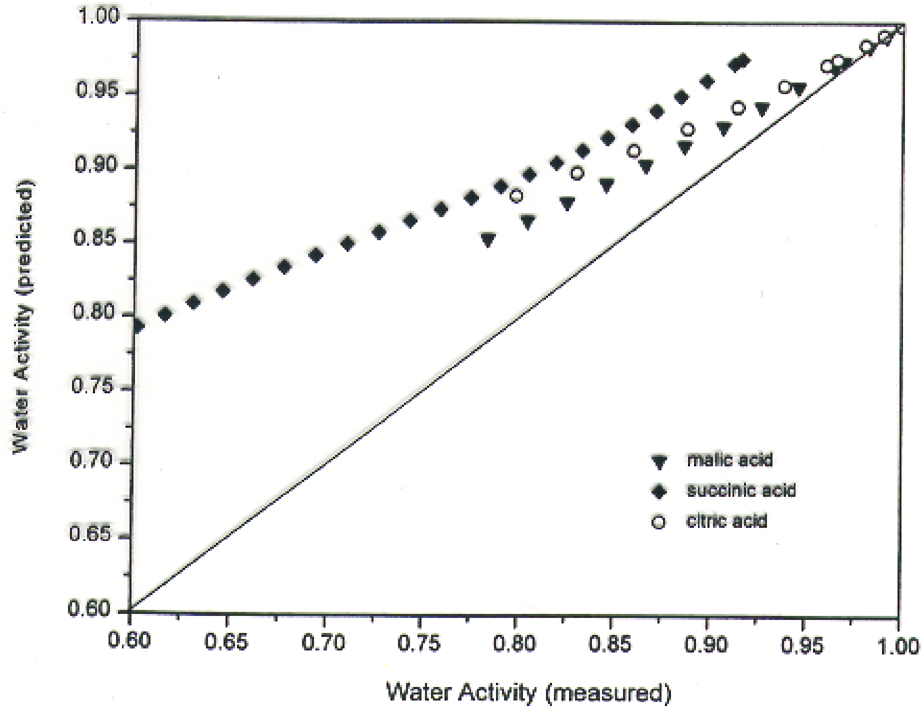


FIGURE 1. Predicted (UNIFAC) versus measured water activity for succinic acid (*24*), malic acid (*48*), and citric acid (*48*).

(from Ansari and Pandis, *ES&T* 34:71-77, 2000)

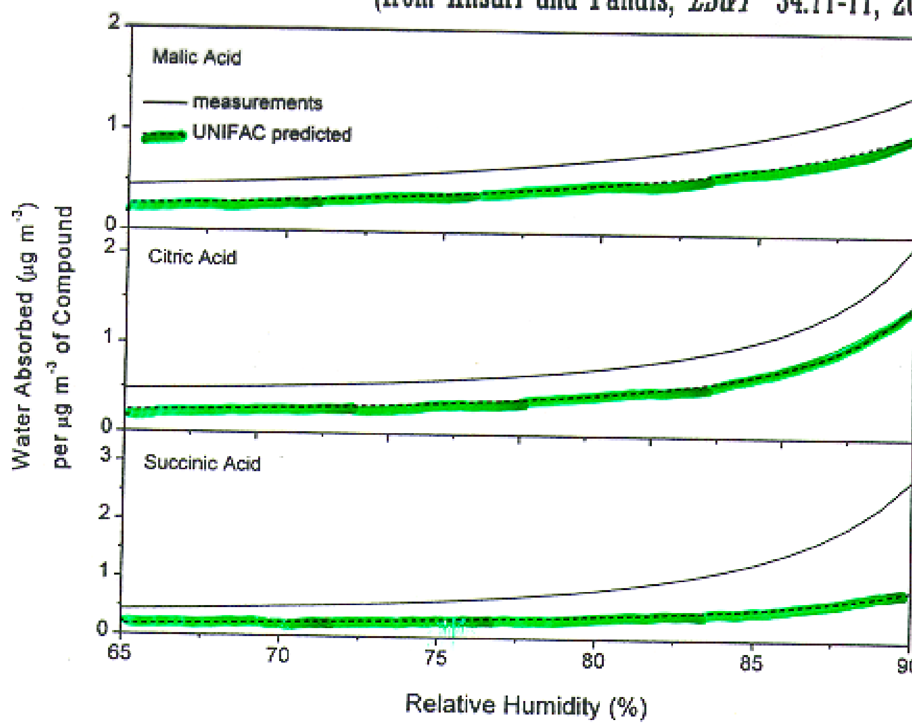


FIGURE 2. Predictions (UNIFAC) for water absorbed ($\mu g\ m^{-3}$) versus those based on measurements for 1 $\mu g\ m^{-3}$ of succinic, malic, and citric acids.

(from Ansari and Pandis, *ES&T* 34:71-77, 2000)

How do Organics Co-Exist with Inorganic Aerosols?

- As a uniform organic coating on a solid/liquid core?
- As a lens of organic?
- As a "blob" attached to the inorganic aerosol?
- As a homogeneous mixture?

When will SOAs Contribute Most Substantially to Haze Formation?

- Under lower relative humidity conditions (below the deliquescence point of sulfates and nitrates)

- In geographic locations where concentrations of highly hygroscopic inorganic aerosols (like the ammonium sulfates) are low

What are Important Areas for Additional Research?

(1) Chemical characterization of polar organic aerosols in ambient air

(2) Theoretical modeling of the hygroscopic behavior of aqueous mixtures containing organics

(3) Laboratory experiments on the hygroscopic behavior of aerosols with organic and inorganic components

- Influence of inorganic composition?
- Influence of organic composition?
- Influence of what fraction of aerosol is organic?
- Influence of aerosol size?

(4) Investigation of the nature/shape of aerosols containing both inorganic and organic components

(5) Analysis of how light extinction changes when particles are nonspherical and/or nonuniform

What impact do SOAs have on light extinction?

(1) Condense onto existing particulate matter

- Increases the total PM mass

- Alters the size distribution

Both of these effects will tend to enhance the light scattering efficiency of the particles

(2) Condensed coating may enhance or inhibit the water-uptake characteristics of core particles originally present

- Polar organics will take up water
- Nonpolar organics may inhibit water uptake by the core particles

What are Important Areas for Additional Research?

- Better chemical characterization of what polar organic species are present in the ambient air

- Insights on the nature/shape of aerosols containing both inorganic and organic components

- Experimental and theoretical work on hygroscopic behavior of complex mixtures containing organics

  -- Influence of particle size?
  -- Influence of inorganic composition?
  -- Influence of organic composition?
  -- Influence of how much organic is present?

Evidence for Hygroscopic Behavior of Organics:

(1) Analysis of Field Experimental Data:

The amount of "extra" water uptake observed correlated with the amount of organic aerosol present:

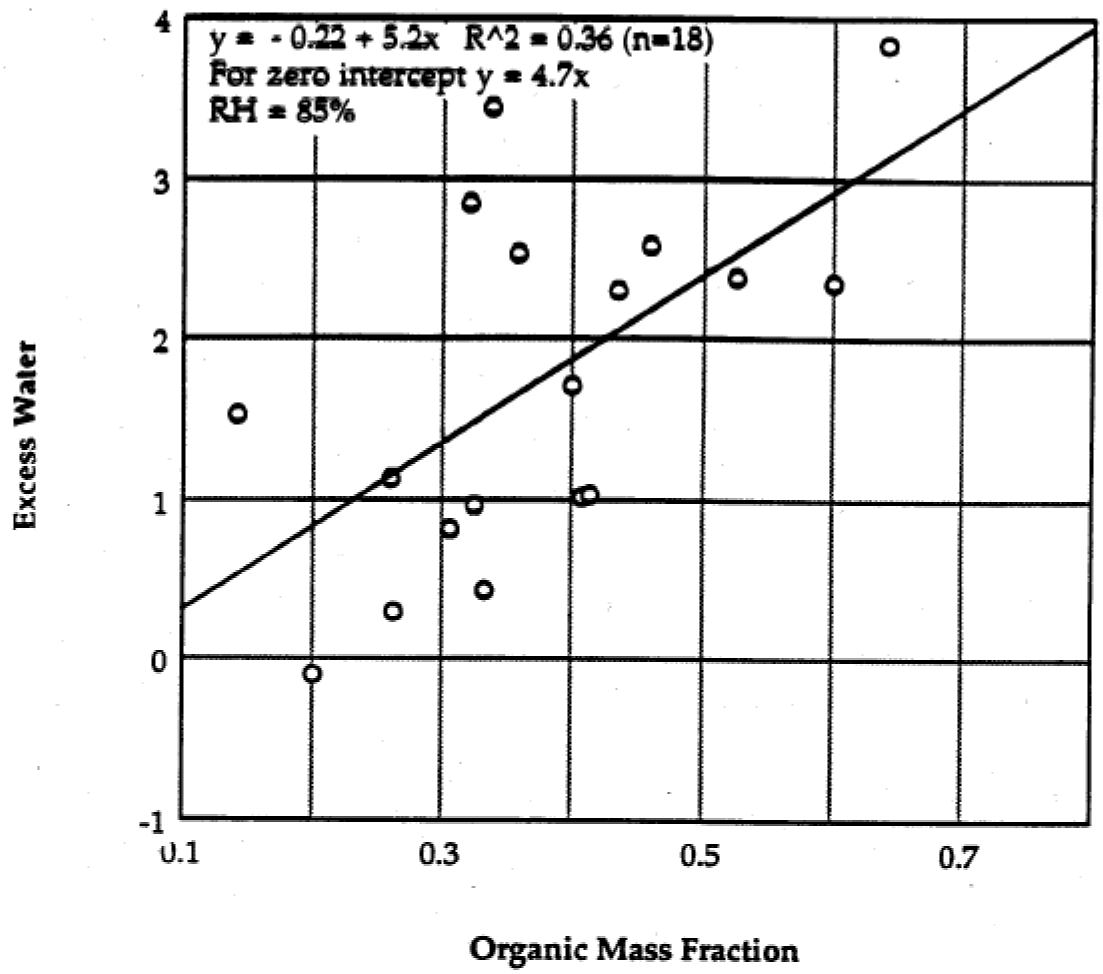


Figure 4. Excess water ($v_{wt} - v_{wi}$) as a function of organic fraction of total particle mass: (a) Dp = 0.4 or 0.5 μm; (b) Dp = 0.2 μm; (c) Dp = 0.1 μm. Solid line denotes least squares fit. Data are for Meadview, summer 1992.

(from Saxena et al., *JGR* 100:18755-70, 1995)

$p_{sat} = 10^{-5}-10^{-7}$ vs

4×10^{-2} for C6 Alkanoic Acid

(hexanoic)

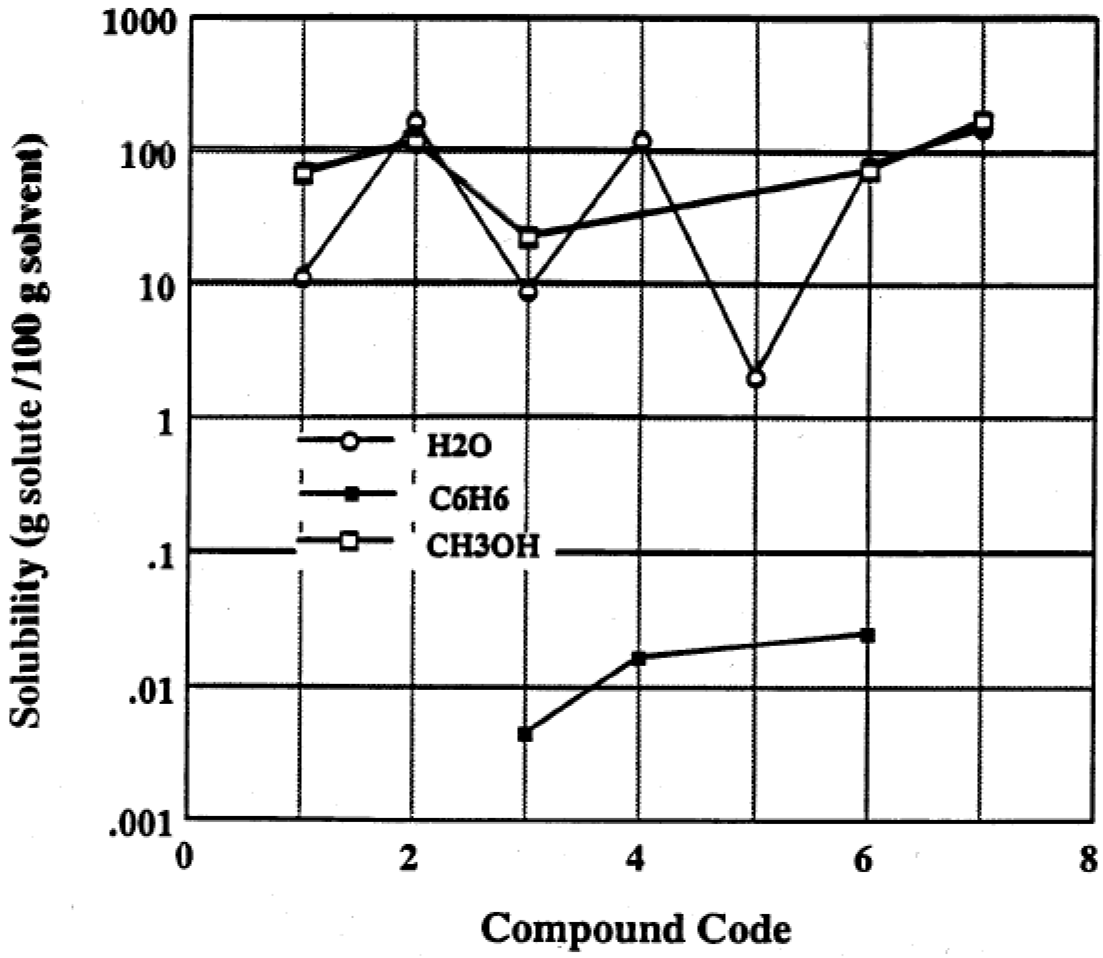


Figure 3-2. Solubility of dicarboxylic acids in water, methanol and benzene

(from Saxena and Hildemann, *J.Atmos.Chem.* 24:57-109, 1996)