Aerosol hygroscopicity at high (99 to 100%) relative humidities

C. R. Ruehl¹, P. Y. Chuang¹, and A. Nenes²

¹Earth & Planetary Sciences, University of California, Santa Cruz, USA
²Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, USA

Abstract. The hygroscopicity of an aerosol strongly influences its effects on climate and, for smaller particles, atmospheric lifetime. While many aerosol hygroscopicity measurements have been made at lower relative humidities (RH) and under cloud formation conditions (RH > 100%), relatively few have been made at high RH (99 to 100%), where the Kelvin (curvature) effect is comparable to the Raoult (solute) effect. We measured the size of droplets at high RH that had formed on particles composed of one of seven compounds with dry diameters between 0.1 and 0.5 µm. We report the hygroscopicity of these compounds using a parameterization of the Kelvin term, in addition to a standard parameterization (κ) of the Raoult term. For inorganic compounds, hygroscopicity could reliably be predicted using water activity data (measured in macroscopic solutions) and assuming a surface tension of pure water. In contrast, most organics exhibited a slight to mild increase in hygroscopicity with droplet diameter. This trend was strongest for sodium dodecyl sulfate (SDS), the most surface-active compound studied. The results suggest that, for single-component aerosols at high RH, partitioning of solute to the particle-air interface reduces particle hygroscopicity by reducing the bulk solute concentration. This partitioning effect is more important than the increase in hygroscopicity due to surface tension reduction. Furthermore, we found no evidence that micellization limits SDS activity in micron-sized solution droplets, as observed in macroscopic solutions. We conclude that while the high-RH hygroscopicity of inorganic compounds can be reliably predicted using readily available data, surface-activity parameters obtained from macroscopic solutions with organic solutes may be inappropriate for calculations involving micron-sized droplets.

1 Introduction

Several mechanisms by which aerosols affect climate have been the subject of a great deal of recent study. These have broadly been classified as direct effects, in which particles interact directly with radiation, or indirect effects, in which variations in aerosol properties cause changes in cloud properties. The magnitude of both direct and indirect effects depends strongly on aerosol hygroscopicity, which we define as the amount of water absorbed by a particle with a given dry diameter at a given relative humidity (RH). Particles that readily absorb water at elevated RH have larger scattering cross-sectional areas than less hygroscopic particles, and are also more likely to act as cloud condensation nuclei (CCN), allowing them to indirectly affect climate. Accurate assessment of the effects of aerosols on climate therefore requires a detailed description of their hygroscopicities. In addition, wet deposition is the most efficient removal mechanism for particles with dry diameters (D_{dry}) less than 1 µm (Textor et al., 2006), and therefore hygroscopicity and CCN activity strongly influence particle lifetime and consequently total aerosol burden.

Aerosol hygroscopicity depends on two properties of the compounds present in a particle: their ability to lower the water activity (a_{w}) of an aqueous solution droplet, and their influence on the surface tension (σ) of the droplet-air interface. Measurements of both a_{w} and σ, however, have typically been made using macroscopic solutions. (Henceforth we use the term “macroscopic” to describe these larger solutions with flat interfaces, in the same way that others have used the term “bulk.” We reserve the term “bulk” for the portion of the droplet not at its surface.) Here, we explore the suitability and limitations of applying properties of macroscopic solutions to micron-sized drops.

It has been argued that the surface activity of aerosols influences climate by reducing droplet σ below the value for pure water (σ_{H₂O}=72.8 mJ m⁻² at 25°C). This would
increase their hygroscopicity, resulting in higher cloud droplet concentrations and consequently greater cloud albedo (Facchini et al., 1999). Many calculations of aerosol particle hygroscopicity have used the reduced σ measured in a macroscopic aqueous solutions (e.g., Facchini et al., 1999; Shulman et al., 1996; Lohmann and Leck, 2005; Rissman et al., 2004). Values of σ obtained in macroscopic solutions have also been used in cloud parcel models (e.g., Ervens et al., 2005; Vanhanen et al., 2008), with results indicating an increase in cloud droplet concentrations of ~10% relative to those assuming σ_{H_2O}. However, even when σ is measured in relatively small macroscopic aqueous solution, the surface:volume ratio of the sample is much lower than found in microscopic droplets (Seidl and Hanel, 1983). For example, σ has been measured in solution droplets with wet diameter \( D_{\text{wet}} \sim 1 \) μm, or a surface:volume ratio of 3000 m\(^{-1}\) (e.g., Shulman et al., 1996; Lima and Synovec, 1995; Varga et al., 2007; Dinar et al., 2007; Taranuik et al., 2008), but the surface:volume ratio in ~1 μm droplets is greater than \( 10^6 \) m\(^{-1}\). It is therefore possible that surface activities measured in macroscopic solutions are not germane to the CCN activity (i.e., hygroscopicity at the point of cloud droplet activation) of submicron particles.

There are several techniques that have been used to measure the hygroscopicity of droplets (as opposed to macroscopic solutions). Most involve droplets not with \( D_{\text{wet}} \sim 1 \) μm, but rather larger droplets with a smaller surface:volume ratio, measurements made at RH>99% recently using the LACIS instrument notwithstanding (Wex et al., 2005; Ziese et al., 2008; Niedermeier et al., 2008; Wex et al., 2009). For example, measurements of the hygroscopicity of larger droplets, typically with \( D_{\text{wet}} \) between 20 and 40 μm, have been made using electrodynamic balances (e.g., Chan et al., 2008). High-resolution diameter measurements have also been made of droplets with \( D_{\text{wet}} \sim 3 \) to 7 μm at high RH using optical tweezers (Hanford et al., 2008).

Recently, many studies have attempted to account for the high surface:volume ratio of microscopic droplets by explicitly modeling the adsorption of solute to the droplet-air interface and the resulting depletion of solute in the droplet bulk phase (i.e. the droplet interior away from the air interface). When this “partitioning effect” is taken into account, hygroscopicity can be reduced by one of two mechanisms: (1) if insufficient solute is available to completely cover the interface, σ is reduced to a much lesser extent than in a macroscopic solution (Li et al., 1998; Sorjamaa et al., 2004; Topping et al., 2007), and (2) depletion of solute in the bulk droplet increases droplet water activity (Sorjamaa and Laaksonen, 2006). In both cases the modeled drop concentration is much closer to that obtained using σ_{H_2O} (Kokkola et al., 2006). Although the partitioning effect may strongly limit the increase in hygroscopicity due to solute surface activity, some authors have argued that the CCN activity of organic material can only be accurately predicted if σ is reduced to values similar to those observed in macroscopic solutions (Dinar et al., 2006; Asa-Awuku et al., 2008; Broekhuizen et al., 2004). Others have found that prediction of the CCN activity of known surface-active compounds did not require any reduction in σ (Abbatt et al., 2005; Sorjamaa et al., 2004). Also, recent work on organic aerosol particles produced from ozonolysis of α-pinene has suggested that only minor reductions in σ at activation are required to be consistent with hygroscopicity measured up to RH=99.6% (Wex et al., 2009).

In addition to the ability to partition and reduce surface tension, another property of many surface active compounds in macroscopic solutions is the tendency to form micelles (or more generally, aggregates) above the critical micelle concentration (CMC). The CMC can be determined in macroscopic solutions by slowly adding a surface-active compound; at the CMC, the activity coefficient of that compound in solution, which can be conceptualized as the fraction of “free” (i.e., not in a micelle) molecules in solution, will decrease sharply, and other solution properties related to micellization, such as turbidity, may begin to change. Tabazadeh (2005) used accepted CMC values for typical surface-active compounds in theoretical calculations to argue that micellization occurs in aerosol solution droplets containing surface-active compounds, which would lower their hygroscopicity both by limiting the amount of solute available to partition to the air-droplet interface and by raising the water activity in the droplet relative to a similar droplet in which no micellization occurs. However, as with measurements of the surface tension of macroscopic solutions, it is not clear that CMC values determined in such solutions are relevant to micron-sized droplets, with curved interfaces and much higher surface:volume ratios. In macroscopic solutions, the surface:volume ratio is small enough that the amount of solute at the interface can be neglected, and the CMC is determined by the tendency of free molecules to form micelles. However, in micron-sized droplets, the amount of solute at the interface might no longer be negligible, meaning that “free” surface active molecules can either partition to the interface or form micelles, and thus the CMC would be determined by both of these processes.

In this study, we measure the hygroscopicity of aerosol particles of known composition at high RH. We use droplets with \( D_{\text{wet}} \sim 1 \) μm because, as discussed below, such droplets are most sensitive to the Kelvin effect; consequently, most cloud droplets are approximately this size at the point of activation. Our primary purpose is to determine the extent to which hygroscopicity determined for droplets of this size differ from predictions based on properties of macroscopic solutions with much lower surface:volume ratios. Additionally, we address two general questions related to high-RH hygroscopicity. First, how well can aerosol hygroscopicity be represented with a single parameter, as has been done in numerous recent studies (e.g., Petters and Kreidenweis, 2007; Hudson and Da, 1996; Wex et al., 2007), for relatively well-studied compounds at high values of RH (99.2 to 99.9%)?
Second, if the hygroscopicity of individual compounds does vary within the range of experimental conditions, which processes might be responsible?

2 Theory

2.1 Sensitivity of $D_{\text{wet}}$ to the Raoult and Kelvin effects

At elevated RH, atmospheric particles typically exist as solution droplets. Through condensation or evaporation of water, these droplets grow or shrink until they reach equilibrium with ambient RH. Hygroscopicity is the amount of water absorbed by a particle with a given dry diameter at a given RH, and thus the more hygroscopic a particle, the greater its $D_{\text{wet}}$ at a given RH and $D_{\text{dry}}$. Because hygroscopicity depends on water activity ($a_w$) and surface tension ($\sigma$), these two variables appear in the Köhler equation, which relates the ambient RH in equilibrium with a droplet to various droplet properties:

$$\text{RH} = a_w \exp \left( \frac{4 \sigma V_w}{RT D_{\text{wet}}} \right)$$

(1)

Here $V_w$ is the molar volume of water (which approximates the dilute droplet), $R$ is the gas constant, and $T$ is temperature. $a_w$ depends on the composition of the dry particle, as well as the molar ratio of solute to water in the droplet:

$$a_w = \exp \left( -\frac{\phi \nu n_s}{n_w} \right)$$

(2)

where $\phi$ is the osmotic coefficient, $\nu$ is the van’t Hoff factor (the moles of soluble species per mole solute), and $n_s$ and $n_w$ are the moles of solute and water, respectively, in the droplet. The numerator of the exponential term in Eq. (2) is the number of osmoles in the solution droplet.

The Raoult effect is defined as the influence of the number of osmoles (for which we will use $\phi$ as a proxy) on hygroscopicity, while the Kelvin effect is defined as the effect of $\sigma$ on hygroscopicity. The sensitivity of $D_{\text{wet}}$ to these variables can be defined as the ratio of the resulting fractional change in $D_{\text{wet}}$ to a small fractional change in either variable, e.g.:

$$\frac{d\tilde{D}_{\text{wet}}}{d\phi} = \frac{dD_{\text{wet}}}{d\phi} \times \frac{\phi_o}{D_{\text{wet},o}}$$

(3)

at some reference wet diameter ($D_{\text{wet},o}$) with a corresponding osmotic coefficient ($\phi_o$). The sensitivity of $D_{\text{wet}}$ to $\sigma$ can be defined analogously. To calculate these sensitivities, we assume a dry particle made of a single component with a molar volume equal to a model surfactant (sodium dodecyl sulfate, or SDS). Then Eqs. (1) and (2) can be used to solve for $\frac{d\tilde{D}_{\text{wet}}}{d\phi}$ and $\frac{d\tilde{D}_{\text{wet}}}{d\sigma}$. The sensitivity of $D_{\text{wet}}$ to $\phi$ increases gradually with RH, reaching 20% around RH=90% and 30% around RH=98% (Fig. 1a). In contrast, the sensitivity of $D_{\text{wet}}$ to $\sigma$ is a much stronger function of both $D_{\text{wet}}$ and RH (Fig. 1b), and only reaches 20% when RH$\gtrsim$99% and $D_{\text{wet}}$$\lesssim$2 µm. This is because the magnitude of the Kelvin effect approaches that of the Raoult effect as RH$\rightarrow$100% (Lewis, 2008), and also due to the greater curvature of smaller droplets which increases the importance of the Kelvin effect. Similar conclusions were reached by Wex et al. (2008), who found that the sensitivity of $D_{\text{wet}}$ to $\sigma$ is negligible when RH$<95\%$, but increases sharply as RH approaches 100%. Wex et al. (2008) also found that the sensitivity of $D_{\text{wet}}$ to the number of osmoles was greater for more hygroscopic particles; in our analysis as well the sensitivity of $D_{\text{wet}}$ to $\phi$ increased when we assumed the dry particle was composed of ammonium sulfate instead of SDS.

2.2 Parametrization of aerosol hygroscopicity

Although hygroscopicity is influenced by several physicochemical properties (e.g. molar volume, aqueous solution activity, surface tension), it has been represented for both ambient and lab-generated particles by a single parameter based on Eq. (1), defined similarly but not identically in several studies (e.g., Fitzgerald et al., 1982; Hudson and Da., 1996; Wex et al., 2007; Petters and Kreidenweis, 2007). Because hygroscopicity is more sensitive to the Raoult term than the Kelvin term for all but the smallest particles at the highest RH.
As can be seen in Eq. (5), $\kappa$ is a parametrization of the Raoult term in Eq. (1). To express observed $D_{\text{wet}}$ values as $\kappa$ (when $D_{\text{dry}}$ and RH are known), a surface tension must be assumed. We also parametrize the the Kelvin term by defining a length scale (Lewis, 2008):

$$\delta = \frac{4 \sigma V_w}{RT}$$

and substitute into the Köhler equation:

$$\text{RH} = \exp\left(-\frac{\phi v n_s}{n_w}\right) \exp\left(\frac{\delta}{D_{\text{wet}}}ight)$$  \hspace{1cm} (7)

We use Eq. (7) to calculate $\delta$ given experimentally-determined $D_{\text{wet}}$, $D_{\text{dry}}$, and RH, just as Eq. (5) is used to derive $\kappa$ from these same quantities. As before, we must make an assumption regarding the term that is not parameterized, in this case the Raoult term. Specifically, we must assume the number of osmoles ($\phi v n_s$) in the droplet (given particle composition and $D_{\text{dry}}$). We use the relationship between $\kappa$ and RH discussed above to determine this quantity.

Because any trend in hygroscopicity with RH has been removed from $\delta$, it much more likely that any observed trend in $\delta$ with $D_{\text{wet}}$ is due to changes in surface activity, as opposed to non-ideality. For an ideal droplet at 25°C with the surface tension of pure water, $\delta \approx 2.1$ nm, and because $\delta \propto \sigma$, as hygroscopicity increases, derived $\delta$ decreases.

### 2.3 Predicted values of $\kappa$

Figure 2 shows theoretical predictions of derived $\kappa$ for different solute and RH conditions. Combining Eqs. (2) and (4), it can be shown that, if $\text{RH} \approx 100\%$,

$$\kappa \simeq \nu_s \frac{\phi V_w}{V_s}$$  \hspace{1cm} (8)

For an ideal, non-surface active solute, $\kappa$ is constant throughout the range of RH examined in this study (Fig. 2, black curves). For non-ideal, non-surface active solutes, $\kappa$ is proportional to $\phi$ (Fig. 2a and b, blue curves). For surface-active solutes, $\sigma$ is reduced, which in turn raises derived $\kappa$ an amount that increases with increasing RH (Fig. 2a and b, red curves). While this increase in $\kappa$ is sensitive to RH, it is reasonably insensitive to $D_{\text{dry}}$ (Fig. 2a). Not all dependence on $D_{\text{dry}}$ is removed, however, unless the surface tension of the droplet equals the assumed surface tension used in Eq. (5). Note that the sensitivity of $\kappa$ to $D_{\text{dry}}$ is much greater if one looks for a trend in $\kappa$ with $D_{\text{wet}}$ (Fig. 2b).

We compare our experimental values of $\kappa$ to theoretical predictions. Calculation of theoretical values for $\kappa$ amounts to describing $a_w$ as a function of $D_{\text{dry}}$ and RH. We use Eq. (2), which requires assumptions for $\phi$ and $v$, as well as calculations for $n_s$ and $n_w$. $n_s$ depends on the size of the dry particle:

$$n_s = \frac{\pi D_{\text{dry}}^3}{6V_s}$$  \hspace{1cm} (9)
where $n_w$ depends on $D_{\text{wet}}$ after the volume of solute has been subtracted:

$$n_w = \frac{\pi (D_{\text{wet}}^3 - D_{\text{dry}}^3)}{6V_w}$$  \hspace{1cm} (10)

For most common solutes, including the ones examined here, $\phi$ as a function of $n_w$ is well-known based on measurements of the water activity of macroscopic solutions, even at the upper end of the range of $a_w$ that is the focus of this study. For sodium chloride, ammonium sulfate, and malonic acid, we used the E-AIM water activity model to determine $\phi$ (Clegg et al., 1998, 2001), and use Eqs. (2) and (4) to calculate $\kappa$ as a function of RH. This model is based on experimental water activities measured in macroscopic solutions, and we compare our experimental results to it to determine how valid it may be for microscopic droplets. For sucrose and glucose, we also compared our data to predictions based on macroscopic experimental values (Clegg et al., 2001; Stokes and Robinson, 1966), which indicate that $\phi > 1$ for these sugars.

### 2.4 Predicted values of $\delta$

As discussed previously, we parametrize the Kelvin term in the Köhler equation to examine trends in hygroscopicity with droplet diameter ($D_{\text{wet}}$) using the length scale $\delta$, which is proportional to surface tension ($\sigma$) and defined in Eq. (7). This is analogous to the use of Eq. (5) to parametrize the Raoult term as $\kappa$. We assume a relationship between $\phi$ (again, a proxy for osmoles) and RH based on the regression of $\kappa$ onto RH, and so this dependence of hygroscopicity on RH has been removed from $\delta$. By accounting for any measured RH-dependence of the Raoult term, we can then attribute remaining variability to the Kelvin term, which will show up as variation in $\delta$. This is the primary motivation for using the $\delta$ parameterization. If the surface tension of a solution droplet is lower than that of pure water, but the partitioning effect is negligible, the observed value of $\delta$ will be lower than that of an ideal solution droplet with $\sigma = \sigma_{\text{H}_2\text{O}}$ (Fig. 2c, red curves). $\delta$ is also sensitive to the assumed value of $\phi$; (Fig. 2c, blue curves).

The reduction of $\sigma$ in macroscopic aqueous surfactant solutions is typically limited by formation of micelles above a certain certain bulk solute concentration. For SDS, this so-called Critical Micelle Concentration (CMC) is 8.2 mol m$^{-3}$, at which point $\sigma$ is reduced to $\sim$40 mJ m$^{-2}$. The range of SDS concentrations observed in this study is 110 to 340 mol m$^{-3}$, the entirety of which is more than 10 times greater than the CMC, suggesting that for all SDS solution droplets, excess SDS will be present to reduce $\sigma$ to whatever minimum value corresponds to saturation of the interface by SDS.

The partitioning effect can be accounted for by assuming that the solute is distributed between the bulk solution and the surface (Sorjamaa et al., 2004; Li et al., 1998):

$$n_s^{\text{tot}} = n_s^{\text{bulk}} + n_s^{\text{surf}} \hspace{1cm} (11)$$

Under the SDS concentrations observed here (110 to 340 mol m$^{-3}$), we assume that the surface is saturated, and therefore:

$$n_s^{\text{surf}} = \pi D_{\text{wet}}^2 \Gamma$$  \hspace{1cm} (12)

SDS has a cross-sectional area of $\sim$30 Å$^2$ per molecule (Prosser and Franes, 2001), and therefore a monolayer of SDS is equivalent to an excess surface concentration ($\Gamma$) of $6 \times 10^{-6}$ mol m$^{-2}$. Given a value of $D_{\text{dry}}$, $\Gamma$, and RH, Eq. (12) can be solved iteratively for $n_s^{\text{surf}}$ and $D_{\text{wet}}$. This model of the SDS solution droplet with a complete coating of solute at the droplet-air interface is similar to the “inverted micelle” model of solution droplets with organic solutes that has been previously described (Gill et al., 1983; Ellison et al., 1999), and for which some observational evidence has been obtained (e.g., Husar and Shu, 1975; Tervahattu et al., 2002; Russell et al., 2002). However, this blurs the distinction between soluble (e.g., SDS) and insoluble (e.g., fatty acids) surfactants (Moroi et al., 2004). For a soluble surfactant, the excess surface concentration is not expected to reside exclusively at the interface (e.g., purely in a self-assembled monolayer), but rather as a concentration gradient between

![Fig. 2. Theoretical variation of $\kappa$ with both (a) RH and (b) $D_{\text{wet}}$, and of (c) $\delta$ with $D_{\text{wet}}$. Black curves are for ideal SDS solution droplets with $\sigma_{\text{H}_2\text{O}}$. Red curves assume $\sigma$ reduced by half, and blue curves assume $\phi$=0.75. $D_{\text{dry}}$ is indicated by symbol size.](image-url)
the bulk and surface phases. As a consequence, \( \Gamma \) may be greater than a monolayer equivalent \((\sim 6 \times 10^{-6} \text{ for } SDS)\). To the extent that the partitioning effect does deplete solute from the bulk phase, hygroscopicity will decrease and \( \delta \) will therefore be greater.

2.5 Specific questions addressed by this study

We compare observed hygroscopicity (as expressed by the parameters \( \kappa \) and \( \delta \)) to values calculated under different assumptions regarding the terms \( a_w \) (i.e., the Raoult effect) and \( \sigma \) (i.e., the Kelvin effect) in Eq. (1). We use these observations to answer the following specific questions:

1. How well do \( a_w \) measurements made of macroscopic solutions describe the high-RH hygroscopicity of micron-sized droplets?
2. Does the micellization of SDS limit its hygroscopicity?
3. How well do \( \sigma \) measurements made using macroscopic solutions describe the high-RH hygroscopicity of micron-sized droplets?
4. And finally, for our model surface-active compound (SDS), does partitioning of solute to the droplet-air interface and the resulting depletion in the bulk droplet (i.e., the partitioning effect) need to be taken into account to accurately predict hygroscopic growth?

3 Experimental

Particles of known composition were generated by atomizing aqueous solutions with a high-pressure nitrogen jet. After atomization, particles flowed through two diffusion dryers, which lowered the RH of the flow to below 10%. After drying, particles entered a differential mobility analyzer (DMA, manufactured by TSI), which selected particles of a certain electrical mobility. While this quasi-monodisperse population was primarily made up of singly-charged particles with diameters (\( D_{\text{dry}} \)) between 0.2 and 0.5 \( \mu m \), it always included some larger, multiply-charged particles of equal mobility. The sheath and sample flow rate in the DMA were 2 and 0.2 \( \text{L min}^{-1} \), respectively. The quasi-monodisperse flow was split, with half going to a condensation nucleus counter and half going to a continuous-flow thermal gradient column (CFTGC). A dynamic shape correction factor (\( \chi \)) of 1.08 was used for NaCl aerosol, 1.04 for ammonium sulfate (AS) aerosol, and no shape correction was made (\( \chi = 1 \)) for any of the organic aerosol tested (Zelenyuk et al., 2006; Krämer et al., 2000).

Flow in the CFTGC proceeds through 1 m of stainless steel tubing with an ID of 0.022 m. Temperature is controlled at four locations along the tube with high-precision thermistors and thermo-electric coolers. The inside wall of the tubing is coated with filter paper, which is saturated with water before use. In previous experiments, the CFTGC has been operated in “CCN” mode, in which a positive temperature gradient (\( \Delta T \)) was imposed in the direction of the flow (Ruehl et al., 2008, 2009). Water vapor diffuses more quickly from the inner wall to the centerline than does the bulk gas (due to its lower molecular mass), causing a supersaturation (\( \text{RH}>100\% \)) along the centerline. This technique of producing a supersaturation was described in Roberts and Nenes (2005). In the experiments of this study, the CFTGC was operated in “high-RH” mode: a negative \( \Delta T \) in the direction of flow was applied, and water vapor diffused more rapidly from the centerline to the inner walls, lowering the RH along the centerline below unity, to somewhere in the range of 99.2 to 99.9% (depending on \( \Delta T \)). The overall flow rate in the column was 0.94 \( \text{L min}^{-1} \), of which 0.1 \( \text{L min}^{-1} \) was the quasi-monodisperse flow along the centerline, and the remainder was a humidified, particle-free sheath flow.

Before exiting the CFTGC, the diameter and velocity of droplets along the centerline was measured with a phase Doppler interferometer (PDI) manufactured by Artium Technologies, Inc. (Bachalo, 1980; Bachalo and Houser, 1984). Diameters were binned at 0.1 \( \mu m \) intervals. To get a sense of the precision of these measurements, we measured \( D_{\text{wet}} \) spectra at \( \Delta T = 1 \) K for droplets formed on dry NaCl particles. The mobility diameter of the NaCl particles was increased from 100 nm to 400 nm at 10 nm intervals (Fig. 3). Larger droplets formed on larger, multiply-charged particles were resolved in most spectra. A bimodal (both normally-distributed) fit was found for each spectra, and the smaller \( D_{\text{wet}} \) mode (which was always the more numerous) was assumed to be the singly-changed mode. The standard deviation of this mode ranged from 0.10 to 0.42 \( \mu m \), or from 7 to 22% of the mean. Replica measurements of \( D_{\text{wet}} \) standard deviation were made at several \( D_{\text{dry}} \), and ranged from 0.03 to 0.30 \( \mu m \) (3 to 15% of the mean). However, when restricted to \( D_{\text{wet}} < 2.0 \mu m \), which includes all droplets in this study except those formed on the largest NaCl and AS particles, standard deviations of replicate measurements ranged from 0.03 to 0.13 \( \mu m \) (3 to 9% of the mean).

\( \text{RH} \) in the CFTGC was calibrated with NaCl particles, which required an assumption of \( \kappa \). Based on the E-AIM model (Clegg et al., 1998, 2001), we assumed NaCl \( \kappa \) increased slightly over the relevant RH range, from 1.24 to 1.27, and then used Eq. (5) to relate RH to \( D_{\text{wet}} \) of NaCl solution droplets at a given \( \Delta T \). We found a linear relationship between RH and \( \Delta T \), but saw slight variation in absolute RH (~0.05%) at the same \( \Delta T \) on different days (Fig. 4). Therefore instead of utilizing the linear regression of RH onto \( \Delta T \), for all compounds besides NaCl we transformed \( D_{\text{wet}} \) into \( \kappa \) using the NaCl-calibrated RH for the individual day of the measurements. It should be mentioned that RH is very sensitive to \( T \), such that an increase in \( T \) of only 0.015 K would result in a decrease in RH of 0.1%. This calibration therefore suggests that the temperature in the view volume was stable to within ~0.01 K, which is approximately the precision of the thermistors.
Table 1. High-RH hygroscopicity ($\kappa_{\text{obs}}$) of the NaCl reference and six other compounds. Also $\kappa_{\text{ideal}}$, the theoretical value at RH=100% assuming an ideal solution, infinite solubility, and either complete dissociation (NaCl, AS, and SDS) or no dissociation (malonic and adipic acids, glucose, and sucrose). Also listed are the slopes ($m$) and $p$-values for linear regressions of $\kappa$ onto RH. $p$-values under 5% are in boldface.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\kappa_{\text{obs}}$</th>
<th>$\kappa_{\text{ideal}}$</th>
<th>$n$</th>
<th>$m$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.27±0.11</td>
<td>1.33</td>
<td>77</td>
<td>-1.2</td>
<td>0.84</td>
</tr>
<tr>
<td>AS</td>
<td>0.572±0.074</td>
<td>0.72</td>
<td>54</td>
<td>20</td>
<td>0.068</td>
</tr>
<tr>
<td>malonic acid</td>
<td>0.291±0.057</td>
<td>0.28</td>
<td>35</td>
<td>46</td>
<td>0.009</td>
</tr>
<tr>
<td>adipic acid</td>
<td>0.185±0.040</td>
<td>0.168</td>
<td>13</td>
<td>100</td>
<td>0.050</td>
</tr>
<tr>
<td>glucose</td>
<td>0.165±0.033</td>
<td>0.154</td>
<td>20</td>
<td>63</td>
<td>0.13</td>
</tr>
<tr>
<td>SDS</td>
<td>0.134±0.029</td>
<td>0.147</td>
<td>53</td>
<td>2.72</td>
<td>0.86</td>
</tr>
<tr>
<td>sucrose</td>
<td>0.112±0.020</td>
<td>0.084</td>
<td>27</td>
<td>-54</td>
<td>0.028</td>
</tr>
</tbody>
</table>

* This value was fixed in the RH calibration.

4 Results and discussion

4.1 Overall results

As expected, the high-RH hygroscopicity, expressed as $\kappa$, of both inorganic compounds was greater than that of any of the five organic compounds (Table 1). NaCl was the most hygroscopic compound studied ($\kappa=1.27±0.11$, with the mean value fixed by the CFTGC calibration), followed by ammonium sulfate (AS $\kappa=0.572±0.074$). Average AS $\kappa$ was 21% lower than the ideal value (0.72) but in agreement with the value predicted from macroscopic observations (Timmermans, 1960). If the nonideality of AS is incorporated into the van’t Hoff factor, this is equivalent to an average value of $\nu=2.4$, although as discussed below this value increases over the RH range studied here. Although not found in atmospheric particles (Facchini et al., 2001), sodium dodecyl sulfate (SDS) is a commonly studied surfactant, and as such it was used as a model surface-active compound. The average high-RH hygroscopicity of SDS ($\kappa=0.134±0.029$) was only 9% lower than that predicted for an ideal solution (0.147). In macroscopic solutions, however, SDS does not behave ideally: $\phi$ drops sharply to 0.12 (equivalent to $\kappa=0.02$) once the critical micelle concentration (CMC, 8.2 mol m$^{-3}$) is exceeded, and remains at ~0.12 for all [SDS] observed in this study (>110 mol m$^{-3}$) (Widera et al., 2003). The values of SDS $\kappa$ derived from $D_{\text{wet}}$ observations therefore suggest that a lack of micellization in micron-sized solution droplets enhances SDS aerosol hygroscopicity at high RH relative to that of a macroscopic solution. The relative hygroscopicity of the organic compounds was as predicted from their molar volumes and assuming an ideal solution (Table 1). Malonic
acid was the most hygroscopic organic compound (κ=0.29), followed by adipic acid (0.19), glucose (0.17), sodium dodecyl sulfate (0.13), and sucrose (0.11). Malonic acid κ was only slightly above the theoretical value assuming ideality and no dissociation. Glucose hygroscopicity was also slightly greater than that predicted for an ideal solution. In contrast, sucrose hygroscopicity was 25 to 50% greater than that predicted assuming ideality. Adipic acid hygroscopicity was relatively high, especially in light of negligible adipic acid hygroscopicity at RH up to 95% observed previously (Prenni et al., 2001; Sjogren et al., 2007). This could be due to the relatively large size (D_{dry} ⩾ 250 nm) of adipic acid particles examined, which are not subject to the deiquecence barrier to hygroscopic growth affecting smaller (D_{dry} < 150 nm) particles (Hings et al., 2008).

4.2 Hygroscopicity variation with RH

4.2.1 Inorganic compounds

Because NaCl was used as the reference substance (Fig. 4), variation of κ with RH was determined by experimental NaCl water activity data, as incorporated into the E-AIM water activity model, and increased from 1.24 at RH=99.2% to 1.27 at RH=99.9%, a small variation relative to that due to experimental uncertainty (Fig. 5a). κ of ammonium sulfate (derived from observations of D_{wet}) increased slightly as RH increased from 99 to 100%, as predicted using macroscopic water activity measurements (represented by E-AIM, see Fig. 5b). Although this trend had only mild statistical significance (p=0.068, see Table 1), the excellent match between the observations and the E-AIM predictions suggests that micron-sized AS solution droplets can be described by macroscopic data. If this nonideality were to be incorporated into the van’t Hoff factor, it would increase from ν=2.2 to 2.5 as RH increases from 99.2 to 99.9%, suggesting that a value larger than 2.5 should be used in calculations involving activation of AS particles under supersaturated conditions.

4.2.2 SDS

In macroscopic aqueous solutions, the ability of SDS to lower water activity (a_w) is strongly limited by its tendency to form micelles, and therefore the hygroscopicity of an SDS particle might be expected to increase with increasing RH, as greater dilution would reduce the proportion of SDS found in micelles. However, as with NaCl, SDS κ did not vary with RH (Fig. 6a). This indicates either that SDS φ is relatively
constant at high RH, or that variation in $\phi$ is roughly canceled out by SDS surface activity in terms of its influence on hygroscopicity. To further investigate this lack of variation, we make several assumptions regarding the water activity of SDS solution droplets, and compare the predicted variation in SDS $\kappa$ with RH to observations. Some of these predictions are based on the CMC of SDS (8.2 mol m$^{-3}$), and we note again that based on measured $D_{\text{dry}}$ and $D_{\text{wet}}$, the range of SDS concentrations observed in this study is 110 to 340 mol m$^{-3}$.

Our first two cases assume that SDS either behaves ideally ($\phi=1$) or $\phi=0.91$ (as required to match observed $\kappa$). In both cases, the surface tension of the droplet is assumed to be equal to that of pure water. The resulting values of SDS $\kappa$ are constant with RH (Fig. 7a) both because $\phi$ is constant and $\sigma=72.8$ mJ m$^{-2}$ (the assumed value in the $\kappa$ formulation, see Eq. 5). Additionally, the theoretical $\kappa$ values are roughly consistent with the observed values. However, if it is instead assumed that $\phi=0.12$, as derived from macroscopic SDS solutions, $\kappa$ is much smaller than in our observations (Fig. 7a, red curve). Not even the assumption that $\sigma$ is reduced to zero can make the choice of $\phi=0.12$ consistent with the observations. We therefore conclude that micellization in micron-sized SDS solution droplets does not increase $a_w$ at RH from 99 to 100% in a manner analogous to macroscopic solutions; and therefore, CMC values obtained from measurements of such solutions may not be appropriate for calculations involving aerosol particles of typical atmospheric sizes (e.g., Tabazadeh, 2005).

4.2.3 Other organic compounds

The hygroscopicity of the remaining compounds, expressed as $\kappa$, increased with RH, with the exception of sucrose. These trends were significant for malonic acid ($p<0.01$) and sucrose ($p<0.03$, Table 1). Like AS, the increase of malonic acid $\kappa$ with RH was consistent with the E-AIM activity coefficient model (Fig. 8a), and values of $\kappa>\kappa_{\text{ideal}}$ around...
Table 2. Slopes (m) and significance (p-value) of trends in both hygroscopicity parameters (κ and δ) with \( D_{wet} \). P-values under 5% are in boldface.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( m_κ ) [% µm(^{-1})]</th>
<th>( m_δ ) [% um(^{-1})]</th>
<th>( p_κ )</th>
<th>( p_δ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>3.3</td>
<td>−8.1</td>
<td>0.13</td>
<td>0.26</td>
</tr>
<tr>
<td>AS</td>
<td>4.5</td>
<td>−0.5</td>
<td>0.42</td>
<td>0.98</td>
</tr>
<tr>
<td>malonic acid</td>
<td>41</td>
<td>−120</td>
<td>0.001</td>
<td>0.014</td>
</tr>
<tr>
<td>adipic acid</td>
<td>47</td>
<td>−27</td>
<td>0.015</td>
<td>0.52</td>
</tr>
<tr>
<td>glucose</td>
<td>42</td>
<td>−76</td>
<td>0.033</td>
<td>0.085</td>
</tr>
<tr>
<td>SDS</td>
<td>65</td>
<td>−210</td>
<td>1 × 10^{-6}</td>
<td>1 × 10^{-6}</td>
</tr>
<tr>
<td>sucrose</td>
<td>22</td>
<td>−100</td>
<td>0.26</td>
<td>0.051</td>
</tr>
</tbody>
</table>

RH=99.8% are likely due to dissociation (κ was calculated assuming no dissociation).

Glucose κ increased slightly with RH (Fig. 8b). Unlike the inorganic compounds, for glucose φ>1 in aqueous solutions (e.g., Matubayasi and Nishiyama, 2006), from which \( κ>κ_{ideal} \) follows. At the high RH observed in this study, glucose concentration was between 0.11 to 0.45 mol kg\(^{-1}\), which in macroscopic solutions corresponds to an increase in φ of <2% (Stokes and Robinson, 1966), and thus this effect would have to be enhanced in micron-sized droplets to account for the observations.

Sucrose was the only compound studied in which κ decreased with RH (Fig. 8c), although for all RH, \( κ>κ_{ideal} \). Like glucose, the osmotic coefficient of macroscopic sucrose solutions is greater than one, although sucrose deviates further from ideality (which is consistent with our observations). At the maximum sucrose concentration observed (0.53 mol kg\(^{-1}\), φ=1.044 in macroscopic solutions (Clegg et al., 2001), again suggesting that this effect is enhanced in micron-sized droplets relative to macroscopic solutions. The ratio of glucose κ to sucrose κ increases towards 1.8 (the ratio of their molar volumes, as assumed for ideal solutions) as RH→100%. The greater non-ideality of sucrose relative to glucose is already apparent at RH ∼ 99.5%.

An increase in adipic acid κ with RH (Fig. 8d) could also at least partly be caused by its low solubility of 25 kg m\(^{-3}\) (Saxena and Hildemann, 1996). Again assuming φ=1, this solubility limit corresponds to an RH of ∼99.7%. Adipic acid κ does decrease below this limit, although it is consistently larger than predicted without accounting for dissociation (or Kelvin effects).

4.3 Hygroscopicity variation with \( D_{wet} \)

4.3.1 Comparison of κ and δ as a hygroscopicity parameter vs. \( D_{wet} \)

We first compared κ and δ as a parameter for trends in hygroscopicity with \( D_{wet} \) to see if there was any justification for a second parameter. Calculation of δ requires assumption of φ (i.e., the Raoult effect), and we allow φ to vary with RH according to the linear regression of κ onto RH (red lines in Figs. 5, 6a, and 8). Because δ accounts for variation of osmolarity with RH, it is less likely that any trend in δ with \( D_{wet} \) is due to solution non-ideality than if φ were held constant. We therefore expect δ to be a more appropriate metric of Kelvin effects. This can be seen by comparing the p values for these parameters (Table 2), which are generally higher (less significant) for δ. δ for only two compounds (SDS and malonic acid) varied significantly (p<0.05) with \( D_{wet} \), while variation of κ with \( D_{wet} \) was significant for two additional compounds (glucose and adipic acid). Figure 6b and c show the trend in SDS hygroscopicity with \( D_{wet} \) using κ and δ, respectively. The trends are in opposite direction because hygroscopicity decreases with δ, but the significance (Table 2) and the correlation are similar. Based on the results from all compounds, we conclude that a parameterization of the Kelvin term such as δ, that is derived accounting for non-ideality in the Raoult term, is a more conservative and useful metric of Kelvin effects in micron-sized droplets.

4.3.2 Inorganic compounds

Neither NaCl nor AS δ varied with \( D_{wet} \) (Fig. 9), as expected because these salts are not known to be surface-active. The finding that non-ideal behavior of AS, as opposed to surface...
activity, causes variation in high-RH hygroscopicity is consistent with LACIS measurements (Wex et al., 2005).

### 4.3.3 Sodium Dodecyl Sulfate (SDS)

It is well-known that SDS reduces the surface tension (\(\sigma\)) of macroscopic aqueous solutions, and consequently one might expect SDS \(\delta\) to be lower than that of NaCl and AS. SDS hygroscopicity did vary strongly with \(D_{\text{wet}}\) (Fig. 6b and c), although it is not immediately clear why its surface activity causes its hygroscopicity to increase with increasing \(D_{\text{wet}}\), as a given reduction in surface tension would be expected to cause a decrease in \(\delta_{\text{SDS}}\) which does not vary with \(D_{\text{wet}}\) (Fig. 2c). We next seek to explain the trend in \(\delta\) with respect to \(D_{\text{wet}}\) as shown in Fig. 6c (and reproduced in Fig. 10). To do so, we make a series of assumptions regarding SDS surface activity, and discuss the theoretical variation in \(\kappa\) with RH and \(\delta\) with \(D_{\text{wet}}\) resulting from these assumptions.

As can be seen in Eq. (6), \(\delta\) is proportional to surface tension (\(\sigma\)). If SDS solution droplets behave ideally, with a surface tension of pure water, \(\delta\) is equal to 2.1 nm, and \(\delta=0\) if the Kelvin effect is completely neglected (Fig. 10a). Taking the partitioning effect into account has the opposite effect: formation of a monolayer (surface excess concentration, \(\Gamma\), of 6 \(\mu\)mol m\(^{-2}\)) causes \(\delta\) to increase to 3.6 nm (Fig. 10a). With a soluble surfactant such as SDS, the solute excess may exist for some distance below the solution-air interface, and thus concentrations greater than one monolayer equivalent are physically reasonable. Note that like \(\sigma\), the influence of \(\Gamma\) on hygroscopicity goes as \(D_{\text{wet}}^{-1}\), and therefore \(\delta\) is constant with \(D_{\text{wet}}\).

Transformation of observed \(D_{\text{wet}}\) into \(\delta\) requires an assumption of \(\phi\) for the solution droplets. As with all other compounds, for SDS we assumed that \(\phi\) varies with RH according to the linear regression of \(\kappa\) onto RH (for SDS, \(\phi\) was relatively constant, roughly 0.9). To test the sensitivity of the trend in \(\delta\) with \(D_{\text{wet}}\) to this assumption, we repeat the calculations assuming \(\phi=0.75\) (Fig. 10b). This causes a slight downward shift in all \(\delta\), but the trend in \(\delta\) with \(D_{\text{wet}}\) is not fundamentally altered.

It can be seen in Fig. 10a that lowering \(\sigma\) (blue curves) and accounting for the partitioning effect (red curves) have opposite effects on SDS hygroscopicity (parametrized as \(\delta\)). When both are taken into account, they tend to cancel each other out, and if they are roughly in balance, no trend in hygroscopicity with RH would be predicted (Fig. 7b). The lack of a trend in SDS \(\kappa\) with RH therefore suggests the presumed lowering of \(\sigma\) is roughly canceled out by the partitioning effect.

As indicated above, we have not been able to model the observed increase in SDS hygroscopicity (decrease in \(\delta_{\text{SDS}}\)) with \(D_{\text{wet}}\) assuming constant values of \(\phi\), \(\sigma\), and \(\Gamma\). This suggests that at least one of these parameters varies with \(D_{\text{wet}}\). Because \(\kappa\) is roughly proportional to \(\phi\), and the highest observed values of \(\kappa_{\text{SDS}}\) are roughly 2 times greater than the lowest, the range of observed SDS hygroscopicity could correspond to an increase in \(\phi\) from 0.5 to 1. This could result from micellization in smaller droplets, although not to the extent seen in macroscopic solutions. However, \(\phi\) is typically thought to vary with concentration, and thus a trend in \(\kappa_{\text{SDS}}\) with RH would be expected if \(\phi\) is not constant. It is therefore unlikely that the trend in \(\delta\) is the result of micellization.

Figure 7b demonstrates that if both \(\sigma\) and \(\Gamma\) are allowed to vary with \(D_{\text{wet}}\), they can do so in a way that their influences on the \(\kappa\) vs. RH trend cancel out. We found that the following assumptions fit the observations: At the low end of our measured \(D_{\text{wet}}\) (0.8 \(\mu\)m), we set \(\Gamma\) to 18 \(\mu\)mol m\(^{-2}\), and decreased \(\Gamma\) linearly with \(D_{\text{wet}}\) until \(\Gamma=0\) when \(D_{\text{wet}}=1.8 \mu\)m. We held \(\sigma\) constant at 30 mJ m\(^{-2}\). Under these assumptions, \(\kappa\) does not vary with RH (Fig. 11a), but \(\delta\) would decrease with \(D_{\text{wet}}\) at roughly the observed rate (Fig. 11b). We emphasize that because two effects are opposing each other (surface tension reduction and partitioning), we cannot isolate either effect
As with the variation of hygroscopicity for malonic acid, fol-
lar concentration is supported by measurements of evapo-
derent. However the same effect is present. Previous investigations have characterized two types of organic films at aqueous interfaces: "condensed" films formed by insoluble organic matter, which resides only at the aqueous-air interface, and "adsorbed" films formed by soluble organic matter. Because SDS is a soluble surfactant, its surface excess might occur both at the interface, but also as an increased dissolved concentration near the interface (i.e., a gradient from the interface to the bulk). In other words, if the surface excess concentration is 18 µmol m$^{-2}$ but only 6 µmol m$^{-2}$ can reside in a monolayer at the interface, then for every SDS molecule in the monolayer, there are two in solution near the interface in excess of the bulk solution concentration. This interpretation of the surface excess concentration is supported by measurements of evaporation rates from SDS solutions, which are similar to those of pure water. In contrast, a compressed film of insoluble surfactant can substantially reduce evaporation rates from aque-
sous solutions (Moroi et al., 2004). However the same effect could result from any mechanism causing a decrease in SDS solution activity that goes as $D_{wet}^{-1}$. However, if $\sigma$ of these droplets is somewhere between the value for pure water and zero, and micellization is not occurring, then the most likely explanation for the observed trend is an increase in $\Gamma$ with decreasing $D_{wet}$, eventually reaching a value equivalent to approximately three monolayers.

### 4.3.4 Other organic compounds

The hygroscopicity of all other organic compounds increased with size (i.e., $\delta$ decreased with $D_{wet}$, although none as strongly as SDS (Fig. 12). As with the variation of hygroscopicity with RH, this trend was strongest (Fig. 12a) and most significant ($p=0.014$, Table 2) for malonic acid, followed by sucrose. These results therefore provide evidence that both the Raoult and Kelvin effects influence the high-RH
hygroscopicity of malonic acid and, to a lesser extent, sucrose. It is also possible that the Kelvin effect contributes to the hygroscopicity of both sugars. While glucose is known to slightly raise the surface tension of aqueous solutions, sucrose has the opposite effect (Matubayasi and Nishiyama, 2006), and this is consistent with sucrose δ being lower on average than glucose δ. The change in σ of macroscopic solutions caused by these sugars is slight relative to SDS, however, particularly at low concentrations. Furthermore, without independent knowledge of the osmolarity of these droplets, the importance of the Kelvin effect on sugar hygroscopicity cannot be quantified. No impact of the Kelvin effect on adipic acid hygroscopicity was seen once observed variations in ϕ with RH were accounted for (Fig. 12d, Table 2).

5 Conclusions

The hygroscopicity of particles of seven pure compounds was measured at RH ranging from 99.2 to 99.9%, and expressed as κ to examine the Raoult effect and as δ to examine the Kelvin effect. The results were broadly consistent with those predicted based on literature values for molar volume and water activity. Specifically, we draw the following conclusions:

1. Small variations in inorganic hygroscopicity are best explained by non-ideal solution effects. No trends with $D_{\text{wet}}$ were observed, and minor variation in hygroscopicity with RH was consistent with water activity data from macroscopic solutions.

2. Both Kelvin (curvature) and Raoult (solute) effects are important for the hygroscopicity of the tested organic aerosol. Trends with RH, when present, were consistent with water activity data. However, even when this variability was accounted for, organic hygroscopicity generally increased with increasing $D_{\text{wet}}$, particularly for the most surface active compound, sodium dodecyl sulfate (SDS).

3. Surface activity reduces the hygroscopicity of SDS at high RH. This occurs because in this RH range (99 to 100%), the partitioning effect overwhelms the reduction in σ. The concentrations observed in this study are greater than would be found at the point of activation, however, and so it is likely that the surface excess concentration is greater in these droplets than in newly-formed cloud droplets. It is therefore possible that slightly reduced surface tension (∼10%) inferred from recent CCN activity experiments of complex organic solutions (e.g., Engelhart et al., 2008; Abbatt et al., 2005; Ziese et al., 2008; Wex et al., 2009; Moore et al., 2008) could be a result of less partitioning relative to surface tension reduction under supersaturated conditions.

4. No evidence for micellization of SDS is found in these drops, at least to the extent seen in macroscopic solutions. SDS hygroscopicity was several times greater (in terms of water volume absorbed) than predicted based on macroscopic data.

5. Overall, these results suggest that extending the properties of macroscopic solutions to calculations of the hygroscopicity of micron-sized drops can be very misleading.

Acknowledgements. The authors would like to acknowledge funding from the NASA Radiation Sciences Program and the NSF Graduate Research Fellowship program.

Edited by: A. Laaksonen

References


Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: A thermodynamic model of the system $H^+\cdot\text{NH}_4^+\cdot\text{Na}^+\cdot\text{SO}_4^{2-}\cdot\text{NO}_3^-\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$ at 298.15 K, J. Phys. Chem. A, 102, 2155–2171, 1998.
Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: Thermo-
dynamic modelling of aqueous aerosols containing electrolytes
and dissolved organic compounds, J. Aerosol Sci., 32, 713–738,

Dinar, E., Tarianni, I., Graber, E. R., Katsman, S., Moise, T.,
Anttila, T., Mentel, T. F., and Rudich, Y.: Cloud Condensa-
Nuclei properties of model and atmospheric HULIS, Atmos.
Chem. Phys., 6, 2465–2482, 2006,
http://www.atmos-chem-phys.net/6/2465/2006/.

Dinar, E., Tarianni, I., Graber, E. R., Anttila, T., Mentel, T. F.,
and Rudich, Y.: Hygroscopic growth of atmospheric and model

Duplissy, J., Gysel, M., Alfarra, M. R., Dommen, J., Metzger, A.,
Prevot, A. S. H., Weingartner, E., Laaksonen, A., Raatikainen,
T., Good, N., Turner, S. F., McFiggans, G., and Baltensperger,
U.: Cloud forming potential of secondary organic aerosol under
near atmospheric conditions, Geophys. Res. Lett., 35, 1–5, doi:

Ellison, G., Tuck, A., and Vaida, V.: Atmospheric processing of
organic aerosols, J. Geophys. Res.-Atmos., 104, 11633–11641,
1999.

CCN activity and droplet growth kinetics of fresh and aged
monoterpen secondary organic aerosol, Atmos. Chem. Phys.,
8, 3937–3949, 2008,
http://www.atmos-chem-phys.net/8/3937/2008/.

Facchini, M., Mircea, M., Fuzzi, S., and Charlson, R.: Cloud
albedo enhancement by surface-active organic solutes in grow-

Facchini, M., Mircea, M., Fuzzi, S., and Charlson, R.: Comments
on “Influence of soluble surfactant properties on the activation of
aerosol particles containing inorganic solute”. J. Atmos. Sci., 58,

Fitzgerald, J., Hoppel, W., and Vietti, M.: The size and scatter-
ing coefficient of urban aerosol-particles at Washington, DC as
a function of relative-humidity, J. Atmos. Sci., 39, 1838–1852,
1982.

Gill, P., Graedel, T., and Weschler, C.: Organic films on atmo-
spheric aerosol-particles, fog droplets, cloud droplets, raindrops,

Hanford, K. L., Mitchem, L., Reid, J. P., Clegg, S. L., Topping,
D. O., and McFiggans, G. B.: Comparative thermodynamic stud-
ies of aqueous glucaric acid, ammonium sulfate and sodium chlor-
eide aerosol at high humidity, J. Phys. Chem. A, 112, 9413–9422,

Henning, S., Rosenström, T., D’Anna, B., Gola, A. A., Svenningsson,
B., and Bilde, M.: Cloud droplet activation and surface tension of
mixtures of slightly soluble organics and inorganic salt, Atmos.
Chem. Phys., 5, 575–582, 2005,
http://www.atmos-chem-phys.net/5/575/2005/.

Hings, S. S., Wrobel, W. C., Cross, E. S., Worsnop, D. R., Davi-
dovits, P., and Onasch, T. B.: CCN activation experiments with
adipic acid: effect of particle phase and adipic acid coatings on
soluble and insoluble particles, Atmos. Chem. Phys., 8, 3735–
3748, 2008,
http://www.atmos-chem-phys.net/8/3735/2008/.

Hitzenberger, R., Berner, A., Kasper-Giebl, A., Löfflund, M., and
Puxbaum, H.: Surface tension of Rax cloud water and its rela-
tion to the concentration of organic material, J. Geophys. Res.-

Hudson, J. and Da, X.: Volatility and size of cloud condensation

Husar, R. and Shu, W.: Thermal analysis of Los Angeles smog

Kiss, G., Tombacz, E., and Hansson, H.: Surface tension effects
of humic-like substances in the aqueous extract of tropo-
ospheric fine aerosol, J. Atmos. Chem., 50, 279–294, doi:

Kokkola, H., Sorjamaa, R., Peraniemi, A., Raatikainen, T., and
Laaksonen, A.: Cloud formation of particles containing humic-

Krämer, L., Pöschl, U., and Niessner, R.: Microstructural rearrange-
ment of sodium chloride condensation aerosol particles on inter-

Lewis, E. R.: An examination of Köhler theory resulting in an ac-
curate expression for the equilibrium radius ratio of a hygro-
scopic aerosol particle valid up to and including relative hu-

properties on the activation of aerosol particles containing inor-

Lima, L. and Synovec, R.: Laser-based dynamic surface-tension
detection for liquid-chromatography by probing a repeating drop

Loglio, G., Pandolfi, P., Tesei, U., and Noskov, B.: Measure-
ments of interfacial properties with the axisymmetric bubble-
shape analysis technique: effects of vibrations, Colloid. Sur-

Lohmann, U. and Leck, C.: Importance of submicron surface-active
organic aerosols for pristine Arctic clouds, Tellus B, 57, 261–
268, 2005.

Matubayasi, N. and Nishiyama, A.: Thermodynamic quantities of
surface formation of aqueous electrolyte solutions, VI. Compari-
son with typical nonelectrolytes, sucrose and glucose, J. Colloid

Mircea, M., Facchini, M. C., Decesari, S., Cavalli, F., Emblico, L.,
Fuzzi, S., Vestin, A., Rissler, J., Swietlicki, E., Frank, G., An-
dreae, M. O., Maenhaut, W., Rudich, Y., and Artaxo, P.: Impor-
tance of the organic aerosol fraction for modeling aerosol hygro-
scopic growth and activation: a case study in the Amazon Basin,
Atmos. Chem. Phys., 5, 3111–3126, 2005,
http://www.atmos-chem-phys.net/5/3111/2005/.

Moroi, Y., Rusdi, M., and Kubo, I.: Difference in surface prop-
erties between insoluble monolayer and adsorbed film from kine-
ic of water evaporation and BAM image, J. Phys. Chem. B, 108,

mass, surface tension, and droplet growth kinetics of marine or-
ganics from measurements of CCN activity, Geophys. Res. Lett.,


