

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

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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 ($\sigma_{\text{H}_2\text{O}}=72.8 \text{ mJ m}^{-2}$ at 25° C). This would



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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 $\sim 10\%$ relative to those assuming $\sigma_{\text{H}_2\text{O}}$. 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_{wet}) ~ 2 mm, 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; Taraniuk et al., 2008), but the surface:volume ratio in $\sim 1 \mu\text{m}$ 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 $D_{\text{wet}} \sim 1 \mu\text{m}$, but rather larger droplets with a smaller surface:volume ratio, measurements made at $\text{RH} > 99\%$ 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_{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 $\sigma_{\text{H}_2\text{O}}$ (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 $\text{RH} = 99.6\%$ (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 $D_{\text{wet}} \sim 1 \mu\text{m}$ 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_{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_{wet} at a given RH and D_{dry} . Because hygroscopicity depends on water activity (a_w) and surface tension (σ), these two variables appear in the Köhler equation, which relates the ambient RH in equilibrium with a droplet to various droplet properties:

$$\text{RH} = a_w \exp\left(\frac{4 \sigma \bar{V}_w}{RT D_{\text{wet}}}\right) \quad (1)$$

Here \bar{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:

$$a_w = \exp\left(-\frac{\phi \nu n_s}{n_w}\right) \quad (2)$$

where ϕ is the osmotic coefficient, ν 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 ϕ as a proxy) on hygroscopicity, while the Kelvin effect is defined as the effect of σ on hygroscopicity. The sensitivity of D_{wet} to these variables can be defined as the ratio of the resulting fractional change in D_{wet} to a small fractional change in either variable, e.g.:

$$\frac{d\tilde{D}_{\text{wet}}}{d\phi} = \frac{dD_{\text{wet}}}{d\phi} \times \frac{\phi_o}{D_{\text{wet},o}} \quad (3)$$

at some reference wet diameter ($D_{\text{wet},o}$) with a corresponding osmotic coefficient (ϕ_o). The sensitivity of D_{wet} to σ 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_{wet} to ϕ increases gradually with RH, reaching 20% around RH=90% and 30% around RH=98% (Fig. 1a). In contrast, the sensitivity of D_{wet} to σ is a much stronger function of

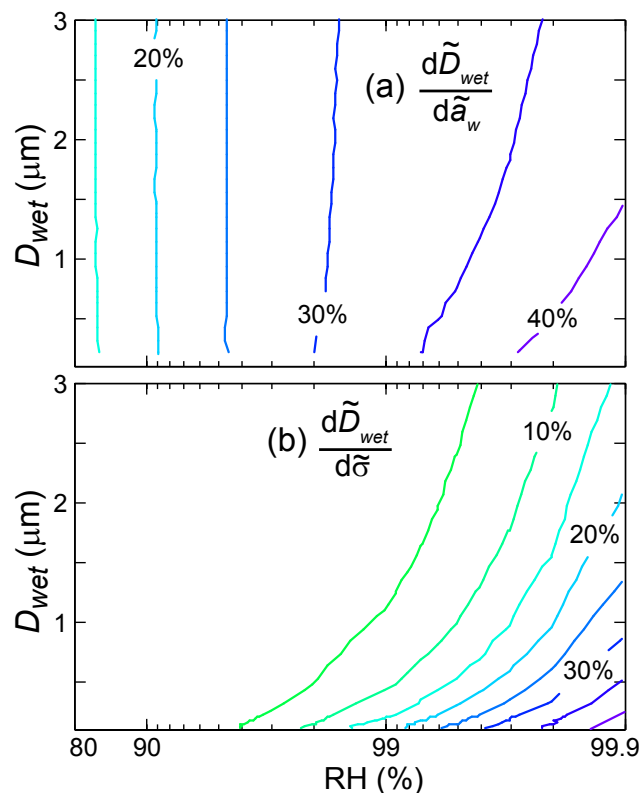


Fig. 1. Sensitivity of D_{wet} to changes in (a) water activity and (b) surface tension. Contour interval is 5%.

both D_{wet} and RH (Fig. 1b), and only reaches 20% when $\text{RH} \gtrsim 99\%$ and $D_{\text{wet}} \lesssim 2 \mu\text{m}$. This is because the magnitude of the Kelvin effect approaches that of the Raoult effect as $\text{RH} \rightarrow 100\%$ (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_{wet} to σ is negligible when $\text{RH} < 95\%$, but increases sharply as RH approaches 100%. Wex et al. (2008) also found that the sensitivity of D_{wet} to the number of osmoles was greater for more hygroscopic particles; in our analysis as well the sensitivity of D_{wet} to ϕ 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

(Fig. 1), most proposed parametrizations are defined through their effect on the water activity (a_w). To facilitate comparison with other studies, we employ the commonly-used κ formulation of Petters and Kreidenweis (2007), in which κ relates a_w to the ratio of the volume of water (V_w) to volume of solute (V_s) in the droplet:

$$\kappa = \frac{V_w}{V_s} \left(\frac{1}{a_w} - 1 \right) \quad (4)$$

In this formulation, κ ranges from zero for an insoluble but wettable substance to a maximum of approximately 1.3 for sodium chloride. Trends in hygroscopicity with RH, which are emphasized in this study, should be similar no matter which parametrization of the Raoult term is used. We wish to incorporate all factors influencing hygroscopicity into a single parameter, without introducing additional parameters such as those in the Szyszkowski equation (Szyszkowski, 1908) which is typically used to express σ as a function of solute concentration. Our approach is therefore to assume $\sigma = \sigma_{\text{H}_2\text{O}}$, and we therefore insert the definition of κ (Eq. 4) into the Köhler equation:

$$\text{RH} = \frac{D_{\text{wet}}^3 - D_{\text{dry}}^3}{D_{\text{wet}}^3 - D_{\text{dry}}^3(1-\kappa)} \exp\left(\frac{4\sigma_{\text{H}_2\text{O}}\bar{V}_w}{RTD_{\text{wet}}}\right) \quad (5)$$

Our experiments involve measuring D_{wet} at selected values of RH and D_{dry} . Equation (5) is used to transform D_{wet} into κ . If the actual surface tension of the droplet is lower than $\sigma_{\text{H}_2\text{O}}$, κ will be overestimated because D_{wet} , and therefore V_w (Eq. 4), will be larger than that of an equivalent droplet with $\sigma = \sigma_{\text{H}_2\text{O}}$.

Any variation in hygroscopicity, regardless of the cause, will be reflected in κ . For example, an increase in κ with RH could be caused by either non-ideal behavior at higher concentrations (i.e., lower RH), or by a surface tension lower than that assumed in the κ formulation (i.e., $\sigma_{\text{H}_2\text{O}}$). Essentially, the issue is that RH and D_{dry} are controlled, and only one experimental variable, D_{wet} , is measured. It is therefore impossible to cleanly separate the multiple effects (e.g., osmolality and surface tension) affecting hygroscopicity. Nevertheless, we attempt to distinguish between solute and surface effects by defining an alternative hygroscopicity parameter, δ . First, we take the linear regression of κ onto RH, and assume that this captures any variation in solution non-ideality that occurs over this RH range. We then incorporate this variation into the definition of δ , described below. δ can thus be thought of as a hygroscopicity parameter that has been detrended with respect to RH, and will be used to look for trends in hygroscopicity with D_{wet} which are likely caused by surface effects. Still, while linear regression of any single hygroscopicity parameter onto RH or D_{wet} has the advantage of simplicity and an ability to determine if trends are statistically significant, caution must be applied when interpreting results, and multiple causes of any observed trends must be considered.

As can be seen in Eq. (5), κ is a parametrization of the Raoult term in Eq. (1). To express observed D_{wet} values as κ (when D_{dry} and RH are known), a surface tension must be assumed. We also parametrize the Kelvin term by defining a length scale (Lewis, 2008):

$$\delta = \frac{4\sigma\bar{V}_w}{RT} \quad (6)$$

and substitute into the Köhler equation:

$$\text{RH} = \exp\left(-\frac{\phi\nu n_s}{n_w}\right) \exp\left(\frac{\delta}{D_{\text{wet}}}\right) \quad (7)$$

We use Eq. (7) to calculate δ given experimentally-determined D_{wet} , D_{dry} , and RH, just as Eq. (5) is used to derive κ 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 ($\phi\nu n_s$) in the droplet (given particle composition and D_{dry}). We use the relationship between κ and RH discussed above to determine this quantity. Because any trend in hygroscopicity with RH has been removed from δ , it is much more likely that any observed trend in δ with D_{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, $\delta = 2.1$ nm, and because $\delta \propto \sigma$, as hygroscopicity increases, derived δ decreases.

2.3 Predicted values of κ

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

$$\kappa \simeq \nu_s \phi \bar{V}_w / \bar{V}_s \quad (8)$$

For an ideal, non-surface active solute, κ is constant throughout the range of RH examined in this study (Fig. 2, black curves). For non-ideal, non-surface active solutes, κ is proportional to ϕ (Fig. 2a and b, blue curves). For surface-active solutes, σ is reduced, which in turn raises derived κ an amount that increases with increasing RH (Fig. 2a and b, red curves). While this increase in κ is sensitive to RH, it is reasonably insensitive to D_{dry} (Fig. 2a). Not all dependence on D_{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 κ to D_{dry} is much greater if one looks for a trend in κ with D_{wet} (Fig. 2b).

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

$$n_s = \frac{\pi D_{\text{dry}}^3}{6\bar{V}_s} \quad (9)$$

where n_w depends on D_{wet} after the volume of solute has been subtracted:

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

For most common solutes, including the ones examined here, ϕ as a function of $\frac{n_s}{n_w}$ 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 ϕ (Clegg et al., 1998, 2001), and use Eqs. (2) and (4) to calculate κ 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 δ

As discussed previously, we parametrize the Kelvin term in the Köhler equation to examine trends in hygroscopicity with droplet diameter (D_{wet}) using the length scale δ , which is proportional to surface tension (σ) and defined in Eq. (7). This is analogous to the use of Eq. (5) to parametrize the Raoult term as κ . We assume a relationship between ϕ (again, a proxy for osmoles) and RH based on the regression of κ onto RH, and so this dependence of hygroscopicity on RH has been removed from δ . 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 δ . This is the primary motivation for using the δ 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 δ will be lower than that of an ideal solution droplet with $\sigma = \sigma_{\text{H}_2\text{O}}$ (Fig. 2c, red curves). δ is also sensitive to the assumed value of ϕ ; (Fig. 2c, blue curves).

The reduction of σ 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 σ is reduced to $\sim 40 \text{ mJ m}^{-2}$. 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 σ 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):

$$n_s^{\text{tot}} = n_s^{\text{bulk}} + n_s^{\text{surf}} \quad (11)$$

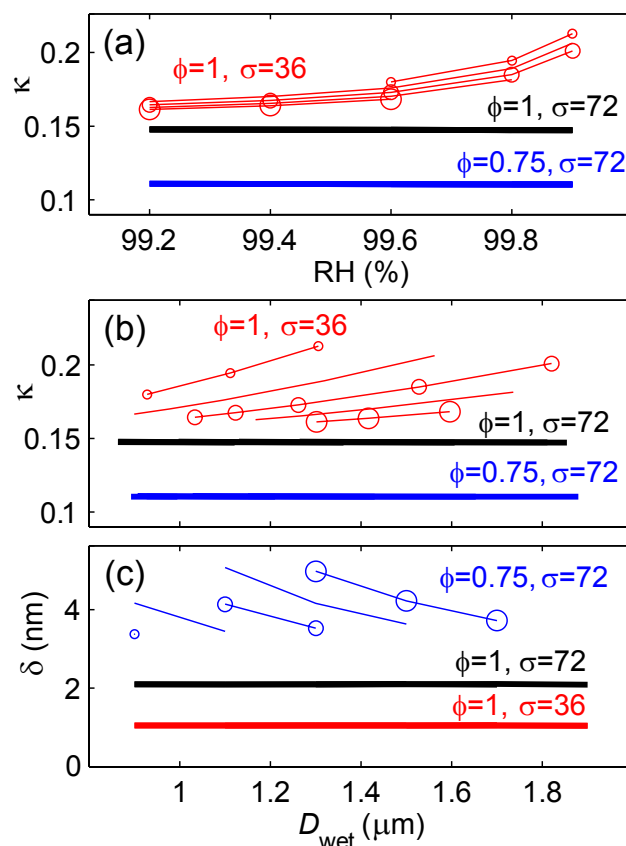


Fig. 2. Theoretical variation of κ with both (a) RH and (b) D_{wet} , and of (c) δ with D_{wet} . Black curves are for ideal SDS solution droplets with $\sigma_{\text{H}_2\text{O}}$, red curves assume σ is reduced by half, and blue curves assume $\phi=0.75$. D_{dry} is indicated by symbol size.

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

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

SDS has a cross-sectional area of $\sim 30 \text{ \AA}^2$ per molecule (Prosser and Franses, 2001), and therefore a monolayer of SDS is equivalent to an excess surface concentration (Γ) of $6 \times 10^{-6} \text{ mol m}^{-2}$. Given a value of D_{dry} , Γ , and RH, Eq. (12) can be solved iteratively for n_s^{surf} and D_{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

the bulk and surface phases. As a consequence, Γ may be greater than a monolayer equivalent ($\sim 6 \times 10^{-6}$ for SDS). To the extent that the partitioning effect does deplete solute from the bulk phase, hygroscopicity will decrease and δ will therefore be greater.

2.5 Specific questions addressed by this study

We compare observed hygroscopicity (as expressed by the parameters κ and δ) to values calculated under different assumptions regarding the terms a_w (i.e., the Raoult effect) and σ (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 σ 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 driers, 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_{dry}) between 0.2 and 0.5 μm , 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 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 (χ) 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 (ΔT) 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 ΔT 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 ΔT). The overall flow rate in the column was 0.94 L min^{-1} , of which 0.1 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 μm intervals. To get a sense of the precision of these measurements, we measured D_{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_{wet} mode (which was always the more numerous) was assumed to be the singly-charged mode. The standard deviation of this mode ranged from 0.10 to 0.42 μm , or from 7 to 22% of the mean. Replicate measurements of D_{wet} standard deviation were made at several D_{dry} , and ranged from 0.03 to 0.30 μm (3 to 15% of the mean). However, when restricted to $D_{\text{wet}} < 2.0 \mu\text{m}$, 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 μm (3 to 9% of the mean).

RH in the CFTGC was calibrated with NaCl particles, which required an assumption of κ . Based on the E-AIM model (Clegg et al., 1998, 2001), we assumed NaCl κ increased slightly over the relevant RH range, from 1.24 to 1.27, and then used Eq. (5) to relate RH to D_{wet} of NaCl solution droplets at a given ΔT . We found a linear relationship between RH and ΔT , but saw slight variation in absolute RH ($\sim 0.05\%$) at the same ΔT on different days (Fig. 4). Therefore instead of utilizing the linear regression of RH onto ΔT , for all compounds besides NaCl we transformed D_{wet} into κ 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.

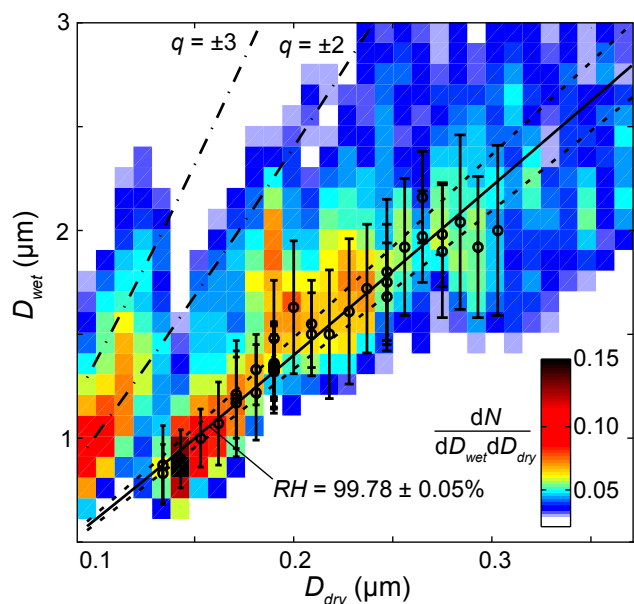


Fig. 3. D_{wet} spectra (color), vs. D_{dry} of NaCl particles. Includes D_{wet} fit peaks (circles) and standard deviations (error bars) used to determine RH, along with a solid line for the best fit RH, dotted lines indicating the precision of the RH calculation, and dash-dot lines representing multiply-charged particles selected by the DMA.

Table 1. High-RH hygroscopicity (κ_{obs}) of the NaCl reference and six other compounds. Also κ_{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 κ onto RH. p -values under 5% are in boldface.

	κ_{obs}	κ_{ideal}	n	m [% % ⁻¹]	p
NaCl	1.27*±0.11	1.33	77	-1.2	0.84
AS	0.572±0.074	0.72	54	20	0.068
malonic acid	0.291±0.057	0.28	35	46	0.009
adipic acid	0.185±0.040	0.168	13	100	0.050
glucose	0.165±0.033	0.154	20	63	0.13
SDS	0.134±0.029	0.147	53	2.72	0.86
sucrose	0.112±0.020	0.084	27	-54	0.028

* This value was fixed in the RH calibration.

4 Results and discussion

4.1 Overall results

As expected, the high-RH hygroscopicity, expressed as κ , of both inorganic compounds was greater than that of any of the five organic compounds (Table 1). NaCl was the most hygroscopic compound studied ($\kappa=1.27\pm 0.11$, with the mean value fixed by the CFTGC calibration), followed by

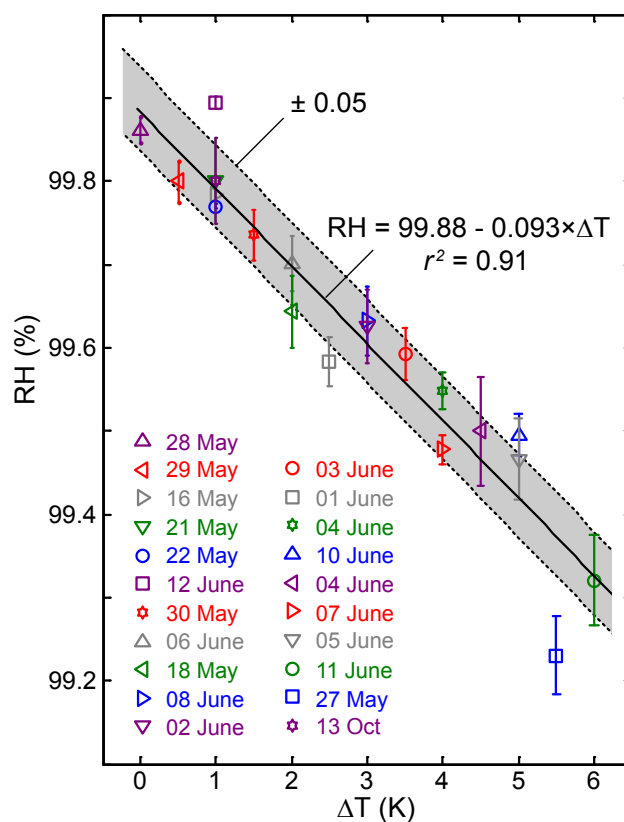


Fig. 4. RH vs. ΔT , with RH derived from observed D_{wet} of NaCl solution droplets, assuming $\kappa=1.24$ to 1.27 (based on the E-AIM model) and shape-corrected diameter ($\chi=1.08$).

ammonium sulfate (AS $\kappa=0.572\pm 0.074$). Average AS κ 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 ($\kappa=0.134\pm 0.029$) was only 9% lower than that predicted for an ideal solution (0.147). In macroscopic solutions, however, SDS does not behave ideally: ϕ 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 ($> 110 \text{ mol m}^{-3}$) (Widera et al., 2003). The values of SDS κ derived from D_{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

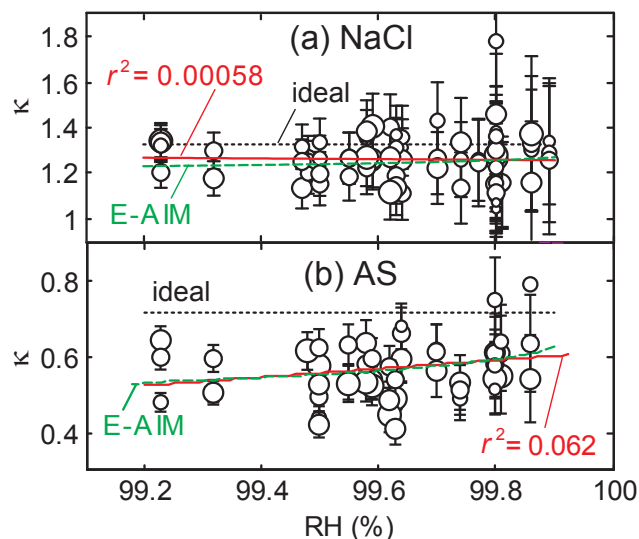


Fig. 5. Hygroscopicity (κ) of (a) NaCl and (b) AS vs. RH. With linear regressions (red solid lines), data from macroscopic solutions as represented in the E-AIM model (green dashed lines), and values for ideal solutions with the surface tension of water (black dotted lines). Symbol size indicates D_{dry} . Error bars indicate the error in κ associated with an error in RH of $\pm 0.5\%$ (absolute).

acid was the most hygroscopic organic compound ($\kappa=0.29$), 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 ($D_{\text{dry}} \geq 250$ nm) of adipic acid particles examined, which are not subject to the deliquescence barrier to hygroscopic growth affecting smaller ($D_{\text{dry}} < 150$ 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

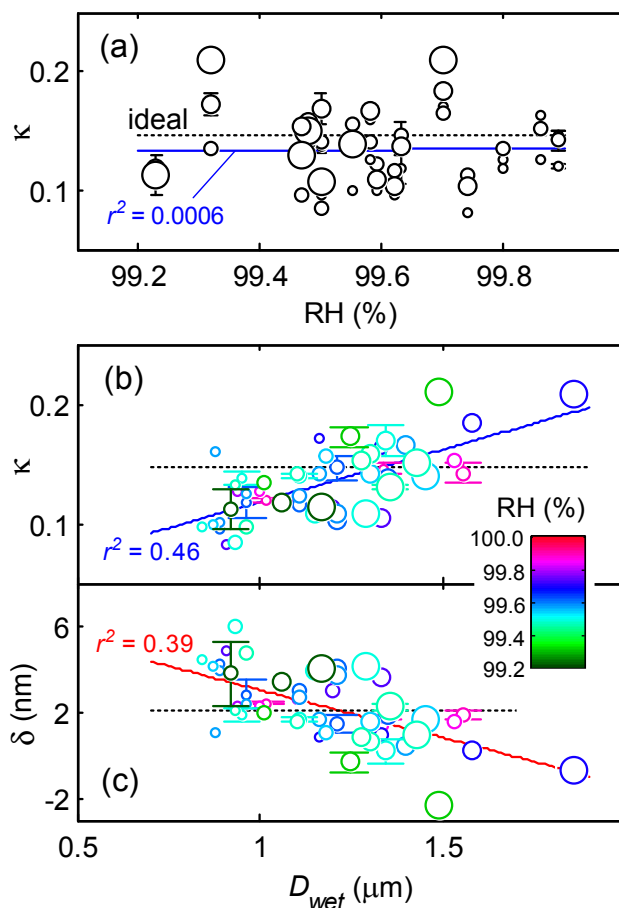


Fig. 6. SDS hygroscopicity, with linear regressions (red solid lines) and values for ideal solutions with the surface tension of water (black dotted lines). Symbol size indicates D_{dry} . Error bars indicate duplicate D_{wet} standard deviations. (a) κ vs. RH. (b) κ vs. D_{wet} . (c) δ vs. D_{wet} .

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 $\nu=2.2$ 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

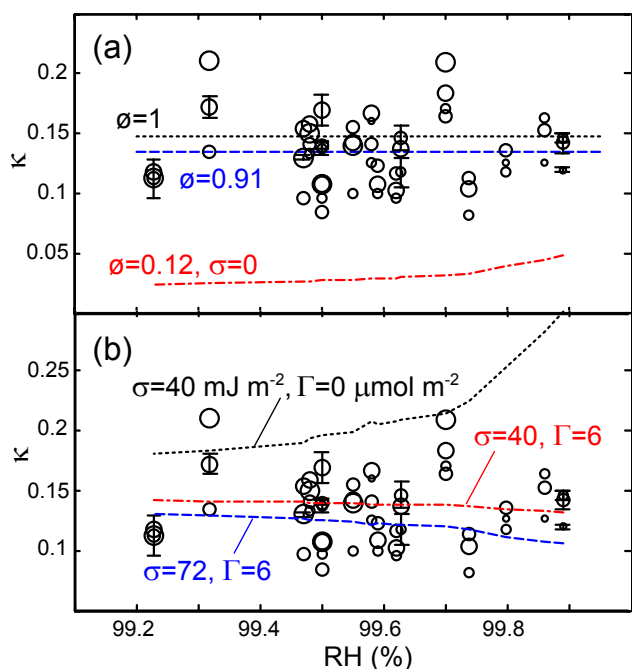


Fig. 7. Theoretical variation in SDS κ with RH (lines) for several cases, with observations (black circles, size indicates D_{dry}). (a) Predicted κ for three cases: an ideal solution droplet with the surface tension of pure water (black dotted line), a droplet with ϕ set to match average observed κ and the surface tension of pure water (blue dashed line), and a droplet with ϕ limited by micellization and a surface tension of zero (red dash-dot line). Even when $\sigma=0$, micellization would result in droplets with $\kappa \sim \frac{1}{2}$ of the observed values. (b) Three cases related to surface activity: only surface tension reduction ($\sigma=40 \text{ mJ m}^{-2}$), only surface partitioning and $\Gamma=6 \mu\text{mol m}^{-2}$ (dashed blue line), and both. When both surface effects are considered, they tend to cancel out in terms of their influence on κ vs. RH.

constant at high RH, or that variation in ϕ 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 κ 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_{dry} and D_{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 κ). In both cases, the surface tension of the droplet is assumed to be equal to that of pure water. The resulting values of SDS κ are constant with RH (Fig. 7a) both because ϕ is constant and $\sigma=72.8 \text{ mJ m}^{-2}$ (the assumed value in the κ formulation, see Eq. 5). Additionally, the theoretical κ values are roughly consistent with the observed values. However, if it is instead assumed that $\phi=0.12$, as derived from macroscopic

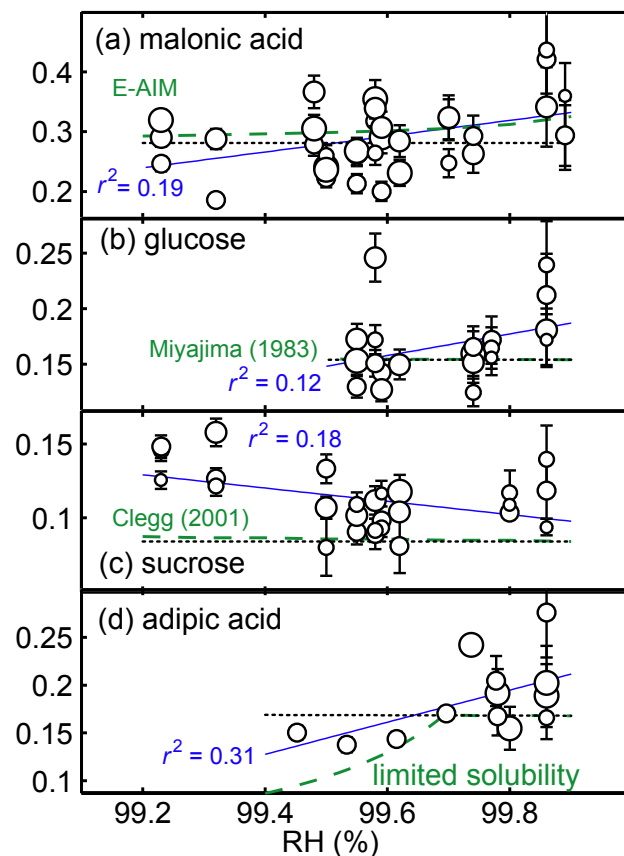


Fig. 8. Organic hygroscopicity (κ) vs. RH. With linear regressions (red solid lines), values for ideal solutions with the surface tension of water (black dotted lines), and theoretical values (green dashed lines). Marker size indicates D_{dry} . Error bars indicate the error in κ associated with an error in RH of $\pm 0.05\%$ (absolute). (a) malonic acid. (b) glucose. (c) sucrose. (d) adipic acid.

SDS solutions, κ is much smaller than in our observations (Fig. 7a, red curve). Not even the assumption that σ 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 κ , 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 κ 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.

	m_{κ} [% μm^{-1}]	m_{δ} [% μm^{-1}]	p_{κ}	p_{δ}
NaCl	3.3	-8.1	0.13	0.26
AS	4.5	-0.5	0.42	0.98
malonic acid	41	-120	0.001	0.014
adipic acid	47	-27	0.015	0.52
glucose	42	-76	0.033	0.085
SDS	65	-210	1×10^{-6}	1×10^{-6}
sucrose	22	-100	0.26	0.051

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 $\phi > 1$ in aqueous solutions (e.g., Matubayasi and Nishiyama, 2006), from which $\kappa > \kappa_{\text{ideal}}$ 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, $\kappa > \kappa_{\text{ideal}}$. 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), $\phi = 1.044$ 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 \rightarrow 100%. The greater non-ideality of sucrose relative to glucose is already apparent at RH \sim 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 $\phi = 1$, this solubility limit corresponds to an RH of \sim 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

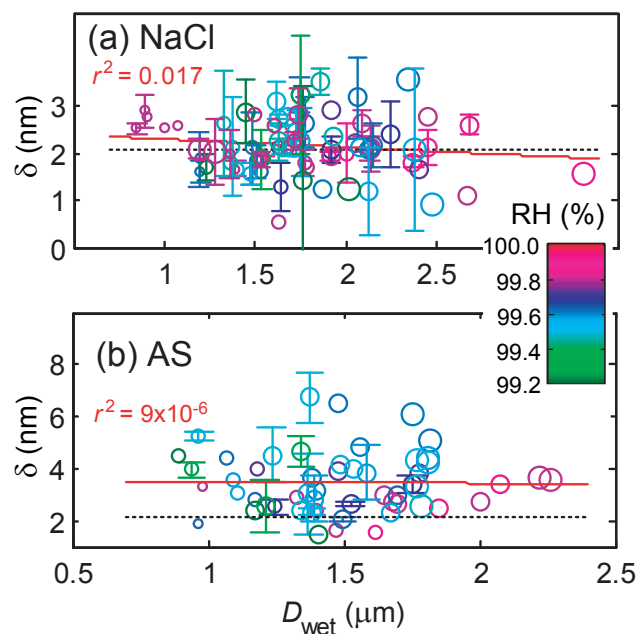


Fig. 9. Hygroscopicity (δ) of (a) NaCl and (b) AS vs. D_{wet} . With linear regressions (red solid lines) and values for ideal solutions with the surface tension of water (black dotted lines). Marker size indicates D_{dry} . Error bars indicate duplicate D_{wet} standard deviations.

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

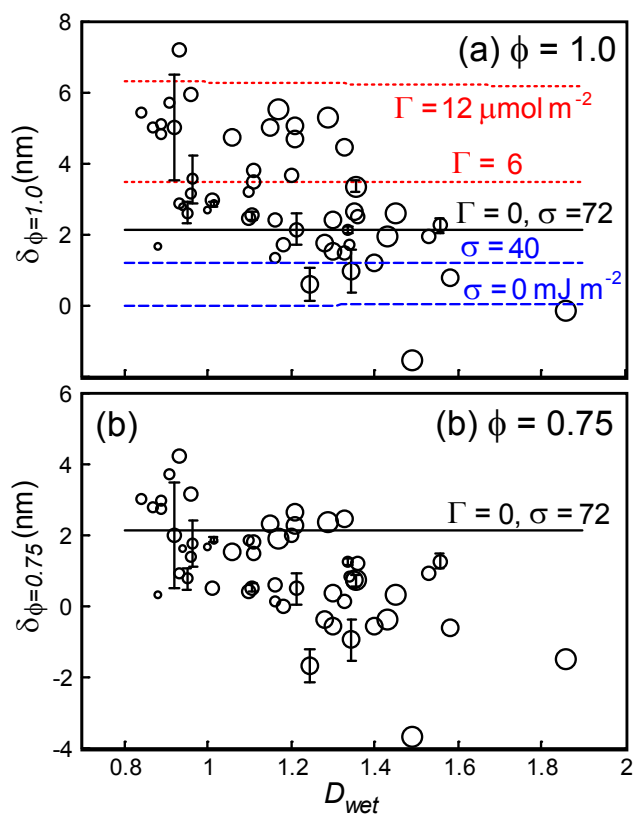


Fig. 10. (a) SDS δ both observed (black circles, size indicates D_{dry}) and predicted (lines) under several assumptions regarding surface activity, versus D_{wet} . Surface partitioning (i.e., $\Gamma > 0$) tends to decrease hygroscopicity, or increase δ , while surface tension reduction ($\sigma; 72 \text{ mJ m}^{-2}$) has the opposite effect. (b) Observed δ with all calculations of δ made assuming $\phi=0.75$. This results in a downward shift in all δ , but has only a minor effect on the trend in δ with D_{wet} .

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 (σ) of macroscopic aqueous solutions, and consequently one might expect SDS δ to be lower than that of NaCl and AS. SDS hygroscopicity did vary strongly with D_{wet} (Fig. 6b and c), although it is not immediately clear why its surface activity causes its hygroscopicity to increase with increasing D_{wet} , as a given reduction in surface tension would be expected to cause a decrease in δ_{SDS} which does not vary with D_{wet} (Fig. 2c). We next seek to explain the trend in δ with respect to D_{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 κ with RH and δ with D_{wet} resulting from these assumptions.

As can be seen in Eq. (6), δ is proportional to surface tension (σ). If SDS solution droplets behave ideally, with a surface tension of pure water, δ 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, Γ , of $6 \mu\text{mol m}^{-2}$) causes δ 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 σ , the influence of Γ on hygroscopicity goes as D_{wet}^{-1} , and therefore δ is constant with D_{wet} .

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

It can be seen in Fig. 10a that lowering σ (blue curves) and accounting for the partitioning effect (red curves) have opposite effects on SDS hygroscopicity (parametrized as δ). 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 κ with RH therefore suggests the presumed lowering of σ 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 δ_{SDS}) with D_{wet} assuming constant values of ϕ , σ , and Γ . This suggests that at least one of these parameters varies with D_{wet} . Because κ is roughly proportional to ϕ , and the highest observed values of κ_{SDS} are roughly 2 times greater than the lowest, the range of observed SDS hygroscopicity could correspond to an increase in ϕ from 0.5 to 1. This could result from micellization in smaller droplets, although not to the extent seen in macroscopic solutions. However, ϕ is typically thought to vary with concentration, and thus a trend in κ_{SDS} with RH would be expected if ϕ is not constant. It is therefore unlikely that the trend in δ is the result of micellization.

Figure 7b demonstrates that if both σ and Γ are allowed to vary with D_{wet} , they can do so in a way that their influences on the κ vs. RH trend cancel out. We found that the following assumptions fit the observations: At the low end of our measured D_{wet} ($0.8 \mu\text{m}$), we set Γ to $18 \mu\text{mol m}^{-2}$, and decreased Γ linearly with D_{wet} until $\Gamma=0$ when $D_{wet}=1.8 \mu\text{m}$. We held σ constant at 30 mJ m^{-2} . Under these assumptions, κ does not vary with RH (Fig. 11a), but δ would decrease with D_{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

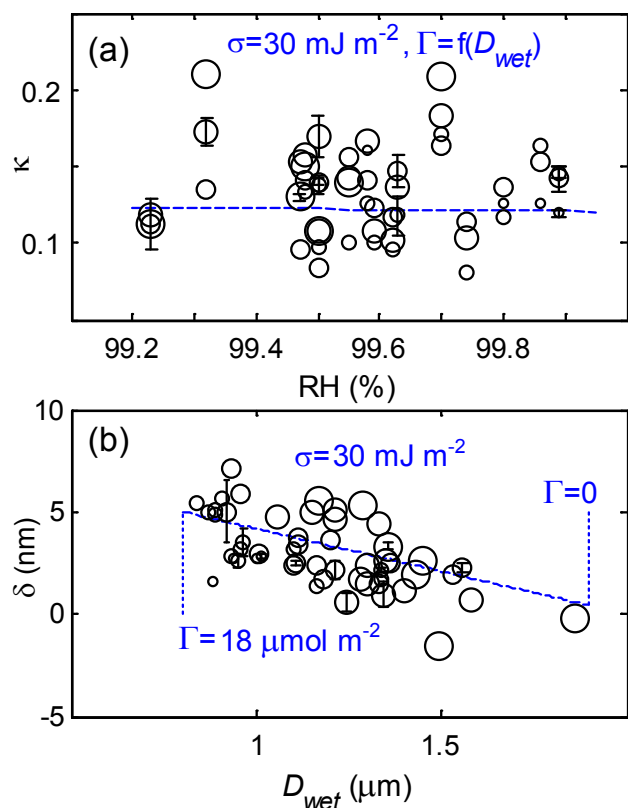


Fig. 11. Observed trends in SDS hygroscopicity with RH and D_{wet} (black circles, size indicates D_{dry}), and predictions (blue dashed lines) assuming $\phi = 1$, and that as D_{wet} increases from 0.8 to 1.8 μm , Γ decreases linearly from 18 to 0 $\mu\text{mol m}^{-2}$. σ is held constant at 30 mJ m^{-2} .

and thus these values can not be considered independent estimates. In other words, this model is an ad hoc fit to the data, and while we can conclude that SDS hygroscopicity increases with increasing D_{wet} , the mechanism responsible for this trend remains unclear.

As discussed previously, a value of Γ corresponding to the actual size of the SDS molecule is 6 $\mu\text{mol m}^{-2}$ if a monolayer 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 $\mu\text{mol m}^{-2}$ but only 6 $\mu\text{mol m}^{-2}$ 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

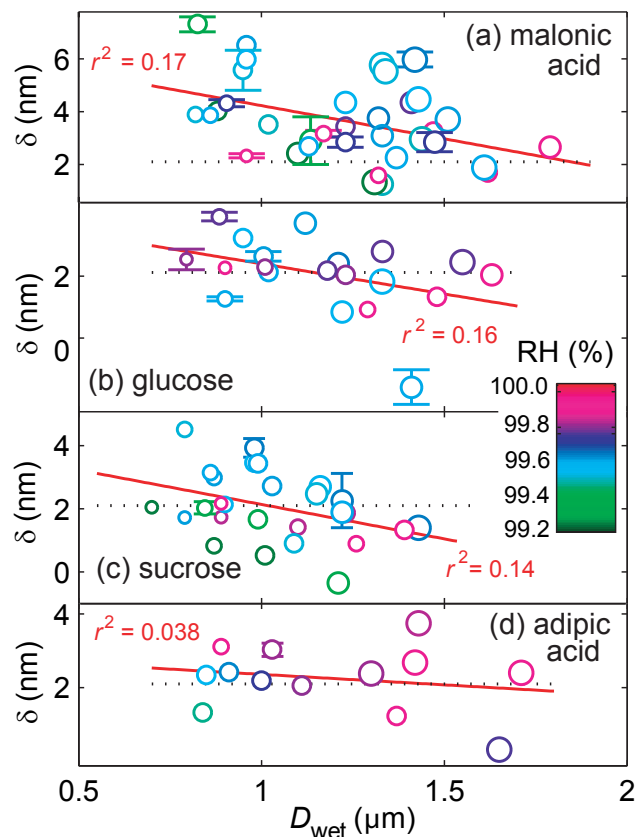


Fig. 12. Organic hygroscopicity (δ) vs. D_{wet} . With linear regressions (red solid lines), and values for ideal solutions with the surface tension of water (black dotted lines). Error bars, symbol size, and color indicate duplicate D_{wet} standard deviations, dry diameter, and RH, respectively. (a) malonic acid. (b) glucose. (c) sucrose. (d) adipic acid.

pure water. In contrast, a compressed film of insoluble surfactant can substantially reduce evaporation rates from aqueous 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 σ 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 Γ 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., δ 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_{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_{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 ($\sim 10\%$) 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.*

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