Accurate Measurements of Aerosol Hygroscopic Growth over a Wide Range in Relative Humidity

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Supporting Information

ABSTRACT: Using a comparative evaporation kinetics approach, we describe a new and accurate method for determining the equilibrium hygroscopic growth of aerosol droplets. The time-evolving size of an aqueous droplet, as it evaporates to a steady size and composition that is in equilibrium with the gas phase relative humidity, is used to determine the time-dependent mass flux of water, yielding information on the vapor pressure of water above the droplet surface at every instant in time. Accurate characterization of the gas phase relative humidity is provided from a control measurement of the evaporation profile of a droplet of know equilibrium properties, either a pure water droplet or a sodium chloride droplet. In combination, and by comparison with simulations that account for both the heat and mass transport governing the droplet evaporation kinetics, these measurements allow accurate retrieval of the equilibrium properties of the solution droplet (i.e., the variations with water activity in the mass fraction of solute, diameter growth factor, osmotic coefficient or number of water molecules per solute molecule). Hygroscopicity measurements can be made over a wide range in water activity (from >0.99 to, in principle, <0.05) on time scales of <10 s for droplets containing involatile or volatile solutes. The approach is benchmarked for binary and ternary inorganic solution aerosols with typical uncertainties in water activity of <±0.2% at water activities >0.9 and ∼±1% below 80% RH, and maximum uncertainties in diameter growth factor of ±0.7%. For all of the inorganic systems examined, the time-dependent data are consistent with large values of the mass accommodation (or evaporation) coefficient (>0.1).

1. INTRODUCTION

Quantifying the equilibrium hygroscopic growth of aerosol is important for understanding the liquid water content and size distributions of atmospheric aerosol and for modeling their optical properties, for predicting cloud droplet number and size distribution following the activation of cloud condensation nuclei (CCN), and for determining the partitioning of semivolatile organic compounds (SVOCs) in the condensed aerosol phase.1,2 The capacity for aerosols to absorb water can also influence their deposition in the respiratory tract on inhalation, potentially influencing the impact of aerosols on health.3 The uncertainties in understanding these processes provide an incentive to improve the characterization of aerosol hygroscopicity. As an example, cloud parcel models have shown that the cloud droplet number can vary by as much as 50% depending on the strength of the assumed hygroscopic growth as saturation is approached.4

Rigorous thermodynamic models for calculating the hygroscopic response of mixed component aerosol have been developed on the basis of bulk phase and aerosol phase measurements of the equilibrium response of binary solutions of a single solute and water.5,6 When combined with treatments of solution density and surface tension, accurate predictions of the variation in equilibrium particle size with relative humidity are possible.7,8 To represent the equilibrium properties of solutions containing the myriad of potential organic compounds found in the atmosphere, it is often necessary to resort to functional group activity models that require consideration of the interactions between electrolytes and organic species.9,10 However, there is also a requirement to provide models of hygroscopic growth that are tractable in computational models of atmospheric chemistry, radiative transfer, and climate models. To achieve this, models such as κ-Köhler theory have been developed to represent the hygroscopicity of aerosol particles using a single value of κ, with a higher value representing more hygroscopic aerosol (κ for ammonium sulfate and sodium chloride) and a lower value representing less hygroscopic aerosol (κ for insoluble fatty acids).11,12 Measurements of κ have been made for aerosols varying in complexity from binary component solution aerosol through to the complex inorganic-aqueous mixtures found in the atmosphere.13−15

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At a fundamental level, both the thermodynamic factors governing hygroscopic growth and the kinetics of condensation must be better quantified to represent the aerosol microphysics underpinning the partitioning of water between the gas and particle phases. A number of significant uncertainties must be addressed to improve the microphysical description of water partitioning. There can be significant differences between hygroscopic growth measurements made on different instruments. Further, estimates of the critical supersaturation for CCN activation inferred from \( \kappa \) values determined from measurements under subsaturated conditions are often inconsistent with values determined directly. The gas–particle partitioning of volatile organic compounds (VOCs) and SVOCs, and co-condensation with water during CCN activation is poorly constrained and has been largely ignored, of hygroscopic growth. Although the molecular complexity of secondary organic aerosol (SOA) precludes an accurate treatment of hygroscopic growth that explicitly accounts for each compound individually, empirical correlations that seek to exploit dependencies on average measures of composition (e.g., the variation of \( \kappa \) with O:C ratio) are often poorly defined and, at best, appropriate only for specific SOA precursors and environmental conditions. The slow deliquescence and low solubility of some organic components present challenges in interpreting measurements of hygroscopic growth. Liquid—liquid phase separation into internal mixtures of hydrophobic and hydrophilic phases in mixed component aerosol remains a challenge in predicting equilibrium properties. The extent of the depression of surface tension by surface active organic components and the interplay of surface and bulk partitioning in determining the critical supersaturation remains difficult to resolve. Finally, the kinetics of water, VOC and SVOC condensation are often poorly determined with few quantitative measurements of the mass accommodation coefficients of organic species in particular.

To address the challenges in quantifying hygroscopicity for aerosols of complex composition, refinements in laboratory and field instrumentation, and improved frameworks for representing hygroscopicity, are required. Hygroscopic growth measurements must be made up to water activities close to 0.999. Such high water activities \( (a_w) \) are required for measurements to be directly relevant to CCN activation and to place tighter constraints on the equilibrium solution compositions required to underpin the development of predictive models.

Building on our previous preliminary report, we present here a more general and wide ranging characterization of a new method for deriving hygroscopic growth curves for coarse mode particles over a wide water activity range (in principle from dry conditions to >0.999). We concentrate on aerosol droplets of well-known composition and containing well-characterized electrolytes to benchmark the technique. Growth curve measurements can be determined rapidly and accurately, potentially opening up the possibility of mapping hygroscopic response for a large number of organic components of SOA and, indeed, complex mixtures and SOA samples directly. In section we review the experimental technique and the analyses methods used before presenting measurements of hygroscopic growth for binary solutions of sodium chloride, ammonium sulfate, sodium sulfate, and sodium nitrate in section. We also consider the accuracy of the approach by exploring the ability of the instrument to resolve small changes in hygroscopic growth for mixed-salt containing aerosol droplets.

### 2. EXPERIMENTAL SECTION

Comparative kinetics measurements for the quantification of the hygroscopicity of aerosols using the cylindrical electrodynamic balance (EDB) experimental setup have been described in previous publications. In this section, an overview of the instrument and of the determination of hygroscopic properties from measurements on multiple droplets is presented, extending our previous work over a wider range in water activity. The adopted treatments for refractive index and density are also introduced.

#### 2.1. Cylindrical EDB

The EDB technique allows the levitation of a single charged aerosol droplet inside an electrical field. Single droplets are generated on-demand from a solution with known initial concentration by applying a pulse voltage to the filled reservoir of a microdispenser (Microfab MJ-ABP-01), placed just outside one of the walls of the EDB chamber. Between droplet generation events, a smaller constant pulse voltage is applied to the microdispenser to continuously flush some solution through its tip, thus assuring that no evaporation of solvent and no variation of the solution concentration can occur from measurement to measurement. The initial radius of the droplets once trapped varies from about 18 to 25 \( \mu m \). Before entering the trapping chamber, a net charge is imparted to every droplet by means of a high-voltage induction electrode. Within 100 ms of its generation, the droplet is tightly confined in the center of the electrodynamic field inside the EDB chamber. An ac signal is applied to the cylindrical electrodes and a dc offset is superimposed, to balance the gravitational and drag forces on the trapped droplet. The cylindrical configuration of the electrodes results in a steep gradient in the potential in the trapping region, guaranteeing a strong confinement of the droplets, with little harmonic oscillation in the position of the particle that is characteristic of other electrode configurations.

The droplet is confined within a gas flow, which results from the mixing of wet and dry nitrogen flows. It is possible to change the ratio between these two flows by means of mass flow controllers (MKS 1179A) and this allows the control of the relative humidity (RH) of the gas phase that surrounds the droplet. The temperature of the chamber is controlled by recirculating a mixture of water and ethylene glycol (50% v/v) from a thermostatic water bath (Julabo, F32-HE) through the lid and the bottom of the chamber. The accessible temperature range is \(-25 \) to \( +50 \) °C. In this study all the measurements were performed at \( 20 \) °C.

The trapped droplet is illuminated by light from a green laser (\( \lambda = 532 \) nm). The resulting elastic scattering pattern is collected every 10 ms over a range of solid angles centered at \( 45^\circ \) by means of a CCD camera and is used to determine the radius of the droplet with the simplified geometrical optics approximation approach, using Equation 1:

\[
a = \frac{\lambda}{\Delta \theta} \left( \cos(\theta/2) + \frac{m \sin(\theta/2)}{\sqrt{1 + m^2 - 2m \cos(\theta/2)}} \right)^{-1}
\]

where \( a \) is the droplet radius, \( \lambda \) is the incident wavelength, \( \theta \) is the central viewing angle, \( \Delta \theta \) is the angular separation between the fringes in the scattering pattern, and \( m \) is the refractive index.
index of the droplet. The error associated with the radius determination with this approach is ±100 nm.

The refractive index of the evaporating droplets is not constant because the solute concentration increases as water evaporates. This variation of the refractive index with time must be taken into account for an accurate determination of the droplet radii. At first, during the data acquisition, m is set constant at 1.335, the value for pure water at 532 nm. In a postacquisition analysis step, the radii data are corrected by taking into account the variation of the refractive index with mass fraction of solute (mfs) by applying the molar refraction mixing rule, which has been demonstrated to be the best mixing rule to describe the refractive index for a number of inorganic systems.38 The molar refraction (R) of a component i is defined as

$$R_i = \frac{(m_i^2 - 1)M_i}{(m_i^2 + 2)p_i} = \frac{(m_i^2 - 1)V_i}{(m_i^2 + 2)}$$  \hspace{1cm} (2)

where $M_i$ is the compound’s molecular mass and $p_i$ is its pure melt density. The ratio of molecular mass to liquid density is equivalent to the molar volume of pure i, $V_i$. The molar refraction for the solution, $R$, is the sum of the molar refractions of each component, including all solutes and water, weighted by their mole fractions ($x_i$):

$$R = \sum_i x_i R_i$$  \hspace{1cm} (3)

In this study, the variation in solution densities with mass fraction of solute and the pure solute melt densities are taken from the work of Clegg and Wexler.39 The melt densities are extrapolations from high-temperature measurements compiled and evaluated by Janz.40 For ease of data processing, the density data are represented as a function of the square root of the mass fraction of solute (mfs) and fitted with a polynomial curve (order ranging from fourth to seventh) such that the residual from the fit is <0.005 g cm$^{-3}$ across the whole mfs range. This density dependence is then used to constrain a least-squares fit of the tabulated data of solution refractive index for solute concentrations below the solubility limit,41 to the functional dependence of the molar refraction mixing rule. The only fit parameter is the value of the pure component refractive index of the molten salt. From this fit, the value of the refractive index of the solution, m, at any solute concentration can then be found from eq 4 by solving for m using the mfs, the estimated density of the solution at this composition $\rho$, a mole fraction weighted molecular mass $M$, and the estimated molar refraction of the solution.

$$R = \frac{(m^2 - 1)M}{(m^2 + 2)p}$$  \hspace{1cm} (4)

The procedure used to take into account the variation in refractive index during the evaporation is the following. There is a time period (~0.1 s) between droplet generation and the first determination of size when the droplet is in transit into the trapping region.32,33 Thus, the initial size of the droplet is estimated with a linear extrapolation of the $a^2$ vs time plot to $t = 0$ s; the initial solute mass fraction and density of solute solution at $t = 0$ s and at this droplet size are known from the prepared solution.43 The elastic light scattering data are first analyzed with $m = 1.335$ to yield an initial estimate of the variation in radius with time, also providing a first estimate of the variation of the solute concentration and of the solution density during the evaporation. A set of corrected refractive indices for the droplet solution at every time step is then calculated on the basis of the change in size using the molar refraction mixing rule (eqs 2–4). These corrected refractive indices at each time point are then used to fit a new set of corrected radii with eq 1. This procedure is repeated for the new set of corrected radii until the refractive indices and radii values converge, typically after 2–3 iterations.

One key feature of this experimental setup is the presence of two microdispensers that can be operated sequentially, thus allowing the generation of aerosol droplets with different chemical compositions in rapid succession. This feature allows comparative kinetics measurements, which consist of levitating a sequence of droplet pairs; one probe droplet (either water or a well-characterized salt solution, such as NaCl), followed by one sample droplet containing the solution of interest. Typically, these kinds of comparative kinetic measurements consist of a series of at least ten pairs of probe and sample droplets. The evaporation kinetics of the probe droplets (when water) or their equilibrated size (when aqueous NaCl) are used to determine the gas phase RH, which is key information for the interpretation of the evaporation profile of the unknown sample droplet, as will be discussed in sections 2.2 and 2.3.

2.2. Modeling Aerosol Droplet Evaporation Kinetics. The mass and heat transport equations from Kulmala and co-workers32 can be used to model the evaporation and condensation kinetics of water or other volatile species from/ to aerosol droplets. For the evaporation case, the mass flux from the droplet ($I$) depends on the concentration gradient of the evaporating species (water in this work) from the droplet surface to infinite distance. We have considered the influence of droplet charge on evaporation rates in previous work,32 showing it to have negligible impact at the imbalance of positive and negative ions induced in the droplets studied in these experiments.44 The mass transfer enhancement resulting from the flowing gas surrounding the droplet is accounted for by the inclusion of a Sherwood number ($Sh$) scaling of the mass flux.33,34 The thermophysical parameters that appear in the mass flux treatment and their uncertainties have been thoroughly discussed in previous publications.32,34,45,46 The resulting expression for the mass flux is the following:

$$I = -2Sha_s(S_{w0} - a_w)\left[\frac{RT_0}{M\beta_u D\rho_0 T_{w0}^2} + \frac{a_L^2 M}{K\beta_T T_0^2}\right]^{-1}$$  \hspace{1cm} (5)

where $Sh$ is the Sherwood number, $S_{w0}$ is the saturation ratio of water in the surrounding gas phase (also referred to as RH in this work), $a_w$ is the water activity in the droplet solution, $R$ is the ideal gas constant, $T_{w0}$ is the gas phase temperature, $L$ is the latent heat of vaporisation, and $M$ is the molar mass of water. $\beta_u$ and $\beta_T$ are the transition correction factors for mass and heat, respectively; these corrections are very small for the coarse mode droplet sizes considered here and this will be demonstrated when we consider the sensitivity of the thermodynamic measurement to the value of the accommodation coefficient. D is the diffusion coefficient of water in the gas phase, $p_0$ is the saturation vapor pressure of water, $A$ is the Stefan flow correction, and $K$ is the thermal conductivity of the gas phase.

As an example of the data acquired during droplet evaporation, a series of seven (NH₄)₂SO₄ solution droplets evaporating into different RHs at 20 °C are shown in Figure 1A.
over the range from 50% to 85% RH. The initial mass fraction of the starting solution was 0.05, and the initial radii of the seven different droplets varied from 23.0 to 23.3 μm. The total amount of water that evaporates from each droplet depends on the gas phase RH and the final equilibrated radius is such that the \( a_w \) in the droplet matches the RH in the surrounding gas phase. The evaporation rate increases with decreasing RH because the mass flux is proportional to the difference between the solution water activity and the RH (eq 5). As shown in Figure 1B, the mass flux (ng s\(^{-1}\)) from the droplet is plotted against time. (C) Variation in time of the difference between the temperature (K) of the droplet surface \( T_{\text{droplet}} \) and the gas phase \( T_{\text{gas}} \), calculated according to eq 9.

2.3. Aerosol Hygroscopic Growth from Comparative Kinetic Measurements in the EDB. The mass and heat transport model presented in section 2.2 is used to compare the evaporation kinetics of probe and sample droplets and to estimate aerosol hygroscopic growth curves from data of the form shown in Figure 1, as follows. The procedure is described below and also outlined in the Supporting Information. First, the probe droplet evaporation profile is analyzed to determine the gas phase RH, which is expressed as a percentage throughout this work; note that \( a_w \) is always represented as a fractional value. The probe droplet can be either pure water or a NaCl solution. Davies et al.\(^{32}\) demonstrated the validity of both methods in the determination of the RH in this kind of comparative kinetic measurements and also estimated the errors on the RH retrieved in both cases.

When a pure water droplet is used as a probe, its experimental radius-squared versus time evaporation profile is compared to simulated evaporation curves at different RH, calculated using eq 4. The mean squared difference (MSD) between the experimental profile and each calculated curve is estimated and the RH corresponding to the curve with the lowest MSD is selected. In this case, the lower and upper values of the RH come from uncertainties in the thermophysical parameters \( D \) (±6%) and \( K \) (±2%)\(^{46}\) in eq 5 and are given by

\[
RH = RH_{e q}^{+}(0.169RH_{e q}^{2} - 0.364RH_{e q} - 0.194) \\
(0.0175RH_{e q}^{2} + 0.0005RH_{e q} + 0.017) \\
(0.169RH_{e q}^{2} - 0.364RH_{e q} - 0.194) \\
(0.0005RH_{e q} + 0.017)
\]

(6)

When a NaCl solution with known initial concentration is used as a probe, the equilibrated size of the droplet after water evaporation may be used to determine the water activity in the solution, and therefore the RH in the gas phase. To do this, the thermodynamic Extended Aerosol Inorganics Model (E-AIM)\(^{5,6,47}\) (http://www.aim.env.uea.ac.uk/) is used to calculate how water activity and density change with the solution composition during evaporation and to predict the equilibrated radius of the droplet after water evaporation has ended at a given RH. For the relationship between water activity and NaCl concentration, the model is based upon the critical review of Archer\(^{48}\) and electrodynamic balance measurements of several authors (see Table 1 of Clegg et al.\(^{49}\)). Densities of aqueous NaCl (up to and including the hypothetical pure liquid salt) were calculated using the equations of Clegg and Wexler.\(^{59}\)

The lowest RH value that can be determined with this method is limited by the efflorescence RH of NaCl, which is around 48%. If this equilibrated size method is used, the uncertainties in RH arise from the accuracy with which the equilibrated radius is known (±100 nm) and the uncertainty in the determination of the initial droplet size at \( t = 0 \) s (±150 nm), which corresponds to an uncertainty of less than 0.8% of the dry radius for the droplet sizes considered in this work. In this case, the lower and upper values of the RH are expressed as

\[
RH = RH_{e q}^{+}(0.0175RH_{e q}^{2} - 0.0005RH_{e q} + 0.017) \\
(-0.0268RH_{e q}^{2} + 0.0086RH_{e q} - 0.017)
\]

(7)

Using a pure water droplet as a probe of RH is preferable as the equilibrated size method includes a further uncertainty from the initial NaCl solution concentration. Nevertheless, NaCl was used as a probe for measurements at RH < 80% because the associated uncertainties on the RH determined with water as a probe droplet would be too significant. Uncertainties in the simulation of pure water evaporation become increasingly large below this RH due to uncertainties in the thermophysical parameters \( D \) and \( K \) because of the approximation that are

\[
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\]

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needed in the expression of the vapor pressure of water at the droplet surface (discussed further in section 3.1).

According to eq 6, the RH can be determined with an uncertainty smaller than $0.3\%$ for RH values above 90% when pure water is used as a probe. At 50% RH, the error in % RH associated with the determination of RH with the equilibrated size method is $1.2\%$, according to eq 7. Knowing the RH with such accuracy is crucial for an accurate application of the kinetics model presented in section 2.2. The uncertainty of commercial RH probes is typically between $0.3\%$ and $1.2\%$, according to the manufacturer's specifications.

The RH of the gas phase in the EDB trapping chamber is kept constant during the evaporation measurements at high RH. The RH of the gas phase is retrieved from the measurements of the RH at which the evaporation rate of water is fastest and, when it is not balanced by the heat flux from the surrounding environment to the droplet, the condensate phase cools down. The temperature depression of the droplet can be considered because the vapor pressure of water at the surface of the droplet is temperature dependent and directly influences the evaporation rate. In the derivation of Kulmala and co-workers' 15 the dependence of the vapor pressure of the evaporating species at the droplet surface ($p_v$) on temperature is calculated from the Clausius–Clapeyron equation. The exponential term in this expression is approximated with the first-order term in a Taylor series expansion:

$$p_v = a_v p^0(T_{gas}) \exp\left(\frac{LM(T_{droplet} - T_{gas})}{RT_{droplet} T_{gas}}\right)$$

$$\approx a_v p^0(T_{gas}) \left(1 + \frac{LM(T_{droplet} - T_{gas})}{RT_{droplet} T_{gas}}\right)$$

where $p^0(T_{gas})$ is the saturation vapor pressure at the temperature of the gas phase ($T_{gas}$) and $T_{droplet}$ is the temperature at the droplet surface.

The approximated expression for the temperature dependence of the vapor pressure of water is only accurate when the difference between the droplet and gas phase temperatures is less than $3 \, ^\circ C$; beyond this threshold value the approximation with the Taylor series expansion results in an underestimation of the value of the exponential larger than 1% at $25 \, ^\circ C$42 with a subsequent underestimation of $p_v$. Consequently, when the droplet temperature depression is large, the vapor pressure of water at the surface of the droplet is increasingly underestimated. Therefore, the only measured points that can be used to reliably calculate the water activity in the evaporating sample droplet are those that satisfy this condition. $T_{droplet} - T_{gas}$ can be estimated according to eq 9:

$$T_{droplet} - T_{gas} = -\frac{IL}{4\pi \beta K_a}$$

Figure 1C shows the time dependence of the temperature difference $T_{droplet} - T_{gas}$ for the same seven $(NH_4)_2SO_4$ droplets as in the two previous panels. The initial temperature
depression can reach −7 K in correspondence to the fastest evaporation rates (at 50% RH), whereas for the three droplets evaporating into a higher RH (about 78%, 81%, and 85%, respectively) the calculated temperature depression is always less than 3 K.

The effect of the droplet temperature depression on the estimated hygroscopic behavior of a sample compound retrieved from the measurements is shown in Figure 2. Panel (Figure 2B) is larger in magnitude than the −3 K threshold, which is satisfied only below a calculated \(a_w\) of 0.73. The absolute error on the calculation of \(a_w\) is shown in Figure 2C. This \(a_w\) error was calculated as the difference between the experimental \(a_w\) calculated with eq 5 and the water activity calculated with the E-AIM model at a certain mfs value. For the averaged data, the absolute errors on the calculated \(a_w\) are very close to 0 at \(a_w\) values below 0.73, whereas they reach values up to about 0.06 when \(T_{\text{droplet}} - T_{\text{gas}}\) is of the order of −5 to −6 K.

As a consequence of this limitation in the kinetics framework, only a portion of about 0.2 in water activity of the mfs curve of a sample compound can be retrieved when measurements are taken into an RH at 50%. As a consequence, evaporation measurements into at least three different RHs are need to determine a full curve from 0.5 to >0.99 \(a_w\). An example of this procedure is shown in Figure 3 for the determination of the relationship between \(a_w\) and mfs for (NH₄)₂SO₄, in which EDB results are compared to the E-AIM model prediction (solid black line). Evaporation measurements with a starting solution of \(\sim 0.05\) mfs were made into three different RHs (54%, 74%, and 87.3%). A fourth data set was collected at high RH (90%, more clearly visible in the inset in Figure 3) using a solution with lower starting concentration (mfs of 0.005) and therefore with a higher starting \(a_w\) (0.997). In this latter case, just a very small section of the mfs curve can be calculated: because the droplet had a very low initial concentration, it was not possible to keep it trapped until its \(a_w\) equilibrated with the surrounding RH, as it undergoes an exceptionally large size change. The open circles represent data points averaged over ten droplets and have been considered acceptable only if the difference in temperature between the droplet and the gas phase is estimated to be smaller than the 3 K limit. In the background, data for all

![Figure 2.](image-url)  
(A) Mass fraction of solute (mfs) vs \(a_w\) plot, calculated from the evaporation kinetics of 10 (NH₄)₂SO₄ droplets evaporating into 58% RH. Symbols: gray dots, data from each individual droplet; black dots, averaged curve calculated over the 10 droplet data set; solid line, mfs vs \(a_w\) for (NH₄)₂SO₄ calculated with the E-AIM model. (B) Difference in temperature between the droplet surface and the surrounding gas phase as a function of \(a_w\), calculated with eq 9. (C) Absolute error in \(a_w\) relative to the reference E-AIM model values. Symbols: gray squares, error on \(a_w\) from each individual droplet; open black squares, error on \(a_w\) relative to the averaged mfs curve.

![Figure 3.](image-url)  
Retrieval of the full mfs vs \(a_w\) curve of ammonium sulfate from measurements into different RHs. Symbols: solid line, calculated mfs vs \(a_w\) curve from the E-AIM model; filled circles, individual data from all 10 droplets in each data set; open circles, averaged data for which the maximum 3 K droplet temperature depression condition is satisfied. Colors: red, purple, and light blue, droplets of 0.05 mfs starting solution evaporating into a gas phase at 54%, 74%, and 87.3% RH, respectively; dark blue, 0.005 mfs starting solution into a gas phase 90% RH. Note: error bars are smaller than the data point when not shown.
the ten droplets in the same four data sets are shown. All the data points can be accepted for the two data sets measured at high RH, with the evaporation sufficiently slow to maintain a small droplet temperature depression, whereas just small portions of the data measured at 54% and 74% RH can be accepted. The agreement with the $a_w$ vs mfs curve calculated with the E-AIM model is very good for the points that lie within the 3 K threshold for the droplet temperature depression.

One of the interesting features of the comparative kinetics measurements in the cylindrical EDB is that hygroscopic growth curves can be measured up to very high $a_w$ values (>0.99). In Figure 4, the very high end for the measured GF, $n_{\text{water}}/n_{\text{solute}}$, and mfs versus water activity plots are shown for (NH$_4$)$_2$SO$_4$ and are compared with simulations from the E-AIM model (solid lines). In this case, the highest $a_w$ reached with this averaged data set is 0.997, corresponding to a GF value of 6.22 (Figure 4A). For the calculation of the radial growth curve, the dry radius of the droplets is calculated from the wet size at $t = 0$, the concentration of the starting solution, and the density of crystalline ammonium sulfate (1.77 g cm$^{-3}$). In Figure 4B, at $a_w = 0.997$ the number of absorbed moles of water per moles of (NH$_4$)$_2$SO$_4$ inferred from the measurements is close to 1000 and the agreement between the measured value and the E-AIM model prediction is remarkable. If the mfs vs $a_w$ plot is considered (Figure 4C), the lowest measured ammonium sulfate mass fraction is 0.005 at $a_w = 0.997$. It is also worth noting that not only is it possible to measure growth curves up to very high water activity values with this technique but also the accuracy on the calculated $a_w$ is highest when the RH at which measurements are taken is high (>90%), according to eqs 6 and 7. It should also be stressed that the growth curve is retrieved in a matter of seconds, potentially allowing accurate hygroscopic growth measurements for droplets containing volatile components, providing their vapor pressure is less than that of water.

3.2. Accuracy of Measurements. Hygroscopicity measurements on four well-characterized inorganic–aqueous systems (NaCl, Na$_2$SO$_4$, NaNO$_3$, and (NH$_4$)$_2$SO$_4$) were performed to confirm the validity of the method over the range in $a_w$ from 0.5 to 0.99. The relationships between mfs and $a_w$ for each solute are shown in Figure 5, compared with the corresponding prediction from the E-AIM model. The level of agreement obtained is excellent for all the systems studied. Na$_2$SO$_4$ was observed to crystallize during measurements at $a_w = 0.57$, and therefore it was not possible to reach lower water activity values during the experiments. In addition, the systematic overpredictions of E-AIM between water activities of 0.75 and 0.85 and underpredictions at the lowest $a_w$ are consistent with previous observations (see, for example, Figure 3 of Clegg et al.49). It should be noted that the measurement for an aqueous sodium chloride droplet provides a consistency check of the approach for inferring the hygroscopicity from kinetics measurements. For control sodium chloride droplets, measurements of the final equilibrated size are used to infer the RH of the gas flow. This value is then used in the retrieval of the mfs data from the kinetic measurement at all intermediate nonequilibrated $a_w$ values; in combination, this allows confirmation of the shape of the mfs vs $a_w$ dependence at all intermediate water activities.

Osmotic coefficients, $\phi_i$, provide a convenient way to characterize the departure of solutes from ideality and can be determined from the equation

$$\phi_i = \frac{M wi}{\ln(a_{wi})}$$

where $M wi$ is the molecular weight of water, $m_i$ is the molality of the solute $i$, and $\nu_i$ is the stoichiometric coefficient of solute $i$. As the water activity tends to unity at zero solute molality, the osmotic coefficient should tend to 1 with the expected Debye–Hückel limiting law behavior. In Figure 6 we report the dependence of the osmotic coefficient on solute molality for the four binary systems studied, providing a stringent examination of the retrieved hygroscopic behavior particularly at the dilute solution limit. As expected, the dependence of the osmotic coefficient on water activity leads to large uncertainties at low molality, a consequence of the large uncertainties in water activity in the early stages of evaporation (high mass flux) of dilute solution droplets. At molalities higher than 1 mol kg$^{-1}$, the close agreement between the measured and modeled osmotic coefficients for all systems suggests that the

Figure 4. GF, $n_{\text{water}}/n_{\text{solvent}}$, and mfs for $a_w$ values between 0.88 and 1 for (NH$_4$)$_2$SO$_4$. Symbols: filled circles, experimental data points averaged over a minimum of 10 droplets; solid lines, calculated curves from the E-AIM model. Note: error bars are smaller than the data point when not shown.
uncertainties attributed to measurements at these molalities are conservative. Deviations are typically <0.02 in osmotic coefficient for the (NH$_4$)$_2$SO$_4$, NaNO$_3$, Na$_2$SO$_4$, and NaCl systems, comparable to previous measurements (see, for example, the comparisons of predictions and measurements of osmotic coefficients in the work by Clegg et al.$^{47}$). Larger discrepancies are observed for Na$_2$SO$_4$ at intermediate concentrations and these have already been discussed above.

To better illustrate the agreement between the experimental results and simulations from the E-AIM model, Figure 7 provides a comparison between the measured and modeled $n_{water}/n_{solute}$ ratios for the four inorganic systems, spanning the

Figure 5. Measured mfs vs $a_w$ plots for (NH$_4$)$_2$SO$_4$, NaNO$_3$, Na$_2$SO$_4$, and NaCl (panels A–D). Symbols: filled circles, experimental data; solid lines, calculation from the E-AIM model. Note: error bars are smaller than the data point when not shown.

Figure 6. Dependence of osmotic coefficient on molality of solute (mol kg$^{-1}$) for (NH$_4$)$_2$SO$_4$, NaNO$_3$, Na$_2$SO$_4$, and NaCl (panels A–D). Symbols: filled circles, experimental data; solid lines, calculation from the E-AIM model.
range from just 3 water molecules per ion pair up to 1000. For each point in the plot, \( n_{\text{water}}/n_{\text{solute}} \) was calculated with the E-AIM model at the exact \( a_w \) value of the experimental data point. For \( n_{\text{water}}/n_{\text{solute}} \) values up to about 100 (corresponding to \( a_w \) of up to about 0.98, depending on the salt), all the points lie close to the 1:1 line, thus revealing a very good agreement of the experimental results with the E-AIM model calculations. For \( n_{\text{water}}/n_{\text{solute}} > 100 \), the points appear a little more scattered. This is due to the fact that at very high \( a_w \) values, even a slight variation in water activity results in a significant variation in the calculated water moles values, with the hygroscopic growth curve extremely steep in this region. As an example, the highest measured data point for (NH₄)₂SO₄ can be considered: the measured \( a_w \) is 0.997 and it corresponds to 799 \( n_{\text{water}}/n_{\text{solute}} \) calculated with the E-AIM model; if an uncertainty of ±0.001 in \( a_w \) is considered, the calculated \( n_{\text{water}}/n_{\text{solute}} \) values are 585 and 1236 for water activity values of 0.996 and 0.998, respectively. To show the effect of such a small uncertainty on water activity, in Figure 7 the uncertainty on the calculated \( n_{\text{water}}/n_{\text{solute}} \) for ammonium sulfate is represented with dark and light gray envelopes if an error of ±0.001 and ±0.002 in \( a_w \) is considered, respectively. These envelopes become increasingly large when the amount of absorbed water increases because of the steepness of the hygroscopic growth curve in that region.

### 3.3. Sensitivity to Small Changes in Chemical Composition.

Hygroscopic growth measurements on mixtures of NaCl and (NH₄)₂SO₄ were also taken to evaluate the sensitivity of the experimental method to small changes in the chemical composition of the aerosol droplets. Three different (NH₄)₂SO₄/NaCl mass ratios were considered (50/50, 90/10, and 95/5) and the mfs and GFr vs \( a_w \) experimental curves (circles) are compared with simulations from the E-AIM model (dashed lines) in Figure 8. For the calculation of growth factors of these mixtures, the reference dry state is considered to be a solid particle made of nonmixed crystalline ammonium sulfate and sodium chloride. The dry density is calculated estimating the dry volumes separately for NaCl and (NH₄)₂SO₄ and calculating the ratio between the total mass and the total volume of the two dry salts.

The experimental results show an overall good agreement with the curves predicted by the E-AIM model for all three mixtures considered, both for the mfs and for the GFr curves. The obtained mfs vs \( a_w \) plot (Figure 8A) shows that it is possible to successfully characterize the different hygroscopic behaviors of the 90/10 and 95/5 mixtures up to about \( a_w = 0.93 \). Above this value, the trends for the 90/10 and 95/5 mixtures.

![Figure 7](image_url)  
*Figure 7.* Correlation plot showing the experimentally measured and E-AIM predicted values for \( n_{\text{water}}/n_{\text{solute}} \), displayed on a logarithmic scale in the main graph and on a linear scale in the inset. Symbols: green, (NH₄)₂SO₄; red, NaNO₃; blue, Na₂SO₄; purple, NaCl; solid line, 1:1 correlation line. Gray shading: uncertainty on \( n_{\text{water}}/n_{\text{solute}} \) for (NH₄)₂SO₄, corresponding to an error in \( a_w \) of ±0.001 (dark gray) and 0.002 (light gray).

![Figure 8](image_url)  
*Figure 8.* mfs vs \( a_w \) (panel A) and GFr vs \( a_w \) (panel B) plots for (NH₄)₂SO₄ and NaCl mixtures at different mass ratios, represented in the form (NH₄)₂SO₄/NaCl. Symbols: filled circles, experimental data; solid lines, calculations from the E-AIM model for pure (NH₄)₂SO₄ and NaCl; dashed lines, calculations from the E-AIM model for the mixtures. From top to bottom in (A) (bottom to top in (B)), the lines/symbols are for pure NaCl (violet), 50/50 ratio (pink), 90/10 ratio (orange), 95/5 ratio (light green), pure (NH₄)₂SO₄ (dark green). Note: error bars are smaller than the data point when not shown.
mixtures become very similar: the difference between the two curves is less than 0.01 mfs, and discriminating between them is not possible. When the experimental results are plotted as GF, vs $a_w$ (Figure 8B), the predicted curves for the same two mass ratios differ by 0.021 in GF, at $a_w = 0.65$ and by 0.058 in GF, at $a_w = 0.95$; in this range, it was possible to discriminate between their GF trends with the EDB measurements. For higher water activity values, the hygroscopic growth curve becomes steep and differences between the two trends are not discernible. The comparison could not be carried out for the ratio $n_{water}/n_{solvent}$ because the curves predicted by the E-AIM model for the 90/10 and 95/5 mixtures are both essentially indistinguishable from that of ammonium sulfate.

These results show that it is possible with this technique to detect variations in the hygroscopicity of solutions with only slight differences in chemical compositions, down to a 5% difference on a mass basis for mixtures of NaCl and (NH$_4$)$_2$SO$_4$. In the case of different mixtures, the minimum detectable variation would depend on the nature of their components: greater discrimination would be achieved if the individual pure components were to much more dissimilar hygroscopic properties.

3.4. Sensitivity to the Value of the Mass Accommodation Coefficient. The sensitivity of these hygroscopicity measurements to variations in the mass accommodation coefficient ($\alpha_M$) was also investigated. The mass accommodation coefficient represents the fraction of water molecules that is absorbed into the droplet bulk on collision with the surface, considered equivalent to the evaporation coefficient by the principle of microscopic reversibility. In the literature, measurements of the mass accommodation coefficient have been performed with a number of different techniques, resulting in a considerable range of different $\alpha_M$ values. $\alpha_M$ contributes to the mass transition correction factor ($\beta_M$, eq 5) in the kinetics model used here. Up to this point we have assumed that $\alpha_M$ has a value equal to 1, in agreement with previous studies which have reported the value of $\alpha_M$ for water accommodating/evaporation from a water surface. $\alpha_M$ is varied, especially for $a_w$ values above 0.95 where the growth curve becomes very steep. Nevertheless, the two curves can be considered to be very similar within the experimental errors. The superior agreement of the curve calculated with $\alpha_M = 1$ (black circles) and the prediction from the E-AIM model (black solid line) at very high $a_w$, together with the very good results obtained for all the aerosol systems presented in sections 3.2 and 3.3, suggests that assuming a value of $\alpha_M = 1$ most accurately characterizes the mass transport behavior observed in the evaporating droplets for all of the binary and ternary systems studied here.

4. CONCLUSIONS
Using the comparative kinetics technique, we have shown that equilibrium hygroscopic growth measurements can be made with typical accuracies in water activity of better than $\pm 0.2\%$ at water activities >0.9 (see, for example, Figure 7) and $\pm 1\%$ below 80% RH. Conventional instruments report growth under subsaturated conditions with accuracies of $\pm 1\%$ in $a_w$ below 95% RH and $\pm 0.1\%$ for high-humidity instruments at >99% RH. In CCN activation measurements, the uncertainty in the critical supersaturation value is typically between 30% at supersaturations between 0.1 and 1%, equivalent to uncertainties of 0.03 to 0.3% at $a_w > 0.99$. In addition, the largest uncertainties in diameter growth factor from this technique are of order $\sim 0.7\%$ (see, for example, the points that have error bars larger than the point size in Figure 8); subsaturated growth measurements by conventional instruments have associated uncertainties of $\pm 5\%$ with large interinstrument variabilities.

Indeed, the hygroscopic growth curves for mixed component aerosol containing (NH$_4$)$_2$SO$_4$/NaCl mass ratios of 90/10 and 95/5 shown in Figure 8 are clearly resolved: the difference between growth factors for these two systems varies from 0.02 at 65% RH (at growth factors of $\sim 1.34$, i.e., a 1.5% difference) up to 0.07 at 98% RH (at growth factors of $\sim 3.20$, mixing ratios).
i.e., a 2% difference). Such a small effect would unlikely be resolved in conventional instruments.

The instrument described here has some significant benefits for rapidly surveying the hygroscopic growth of laboratory generated aerosols of known composition or, indeed, samples from field measurements. Determinations of hygroscopic growth can be made over a wide range in water activity by measuring the time-dependent profiles of droplets evaporating into a selected sequence of RHs (potentially down to fully dry conditions and up to water activities greater than 0.99) with a similar level of accuracy and without particular refinement to address specific water activity ranges. The opportunity to measure hygroscopic growth to such high water activity should provide an opportunity to address some of the challenges in resolving the discrepancies between determinations of $\kappa$ from measurements made under subsaturated and supersaturated conditions. An advantage of performing measurements on coarse mode particles (>5 μm in diameter) is that the Kelvin component of the equilibrium response is negligible when compared with the solute component. Thus, the surface curvature component can be ignored, providing the most unambiguous route to accurate measurements of the solute effect. In addition, this approach yields growth curves in a few seconds starting from the limit of high water activity, particularly valuable for studying organic compounds of low solubility or high volatility by avoiding the complications that follow when changes in the particle-gas partitioning of the VOC/SVOC must be considered. Hygroscopic growth measurements can also be made over a wide temperature range from <250 to >320 K although we focus on ambient temperatures in this publication. Although not appropriate for direct field measurements on accumulation mode particles, the technique can be used to characterize samples with volumes of only a few tens of microliters, the minimum volume required to load the piezoelectric droplet-on-demand generators used to deliver droplets to the electrodynamic balance. Benefiting from these advantages, studies are underway to provide accurate measurements of hygroscopic growth for a wide range of organic compounds found in ambient aerosol containing disparate functional groups and containing multiple functionalities in the same solute molecule.

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