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Discussions

Dependence of the hygroscopicity parameter *κ* on particle size, humidity and solute concentration: implications for laboratory experiments, field measurements and model studies

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Abstract

The hygroscopicity parameter κ has been intensively used in the investigation of the water uptake, cloud condensation nuclei (CCN) activity and chemical composition of atmospheric aerosol particles. A representative value of κ is often assigned to individual species or sources. Such treatment may lead to confusion in closure studies of κ derived from hygroscopic growth factor measurements (κ_{gf}) and CCN activity measurements (κ_{CCN}), and in studies of aerosols at the sub-10 nm size range. Here we show that for particles of the same dry composition, κ may differ as a function of water content, solute concentration and particle size. The concentration- and size-dependence of κ are demonstrated for representative inorganic and organic compounds, i.e., ammonium sulfate (AS), sodium chloride (NaCl) and sucrose. Our results illustrate that an absolute closure between κ_{gf} and κ_{CCN} should not be expected, and how the deviations observed in field and laboratory experiments can be quantitatively explained and reconciled. The difference between κ_{gf} and κ_{CCN} increases as particle size decreases reaching up to 40% and 30% for 10 nm AS and NaCl particles, respectively. Moreover, we show that the deviations of κ_{CCN} vary from ~10% for 30 nm and ~40% for 200 nm, indicating a strong dependence on the Köhler models and thermodynamic parameterizations used for instrument calibration (e.g., effective water vapor supersaturation in CCN counter). By taking these factors into account, we can largely explain apparent discrepancies between κ_{gf} and κ_{CCN} values reported in the scientific literature. Our results help to understand and interpret κ values determined at different water vapor ratios and at different size ranges (especially sub-10 nm). We highlight the importance of self-consistent thermodynamic parameterizations when using AS for calibration aerosol and taking it as a reference substance representing inorganics in closure study between chemical composition and hygroscopicity of aerosol particles.

1. Introduction

Hygroscopicity and cloud condensation nuclei (CCN) activity represent the ability of aerosol particles to interact with water, which is essential for the understanding of aerosol climate effects (Andreae and Rosenfeld, 2008). These properties can be described by the Köhler theory (Köhler, 1936), which accounts for both Kelvin and solute effects. Water activity and surface tension are two key parameters in the Köhler equation, both of which are functions of the aerosol composition and solution concentration. The concentration dependence of water activity and surface tension has been determined for many compounds, e.g., ammonium sulfate (AS) and sodium chloride (NaCl) etc. (Tang and Munkelwitz, 1994; Tang, 1996; Pruppacher and Klett, 1997). Yet we are in lack of such information for a large number of aerosol species and mixtures.

To describe the relationship between particle dry diameter and CCN activity, Petters and Kreidenweis (2007) proposed a method using a single hygroscopicity parameter κ. The κ parameter has several advantages: (1) representative values of κ may be assigned to a specific aerosol species or source; (2) values of κ for mixtures may be determined from volume-weighted average κ of individual components (Petters and Kreidenweis, 2007); and (3) the experimentally-determined κ has already accounted for the impacts of aerosol size, composition and surfactants (Facchini et al., 1999). This approach has been proved useful in describing and predicting the CCN activity of single components and aerosol mixtures (Farmer et al., 2015, and references therein), and the simplified parameterization of κ have been implemented in cloud modeling studies (Spracklen et al., 2008; Reutter et al., 2009; Pringle et al., 2010; Chang et al., 2015).

The original purpose of introducing κ is to achieve a simple prediction of critical activation dry diameter and supersaturation for the CCN activation of aerosol particles (Petters and Kreidenweis, 2007). Since representative κ value is assigned to an aerosol species, it is legitimate to ask if the experimentally determined κ can be used to estimate the aerosol composition. Such efforts have been encouraged by the finding of a simple near linear relationship between hygroscopicity parameter κ and the organic mass fraction (Petters and Kreidenweis, 2007; Gunthe et al., 2009), which has been confirmed by results from different locations and sources (Dusek et al., 2010; Cerully et al., 2011; Gunthe et al., 2011; Kawana et al., 2016; Vogel et al., 2016). In addition, the change of κ values was regarded as an indicator for the evolution of chemical composition or mixing state in the aging process of aerosol particles (Chang et al., 2010; Massoli et al., 2010; Wang et al., 2010; Alfarra et al., 2013; Lathem et al., 2013; Mei et al., 2013a; Mei et al., 2013b; Zhao et al., 2015), and the size-dependent κ values have also been used as an evidence of size-dependent chemical compositions (Su et al., 2010; Cerully et al., 2011; Rose et al., 2011; Lance et al., 2013).

The Köhler equation describes not only the CCN activation under supersaturated conditions but also the hygroscopic growth under subsaturated conditions. Accordingly, κ values can also be determined from hygroscopic growth data measured by hygroscopic tandem differential mobility analyzer (HTDMA). Hence closure studies have been performed to compare κ values determined by hygroscopic growth factor measurements (κ_{gf}) to those determined by CCN activity measurements (κ_{CCN}). Instead of a closure, most laboratory (Carrico et al., 2008; Massoli et al., 2010; Dusek et al., 2011; Alfarra et al., 2013; Hansen et al., 2015; Dawson et al., 2016) and field measurements (Good et al., 2010; Irwin et al., 2010; Cerully et al., 2011; Wu et al., 2013; Bougiatioti et al., 2016; Kim et al., 2016) showed that κ_{CCN} is usually larger than κ_{gf}. Wex et al., (2009) demonstrated that the constant κ value over different concentrations should be reconsidered due to the non-ideality effects in the solution droplet and surface tension variation. Especially in mixed particles, the organic coating or the presence slightly soluble substances can reduce the water transport across the surface by acting as a physical barrier, which may lead to a discrepancy by a factor of 5–10 between κ_{CCN} and κ_{gf} for secondary organic aerosol (Petters et al., 2009; Hansen et al., 2015; Mikhailov et al., 2015; Pajunoja et al., 2015). Hersey et al., (2013) found that the aerosol aging and biomass burning can lead to the discrepancies between κ_{CCN} and κ_{gf} values that may be related to mixing state. Conversely, higher κ_{gf} compared to κ_{CCN} was also observed, and the discrepancies were more attributed to the instrument technical differences (Irwin et al., 2011). Moreover, recent studies (Keskinen et al., 2013; Kim et al., 2016) tried to related the experimentally-determined κ value to chemical composition during new particle formation and initial growth stage, based on the κ-composition relationship built for much larger particles (dry diameter larger than ~50 nm). Wang et al. (2015), however, reported much smaller κ values for the sub-10 nm aerosols than to the hundred nanometer particles with the same chemical composition. A question is hence raised, if and how accurate a single κ value can be used to represent the whole Köhler curve for the whole dry size range. The answer to this question is especially critical and sensitive for the understanding of multiphase chemistry (Herrmann et al., 2015; Pöschl and Shiraiwa, 2015; Cheng et al., 2016) and for accurate climate modeling (Pajunoja et al., 2015).

Another critical issue concerning the application of κ is that its exact value is subject to the selection of thermodynamic parameterizations in Köhler models (Rose et al., 2008; Mikhailov et al., 2013). This is because different thermodynamic parameterizations may lead to different Köhler curves (Cheng et al., 2015; see Fig. 1 and references therein), resulting in different calibrations of effective water vapor supersaturation (S_{e}) in CCN counter (CCNC) and column relative humidity (RH) in HTDMA and consequently different κ values.

In this study, we address the question whether the same compound always has the same κ value; if not, what contributes to the difference. In the following, we first present the theoretical basis and data retrieval methodology. Then we demonstrate the concentration and size dependence of κ for exemplary substances. Finally, we discuss the closure studies between κ_{gf} and κ_{CCN}, and emphasize the importance of the usage of a consistent Köhler model for both calibration with AS and the retrieval of AS κ value when taking it as a reference substance in the inorganic/organic mixing ratio analyses.

2. Methodology

2.1 κ-Köhler model

The Köhler theory describes the equilibrium saturation ratio (s) over a spherical aqueous droplet (Köhler, 1936):

$$s = a_{\mathrm{w}} \exp\left(\frac{4\sigma_{\mathrm{sol}} v_{\mathrm{w}}}{RTD_{\mathrm{d}} gf}\right) \quad (1)$$

where a_{w} is the water activity, σ_{sol} is the surface tension of solution droplet, v_{w} is the partial molar volume of water, D_{d} is the particle dry diameter (mass equivalent diameter), gf is the growth factor of particle diameter relative to the dry particle diameter ($gf = D/D_{\mathrm{d}}$), which is related with solute concentration by concentration-dependent solution density. R and T are the universal gas constant and absolute temperature, respectively.

For AS and NaCl aerosols, we choose the original models used by Biskos et al. (2006a; 2006b), which agree well with the observation data from HTDMA experiments (Cheng et al., 2015). a_{w} and σ_{sol} are expressed as a function of solute mass fraction x_{s}, which are derived from the best fit to the literature measurement data (Tang and Munkelwitz, 1994; Tang, 1996; Pruppacher and Klett, 1997). The parameterizations are detailed in the Appendix.

Petters and Kreidenweis (2007) proposed a hygroscopicity parameter κ for the parameterization of water activity:

$$\frac{1}{a_{\mathrm{w}}} = 1 + \kappa \frac{V_{\mathrm{s}}}{V_{\mathrm{w}}} \tag{2}$$

where V_{s} and V_{w} are the volumes of the dry aerosol particle and water, respectively. For ideal solution, κ have a unique value for certain species while it may vary for non-ideal solution.

Substituting the expression of κ into Eq. (1), we have the κ-Köhler equation as:

$$s = \frac{gf^3 - 1}{gf^3 - (1-\kappa)} \exp\left(\frac{4\sigma_{\mathrm{sol}} v_{\mathrm{w}}}{RTD_{\mathrm{d}} gf}\right) \tag{3}$$

Due to the lack of thermodynamic data for the mixed or unknown system, surface tension of water (σ_{w}) is used instead of σ_{sol} and v_{w} is simplified as $M_{\mathrm{w}}/\rho_{\mathrm{w}}$ in the κ calculation (Petters and Kreidenweis, 2007; Su et al., 2010), where M_{w} and ρ_{w} are the molar mass and density of water, respectively.

2.2 Determination of κ

To elucidate the concentration and size dependence of κ, we use AS, NaCl and sucrose as exemplary substances. The 'real' s-gf relations for these substances at different sizes (i.e., D_{d}) are first calculated by Eq. (1) with well-documented thermodynamic data (i.e., a_{w} and σ_{sol}). We then retrieve the corresponding κ values for each s-gf-D_{d} pair with Eq. (4):

$$\kappa = \frac{gf^3 - 1}{s} \exp\left(\frac{A}{D_{\mathrm{d}} gf}\right) - gf^3 + 1 \text{ and } A = \frac{4\sigma_{\mathrm{w}} M_{\mathrm{w}}}{\rho_{\mathrm{w}} RT} \tag{4}$$

3. Results and discussion

3.1 Concentration and size dependence of κ

In reality, the aerosol or cloud droplets are often not ideal solutions, especially at concentrated state, and the Zdanovskii-Stokes-Robinson (ZSR) volume additivity assumption would not hold anymore. To maintain the κ-Köhler equation (Eq.3), these non-ideality effects have to be compensated, which is reflected by a change in κ. That is why a single species does not correspond to a unique κ value. In addition, since σ_w is often used instead of σ_{sol}, their difference also needs to be compensated through a change in κ values. In a word, the κ in practical application is subject to both the non-ideality effect and simple treatment of surface tensions. The nano-size effects (e.g., the Tolman effect) on the thermodynamic properties of aerosol particles may result in additional size dependence as well (Cheng et al., 2015).

Concentration dependence. Figure 1 shows the κ values as a function of solute concentration (expressed as *gf* or solute molality μ_s) for different aerosol particles with dry diameters of 10 nm, 50 nm and 100 nm, respectively. Here the change of *gf* reflects the change of solution concentration, i.e., larger *gf* corresponds to more dilute solution (see Eq. A5). Our theoretical calculations illustrate a strong concentration dependence of κ values for AS, NaCl and sucrose. Similar findings in sub-saturation range (RH < 100%) have been shown by Mikhailov et al. (2009; 2013), as water activity dependent κ for AS and levoglucosan. However, in some cases, κ does not show strong concentration dependence, e.g., oxalic acid (Mikhailov et al., 2009) and a mixture system of AS and five dicarboxylic acids (Marcolli et al., 2004), which may infer ideal solution or result from the compensation of simplified surface tension and solution non-ideality. For AS and NaCl aerosols (Fig. 1a-b), κ first decreases with increasing *gf* (decreasing μ_s). After reaching a minimum, κ gradually increases and finally approaches a plateau. For example, the κ values of 100 nm AS particles vary from 0.57 at the deliquescence point (RH~80%) to a minimum value of ~0.42, and retain ~0.48 at larger *gf*. The concentration dependence of NaCl shows a similar shape as AS with κ values eventually approaching ~1.4 (Petters and Kreidenweis, 2007). However, κ of sucrose aerosols has a different concentration dependence which shows a monotonic decrease down to ~0.08. Compared to the 100 nm aerosols, the 10 nm and 50 nm aerosols show similar concentration dependence but lower κ values.

Size dependence. Beside the concentration dependence, Fig. 1 also shows a size dependence of κ. This feature can be more clearly seen in Fig. 2, where κ values are plotted against the particle diameter. The same color-coding represents the same solution concentration, which helps to separate the size effect from the concentration effect. Given the same *gf*, the κ values increase with increasing particle diameter and finally approaching a plateau, i.e., ~0.56 for AS (*gf* ~1.5), ~1.8 for NaCl (*gf* ~2.0) and ~0.14 for sucrose (*gf* ~1.2), respectively. The size dependence of κ is more prominent for AS aerosols, especially for smaller particles. For the same concentration (*gf* of ~ 1.5), the κ values of AS vary from 0.40 for 6 nm to 0.51 for 20 nm, and then slowly grow to 0.56 for 300 nm.

3.2 Comparison of HTDMA and CCNC measurements

3.2.1 Theoretical calculation

According to Eq. (4), κ can be derived experimentally from both hygroscopic growth and CCN activity measurements. Thus direct comparison of κ_{gf} and κ_{CCN} were often performed. The concentration and size dependence of κ, however, challenges the possibility of reaching a closure of κ value determined from different RH or saturation conditions.

On the basis of reliable thermodynamic models (see Appendix), we calculate the theoretical κ values (AS, NaCl and sucrose) at RH=90% as for hygroscopic growth factor measurement and at empirical critical supersaturation (S_{cri}) as for CCN activity measurement. Indeed, the retrieved κ is a combined presence of both concentration and size dependence. As demonstrated in Fig. 3 (left panel), κ_{gf} decrease with increasing particle dry diameter while κ_{CCN} shows a contrary trend. The gap between HTDMA and CCNC results narrows down with the increasing particle dry diameter which is also reflected in Fig. 1. Finally, both of the predicted κ approach a value of ~0.48 and ~1.4 for AS and NaCl particles, respectively, while no convergence is observed for sucrose at 200 nm.

We also notice weaker size dependence toward the larger size range. To identify the size range with negligible size effects, we calculate the size dependence of κ values as shown in the right panel of Fig. 3. The size dependence is more prominent for smaller aerosols. For example, a relative variation ($\mathrm{dlog}\kappa/\mathrm{dlog}D_{\mathrm{d}}$) of ~0.24 is found for 10 nm AS aerosols while a $\mathrm{dlog}\kappa/\mathrm{dlog}D_{\mathrm{d}}$ for 50 nm aerosols is only 0.04 (CCN activity methods). This size effect should be specifically taking into account when study the properties of nanoparticles during new particle formation and initial growth.

3.2.2 Revisit of literature data

Figure 4 summarized the comparisons of κ values from HTDMA and CCNC measurements of field and laboratory aerosols (~50-300 nm) in literatures. Different from our theoretical calculations ($\kappa_{\mathrm{CCN}} < \kappa_{\mathrm{gf}}$), the literature comparison generally shows larger κ_{CCN} than κ_{gf}. Though it was mostly attributed to potential measurement uncertainty (Good et al., 2010) and non-ideality of solution (Wex et al., 2009), we provide an alternative explanation that the selection of parameterization methods in the instrument calibration (specifically for CCN activation experiments) may contribute largely to such differences.

Rose et al. (2008) demonstrated the commonly used Köhler models and thermodynamic parameterizations for the calibration of the S_{e} in CCNC. The results showed that the relative deviations of theoretical S_{e} are as high as 25% and 12% for AS and NaCl particles, which is mainly caused by the different parameterizations for a_{w} in dilute aqueous solutions of these two salts. Figure 5a-b shows the deviations of activity parameterizations (AP) models for AS particles, such as Aerosol Inorganics Model (AIM)-based (referred as AP3) and Electrodynamic Balance method (EDB)-based (referred as AP1, roughly corresponding to the models used in this study, see details in the Appendix) a_w parameterizations (Rose et al., 2008). For the range of solute molality up to 0.3 mol kg^{-1}, the a_w differences are on the order of ~10^{-3}, resulting in the relative differences of retrieved S_e vary between 8% and 18% in the size range of 20-200 nm (Figs. 5c and 5e), the size range where the CCNC calibration commonly performed (Rose et al., 2008). Accordingly, the estimated hygroscopicity κ is higher when applying AP3 model in CCN activity measurements compared to AP1 model ($\kappa_{AS} \approx 0.66$ with AP3 and $\kappa_{AS} \approx 0.48$ with AP1 at 200 nm). As demonstrated in Figs. 3a and 6a, the deviations appear to be size dependence, varying from ~10% for 30 nm to ~40% for 200 nm. Conversely, the influences of selecting different AP models will largely cancel out when performing RH calibration in HTDMA studies (Fig. 5d-e). In other words, the predicted κ values are not sensitive to the selected thermodynamic parameterizations and Köhler models in hygroscopic growth measurements.

Although previous studies attributed the inconsistencies between κ_{gf} and κ_{CCN} to the non-ideality effects in the solution droplet and surface tension variation, etc. (Wex et al., 2009; Wu et al., 2013; Hong et al., 2014; Pajunoja et al., 2015; Zhao et al., 2016), we find that the key factor to explain the differences is indeed the distinct Köhler models and thermodynamic parameterizations used in the CCNC calibration. AIM-based Köhler model (AP3) are recommended because it provides an accurate prediction of a_w for highly dilute solution (Rose et al., 2008). However, our theoretical calculations indicate that the AP3 model could lead to a systematic overestimation of up to ~40% in predicting κ_{CCN} than κ_{gf}. In addition, for certain chemical compounds, their hygroscopic behavior in subsaturated and supersaturated conditions is innate distinct, with no apparent closure between κ_{gf} and κ_{CCN}. For example, we find that the κ_{gf} exceeding κ_{CCN} by a factor of 1.5 for sucrose at particle size larger than 50 nm (Fig. 3e).

Our results demonstrate that besides the measurement uncertainty, the discrepancies in previous hygroscopicity closure studies may be to a large extent reconciled by the systematic calibration differences and the inherent concentration dependence of κ for specific compounds. Based on our calculations, the ratios of κ_{CCN} to κ_{gf} (κ_{CCN}/κ_{gf}) may vary from 1.1 to 1.4 due to systematic calibration differences (Fig. 6a) and from 0.7 to 1.4 due to the inherent concentration dependence for different chemical composition (Figs. 3a and 3e). Taking these effects into account, we find that the observed discrepancy between κ_{gf} and κ_{CCN} could be partially explained (shaded area in Fig. 6b). Therefore, we suggest that hygroscopicity studies should always report exactly which Köhler models and thermodynamic parameterizations to ensure the comparability of results.

3.3 Application to atmospheric closure study between chemical composition and hygroscopicity of aerosol particles

In practice, with precise measurement techniques and reliable calibration procedure, we can accurately measure the particle *gf* at certain RH (HTDMA) and determine the D_d-S_e relation (CCNC). Hence, the predicted κ value has already considered the impacts of aerosol size, composition and unknown thermodynamic properties, and it can well describe the hygroscopicity and CCN activity. Still, the following issues should be addressed when applying κ:

1. The simple near linear κ-composition relationship establishes the fundamental for estimating κ or mass fraction of organic or inorganic compounds (Dusek et al., 2010; Mei et al., 2013a; Mei et al., 2013b; Wang et al., 2015; Kim et al., 2016; Vogel et al., 2016). In view of such application, the self-consistent approaches should be strictly followed to determine κ value, especially for AS, which is the commonly

adopted calibration aerosol and the dominating inorganics of ambient aerosol particles. As previously demonstrated, the retrieval of S_{cri} is very sensitive to the selection of Köhler models and thermodynamic parameterizations, resulting in the representative κ for AS particles vary in a wide range (~0.4-0.8) in closure study (Petters and Kreidenweis, 2007; Rose et al., 2008; Mikhailov et al., 2009; Mikhailov et al., 2013; Wang et al., 2015). Therefore, the chosen κ value should always be correspondingly associated with the calibration method. Otherwise, the inconsistent thermodynamic data will introduce additional uncertainty in retrieving κ value, which may in turn lead to the unreliable estimation of organics/inorganics fractions or hygroscopicity κ for unknown chemical component. For instance, the bias in the estimation of organic mass fraction is within 10% when choosing the identical thermodynamic data to calibrate nano-CCNC and determine κ value for 2.5 nm AS particles, as shown in Fig.9 of Wang et al. (2015). This uncertainty can reach a level of 50% in case of inconsistent parameters are used.

2. Size-resolved aerosol hygroscopicity and its link to chemical composition were also investigated in many closure studies (Dusek et al., 2010; Bezantakos et al., 2013; Wu et al., 2013; Liu et al., 2014; Zhang et al., 2014). However, only one κ value is commonly used to describe hygroscopicity of the typical inorganics, i.e., ~0.6 for AS and ~0.7 for NH_4NO_3 in the entire investigated size range. According to our simulation, this hypothesis may not hold for smaller aerosols due to the significant size dependence of κ at that size range (Fig. 3). Experimentally determined κ value is found to be 0.43 for 10 nm AS particles, which is approximately 11% lower than that for particles larger than 100 nm. This gap becomes more obvious for sub-10 nm aerosol particles, and the relative deviation is up to ~45%. These findings suggest when performing hygroscopicity closure studies, special attention should be paid to size-resolved κ values used in the calculation to obtain accurate results, especially for aerosol particles in nano-size range. In addition, there exist large discrepancies

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between observations and model predictions of the hygroscopic growth of salt nanoparticles when ignoring particle size effects in Köhler models (Biskos et al., 2006b; Cheng et al., 2015). This prompts the precise thermodynamic data for nanoparticles needs to be investigated more systematically.

4. Conclusion

In this study, we present the differences in particle hygroscopicity behavior (represented as κ) in subsaturated and supersaturated conditions. The proof-of-principle demonstration is performed with AS, NaCl and sucrose particles. Our results indicate that the theoretical κ value shows relatively strong concentration and size dependence, suggesting its value for individual chemical substance should be specifically assessed according to the concerned particle size and saturation regime, especially for sub-10 nm particles.

We demonstrate that the observed κ is a compromised product between its inherent concentration dependence (i.e., solution non-ideality & simplification of surface tension) and systematic calibration differences (i.e., different thermodynamic parameterizations in Köhler models). By taking these factors into account, we can largely explain the observed inconsistency of κ values derived from hygroscopic growth factor and CCN activity measurements in literatures. Our results highlight the importance of self-consistent thermodynamic data in the closure studies concerning particle hygroscopicity.

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Appendix

In this appendix, we present the parameterizations to retrieve Köhler curve of AS, NaCl and sucrose aerosol particles.

1. AS and NaCl

Water activity a_w was derived from the single particle experiments by the Electrodynamic Balance (EDB) method (Tang and Munkelwitz, 1994; Tang, 1996), which can be expressed as polynomial fit functions of solute mass fraction x_s:

$$a_w = 1 + \sum_q A_q (100 \cdot x_s)^q \tag{A1}$$

The polynomial coefficients A_q for AS at 298 K are $A_1 = -2.715\times10^{-3}$, $A_2 = 3.113\times10^{-5}$, $A_3 = -2.336\times10^{-6}$, and $A_4 = 1.412\times10^{-8}$. The polynomial coefficients A_q for NaCl at 298 K are $A_1 = -6.366\times10^{-3}$, $A_2 = 8.624\times10^{-5}$, $A_3 = -1.158\times10^{-5}$, and $A_4 = 1.518\times10^{-7}$.

For the surface tension (σ_{sol}) of aqueous AS and NaCl droplet, Pruppacher and Klett (1997) proposed the following parameterization:

$$\sigma_{sol} = 0.072 + \frac{2.34\times10^{-2}\cdot x_s}{1-x_s} \text{ for AS} \tag{A2}$$

$$\sigma_{sol} = 0.072 + \frac{2.9\times10^{-2}\cdot x_s}{1-x_s} \text{ for NaCl} \tag{A3}$$

of which the validated range is $x_s < 0.78$ for AS and $x_s < 0.45$ for NaCl.

Solution density ρ_{sol} is also a function of x_s, which is parameterized based on the EDB measurements (Tang and Munkelwitz, 1994; Tang, 1996):

$$\rho_{sol} = \rho_w + \sum_q d_q (100 \cdot x_s)^q \tag{A4}$$

The polynomial coefficients d_q for AS at 298 K are $d_1 = 5.92$, $d_2 = -5.036\times10^{-3}$ and $d_3 = 1.024\times10^{-5}$. The polynomial coefficients d_q for NaCl at 298 K are $d_1 = 7.41$, $d_2 = -3.741\times10^{-2}$, $d_3 = -2.252\times10^{-3}$, and $d_4 = -2.06\times10^{-5}$.

Growth factor *gf* can be calculated as:

$$gf = \left(\frac{\rho_s}{x_s \rho_{\mathrm{sol}}}\right)^{1/3} \tag{A5}$$

where ρ_s is the density of dry solute.

To be consistent with previous work (Biskos et al., 2006a), the molar volume of pure water was used instead of the partial molar volume and shaper factor correction for dry equivalent spherical mobility diameter were performed based on the methods of Biskos et al. (2006a) for AS and DeCarlo et al. (2004) and Biskos et al. (2006b) for NaCl, respectively.

We also compare the AP1 and AP3 models (section 3.2.2) by following the parameterizations described in Rose et al. (2008). Note that the difference between our present model and AP1 is the different selection of σ_{sol} parameterization. We adopt the parameterization proposed by Pruppacher and Klett (1997) due to the better agreement between calculations and observations for nanoparticles down to 6 nm (Cheng et al., 2015).

2. Sucrose

For sucrose aerosols, water activity a_{w} was calculate based on the model provided by Chen (1989):

$$a_{\mathrm{w}} = \frac{1}{1+0.018\times 0.1136\times \mu_s^{0.955}\mu_s} \tag{A6}$$

where μ_s is the solute molality.

Under the assumption of volume additivity (Mikhailov et al., 2004), ρ_{sol} can be calculated by:

$$\rho_{\mathrm{sol}} = \left(\frac{1-x_s}{\rho_{\mathrm{w}}} + \frac{x_s}{\rho_s}\right)^{-1} \tag{A7}$$

where ρ_{w} is the density of pure water.

Surface tension (σ_{sol}) parameters were adopted by the work of Matubayasi and

Nishiyama (2006), which measured the surface tension (σ_{sol}) of aqueous sucrose solation in the concentration range 0 to 0.5 mol kg^{-1} using drop volume method. Growth factor *gf* can be calculated with Eq. A5.

Figures

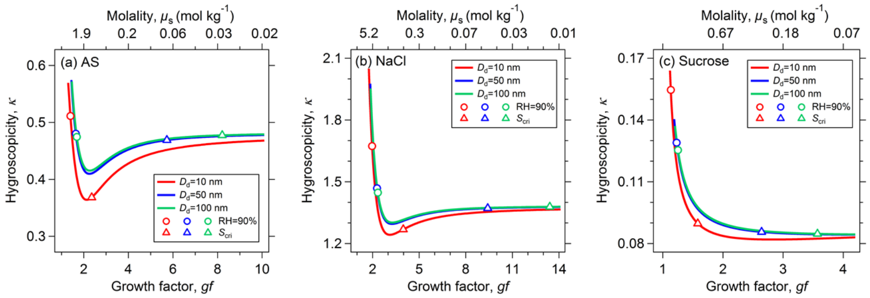

Figure 1: Concentration dependence of the hygroscopicity parameter κ calculated for deliquesced aerosol particles of (a) ammonium sulfate (AS), (b) sodium chloride (NaCl) and (c) sucrose with dry diameters of 10 nm (red), 50 nm (blue) and 100 nm (green). Lower limit values of the particle diameter growth factors (*gf*) correspond to the deliquescence point of crystalline particles. Open circles and triangles indicate the values of κ and solute molality (or diameter *gf*) calculated at 90% RH and at the theoretical critical supersaturation of CCN activation (S_{cri}), respectively. Thermodynamic parameterizations are described in the Appendix.

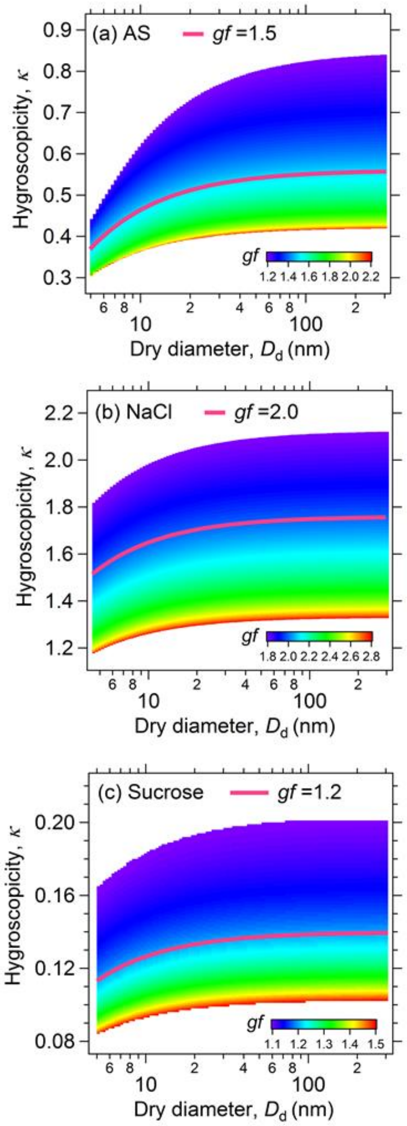

Figure 2: Size dependence of the hygroscopicity parameter κ calculated as a function of particle dry diameter (D_d, x axis) and growth factor (*gf*, color coding) for deliquesced (a) ammonium sulfate (AS), (b) sodium chloride (NaCl) and (c) sucrose aerosols. The pink lines represent the dependence of κ on D_d for fixed *gf* values: (a) *gf* = 1.5 for AS, (b) *gf* = 2.0 for NaCl, and (c) *gf* = 1.2 for sucrose.

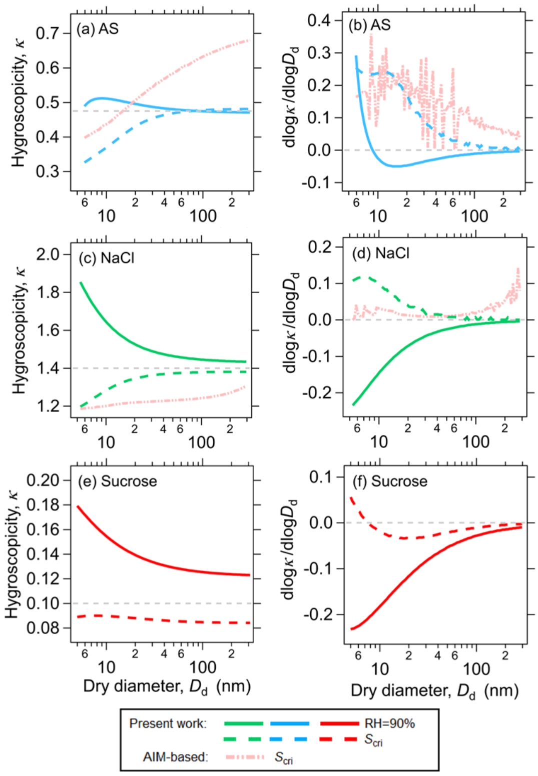

Figure 3: Left Panel: Size dependence of the hygroscopicity parameter κ calculated as a function of dry diameter (D_d, x axis) for different types of aerosol particles at a typical level of relative humidity applied in HTDMA measurements (RH = 90%, solid lines) and at the critical supersaturation of CCN activation (S_{cri}, dashed and dash-dotted lines): (a) ammonium sulfate (AS), (c) sodium chloride (NaCl) and (e) sucrose. Right panel: The relative sensitivity of κ to changes in dry particle diameter (dlogκ/dlogD_d). Solid lines and dash lines were determined with the parameterizations described in the Appendix. Pink dash-dotted lines are determined with the Aerosol Inorganics Model (AIM)-based parameterizations (Clegg et al., 1998). Gray dash lines are to guide the eye.

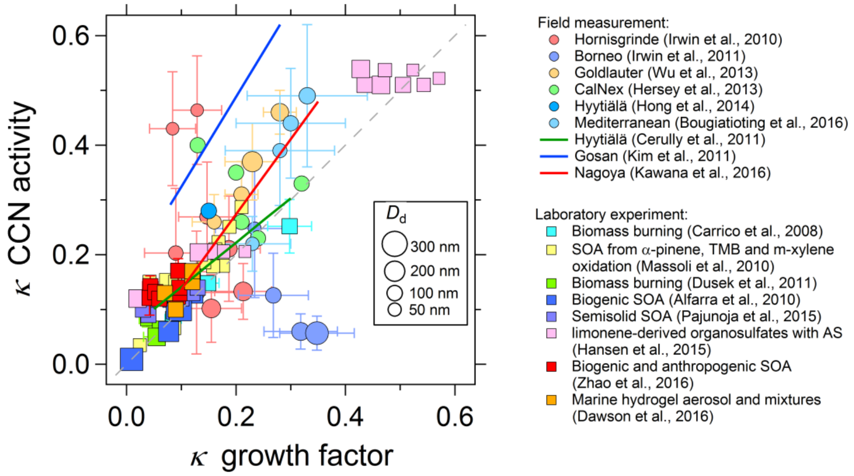

Figure 4: Comparison of reported κ values from field measurements (circles and solid lines) and laboratory experiments (squares) based on hygroscopic growth factor (x axis) and CCN activity measurements (y axis). The gray dashed line shows 1:1 ratio. The size of symbols indicates the particle diameter. Note for the studies which did not provide the specific particle size (Carrico et al., 2008; Hersey et al., 2013; Zhao et al., 2016), we use 100 nm to present the results.

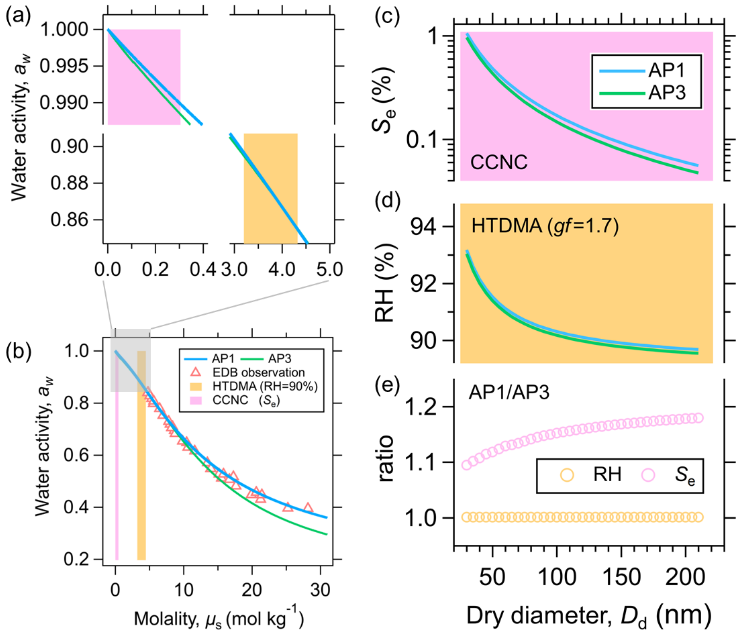

Figure 5: Left panel: (a-b) Dependence of water activity (a_w) on solute concentration (molality μ_s) in aqueous ammonium sulfate (bulk solution). Pink triangles indicate the electrodynamic balance (EDB) measurement data (Clegg et al., 1995). Blue and green lines represent different parameterizations of a_w as a function of μ_s based on EDB method (AP1) and on the Aerosol Inorganics Model (AP3). Right panel: (b) Comparison of results when applying different AP models in calibrating (c) the effective supersaturation (S_e) in a CCNC instrument and (d) the effective relative humidity (RH) in a HTDMA instrument. (e) Ratio of calibration values (AP1 to AP3 models) for HTDMA (e.g., RH at *gf*=1.7) and CCNC (S_e). The corresponding concentration and saturation ranges for HTDMA and CCNC measurements are respectively marked as yellow and pink.

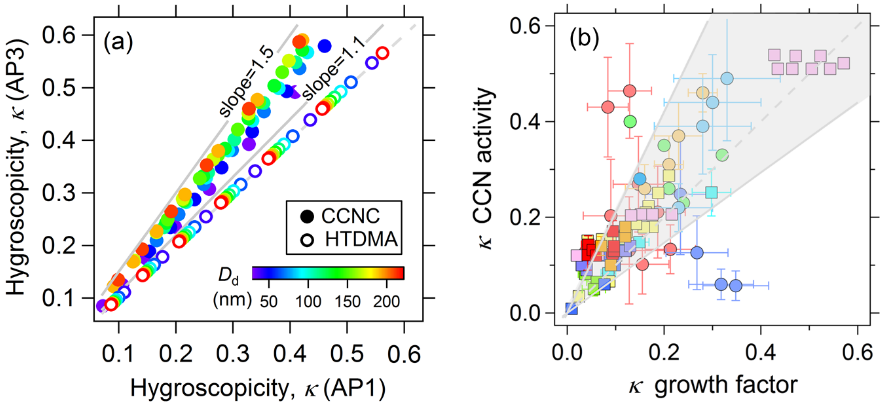

Figure 6: (a) Comparison of retrieved hygroscopicity κ using different Activity Parameterization (AP) model (Rose et al., 2008) for the calibration of HTDMA and CCNC. The dashed line shows the 1:1 ratio, and the solid lines correspond to 10% and 50% uncertainties. (b) The shaded area represents the region where the measured κ values might be located when considering systematic calibration differences (κ_{CCN}/κ_{gf} ~1.1-1.5) and inherent concentration dependence (κ_{CCN}/κ_{gf} ~0.7-1.4) of κ. The upper and lower bounds corresponding to the fit lines of κ_{CCN}=2.1 κ_{gf} and κ_{CCN}=0.7 κ_{gf}, respectively. Reported κ values from field measurements and laboratory experiments corresponding to Fig. 4.

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