

Strong evidence of surface tension reduction in microscopic aqueous droplets

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The ability of airborne particles to take up water may be enhanced by surface-active components, but the importance of this effect is controversial because direct measurement of the surface tension of microscopic droplets has not been possible. Here we infer droplet surface tension from water uptake measurements of mixed organic-inorganic particles at relative humidities just below saturation (99.3 - 99.9%). The surface tension of droplets formed on particles composed of NaCl and α -pinene ozonolysis products was reduced by 50 - 75%, but only when enough organic material was present to form a film on the droplet surface at least 0.8 nm thick. This study suggests that if atmospheric particles are predominantly ($\gtrsim 80\%$) composed of surface-active material, their influence on cloud properties and thus climate could be enhanced, and their atmospheric lifetimes could be reduced.

1. Introduction

If two airborne particles with the same dry diameter (D_{dry}) are in equilibrium with ambient relative humidity (RH), the more hygroscopic of the two will have a greater wet diameter (D_{wet}). It will therefore scatter more light, act as a greater condensational sink for soluble compounds, and more readily act as a cloud condensation nucleus (CCN). Since wet deposition is the dominant process removing sub-micron particles from the atmosphere [Textor *et al.*, 2006], and the chemistry of dilute cloud droplets is distinct from that of aerosol particles [Ervens *et al.*, 2011], an aerosol's hygroscopicity largely determines its chemical evolution, its lifetime and atmospheric burden, and hence its influence on air quality and climate.

Particle hygroscopicity under supersaturated ("CCN") conditions is often greater than predicted from subsaturated water uptake measurements (typically at RH $\lesssim 90\%$). Several explanations for this behavior have been discussed in the literature, including reductions in droplet surface tension (σ , e.g., Dinar *et al.* [2007]; Asa-Awuku *et al.* [2008]; Ovadnevaite *et al.* [2011]). Currently no known method can directly measure σ of microscopic ($D_{wet} \sim 1 \mu\text{m}$) droplets. Thus while many studies have shown that atmospheric organic matter can reduce σ of macroscopic aqueous solutions [Facchini *et al.*, 1999; Dinar *et al.*, 2006; Asa-Awuku *et al.*, 2008], conclusive evidence of reduced σ in microscopic droplets has been elusive [Abbatt *et al.*, 2005]. The σ values of microscopic droplets and macroscopic solutions may differ because surface area to volume ratios are several orders of magnitude greater in the former. This tends to reduce surface excess concentrations of surface-active compounds,

potentially inhibiting σ reduction relative to macroscopic solutions. Furthermore, for soluble surfactants, surface partitioning reduces bulk solute concentration, raising water activity and thus decreasing hygroscopicity [Sorjamaa *et al.*, 2004]. It may therefore be inappropriate to apply macroscopic σ to microscopic droplets.

Although σ in microscopic droplets cannot be directly measured, it can be inferred from measurements of droplet hygroscopicity, which is determined by two components: (1) the Kelvin effect, which is the increase in equilibrium water vapor pressure over a curved surface, and is proportional to σ ; and (2) the Raoult effect, which is the reduction in water activity associated with solute dissolution, and does not explicitly depend on σ . Such an inference requires that these two effects can be separated, and that the measurements are sensitive to σ . Previously, σ has been inferred from measurements of CCN activity. However, for an aerosol of a given composition, such a measurement involves only a single independent variable - either the critical supersaturation or D_{dry} at the point of cloud droplet activation. Thus any enhanced CCN activity cannot be unambiguously attributed to reduced σ , as it could also be caused by an increased Raoult effect. Subsaturated hygroscopicity experiments allow for two independent variables (RH and or D_{dry}), but the Kelvin effect is negligible at RH $< 95\%$, and thus hygroscopicity is dominated by the Raoult effect. Since RH $> 95\%$ is difficult to maintain accurately in most experimental setups, most previous observations of subsaturated hygroscopic growth have not been sensitive to σ .

These issues likely have contributed to disagreements among previous studies regarding the role of reduced σ in determining CCN activity, with some studies concluding that the CCN activity of surfactants is overestimated unless surface partitioning is taken into account [Li *et al.*, 1998; Sorjamaa and Laaksonen, 2006; Prisle *et al.*, 2010], while others have found that organic CCN activity can only be accurately predicted if σ is reduced to values similar to macroscopic solutions [Dinar *et al.*, 2006; Broekhuizen *et al.*, 2004; Asa-Awuku *et al.*, 2008; Moore *et al.*, 2008]. Another set of studies have concluded that only slight reductions in σ ($\sim 10 - 15\%$) are most consistent with observed CCN activity [Engelhart *et al.*, 2008; Wex *et al.*, 2009; King *et al.*, 2009; Duplissy *et al.*, 2008; Padr pure *et al.*, 2010; Asa-Awuku *et al.*, 2010].

Here we report measurements of equilibrium water uptake at high but subsaturated RH (99.2 to 99.9%), to unambiguously determine if σ can be reduced in microscopic droplets. This is possible because measurements over this RH range allow for clear separation of the Kelvin and Raoult effects. These measurements are relevant to CCN activity because the water activity of the droplets is similar to that of typical atmospheric CCN at the point of activation. Our experiments utilize particles generated via dark ozonolysis of α -pinene because they mimic the complexity of ambient organic aerosols, and because α -pinene is an important precursor of ambient secondary organic aerosol (SOA). We address the following questions:

1. Do we see evidence of σ reduction in microscopic droplets at RH near 100%? If so, to what extent?

2. How much surface-active material is required to achieve any such reductions in σ ?

3. Under what conditions might reduced σ increase the CCN activity of aerosols?

2. Experimental

Reagent grade (>99% purity, VWR International) NaCl was dissolved in ultrapure water (resistivity ≥ 18.2 M Ω cm) and used in a constant-output atomizer (TSI, model 3079) followed by a diffusion drier (output RH < 10%) to generate seed particles. SOA particles were generated by dark ozonolysis of α -pinene, either via homogeneous nucleation or condensation onto NaCl seed particles. No radical scavenger was used. Ozone was produced with a Hg penray lamp and diluted with a dry nitrogen flow to a concentration of either 350 ppb for seed experiments, or 560 ppb for homogeneous nucleation. The larger [O₃] in the homogeneous nucleation experiments was necessary to ensure that droplets were large enough to measure. Liquid α -pinene was delivered via a syringe pump into a dry nitrogen flow, at a rate ensuring that O₃ was the limiting reagent. The α -pinene and O₃ reacted to form SOA in a small stainless steel reaction chamber with a residence time of approximately 30 s. For the mixed SOA-NaCl particles, the SOA volume fractions were determined from the measured dry particle diameters of the pure NaCl and mixed particles. For inorganic particles, shape correction factors of 1.08 for NaCl and 1.04 for AS was applied. For pure organic or mixed organic-inorganic particles, no shape correction factor was used [Zelenyuk *et al.*, 2006].

High RHs just below (99.3 – 99.9%) and just above (100.2 – 100.6%) saturation were generated with a continuous-flow streamwise thermal gradient chamber based on the design of Roberts and Nenes [2005] and described in detail previously [Ruehl *et al.*, 2010]. The flow rate in the chamber was fixed at 0.82 lpm, resulting in a residence time of ~ 12 s. Before exiting the chamber, and while still flowing along the chamber centerline, droplets were counted and sized with a phase Doppler interferometer (PDI; Artium, Inc.).

In subsaturated experiments, hygroscopicity is reported as κ [Petters and Kreidenweis, 2007]:

$$\text{RH} = \frac{D_{\text{wet}}^3 - D_{\text{dry}}^3}{D_{\text{wet}}^3 - D_{\text{dry}}^3(1 - \kappa)} \exp\left(\frac{4\sigma\bar{V}_w}{RTD_{\text{wet}}}\right), \quad (1)$$

where \bar{V}_w is the molar volume of the water in the droplet solution (assumed to be equal to that of pure water because droplets are very dilute when RH is near 100%), R is the gas constant, and T is temperature. The largest source of experimental uncertainty is the RH in the chamber, as RH is extremely sensitive to T near saturation. The chamber T is controlled to within 0.01 K using high-precision thermistors, which corresponds to an uncertainty in RH of $\pm 0.05\%$ (absolute). All quoted uncertainty and error bars depicted in plots are those associated with the 0.01 K uncertainty in T , unless otherwise indicated. For CCN measurements, κ is determined via measurement of the critical supersaturation (S_c), from the following relationship:

$$\kappa = \frac{4}{27D_{\text{dry},c}^3 \ln^2(S_c)} \left(\frac{4\sigma\bar{V}_w}{RT}\right)^3, \quad (2)$$

where $D_{\text{dry},c}$ is the dry diameter that activates at a given S_c . Both RH and S (for CCN experiments) were calibrated with pure AS particles, taking into account non-ideality [Rose *et al.*, 2008].

3. Results

3.1. Observed κ values

Under subsaturated conditions, κ of pure secondary organic aerosol ($\kappa_{\text{SOA}}^{\text{pure}}$) generated by ozonolysis of α -pinene ranged from 0.011 to 0.042 (mean $\pm 1\sigma = 0.026 \pm 0.010$) (Table 1), increasing with RH (Fig. S1a). This low value of $\kappa_{\text{SOA}}^{\text{pure}}$ is consistent with Wex *et al.* [2009], who found that for α -pinene ozonolysis $\kappa_{\text{SOA}}^{\text{pure}} \sim 0.02$ at RH = 99.6%. Such a low $\kappa_{\text{SOA}}^{\text{pure}}$ is also consistent measured $D_{\text{wet}}/D_{\text{dry}}$ ratios less than 1.1 at 85% < RH < 90% (e.g., Prenni *et al.* [2007]). Due to the Kelvin effect, the water activity (a_w) in these droplets is at least as high as the ambient RH, and so while non-idealities cause $\kappa_{\text{SOA}}^{\text{pure}}$ to increase slightly with a_w (and thus RH), $\kappa_{\text{SOA}}^{\text{pure}} \lesssim 0.04$ even when $a_w \gtrsim 0.999$ (Fig. S1b). After the RH dependence of $\kappa_{\text{SOA}}^{\text{pure}}$ is removed, it still increased with D_{wet} (Fig. S1c). Using this technique, Ruehl *et al.* [2010] also observed an increase in hygroscopicity with D_{wet} for sodium dodecyl sulfate, a well-known surfactant, suggesting that the SOA used in these experiments was also surface-active.

In the experiments on SOA-NaCl particles, the κ value for the SOA component alone (κ_{SOA}) can be determined using the Zadanovkii-Stokes-Robinson (ZSR) mixing rule [Stokes and Robinson, 1966], which assumes that κ_{tot} is the volume-weighted average of the individual components. In most of our mixed SOA-NaCl experiments, the inferred value of κ_{SOA} was much greater than $\kappa_{\text{SOA}}^{\text{pure}}$ (Table 1). For example, for mixed particles with a dry SOA volume fraction (f_{SOA}) of 88% had $\kappa = 0.52 \pm 0.18$, which yields $\kappa_{\text{SOA}} = 0.41$, given $\kappa_{\text{NaCl}} = 1.26$ and using ZSR. This κ_{SOA} is a factor of 15 larger than $\kappa_{\text{SOA}}^{\text{pure}}$, and well beyond what could be explained by variation in RH. Measurements of $f_{\text{SOA}} = 80\%$ and 90% SOA particles yielded similarly high values of κ_{SOA} (Table 1). However, in deriving all of these κ values, we have assumed σ is that of pure water (72 mJ m⁻²). If, instead, we assume σ is reduced by a factor of ~ 2 , the calculated κ_{SOA} decreases by an order of magnitude, and is thus similar to $\kappa_{\text{SOA}}^{\text{pure}}$.

When f_{SOA} was decreased to 67%, however, κ actually decreased to 0.22 ± 0.11 (Fig. 1, Table 1). The ZSR-derived value of κ_{SOA} for these particles was actually lower than $\kappa_{\text{SOA}}^{\text{pure}}$, and in fact was negative. This suggests that interactions between SOA and NaCl reduced their combined water uptake. Vaden *et al.* [2010] found that in similar SOA-NaCl particles, some NaCl actually dissolved in the SOA coating; such an interaction could be the cause of $\kappa_{\text{SOA}} < 0$. In summary, enhanced hygroscopicity was observed in mixed SOA-NaCl particles, but only when f_{SOA} was greater than 67%.

To further explore the dependence of hygroscopicity on SOA:NaCl ratio, NaCl particles with a constant $D_{\text{dry}} = 0.14$ μm were coated with a variable amount of SOA, resulting in mixed particles with D_{dry} between 0.19 to 0.28 μm (f_{SOA} from 60 to 88%). The hygroscopicity of the coated particles was measured at RH = $99.92 \pm 0.05\%$. When $f_{\text{SOA}} \leq 70\%$, κ_{SOA} was approximately equal to $\kappa_{\text{SOA}}^{\text{pure}}$. As f_{SOA} increased above 70%, κ_{SOA} increased, eventually attaining a maximal value of ~ 0.4 at $f_{\text{SOA}} \sim 80\%$ (Fig. 2a). This observation is consistent with the above finding that κ_{org} values were above the ZSR line only when f_{SOA} was at least 67% (Fig. 1).

3.2. Derived σ values

To better distinguish between the Kelvin and Raoult effects, it is helpful to examine the measured D_{wet} distributions. The sharp increase in D_{wet} over the range

70% < f_{SOA} < 77% (Fig. 2b) cannot be adequately explained solely with the Raoult effect. If κ_{SOA} is constant (dashed grey lines in Fig. 2b), D_{wet} would increase proportionally to D_{dry} . Instead, D_{wet} increases much more rapidly. Since RH is constant, an increase in SOA solubility also cannot explain these results. Therefore the Kelvin effect must contribute to this rapid change in hygroscopicity. Because all other variables in the Kelvin term are constant, droplet σ must be changing in response to an increase in f_{SOA} of the dry particle.

Using Eq. 1, we calculate values of σ that fit our experimental data, using observed D_{wet} , D_{dry} , and RH, and assuming $\kappa_{NaCl} = 1.26$ and $\kappa_{SOA} = 0.026$ (Table 1). When $f_{SOA} \geq 77\%$, σ is reduced to below 18 mJ m⁻², or by at least 75% from that of pure water (Fig. 2c). If we use instead $\kappa_{SOA} = 0.1$, an upper-limit based on previous studies, we find that $\sigma < 27$ mJ m² (a 62% reduction). This value of $\kappa_{SOA} = 0.1$ is greater than that observed for pure SOA particles, even at water activities $\gtrsim 0.999$. Thus, for all reasonable values of κ_{SOA} and accounting for experimental uncertainties, sufficient amounts of organics reduce σ by at least 50%, and likely up to $\sim 75\%$. These reductions are greater than typically observed of macroscopic aqueous surfactants. This could be due to the smaller length scale of our droplets, and/or the lack mechanical manipulation (including creation or destruction) of the aqueous surface in our experiments. The creation of new surface in particular is known to delay the equilibration of σ [Eastoe and Dalton, 2000], resulting in a higher σ value.

To better understand the decrease in σ as f_{SOA} increases from 70 to 77%, Figure 2b includes lines of constant aqueous SOA film thickness (assuming all SOA partitions to the droplet surface). These lines are much steeper than those corresponding to constant κ_{SOA} , going as $D_{dry}^{1.5}$ instead of D_{dry} , and thus better match the observations. The reduction in σ occurs when the droplet is covered in an SOA film of at least 0.8 nm thickness. Although some of the SOA may remain in the droplet bulk, 0.8 nm is on the low end of typical surfactant monolayer thicknesses, suggesting that a large fraction of the SOA partitions to the surface. In the transitional interval ($0.21 < D_{dry} < 0.23$ μ m), the droplet grows to the point at which this thickness is reached. When $f_{SOA} > 80\%$, this point is not reached before the droplets attain their equilibrium size at the minimum value of σ . Therefore D_{wet} is limited by whatever minimum value of σ is possible. Overall, this behavior is more consistent with the model of an insoluble surfactant; soluble surfactants would be expected to have a much more gradual change in σ with f_{SOA} .

3.3. Relationship to CCN activation

The previous results describe droplets at equilibrium with high RH (i.e., just below the critical supersaturation); next, we consider the minimum value of f_{SOA} required for σ reduction to still be relevant at the point of CCN activation. The film thickness at this point is determined primarily by f_{SOA} , but also varies with σ and the hygroscopicity (κ_{inorg}) of the non-surface-active fraction of the particle, as these influence D_{wet} . If σ and κ_{inorg} at activation do not vary with D_{wet} , then D_{wet} at activation is proportional to $D_{dry}^{1.5}$ [Lewis, 2008]. Therefore, the droplet surface area at activation is proportional to the dry particle volume, and thus the assumed film thickness is independent of D_{dry} . For reasonable assumptions of σ and κ_{inorg} , a film at least 0.8 nm thick will only exist on an activating droplet if the dry particle is composed of at least $\sim 80\%$ SOA (Fig. S2).

These theoretical predictions are consistent with observations of mixed SOA-NaCl CCN activity. κ_{tot} derived from these experiments for both 67% and 88% SOA-NaCl particles was relatively low (0.13 and 0.12, respectively), similar

to κ_{tot} of 67% SOA:NaCl particles at high but subsaturated RH (Table 1). Because NaCl is so hygroscopic, a film on an organic-NaCl particle will be thicker than 0.8 nm at activation only if $f_{SOA} > 0.9$ (Fig. S2).

Finally, unlike water uptake measurements made at lower RH, these experiments are directly applicable to supersaturated conditions. This is because a_w is similar to what would be expected for smaller (dry) particles at the point of CCN activation. Specifically, a_w of the solution droplets in Fig. 2 ranges from 0.997 to 0.999, and a_w of droplets formed on pure SOA particles was at least 0.998 (Fig. S1b). Because Köhler theory predicts that the Kelvin effect is three times the magnitude of the Raoult effect at activation, an activating CCN with $a_w = 0.998$ (i.e., reduced from pure water by 0.2%) would have a Kelvin effect that increases the equilibrium RH by 0.6%. It would thus have a $S_c = 0.4\%$, a fairly typical value for atmospheric CCN.

4. Conclusions

This study presents strong evidence that surface tension reduction can occur in microscopic droplets and augment their hygroscopicity. Low water uptake was observed for pure SOA formed via α -pinene ozonolysis ($\kappa_{SOA}^{pure} = 0.026 \pm 0.010$), even at high RH (99.7 – 99.9%). The SOA was much more hygroscopic ($\kappa_{SOA} \sim 0.4$) when internally mixed with NaCl, which is attributed to a $\sim 75\%$ reduction in surface tension. This only occurred, however, if enough SOA was present to form a surface layer with a minimum thickness of about 0.8 nm on the wet droplet. Our results suggest that only particles that are predominantly (i.e., $\gtrsim 80\%$) composed of surface-active material will have films sufficiently thick to experience enhanced CCN activity due to σ reduction.

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Table 1. Summary of high-RH hygroscopicity measurements (excluding those in Fig. 2).

composition ^a	<i>n</i>	<i>D_{dry}</i> (μm)	RH (%)	<i>f_{SOA}</i>	<i>κ_{tot}</i>	<i>κ_{org}</i>	<i>κ_{CCN}</i>
SOA	20	0.350–0.650	99.60–99.84	1	0.026	0.026	
9SOA:1NaCl	3	0.215–0.366	99.87–99.87	0.90	0.72	0.66	
7SOA:1NaCl	21	0.176–0.525	99.71–99.92	0.88	0.52	0.41	0.12
4SOA:1NaCl	3	0.222–0.291	99.81–99.87	0.80	0.72	0.59	
2SOA:1NaCl	22	0.144–0.288	99.71–99.92	0.67	0.22	-0.30	0.13

^a SOA=α-pinene ozonolysis SOA

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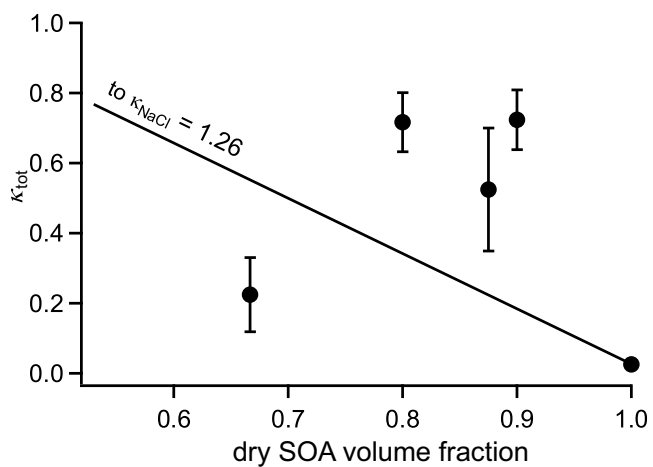


Figure 1. Hygroscopicity (κ) vs. dry SOA volume fraction for all SOA-coated NaCl particles (RH 99.60-99.92%). Solid line assumes ZSR (additive) mixing rule with κ_{org} equal to the value for pure SOA (0.026). Error bars indicate the standard deviation of measurements made at various particle diameters and RH.

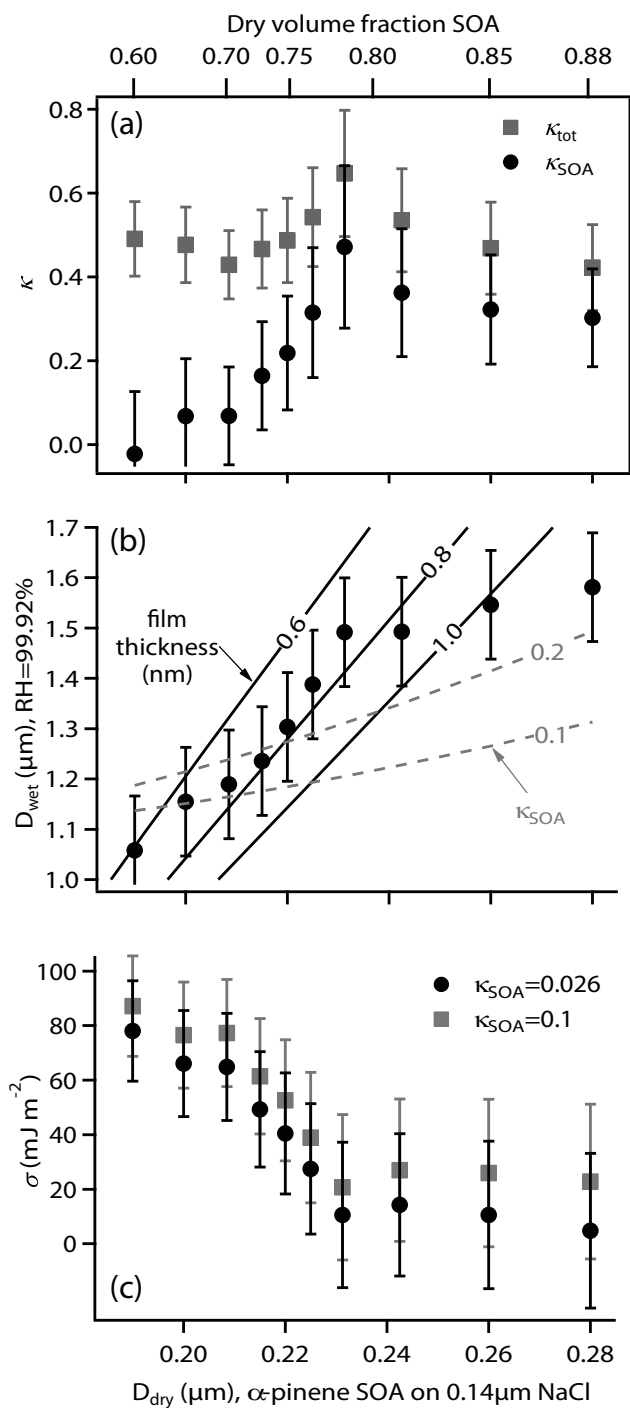


Figure 2. Hygroscopicity of particles composed of α -pinene SOA condensed onto $0.14 \mu\text{m}$ NaCl at $\text{RH} = 99.92 \pm 0.05\%$, vs. D_{dry} (bottom axis) and dry volume fraction SOA (top axis). All error bars correspond to 0.01 K uncertainty in T . (a) κ of the total particle (κ_{tot} and of the SOA component (κ_{SOA}). Error bars correspond to 0.01 K uncertainty in T . (b) Peaks in the D_{wet} distributions, with lines of constant SOA film thickness ($\sim D_{\text{dry}}^{1.5}$, solid black) and constant κ_{SOA} ($\sim D_{\text{dry}}$, dashed grey). Error bars correspond to 95% CI of RH calibration. (c) Calculated surface tension (σ) given different assumptions of κ_{SOA} . Error bars correspond to 0.01 K uncertainty in T .