Ozone oxidation of oleic acid surface films decreases aerosol CCN activity

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Abstract

Heterogeneous oxidation of aerosols composed of pure oleic acid ($C_{18}H_{34}O_2$, an unsaturated fatty acid commonly foundin continental and marine aerosol)by gas-phase O_3 is known to increase aerosol hygroscopicity and activity as Cloud Condensation Nuclei (CCN). Whether this trend is preserved when the oleic acid is internally mixed with other electrolytes is unknown and addressed in this study. We quantify the CCN activity of sodium salt aerosols (NaCl, Na_2SO_4) internally mixed with sodium oleate (SO) and oleic acid (OA). We find that particles containing roughly one monolayer of SO/OA show similar CCN activity to pure salt particles, whereas a tenfold increase in organicconcentration slightly depresses CCN activity. O_3 oxidation of these multicomponent aerosols has little effect on the critical diameter for CCN activation for unacidifiedparticles at all conditions studied, and the activation kinetics of the CCN are similar in each case to those of pure salts.SO-containing particles which are acidified to atmospherically relevant pH before analysis in order to form oleic acid, however, show depressed CCN activity upon oxidation. This effect is more pronounced at higher organicconcentrations.The behavior after oxidation is consistent with the disappearance of the organic surface film, supported by Köhler Theory Analysis (KTA).κ-Köhler calculations show a small decrease in hygroscopicity after oxidation.The important implication of this finding is that oxidative aging may not always enhance the hygroscopicity of internally mixed inorganic-organic aerosols.

1. Introduction

Surface-active molecules contain both hydrophilic and hydrophobic moieties;therefore, they tend to partition at the gas-liquid interface of aqueous solutions. Given that both water and surface-active organics are ubiquitous in tropospheric aerosols,organic films have long been hypothesizedto exist on aerosol surfaces[*Ellison et al.*, 1999; *Gill et al.*, 1983] with potentially important consequences for atmospheric chemistry and climate. Organic films may affect the ability of the aerosol to act as CCN[*Andrews and Larson*, 1993; *Asa-Awuku et al.*, 2008; *Chuang et al.*, 1997; *Ervens et al.*, 2005; *Facchini et al.*, 1999; *Novakov and Penner*, 1993; *Shulman et al.*, 1996], ice nuclei[*Cziczo et al.*, 2004; *DeMott et al.*, 2003; *Kärcher and Koop*, 2005],and alter aerosoloptical properties[*Bond and Bergstrom*, 2006; *Dinar et al.*, 2008; *Kanakidou et al.*, 2005; *Malm and Kreidenweis*, 1997; *Mircea et al.*, 2005]. These films may act as a barrier to mass transport across the gas-liquid interface, with implications for aerosol heterogeneous chemistry[*Folkers et al.*, 2003; *McNeill et al.*, 2006; *Thornton and Abbatt*, 2005] and the rate of water uptake[*Asa-Awuku et al.*, 2009; *Cruz and Pandis*, 2000; *Demou et al.*, 2003; *Garland et al.*, 2005; *Gill et al.*, 1983; *Hemming and Seinfeld*, 2001; *Nenes et al.*, 2002; *Rubel and Gentry*, 1984; *Rudich et al.*, 2000; *Saxena and Hildemann*, 1997]. Surface-active organics can impact CCN activity by lowering aerosol surface tension, thus affecting the Kelvin term of the Köhler equation[*Shulman et al.*, 1996], but they can also affect the Raoult term by altering n_s, the number of moles of solute, especiallywhen surface-bulk partitioning of solute is taken into account[*Kokkola et al.*, 2006; *Sorjamaa et al.*, 2004; *Sorjamaa and Laaksonen*, 2006].

Oleic acid ($C_{18}H_{34}O_2$), a surface-active monounsaturated long-chain fatty acid, has been detected in urban, rural and marine aerosols[*Cheng and Li*, 2005; *Graham et al.*, 2003; *Kawamura et al.*,

2003; *Limbeck and Puxbaum*, 1999; *Robinson et al.*, 2006; *Schauer et al.*, 1996, 2002; *Simoneit et al.*, 2004; *Stephanou and Stratigakis*, 1993; *Yue and Fraser*, 2004]. It is the most common fatty acid found in plant membranes, is prevalent in many cooking oils, and it is used as a marker for meat cooking aerosols[*Rogge et al.*, 1991].Ozonolysis of oleic acid yields nonanal, nonanoic acid, 9-oxononanoic acid, and azelaic acid under humid conditions, and high molecular weight products under dry conditions[*Hearn et al.*, 2005; *Hearn and Smith*, 2004; *Katrib et al.*, 2005a; *McNeill et al.*, 2007; *Rudich et al.*, 2007; *Smith et al.*, 2002; *Thornberry and Abbatt*, 2004; *Vesna et al.*, 2008, 2009; *Zahardis et al.*, 2005, 2006a; *Zahardis and Petrucci*, 2007].Under atmospherically-relevant conditions, nonanal primarily partitions to the gas phase, while the other products remain in the condensed phase. Dueto the importance of oleic acid as a tracerspecies[*Rogge et al.*, 1991] and its relatively well-understood O_3 oxidation mechanism, many studies of the kinetics of oleicacid oxidation have been performed on systems of varying morphology, including pure oleic acid particles[*Broekhuizen et al.*, 2004b; *Hearn et al.*, 2005; *Hearn and Smith*, 2004; *Hung et al.*, 2005; *Katrib et al.*, 2005a; *Lee and Chan*, 2007; *Morris et al.*, 2002; *Pfrang et al.*, 2010; *Reynolds et al.*, 2006; *Sage et al.*, 2009; *Smith et al.*, 2002; *Vesna et al.*, 2008; *Zahardis et al.*, 2005, 2006a, 2006b; *Ziemann*, 2005], mixed organic particles[*Hearn and Smith*, 2005; *Hung and Ariya*, 2007; *Nash et al.*, 2005], films on polystyrene beads[*Katrib et al.*, 2004, 2005b], films on aqueous sea salt aerosol[*King et al.*, 2004], films in coated wall flow tube studies[*de Gouw and Lovejoy*, 1998; *Knopf et al.*, 2005; *Moise and Rudich*, 2000, 2002; *Thornberry and Abbatt*, 2004], and films on crystal surfaces[*Asad et al.*, 2004].

Pure organic aerosols are generally less hygroscopic and CCN active than deliquescent inorganic particles (such as NaCl or $(NH_4)_2SO_4$)[*Petters and Kreidenweis*, 2007]. Oxidation of organic

aerosol material can increase the number of polar, hydrophilic functional groups present in the condensed phase, potentially leading to increased hygroscopicity and CCN activity. Oleic acid particles have been used extensively as a model system to study the effect of oxidation on the CCN activity of organic particles.*Kumar et al.*[2003] created pure oleic acid particles through homogenous nucleation and observed no activation for particle sizes up to 140 nm and ≤ 0.6% supersaturation (SS). *Abbatt et al.*[2005] studied the CCN activity of ammonium sulfate aerosols coated with oleic acid and found that particles with thin (~2.5-5 nm) coatings of oleic acid were not CCN active, but that CCN activity increased when the organic mole fraction increased. This somewhat counterintuitive result was attributed to the fact that the particle diameter increased with increasing organic mass fraction, reducing the magnitude of the Kelvin effect.*Broekhuizen et al.*[2004a] found that oxidation products of oleic acid(nonanoic acid and azelaic acid) were highly CCN active. In a separate study, they found that CCN activity was enhanced after oxidation for both pure oleic acid particles and particles formed by atomizing a solution of oleic acid in methanol[*Broekhuizen et al.,* 2004b]. The enhancement in CCN activity occurred at very high ozone exposures (~0.4 atms) for pure oleic acid particles, and at atmospherically relevant exposures ($<1x10^{-4}$atms) for the oleic acid/methanol particles.*Shilling et al.*[2007] determined that 200 nm mobility diameter oleic acid particles, generated through either homogenous nucleation or atomization, became CCN active at 0.66(±0.06)%supersaturation after exposure to greater than 0.01 atmsO_3.

Despite its atmospheric relevance, the response of mixed inorganic/oleic acid particles to oxidation has not been considered in published CCN activity studies. This is an important omission, because the acid almost always coexists in the atmosphere with inorganic salts. Little

115 is known about the interactions of oleic acid and its oxidation products with water in a high ionic
116 strength environment. These issues are addressed in this study. An aerosol flow tube reactor
117 coupled with a continuous flowcloud condensation nucleus counter is used to examine the effect
118 of ozone oxidation on the CCN activity of aerosol particles containing mixtures of sodium oleate
119 (SO)/oleic acid (OA) with inorganic salts (NaCl or Na_2SO_4).

120 ## *2. Methods*

121 **2.1. Experimental.**Sodium oleate ($C_{18}H_{33}O_2^- \cdot Na^+$), the sodium salt of oleic acid ($C_{18}H_{34}O_2$), has
122 much higher solubility in water than oleic acid. It was used in these experiments to simplify the
123 preparation of aerosols containing a small, controlled amount of organic material. When the pH
124 of aerosols containing SO is lowered to atmospherically relevant values via acidification (see
125 details below), the oleateion converts to oleic acid according to:

126 $$C_{18}H_{33}O_2^- \cdot Na^+ + H_3O^+ \leftrightarrow C_{18}H_{34}O_2 + H_2O + Na^+ \quad (1)$$

127

128 For the experiments performed, the setup is shown in Figure 1. Polydisperse submicron aerosols
129 were generated using a constant output atomizer (TSI 3076). Atomizer solutions were prepared
130 using Millipore water with 0.001 M or 0.01 M SO (Sigma Aldrich) and 0.05 M NaCl. This
131 technique, using 0.001 M SO, was used by *McNeill et al.*[2007]to generate aerosols with an
132 inferred population-averaged oleate surface coverage of ~92%. The atomizer output was
133 combined with a humidified N_2 dilution stream. This combined stream was sent through an
134 aerosol flow tube reactor (7.5 cm ID, 55 cm length). Relative humidity was measured at the
135 outlet of the flow tube reactor using a commercial hygrometer (Vaisala) and was maintained
136 between 62-67%. Ozone was generated by flowing O_2 in an N_2 carrier stream through a

137 photoreactor containing a Hg lamp (Jelight, Inc.). This stream entered the flow tube reactor
138 through a moveable stainless steel injector tube. Ozone concentrations of 0.2and1 ppm were
139 used. Total flow through the reactor was 0.8 LPM, with a reaction time of 3minutes.Processed
140 aerosols in the reactor effluent flowed through a diffusion drier before being characterized by a
141 Differential Mobility Analyzer (DMA, TSI 3080), a Condensation Particle Counter (CPC, TSI
142 3775) and a Continuous Flow Streamwise Thermal Gradient CCNChamber (CFSTGC, Droplet
143 Measurement Technologies)[*Lance et al.*, 2006; *Roberts and Nenes*, 2005]. Aerosols were size-
144 selected using the DMA, and the DMA output flow was split between the CPC and the CFSTGC.
145 0.8 LPM entered the DMA and split 0.5 LPM to the CFSTGC, 0.3 LPM to the CPC. Scanning
146 Mobility CCN Analysis[*Moore et al.*, 2010] was used to determine the size-resolved CCN
147 activity of the aerosol, where the voltage applied to the DMA is scanned so that a complete
148 activation curve (fraction of classified particles acting as CCN) is obtained every 2 minutes. The
149 average total aerosol number concentration in the reactor output was $9.6 \pm 2.0 \times 10^4 cm^{-3}$. The size
150 distribution of NaCl particles had a geometric surface area-weighted mean particle diameter of
151 202 ± 7nm with a geometric standard deviation of 1.59. Na_2SO_4 particles had a particle diameter
152 of 194 ± 5 nm with a geometric standard deviation of 1.63.

153

154 A second series of experiments was performed in order to test the sensitivity of CCN activity in
155 the mixed inorganic-SO aerosols to particle pH because atmospheric aerosols are typically
156 acidic[*Keene et al.*, 2004; *Zhang et al.*, 2007]. Under acidic conditions oleateexists in its un-
157 ionized, lower-solubility form, oleic acid, according to Reaction 1. The atomizer output was
158 passed over an H_2SO_4 reservoir before combining with humidified N_2 and entering the flow tube
159 reactor. Assuming an uptake coefficient γ=0.5[*ten Brink*, 1998], an aerosol surface area of S_a=6.2

160 ±1.4x10^{-5} cm^2cm^{-3}, geometric volume-weighted mean diameter D_p=232 nm, and a residence time
161 of ~0.8 s in the H_2SO_4 reservoir, we estimate that the particles are acidified from an initial pH=8
162 to pH~0.4.The calculation methodology is shown in the supplementary material. Giventhat
163 thepKa of oleic acid = 5.02 [*Riddick et al.*, 1986] and pH = 0.4, the ratio of oleate to non-
164 dissociated oleic acid in the particles ($[C_{18}H_{33}O_2^-]/[C_{18}H_{34}O_2]$) = 2.3988 x$10^{-5}$, that is,nearly all
165 of the organic will be present as oleic acid under these conditions.For the acidification
166 experiments the total aerosol number concentration was 9.9 ± 1.4 x10^4 cm^{-3}.
167

168 The following control experiments were also performed: "pure" sodium oleate particles were
169 generated by atomizing an aqueous solution of 0.001 M SO. In order to investigate possible
170 variations in pH buffering by differentcounterions,experiments were also performed using
171 aerosols atomized from solutions containing 0.001 M or 0.01 M SO and 0.06 M Na_2SO_4.Finally,
172 pure inorganic aerosols prepared from solutions containing 0.05 M NaClor 0.06 M Na_2SO_4 were
173 oxidized with 1 ppm O_3 in the flow tube reactor, showing no significant deviation in CCN
174 activity from the pure salt calibrations without oxidation.
175

176 **2.2 Data Analysis.** Köhler Theory provides the framework used to describe cloud droplet
177 formation from activation of soluble particles [*Cruz and Pandis*, 1997; *Gerber et al.*, 1977; *Katz*
178 *and Kocmond*, 1973]. A single-parameter expression of Köhler theory, referred to asκ-Köhler
179 theory, was introduced by *Petters and Kreidenweis*[2007]to account for the effect of variations in
180 solute hygroscopicity on CCN activity. Values of the hygroscopicity factor, κ, of 0.5<κ<1.4 are
181 typical for inorganic particles in the atmosphere. For hygroscopic organic particles, 0.01<κ<0.5,

whereas for non-hygroscopic materials (including highly hydrophobic organics)κapproaches zero.κis derived from the CCN activity data as follows[*Petters and Kreidenweis*, 2007],

$$\kappa = \frac{4A^3}{27 d_d^3 \ln^2 S} \tag{2}$$

$$\text{where } A = \frac{4\sigma_{s/a} M_w}{RT\rho_w} \tag{3}$$

Here, d_d is the critical dry activation diameter of the particle[m] (determined from CCN activation experiments), $S$is the water saturation ratio (S= 1 + 0.01S_c, where S_c is critical supersaturation[%]), $\sigma_{s/a}$ is the surface tension of water at the surface/air interface at the median temperature of the CFSTGCcolumn, M_w is the molecular weight of water, R is the universal gas constant, T isthe mediantemperature of the CFSTGCcolumn [K], and ρ_w is the density of water.

Köhler Theory Analysis (KTA) was also used to infer the surface tension of the mixed aerosol before and after oxidation[*Padro et al.*, 2007]. The following equations were used[*Padro et al.*, 2007]:

$$\frac{M_o}{\rho_o} = \frac{\varepsilon_o \upsilon_o}{\frac{256}{27}\left(\frac{M_w}{\rho_w}\right)^2 \left(\frac{1}{RT}\right)^3 {\sigma_{s/a}}^3 \omega^{-2} - \frac{\rho_i}{M_i}\varepsilon_i \upsilon_i} \tag{4}$$

$$\text{where } \varepsilon_i = \frac{\frac{m_i}{\rho_i}}{\frac{m_i}{\rho_i} + \frac{m_o}{\rho_o}} \tag{5}$$

Here, M_o, M_i,$\rho_o$and $\rho_i$refer to the average molecular weight and density of the organic and inorganic components of the aerosol, while υ_o andυ_i are effective van't Hoff factors,$\varepsilon_o$and$\varepsilon_i$are volume fractions, and m_o, m_i are the mass fractions of the organic and inorganic components,

201 respectively. The fitted CCN activity factor, ω, is determined from the log-log plots of
202 $S_c$versusd_d, fit to the equation[*Asa-Awuku et al.*, 2010],

203 $$S_c = \omega d_d^{-3/2} \quad (6)$$

204 κandω are related by $\omega = (4A^3/27\kappa)^{1/2}$.

205 ## *3. Results*

206 The results of our CFSTGC measurements for the SO/OA/NaCl and SO/OA/Na_2SO_4 systems are
207 shown in Figures 2-5. A complete list of calculated κ values (derived from eqs. (2) and (3)) and
208 power law exponents for the CCN activity data is available in the supplementary material.

209

210 **3.1 SO/NaCl.** As expected, pure SO/H_2O aerosols are much less CCN active than NaCl aerosols
211 (Figure S1), withκ= 0.12 ± 0.004. As shown in Figures 2a and S1, the CCN activity of mixed
212 SO/NaCl particles generated from 0.001 M SO/0.05 M NaCl solutions (κ= 1.19 ± 0.03) is similar
213 to that of pure NaCl particles. The mixed particles with higher SOcontent show intermediate
214 CCN activity(κ= 0.87 ± 0.06) compared to particles with lower SO content and pure SO/H_2O
215 particles. The mixed SO/NaCl aerosols exhibit similar wet activated diameter profiles to NaCl
216 particles (Figure 2b), indicating that the presence of oleate does not retard the activation kinetics
217 of the aerosol on the timescale of the CCN measurements[*Engelhart et al.*, 2008; *Moore et al.*,
218 2008]. Furthermore, for all these systems the critical supersaturation shows a power law
219 dependence of $S_c \sim d_d^{-1.42\pm0.04}$, suggesting that the CCN activity of these particles is described
220 fairly well by Köhler theory, with no significant solubility limitations or size-dependent surface-
221 bulk partitioning effects. For a system that is perfectly described by Köhler Theory, we expect
222 the relationship to follow $S_c \sim d_d^{-1.5}$, as shown in eq. (6)[*Padro et al.*, 2007].

CCN activity did not significantly change upon exposure to O_3 for theunacidifiedmixed SO/NaCl aerosols studied. Critical dry diameters changedby ~0.5% for the particles generated from 0.001 M SO/0.05 M NaCl solutions and ~1.6% for the particles generated from 0.01 M SO/0.05 M NaCl solutions (Figure 2a); this leads to a changeof particle critical supersaturation by ~1% for the former and ~3% for the latter. The change in CCN activity due to oxidation effectively falls within the standard deviation of the non-oxidized data, showing relatively little effect of oxidation to unacidifiedmixed SO/NaCl particles. Calculatedκvalues after oxidation for all SO/NaCl aerosols were similar to the κ values prior to oxidation;$\kappa = 1.14 \pm 0.02$ for 0.001 M SO/0.05 M NaCl and $\kappa = 0.83 \pm 0.04$ for 0.01 M SO/0.05 M NaCl. The change in CCN activity wasnot dependent on the concentration of ozone used within the range studied here (0.2 – 1 ppm). The wet diameter profiles after oxidation are nearly identical to the non-oxidized SO/NaCl particle wet diameters. This suggests that surface films, if present, do not retard CCN activation kinetics and growth.

3.2 SO/Na_2SO_4. Because oleate oxidation generates organic acid products, it is possible that the particle pH changes during oxidation, with implications forfatty acid solubility[*Cistola et al.*, 1988]. In the unacidifiedSO/NaCl system, the formation of organic acidoxidation products may result in the formation, and possible subsequent volatilization, of HCl, due to its high vapor pressure. The net pH change is expected to differ in the SO/Na_2SO_4 system. The CCN activity data for the SO/Na_2SO_4 experiments are shown in Figure 3.

245 The CCN activity of the SO/Na_2SO_4 particles follows trends similar to what we observed for the
246 SO/NaCl particles. The CCN activity of the particles generated from 0.001 M SO/0.06 M
247 Na_2SO_4 solutions(κ= 0.71 ± 0.04) and 0.01 M SO/0.06 M Na_2SO_4 solutions (κ= 0.68 ± 0.03) is
248 roughly similar to that of pure Na_2SO_4 particles. The CCN activity changes littleupon oxidation,
249 and the resulting hygroscopic parameters (κ= 0.71± 0.02 and κ= 0.67 ± 0.03, respectively) are
250 similar to the non-oxidized SO/Na_2SO_4 particles, analogous to our observations for the
251 SO/NaClsystem. The wet diameter profiles are again very similar both before and after
252 oxidation, suggesting that there is no kinetic limitation to water uptake.

253

254 **3.3 Acidified experiments: OA/NaCland Na_2SO_4.** As an additional test of the effect of pH on
255 our observations of CCN activity for the SO/NaCl and SO/Na_2SO_4 systems, we performed a set
256 of experiments in which the atomized mixed particles were exposed to gas-phase H_2SO_4 before
257 oxidation. The goal of these experiments was to create a particle with a low pH typical of that of
258 atmospheric aerosols, conditions under which sodium oleate and the organic acid oxidation
259 products are in their un-ionized, lower-solubility forms (cf. Reaction (1)). As demonstrated in
260 Section 2, nearly all of the SO will be present as oleic acid under these conditions.The results of
261 these experiments are shown in Figure 4 and 5.

262

263 The CCN activity of acidified 0.001 M SO/0.05 M NaCl (κ= 1.14 ± 0.05) and 0.01 M SO/0.05 M
264 NaCl (κ= 0.97 ± 0.08) decreased after oxidation (κ= 1.07 ± 0.05 and 0.79 ± 0.02, respectively),
265 more noticeably at higher instrument supersaturations and SO concentrations (Figure 4 and
266 inset). The wet activated diameters do not show any kinetic limitations to water uptake.

Similarly, the acidified SO/Na_2SO_4 data shows similar CCN activity behavior to the acidified SO/NaCl particles (Figure 5). The hygroscopicity values for both 0.001 M and 0.01 M SO/0.06 M Na_2SO_4 decrease after oxidation, and both follow the power law dependence expected from Köhler theory (where $S_c \sim d_d^{-1.46\pm0.005}$ and $S_c \sim d_d^{-1.37\pm0.002}$, respectively).

3.4 Köhler Theory Analysis. The parameters and results of the KTA calculations can be seen in Tables 1-3. The initial in-particle concentrations of oleate and the inorganic salt were calculated following*McNeill et al.*[2007]. After oxidation, we assume the oleate is completely oxidized to form nonanal and azelaic, nonanoic, and 9-oxononanoic acids. The product yields reported by*Vesna et al.*[2009] were used. The density of 9-oxononanoic acid is unknown and was assumed to be 1 g cm^{-3}. The inorganic effective van't Hoff parameter (υ_i), T, the fitted CCN activity factor (ω), and ρ_w all varied with varying S_c and d_d.To account for dissociation of the organics, υ_o = 1 and 2 were tested, but the results for both salts at varying ozone concentrations, regardless of the υ_o used,were the same to within 3%; the data for υ_o = 2 is shown.

The results suggest that the surface tension of the aerosols increases slightly after oxidation, which is consistent with the breakup of the oleate monolayer (we have measured the surface tension of bulk solutions saturated in NaCl and SOusing pendant drop tensiometry to be 44.4 ± 0.8dyn cm^{-1}).The calculated surface tension values after oxidationfall between 64-75dyn cm^{-1}, slightly less thanthe surface tension of saturated NaCl and Na_2SO_4 solutions[*Washburn*, 2003].*Vesna et al.*[2009] found thata large portion of the aerosol organic mass after oleic acid oxidation consisted of unidentified products (UP). Including these products inour KTA

289 calculations (assuming an average molar mass of 500 g mol^{-1}anddensity of 1.4 g cm^{-3},[*Turpin*
290 *and Lim*, 2001]), gave very similar surface tension results compared to when only the 4 main
291 oxidation species are considered. Therefore, the single-phase approximationrepresents our
292 system well.

293

294 ## *4. Discussion*

295 The particles generated using 0.001 M SOatomizer solutions were designed such that the
296 particles with the surface-area weighted average diameter would be covered with approximately
297 1 monolayer of oleate/OA at 65% RH. Following *McNeill et al.*[2006], we estimated the
298 organicfractional coverage of the total available surface area of our aerosol population by,

299 $$\Theta = \frac{\sum_i \theta_i N_i}{\sum_i N_i} \qquad (7)$$

300 where$\theta_i$and N_i are the fractional surface coverage of the aerosol and the number density in the
301 DMA size bin i,and Θis the overall fractional surface coverage. Assuming three things: that all
302 the organic partitions to the surface until saturated coverage is reached,that it is equally
303 distributed across the aerosol population in constant proportion to either NaCl or Na_2SO_4, and an
304 oleatefootprint of 48 $Å^2$[*Langmuir,* 1917], we find that for the particles generated using 0.001 M
305 SO/0.05 M NaCl or 0.001 M SO/0.06 M Na_2SO_4 atomizer solutions, Θ≈0.83 (83% overall
306 surface coverage) and Θ≈1.01 (100%), respectively. This calculation also implies that smaller
307 particleswith larger surfacearea-to-volume ratios will not contain enough oleate for full
308 monolayer coverage, while thelarger particles will have complete monolayer coverage.There is
309 indirect evidence of monolayer formation at similar conditions from N_2O_5 uptake experiments by

310 *McNeill et al.*[2007]. In addition, *McNeill et al.*[2007] analyzed SO/NaCl particles formed using
311 this techniqueby SEM-EDAX,which showed the existence of uniform coatings of SO on the
312 particles.Using kinetic data from*McNeill et al.*[2007], we calculate the extent of oxidation in
313 particles with lower SO content to be76-100%, varying with O_3 concentration. The reacto-
314 diffusive length in the OA-O_3 system is ~20 nm, so for particles with higher SO content, the
315 kinetic model of *Smith et al.* [2002], for reactions occurring in a near-surface layer of a pure
316 oleic acid particle, can be applied. Using their kinetic model and parameters, we calculate ~100%
317 oxidation.

318 Several studies on bulk systems have shown that when an oleic acid monolayer at the air-
319 aqueous interface is exposed to ozone, the organic film breaks down, as evidenced by a decrease
320 in surface pressure[*González-Labrada et al.*, 2006, 2007], disappearance of the vibrational sum
321 frequency generation signal [*Voss et al.*, 2006, 2007], or neutron reflection[*King et al.*, 2009].
322 From these studies, it appears that the oxidation products leave the gas-particle interface soon
323 after oxidation. Nonanoic acid, 9-oxononanoic acid, and azelaic acid are more soluble in water
324 than oleic acid, and they may partition into the aqueous solution after they are formed. However,
325 there is evidence that azelaic acid[*Tuckermann*, 2007; *Tuckermann and Cammenga*, 2004] and
326 nonanoic acid[*Caetano et al.*, 2007; *Gilman et al.*, 2004; *King et al.*, 2009] are surface-active and
327 CCN active[*Broekhuizen et al.*, 2004a].*McNeill et al.*[2007]observed that nonanoic acid in wet
328 NaCl aerosols, in the absence of other oleic acid oxidation products, was volatile at room
329 temperature.Nonanal has been reported to enter the gas phase after it is formed[*Katrib et al.*,
330 2004; *Moise and Rudich*, 2002; *Thornberry and Abbatt*, 2004; *Voss et al.*, 2006; *Wadia et al.*,
331 2000].*Hung and Ariya*[2007] analyzed the oxidation of mixed OA/NaCl particles using ATR-
332 FTIR, and showedthat before oxidation, while increasing RH, there was no increase in the water

content of the particles, but after oxidation, there was an initial increase, then decrease in the liquid water content. They determined that the hygroscopicity of OA/NaCl particles changed after oxidation, but could vary and was affected by relative humidity levels. *King et al.*[2009] used neutron scattering and surface pressure measurements to study the disappearance of an oleic acid surface film on an aqueous subphase upon exposure to O_3. They observed that roughly half of the oxidation products remained at the surface, while the remainder were either released into the gas phase or incorporated into the bulk. Consistent with our observations that CCN activity was not enhanced compared to the pure salt for the particles generated using 0.001 M SO/0.05 M NaCl or 0.001 M SO/0.06 M Na_2SO_4 atomizer solutions,they calculated, using Köhler theory, that one monolayer of oleic acid on a 100 nm radius particle would not depress surface tension during cloud droplet formation enough to affect the critical supersaturation point of the droplet. Based on the assumption that the oleic acid oxidation would be complete and would lead to a surface film of nonanoic acid, with azelaic acid dissolving into the bulk phase, they predicted that the oxidation of an oleic acid surface film on an aerosol particle would decrease the critical supersaturation required for droplet formation, increasing CCN activity. Surface-bulk partitioning was not taken into account in that calculation[*Kokkola et al.*, 2006; *Sorjamaa et al.*, 2004; *Sorjamaa and Laaksonen*, 2006].

Our KTA calculations show support for a smallincrease in particle surface tension upon oxidation. Such an increase in surface tension could occur with the disappearance of a surfactant film at the interface. However,our observation that the mixed inorganic/organic particles become more organic-like in their CCN activity after oxidation is not inconsistent with the oxidation products remaining at the interface.The high salt content of the particles prior to activation and

the acidic conditions would decrease the solubility of the oxidation products in these aerosols as compared to the bulk films studied by other groups, possibly leading to phase separation. If oxidation of an oleate surface layer is complete, it would result in the doubling of the number of organic molecules present at the interface. In the absence of external pressure, oleate forms expanded-state monolayers on aqueous surfaces, that is, the surface layer formed by the hydrophobic tail groups is not well-ordered[*Rideal*, 1925; *Schofield and Rideal*, 1926]. Immediately after forming, the oxidation products exist in a disordered double layer until they dissolve into the bulk or are released into the gas phase, or sufficient water is taken up by the particle to dissolve them. Transport to and self-assembly of surfactant products at the interface may be slow after oxidation, occurring on timescales much longer than the residence time in our experimental system[*Lass et al.*, 2010; *McIntire et al.*, 2010]. The work of *McIntire et al.*[2010]on the ozonolysis of alkene self-assembled monolayers (SAMs) with internal double bonds provides support for the formation of a complex, low-hygroscopicity organic surface layer upon ozonolysis. They reported that ozonolysis did not increase the hygroscopicity of surface-bound alkenes, and it was hypothesized that the polar head groups of the oxidation products were buried in a mixed organic layer after oxidation rather than at the air-organic interface. They concluded that the three-dimensional structure of particles was critical for predicting aerosol hygroscopicity and CCN activity.

For internal mixtures, κ can be described by a weighted linear sum of the components in the system [*Petters and Kreidenweis*, 2007]. κ of azelaic acid was found to be ~0.1, while κ of the other oxidation products is unknown. If we assume that κ for all oxidation products is 0.1 and use the weighted sum approach, we find that the theoretical κ values after oxidation from 0.001

379 M SO/0.05 M NaCl and 0.001 M SO/0.06 M $Na_2SO_4$are 1.23 and 0.83, respectively.Possible
380 sources of error include the assumption of one κ value for the four main oxidation products. The
381 small difference between these theoretical κ valuesand our observations (κ= 1.19 and 0.71,
382 respectively) suggests that these particles can be accurately described as internally well-mixed.

383

384 Since most of the expected oleateozonolysis products are organic acids, a change in aerosol pH is
385 possible upon oxidation in the unacidified particles. Due to the possible formation of sodium
386 salts as well as organic acids, this maximum pH change assumes that only the three soluble
387 organic acid oleate oxidation products are formed and dissolve in the aqueous phase.Using the
388 pKa of each acid (azelaic acid (pKa=4.55), nonanoic acid (4.95), 9-oxononanoic acid (assumed
389 to be 4.95)), we can estimate the concentration of $[H^+]$ in our system after oxidation. The
390 calculation methodology is shown in the supplementary material. Assuming pH = 8 initiallyand
391 using product yields from*Vesna et al.*[2009], after complete oxidation of an aerosol with in-
392 particle oleate concentration of 0.176 M[*McNeill et al.*, 2007], the particles would have $[H^+]$ =
393 1.38mM, resulting in a final pH of ~3. This pH change is expected to be less in the SO/Na_2SO_4
394 system due to buffering by SO_4^{-2}, and negligible in the acidified particles. Fatty acid solubility
395 increases with increasing pH (basic conditions), complementing our observation that CCN
396 activity decreases upon oxidation for acidifiedparticles but shows little change for unacidified
397 particles.This highlights the importance of using atmospherically relevant pH in laboratory
398 studies involving fatty acid surface-bulk partitioning in aerosols.The activated droplet diameters
399 of the studied systems did not change after oxidation; this suggests that if there are any kinetic
400 barriers to hygroscopic growth in these systems, they may be due to the finite dissolution
401 timescale and not a water uptake barrier from the action of the organic surface layer.

5. Conclusions

We examined the effect of ozone oxidation on the CCN activity of aerosol particles containing mixtures of sodium oleate (SO)/oleic acid (OA) with inorganic salts (NaCl or Na_2SO_4).Exposure to O_3led to decreased CCN activity for particles at atmospherically relevant pH. Wet (activation) diameters of these particles were not significantly different frominorganic calibration standards, suggesting that the activation kinetics are not affected by organic surface films. KTA indicatesa slight increase in particle surface tension uponoxidation, consistent with breakup of the organic film after oxidation.The κ values were calculated here for a reaction timescale of up to 3 minutes, and might not accurately represent the real water uptake properties of an aged atmospheric particle.We find that oxidative aging of mixed inorganic-organic aerosols may negatively affect their hygroscopicity and CCN ability.

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Figure Captions

Figure 1. Experimental setup. The solutions were atomized, and combined with humidified N_2; this flow entered the flow tube reactor simultaneously with O_3 in an N_2 stream. The reactor effluent passed through a drier before being characterized with a Differential Mobility Analyzer (DMA), Condensation Particle Counter (CPC) and a Continuous Flow Streamwise Thermal Gradient CCN Chamber (CFSTGC).

Figure 2.CCN activity of SO/NaCl particles. Particles generated from solutions containing 0.001 M or 0.01 M SO mixed with 0.05 M NaCl were exposed to O_3 concentrations ranging between 0.2-1ppm in an aerosol flow tube reactor. Instrument supersaturation is shown as a function of A) critical dry diameter and B) activated wet diameter. In both plots, the red dots represent the salt calibration, and the red lines are guides to the eye. In panel A) an inset focuses on higher supersaturations. In panel B) the gray lines indicate the standard deviation in the salt calibration.

Figure 3.CCN activity of SO/Na_2SO_4 particles. Particles generated from solutions containing 0.001 M or 0.01 M SO mixed with 0.06 M Na_2SO_4, were oxidized with 1 ppm O_3 in an aerosol flow tube reactor. Instrument supersaturation is shown as a function of A) critical dry diameter and B) activated wet diameter. In both plots, the red dots represent the salt calibration, and the red lines are guides to the eye. In panel A) an inset focuses on higher supersaturations. In panel B) the gray lines indicate the standard deviation in the salt calibration.

Figure 4. CCN activity of SO/NaCl particles exposed to H_2SO_4. Particles generated from solutions containing 0.001 M or 0.01 M SO mixed with 0.05 M NaCl were oxidized with 1 ppm O_3 in a flow tube reactor. Instrument supersaturation is shown as a function of A) critical dry diameter and B) activated wet diameter. In both plots, the red dots represent the salt calibration, and the red lines are guides to the eye. In panel A) an inset focuses on higher supersaturations. In panel B) the gray lines indicate the standard deviation in the salt calibration.

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Tables

Table 1. KTA Parameters used before and after oxidation, based on in-particle concentrations of 0.176 or 1.76 M oleate and either 8.6 M NaCl or 10.6 M Na_2SO_4 .

KTA Parameters	0.176 M				1.76 M			
	Before Oxidation		After Oxidation (0.2-1ppm)		Before Oxidation		After Oxidation (1ppm)	
	NaCl	Na_2SO_4	NaCl	Na_2SO_4	NaCl	Na_2SO_4	NaCl	Na_2SO_4
ε_o	0.19	0.09	0.12	0.05	0.71	0.50	0.57	0.35
M_o(g/mol)	282.46		169.93		282.46		169.93	
ρ_o(g/m^3)	8.95×10^5		9.94×10^5		8.95×10^5		9.94×10^5	
υ_o	2		2		2		2	

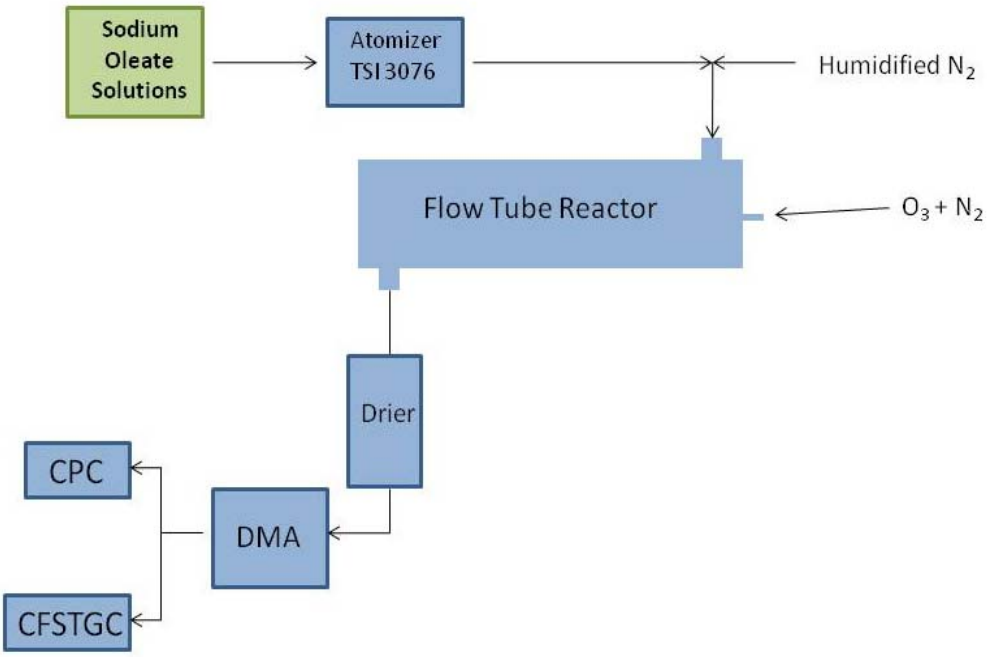
Table 2. Inferred surface tension for unacidified aerosols from eqns. (3-5), assuming in-particle concentrations of 0.176 or 1.76 Moleate in either 8.6 M NaCl or 10.6 M Na_2SO_4.

	σ (mN/m) [0.176 M]			σ (mN/m) [1.76 M]		
	Before Oxidation	After Oxidation (1ppm)	After Oxidation (0.2ppm)	Before Oxidation	After Oxidation (1ppm)	After Oxidation (0.2ppm)
NaCl	68.1	70.5	71.7	57.5	64.4	68.6
Na_2SO_4	73.9	74.8	-	63.7	69.9	-

Table 3. Inferred surface tension for acidified aerosols from eqns. (3-5), assuming in-particle concentrations of 0.176 or 1.76 M oleate in either 8.6 M NaCl or 10.6 M Na_2SO_4.

	σ (mN/m) [0.176 M]		σ (mN/m) [1.76 M]	
	Before Oxidation	After Oxidation (1ppm)	Before Oxidation	After Oxidation (1ppm)
NaCl	69.1	72.9	55.5	67.4
Na_2SO_4	72.4	74.8	66.1	74.8

Figures



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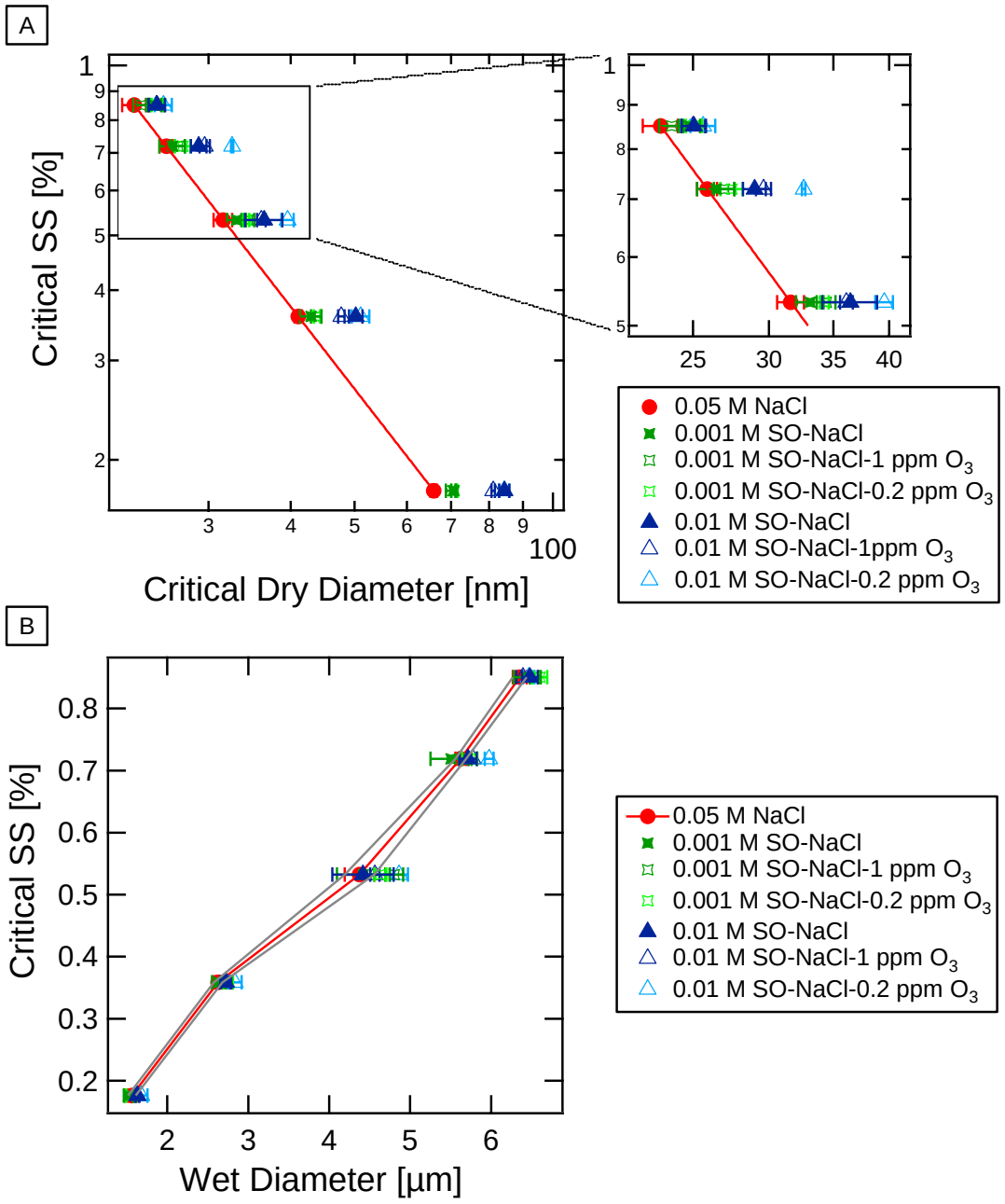

841

842 **Figure 2.**CCN activity of SO/NaCl particles. Particles generated from solutions containing 0.001
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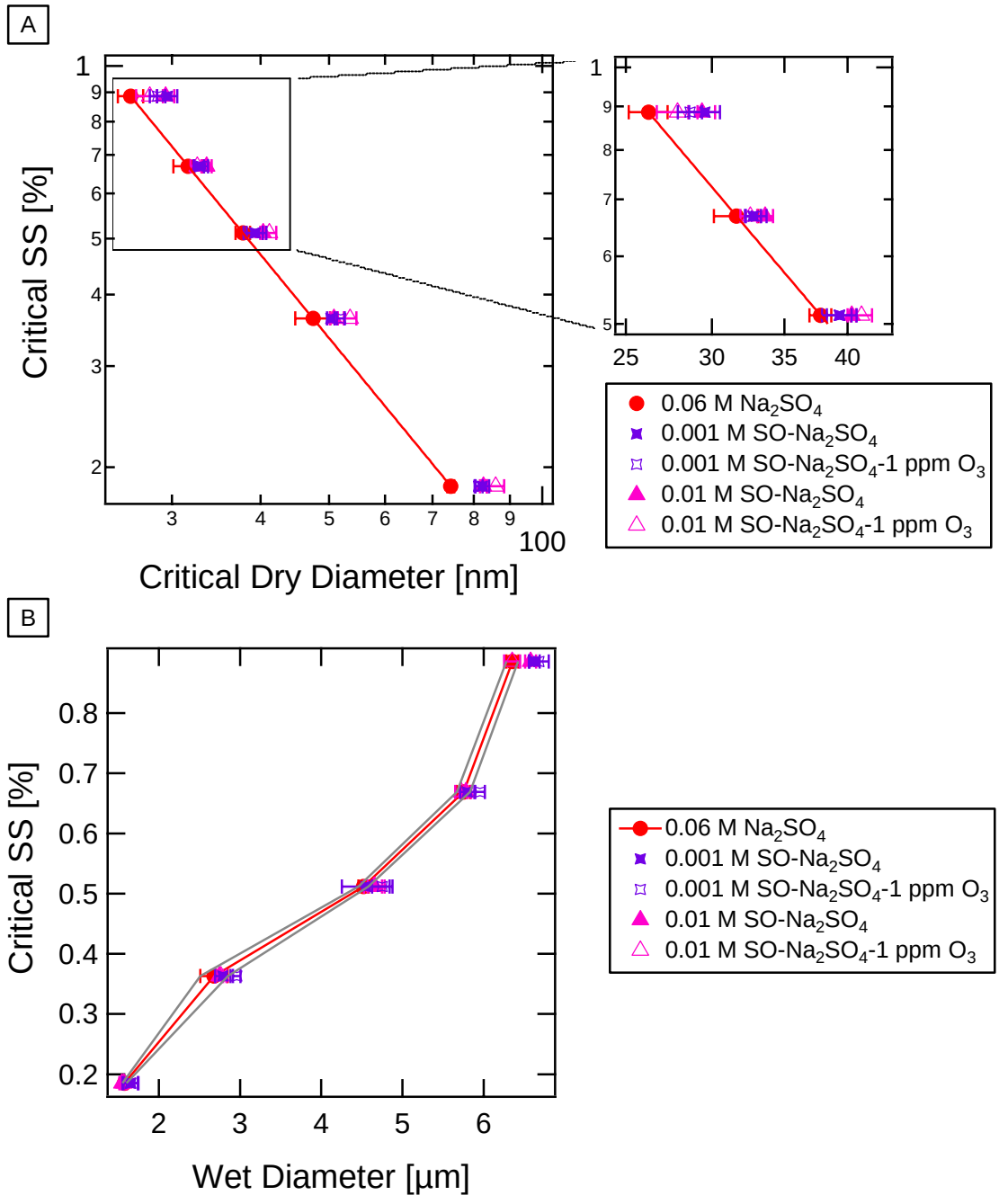

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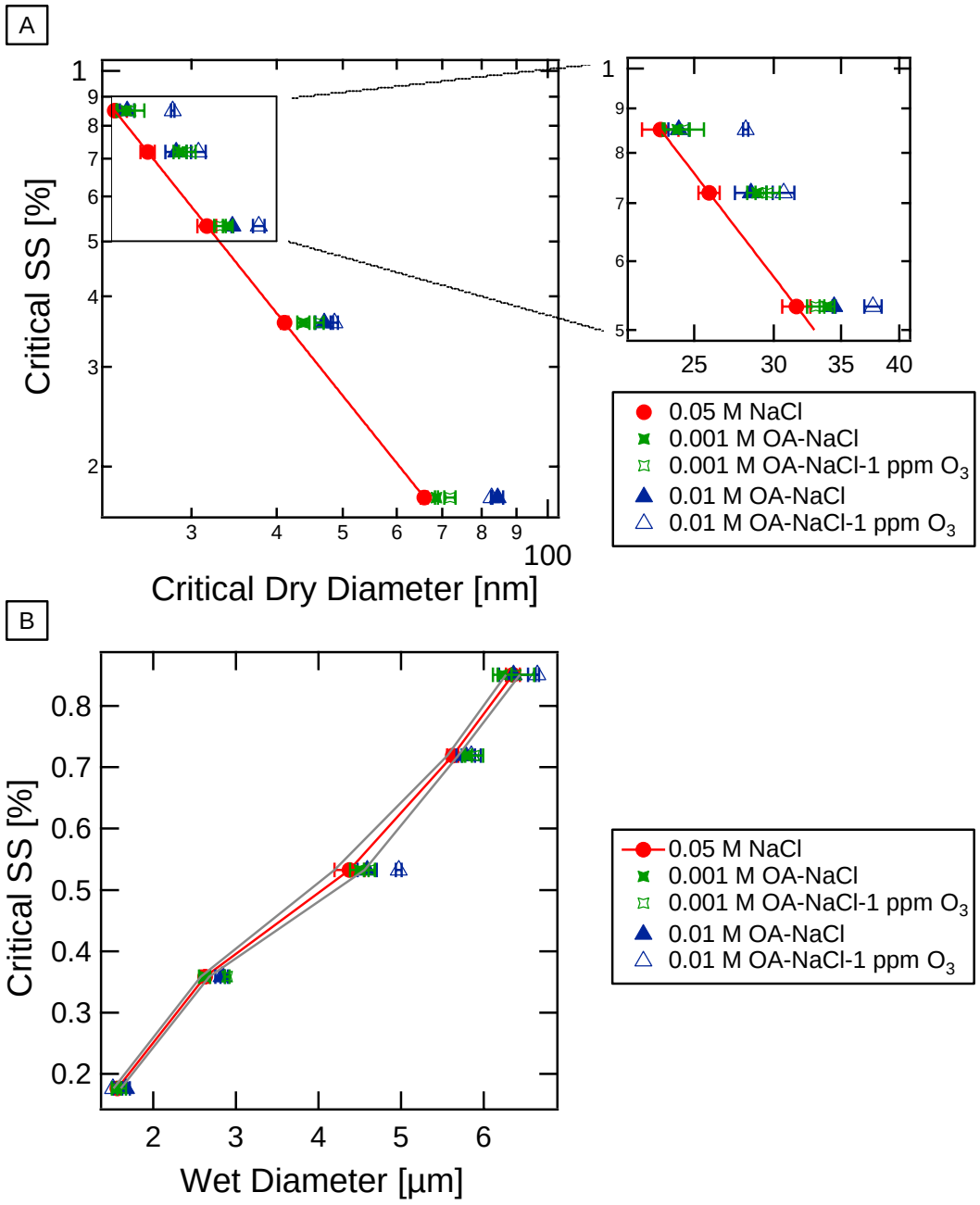

856

857 **Figure 4.** CCN activity of SO/NaCl particles exposed to H_2SO_4. Particles generated from
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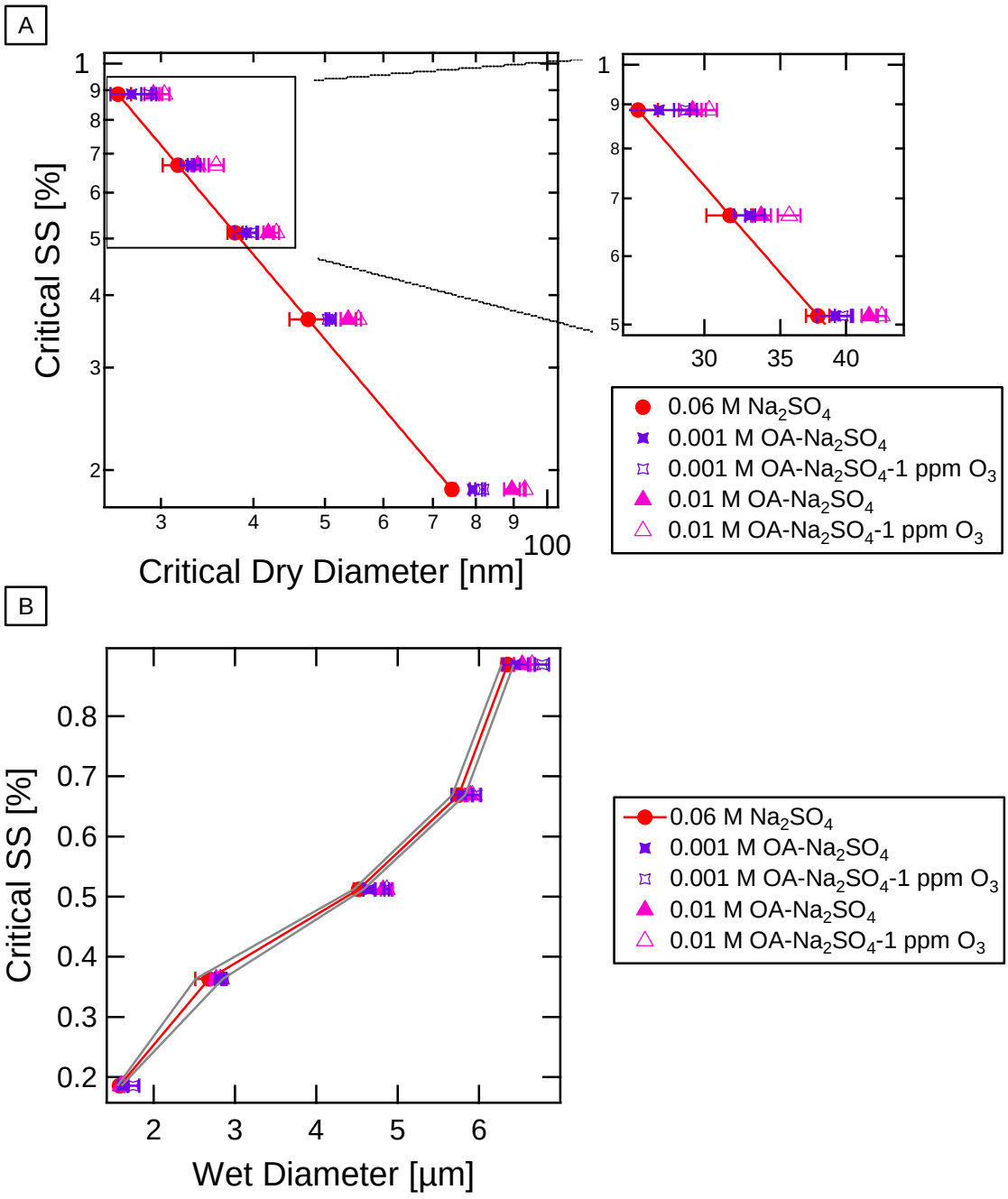

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