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Impacts of methanesulfonate on the cloud condensation nucleation activity of sea salt aerosol

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ABSTRACT

Methanesulfonate, an important oxidation product of dimethyl sulfide, is abundant in marine aerosol particles. However, its impact on the cloud condensation nucleation (CCN) activity of marine aerosol is yet to be elucidated, largely because the CCN activity of methanesulfonate has been seldom investigated. In this work, we measured the CCN activities of three common methanesulfonates, and the single hygroscopicity parameters (κ) were determined to be 0.46 ± 0.02 for sodium methanesulfonate (NaMS), 0.37 ± 0.01 for calcium methanesulfonate, and 0.47 ± 0.02 for potassium methanesulfonate, respectively. In addition, we explored the effect of NaMS on the CCN activities of NaCl and synthetic sea salt. It was found that if presented with a mass ratio of 1:1, NaMS would significantly reduce the CCN activities of NaCl and sea salt, and the κ values of binary mixtures could be estimated using the simple mixing rule. Nevertheless, if only presented with a mass ratio of 1:10 (an environmentally relevant value), the effect of NaMS on the CCN activities of NaCl and sea salt was found to be small. Overall, we conclude that from our experimental data and its levels found in the troposphere, methanesulfonate may only have minor impacts on the CCN activity of marine aerosol.

1. Introduction

Dimethyl sulfide (DMS), one of the most abundant biogenic sulfur compounds in the troposphere (Andreae, 1990; Barnes et al., 2006; Seinfeld and Pandis, 2016), is emitted mainly from oceans into the atmosphere, and its global flux is estimated to be ~28 Tg S per year (Carpenter et al., 2012). After emitted into the atmosphere, DMS will be oxidized by several oxidants (e.g., OH, NO_3 and O_3), eventually leading to the formation of sulfate aerosol (Yin et al., 1990; Barnes et al., 2006). The oxidation of DMS is an important source of non-sea-salt sulfate aerosol in marine and oceanic regions (Chin and Jacob, 1996; Gondwe et al., 2004), and thus may affect tropospheric cloud condensation nuclei (CCN) concentrations to some extent (Korhonen et al., 2008; Woodhouse et al., 2013). The CLAW hypothesis, which proposed a feedback loop between DMS emission and climate change (Charlson et al., 1987), has gained much attention in the last few decades and is still under debate (Ayers and Cainey, 2007; Quinn and Bates, 2011). Due to projected decline in anthropogenic SO_2 emission, the relative contribution of DMS to sulfate and CCN concentrations may increase in future.

In addition to sulfate, methanesulfonic acid (MSA) is also formed in the atmospheric oxidation of DMS (Barnes et al., 2006; Hoffmann et al., 2016). Once formed, gaseous MSA will condense onto or undergo heterogeneous reactions with existing particles, leading to the formation of particulate methanesulfonate (Debruyn et al., 1994; Hanson, 2005; Tang and Zhu, 2009; Tang et al., 2010), and gaseous MSA can also be involved in new particle formation (Dawson et al., 2012; Chen et al., 2016; Zhao et al., 2017). Furthermore, methanesulfonate can be

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formed via aqueous oxidation of DMS (Hoffmann et al., 2016). Methanesulfonate has been detected in various locations around the globe (Bates et al., 1992; Davis et al., 1998; Bardouki et al., 2003; Gondwe et al., 2004; Zorn et al., 2008; Lin et al., 2012; Ovadnevaite et al., 2014; van Pinxteren et al., 2015; Willis et al., 2016; Huang et al., 2017). It has been widely used as a tracer to assess the contribution of DMS oxidation to non-sea-salt sulfate aerosol, because the exclusive source of methanesulfonate in the atmosphere is DMS oxidation. Recently it was suggested that methanesulfonate in the troposphere may also have other sources (Sorooshian et al., 2015). In addition to dry and wet deposition, heterogeneous oxidation by OH radicals may also be an important sink for methanesulfonate (Kwong et al., 2018; Mungall et al., 2018).

Methanesulfonate is an important product in DMS oxidation and ubiquitously found in marine aerosols, and increased aerosol CCN activities were reported during periods with higher marine biogenic emissions (and thus probably larger methanesulfonate fractions in aerosol particles) (Sorooshian et al., 2009). Nevertheless, it is not clear yet to which extent the presence of methanesulfonate would affect the CCN activities of marine aerosol particles, and one major reason is that the CCN activity of methanesulfonate has not been well understood. To our knowledge, only one previous study (Tang et al., 2015) explored the CCN activity of calcium methanesulfonate, and the single hygroscopicity parameter (κ) (Petters and Kreidenweis, 2007) was determined to be 0.30–0.38. A few previous studies (Peng and Chan, 2001; Liu and Laskin, 2009; Liu et al., 2011; Zeng et al., 2014) examined hygroscopic properties of methanesulfonates under sub-saturation. For example, in an electrodynamic balance study (Peng and Chan, 2001), sodium methanesulfonate was found to deliquesce at 60–70% RH (relative humidity), and its growth factor was derived to be 1.80 at 90% RH. In another study (Liu and Laskin, 2009), Fourier transform infrared microscopy was used to investigate hygroscopic properties of micrometer-sized sodium, ammonium, calcium and magnesium methanesulfonate (abbreviated as NaMS, NH_4MS, $Ca(MS)_2$ and $Mg(MS)_2$) particles deposited on a substrate. It was found that NaMS underwent deliquescence at 71% RH, while the other three salts showed continuous hygroscopic growth. In addition, hygroscopic properties of NaMS/NaCl (Liu et al., 2011) and the effect of temperature on the deliquescence and efflorescence RH of NaMS (Zeng et al., 2014) were also explored. In the work presented here, we measured the CCN activities of NaMS, $Ca(MS)_2$ and KMS (potassium methanesulfonate), and investigated the CCN activities of internally mixed NaMS/NaCl and NaMS/sea salt particles for the first time. Our experimental data can be very valuable in assessing the impact of methanesulfonate on sea salt aerosol (also known as sea spray aerosol) (Bertram et al., 2018).

2. Experimental methods

The experimental setup employed in this work is similar to those used previously (Sullivan et al., 2009; Tang et al., 2015), and its

schematic diagram is shown in Fig. 1. In brief, high-purity nitrogen from a cylinder was applied to a commercial atomizer (TSI 3076, TSI Incorporated, Shoreview, MN, USA) for aerosol generation, and solutions in the atomizer bottle were typically in the concentration range of 0.2–0.4 g/L. The resulting wet aerosol flow (~3000 mL/min) was first delivered through a silica gel diffusion dryer to reduce the RH, and was then split to two flows. One flow (~2200 mL/min) went through a HEPA filter into the exhaust line. The other flow (800 mL/min) passed through three silica gel diffusion dryers in series to further reduce the RH down to < 5%; after that, the dry aerosol flow was delivered through a RH sensor (to monitor the aerosol RH), an aerosol neutralizer (TSI) and then an electrostatic classifier (TSI) which was coupled to a differential mobility analyzer (DMA, TSI 3081) to produce quasi-monodisperse aerosol. The DMA sheath flow was set to 8000 mL/min so that the flow ratio of the aerosol flow to the sheath flow was 1:10. After exiting the DMA, the aerosol flow was split to two flows again. One flow (300 mL/min) was sampled into a condensation particle counter (CPC, TSI 3775) to measure the total particle number concentration, and the other flow (500 mL/min) was sampled into a cloud condensation nuclei counter (CCNc, CCN-100, Droplet Measurement Technologies, Longmont, CO, USA) to monitor the number concentration of aerosol particles which were activated into cloud droplets. CCN-100 used in this work was a single-column instrument in which aerosol particles were exposed to a constant supersaturation in the range of 0.1–2.0%, and aerosol particles activated to cloud droplets were counted and sized using an optical counter. More details of this instrument can be found elsewhere (Roberts and Nenes, 2005; Rose et al., 2008; Good et al., 2010).

Similar to our previous work (Tang et al., 2015), experiments were carried out by scanning supersaturation (s) at a fixed dry mobility diameter. Each measurement typically contained at least 12 different supersaturations to obtain an activation curve, for which activation fractions, defined as the ratio of number concentrations of activated particles to total particles ([CCN]/[CN]), were plotted versus supersaturation. The contribution by multiply charged particles, though minor for our work, was taken into account, as described elsewhere (Rose et al., 2008; Good et al., 2010). Fig. 1 shows activation fractions of 50 nm (dry mobility diameter) ammonium sulfate, NaMS, sea salt, and NaMS/sea salt internal mixture (with a mass ratio of 1:1) as a function of supersaturation. Following previous studies (Sullivan et al., 2009; Tang et al., 2015), a Boltzmann sigmoid function was used herein to fit the experimental data to derive the corresponding critical supersaturation (s_c). During our measurements, the CCN counter was calibrated and routinely checked using 50, 60 and 70 nm ammonium sulfate aerosols, and the absolute difference between our measured and theoretically predicted supersaturations (Topping et al., 2005) was always within 0.02%. For comparison, the CCN-100 instrument has a stated supersaturation resolution of 0.01%, suggesting that the accuracy and stability of set supersaturations were both satisfactory in our work.
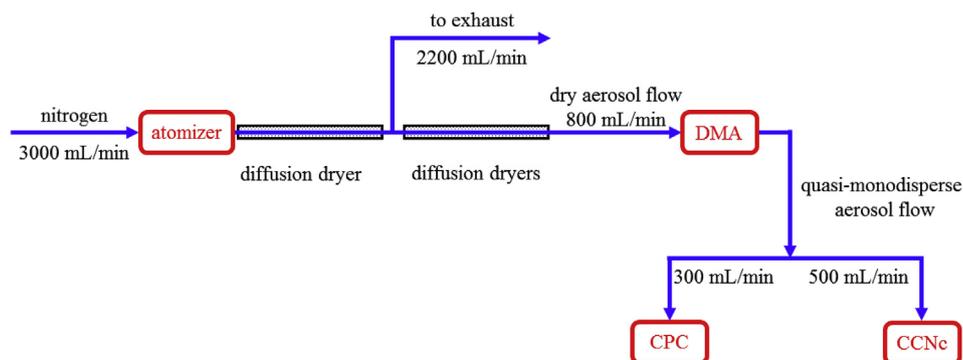

Fig. 1. Schematic diagram of the experimental setup used in this work to measure the CCN activities of aerosol particles.

Table 1
Dry mobility diameters (d_m), critical supersaturations (s_c), and single hygroscopicity parameters (κ) for aerosol particles investigated in this work.

aerosol	d_m (nm)	s_c (%)	κ	average κ	calculated κ
NaMS	50	0.448–0.501	0.44–0.47	0.46 ± 0.02	–
	60	0.361–0.377	0.45–0.49		
Ca(MS)$_2$	50	0.546–0.554	0.36–0.37	0.37 ± 0.01	–
	60	0.403–0.424	0.36–0.40		
KMS	50	0.486–0.497	0.45–0.47	0.47 ± 0.02	–
	60	0.363–0.380	0.44–0.49		
NaCl	40	0.413–0.433	1.16–1.27	1.22 ± 0.09	–
	50	0.285–0.318	1.10–1.37		
NaMS/NaCl (1:1)	50	0.380–0.392	0.72–0.77	0.75 ± 0.02	0.82
NaMS/NaCl (1:10)	50	0.323–0.335	0.99–1.06	1.03 ± 0.03	1.14
sea salt	50	0.339–0.342	0.95–0.97	0.96 ± 0.01	–
NaMS/sea salt (1:1)	50	0.392–0.400	0.69–0.72	0.71 ± 0.01	0.71
NaMS/sea salt (1:10)	50	0.330–0.335	0.99–1.02	1.01 ± 0.01	0.92

The following chemicals were used to prepare aqueous solution to generate aerosol particles: $(NH_4)_2SO_4$ (> 99.999%, Aldrich), NaCl (> 99.5%, Aldrich), sodium methanesulfonate (> 98%, Alfa Aesar), potassium methanesulfonate (> 99%, Alfa Aesar), calcium methanesulfonate (> 98.0%, Tokyo Chemical Industry), and synthetic inorganic sea salt (abbreviated as sea salt, provided by Himedia, Mumbai, India). This synthetic inorganic sea salt, which was commercially available, mimics the water soluble inorganic composition of sea water.

3. Results and discussion

3.1. CCN activity of methanesulfonates

In this work we first measured the CCN activities of quasi-mono-disperse NaMS, Ca(MS)$_2$ and KMS aerosol particles. Measurements were carried out using dry diameters of 50 and 60 nm for all the three compounds, and each measurement was at least repeated for three time. Table 1 summarizes all the experimental results. As shown in Table 1, the critical supersaturations were determined to be ~0.50, ~0.55 and ~0.49% for 50 nm NaMS, Ca(MS)$_2$ and KMS particles, suggesting that the CCN activities were similar for NaMS and KMS, but higher than Ca(MS)$_2$. Correspondingly, the κ values were determined to be 0.46 ± 0.02 for NaMS, 0.37 ± 0.01 for Ca(MS)$_2$, and 0.47 ± 0.02 for KMS. For water-soluble compounds such as the three methanesulfonates examined in the present work, the difference in κ values can be caused by difference in density and molecular weight of the solute as well as the number of ions/molecules formed when one solute molecule is completely dissociated in water (Sullivan et al., 2009; Gaston et al., 2017). For example, once completely dissociated, three ions will be produced for one Ca(MS)$_2$ molecule while only two for one NaMS molecule. The κ values are ~0.61 and ~1.28 for $(NH_4)_2SO_4$ and NaCl (Petters and Kreidenweis, 2007), two typical inorganic compounds found in tropospheric aerosol; therefore, the CCN activity of NaMS is lower than $(NH_4)_2SO_4$ and much lower than NaCl.

One previous study (Tang et al., 2015) measured the CCN activity of Ca(MS)$_2$, and κ was reported to 0.30–0.38; in our current work, κ was determined to be 0.37 ± 0.01, in good agreement with the previous study (Tang et al., 2015). An electrodynamic balance was employed to monitor the mass change of single levitated NaMS particles as a function of RH (Peng and Chan, 2001), and the growth factor (GF) at 90% RH (i.e. the ratio of particle diameter at 90% RH to that at dry condition) was derived to be 1.80. GF can be used to derive κ, according to Eq. (1) (Petters and Kreidenweis, 2007; Tang et al., 2016):

$$\kappa = (GF^3 - 1)\frac{1 - RH}{RH} \tag{1}$$

A GF value of 1.80 at 90% RH gives a κ value of 0.54, considerably larger than that (0.46 ± 0.02) derived from our CCN activity measurement for NaMS. The densities of dry and deliquesced particles were required to calculate GF from the date provided by electrodynamic balance measurements. Peng and Chan (2001) used the estimated densities of dry and deliquesced NaMS particles at 90% RH to derive their reported GF, and difference between the κ value derived from Peng and Chan (2001) and that measured in our work cannot be fully explained by the uncertainties in densities estimated by Peng and Chan (2001). Other independent measurements, especially direct growth factor measurement using the humidity-tandem differential mobility analyzer, would give a better understanding in hygroscopicity and CCN activity of NaMS.

3.2. Impacts of methanesulfonate on CCN activity of NaCl and sea salt

We also investigated the CCN activities of NaCl and sea salt aerosols. As shown in Table 1, critical supersaturations were measured to be 0.413–0.433% and 0.285–0.318% for 40 and 50 nm NaCl particles and 0.339–0.342% for 50 nm sea salt particles. Correspondingly, κ were determined to be 1.22 ± 0.09 for NaCl and 0.96 ± 0.01 for sea salt. The average κ value measured in our work for NaCl is consistent with those reported previously (Petters and Kreidenweis, 2007; Zieger et al., 2017). It has been long recognized that NaCl and sea salt aerosol particles are not spherical, and their actual diameters are smaller than electrical mobility diameters (Rose et al., 2008; Zieger et al., 2017). However, the shape of NaCl and sea salt aerosol particles is quite uncertain and appears to depend on particle size as well as the exact methods used in aerosol generation and conditioning (Zieger et al., 2017). Since the main purpose of our work was to investigate the effect of methanesulfonate on CCN activities of NaCl and sea salt, we did not correct our data for particle non-sphericity. It should be noted that taking into account particle non-sphericity would lead to decrease in actual particle diameter and consequently increase in reported κ values. Our work found that compared to NaCl, the κ value was smaller for sea salt. This result is in good agreement with Zieger et al. (2017), who concluded from their humidity-tandem differential mobility analyzer measurements that the hygroscopicity of sea salt was lower than NaCl. The reason is that in addition to NaCl, sea salt also contains other components such as CaCl$_2$ and MgCl$_2$ and their hydrates (Zieger et al., 2017), the hygroscopicity of which is lower than NaCl (Sullivan et al., 2009; Gupta et al., 2015; Tang et al., 2015; Guo et al., 2018).

To investigate the effect of methanesulfonates on the CCN activities of marine aerosols, we then measured the CCN activities of internal NaMS/NaCl and NaMS/sea salt mixtures with mass ratios of 1:1 and 1:10. The densities are 2.16 and 2.017 g cm^{-3} for NaCl and sea salt (Zieger et al., 2017). The density of dry sea salt aerosol particles may be different from original sea salt powder; however, no density data is available for dry sea salt aerosol particles. Using a gas pycnometers (UltraPyc 1200e, Quantachrome Instruments, Boynton Beach, FL, United Stated), the density of NaMS was determined in our work to be 1.955 g cm^{-3}, larger than that reported in a previous study (1.568 g cm^{-3}) (Peng and Chan, 2001). The NaMS density measured in our work was used together with the densities of NaCl and sea salt to convert the mass ratios to volume ratios. For a binary internal mixture, its κ value can be calculated using the simple mixing rule (Petters and Kreidenweis, 2007):

$$\kappa = \varepsilon_1 \kappa_1 + \varepsilon_2 \kappa_2 \tag{2}$$

where ε_1 and ε_2 are the volume fractions of the first and second components that the binary mixture contains ($\varepsilon_1 + \varepsilon_2 = 1$), and κ_1 and κ_2 are the κ values of the first and second components.

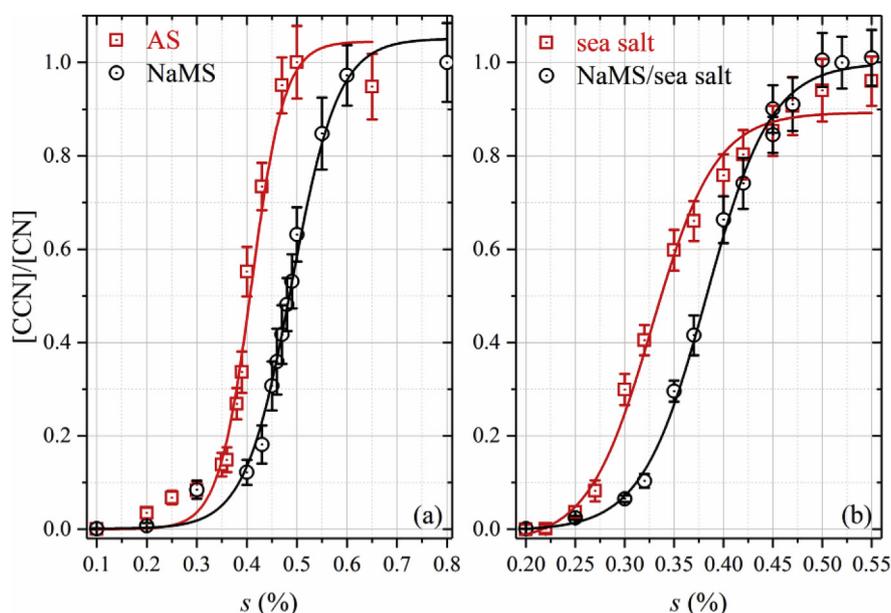Fig. 2b shows the experimental activation curves of sea salt and

Fig. 2. Activation fractions of 50 nm (dry mobility diameters) aerosol particles as a function of supersaturation: (a) ammonium sulfate (AS) and sodium methanesulfonate (NaMS); (b) sea salt and NaMS/sea salt mixture with a mass ratio of 1:1.

NaMS/sea salt aerosol particles (with a mass ratio of 1:1), both with dry mobility diameters of 50 nm. It is evident that compared to sea salt, NaMS/sea salt was activated at higher supersaturation, suggesting that the presence of NaMS with a mass ratio of 1:1 significantly reduced the CCN activity of sea salt. As summarized in Table 1, the average κ values were measured to be 0.75 ± 0.02 and 0.71 ± 0.01 for NaMS/NaCl and NaMS/sea salt, both with a mass ratio of 1:1. For comparison, the calculated average κ values, using Eq. (2), were found to be 0.82 (0.77–0.87) for 1:1 NaMS/NaCl and 0.71 (0.69–0.72) for 1:1 NaMS/sea salt, and the numbers in the parentheses represent the ranges of calculated κ values. Therefore, the measured and calculated κ values agreed well within the uncertainties for the two binary mixtures.

In addition, we also investigated the CCN activities of NaMS/NaCl and NaMS/sea salt mixtures with a mass ratio of 1:10. This mass ratio, chosen to represent methanesulfonate to non-sea-salt sulfate ratios typically found in the troposphere (Bates et al., 1992; Berresheim et al., 1998; Bardouki et al., 2003; Chen et al., 2012; Huang et al., 2017), was environmentally relevant. Please be noted that the mass ratio of methanesulfonate to marine aerosol particles would be much smaller than the mass ratio of methanesulfonate to non-sea-salt sulfate (Berresheim et al., 1998; Chen et al., 2012). The average κ values were measured to be 1.03 ± 0.03 and 1.01 ± 0.01 for 1:10 NaMS/NaCl and 1:10 NaCl/sea salt, showing no significant difference from (or being slightly smaller than) those for NaCl (1.22 ± 0.09) and sea salt (0.96 ± 0.01). As a result, it can be concluded that the presence of sodium methanesulfonate would likely have minor effects on the CCN activities of marine aerosols in the troposphere, and the main reasons include: 1) the mass fraction of methanesulfonate in marine aerosol particles is typically less than 10%; 2) the CCN activity of sodium methanesulfonate is quite high, with an average κ value of ~0.46.

4. Summary and conclusion

Methanesulfonates, produced from atmospheric oxidation of dimethyl sulfide, are abundant in marine aerosols; however, their CCN activities have rarely been studied. In this work, we measured the CCN activities of three common methanesulfonates, including NaMS, Ca(MS)$_2$ and KMS. The single hygroscopicity parameters, κ, were determined to be 0.46 ± 0.02 for NaMS, 0.37 ± 0.01 for Ca(MS)$_2$ and 0.47 ± 0.02 for KMS, respectively, suggesting that methanesulfonates

exhibit relatively high CCN activities (for comparison, the κ value is ~0.61 for ammonium sulfate). In addition, we investigated the impact of methanesulfonates on the CCN activities of marine aerosol particles by measuring the CCN activities of internally mixed NaMS/NaCl and NaMS/sea salt with mass ratios of 1:1 and 1:10. It was found that for the two mixtures with a mass ratio of 1:1, the measured κ values agreed well with those estimated using the simple mixing rule. When the mass ratio of NaMS to NaCl or sea salt was 1:10, the presence of NaMS only had a small or even negligible effect on the measured CCN activities of NaCl and sea salt particles. Due to the relative small contribution of methanesulfonate to the total mass of marine aerosol particles, the impact of methanesulfonates on the CCN activities of marine aerosols is likely to be very minor.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2018.12.034.

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