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Implications for new particle formation in air of the use of monoethanolamine in carbon capture and storage†

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Alkanolamines are currently being deployed in carbon capture and storage (CCS) technology worldwide, and atmospheric emissions have been found to coincide with locations exhibiting elevated concentrations of methanesulfonic acid (MSA). It is thus critical to understand the fate and potential atmospheric reactions of these chemicals. This study reports the characterization of sub-10 nm nanoparticles produced through the acid–base reaction between gas phase monoethanolamine (MEA) and MSA, a product of organosulfur compound oxidation in air, using a flow reactor under dry and humid (up to ∼60% RH) conditions. Number size distribution measurements show that MEA is even more efficient than methylamine in forming nanoparticles on reaction with MSA. This is attributed to the fact that the MEA structure contains both an $-NH_2$ and an $-OH$ group that facilitate hydrogen bonding within the clusters, in addition to the electrostatic interactions. Due to this already strong H-bond network, water has a relatively small influence on new particle formation (NPF) and growth in this system, in contrast to MSA reactions with alkylamines. Acid/base molar ratios of unity for 4–12 nm particles were measured using thermal desorption chemical ionization mass spectrometry. The data indicate that reaction of MEA with MSA may dominate NPF under some atmospheric conditions. Thus, the unique characteristics of alkanolamines in NPF must be taken into account for accurate predictions of impacts of CCS on visibility, health and climate.

Introduction

Monoethanolamine ($NH_2CH_2CH_2OH$, MEA) is a multifunctional amine currently deployed in carbon capture and storage (CCS) technology systems aimed at sequestering CO_2 emissions before release into the atmosphere.[1–5] The most widely used CCS media is a 30% aqueous solution of MEA.[6] Briefly, the solvent medium chemically absorbs CO_2 contained in the flue gas, which leads to a CO_2-depleted gas stream exiting the stack. The solvent is subsequently regenerated and recycled back into the absorber column, while the CO_2 is compressed and captured. A potential drawback from these technologies is the likely release of MEA into the air.[4,5,7–14] For example, concentrations of MEA outside a CCS-equipped plant of the order of several ppb have been reported.[7] MEA is also used as a solvent in various consumer products and industrial processes.[15–19] In air, recognized fates of gas phase MEA to date include its reaction with O_3 and OH,[20–24] the formation of alkylaminium nitrate salts from its interaction with HNO_3[21,24] and acid–base reactions with gas phase and particulate sulfuric acid.[25,26]

Methanesulfonic acid (CH_3SO_3H, MSA) is a strong acid formed along with SO_2 (a sulfuric acid precursor) in the oxidation of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS)[27–32] which have a variety of sources both natural and anthropogenic.[33–59] Therefore, it is not surprising that the oxidation product MSA is detected in the gas phase and in ambient particles worldwide. Ambient gas phase atmospheric concentrations of MSA range from mid-10^4 to 10^7 molecules cm^{-3},[60–69] and can reach levels similar to that of H_2SO_4, which is considered to be a major source of new particles. In some instances, the MSA concentration in air can actually surpass that of co-located H_2SO_4.[68,70] MSA has also been detected in ambient particles worldwide, including in marine and coastal environments,[71–77] in coastal areas affected by biomass burning plumes,[78,79] and near agricultural regions as well as near urban centers.[78,80,81] This acid has been detected in ultrafine and nucleation mode particles measured in the Arctic,[76,82–85] at urban sites[86,87] and in the Antarctic[88] as well as in a boreal

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forest.[67,89] Particulate MSA concentrations in the Arctic summertime have been observed to correlate well with new particle formation (NPF)[85,90–94] suggesting a role for MSA in the earliest stages of NPF and growth. Chen and co-workers[95] predicted that the total annual MSA budget would be 20 Gg S y^{-1} from DMS oxidation reactions alone. However, climate change is dramatically modifying the extent of ice sheet coverage, exposing more sea water, which increases phytoplankton productivity and DMS emissions and thus MSA in air.[94,96–98] The significant contribution of MSA to atmospheric NPF is supported by both laboratory experiments[99–107] and quantum chemical calculations.[108–115]

Amines and MSA are both found in ambient particles.[67,80,116–118] This includes MEA, which has been detected as one of the most abundant amines in ambient particles in various locations around the globe,[119–124] overlapping with sources of both DMS and MSA. MEA has also been detected in biomass burning aerosols collected in St John, Newfoundland, Canada[125] and in both aerosol and precipitation samples over the North Atlantic Ocean.[126]

It is thought that NPF is responsible for a significant portion of the global cloud condensation nuclei budget.[127] In addition to influencing cloud properties, airborne particles are well known to interact with solar radiation, thus playing a critical role in the Earth's climate.[128,129] In a recent study, Hodshire *et al.*[130] predicted, using a simplified DMS oxidation model, that inclusion of MSA formation and its role in aerosol processes (either acting as condensable non- or semi-volatile species, or participating in NPF) influenced the cloud-albedo aerosol indirect and the direct radiative effect.

While recent theoretical studies predicted that MEA may play an important role in NPF,[108] to date there have been no direct experimental investigations of particle formation from MEA and MSA. We present the first measurements of 4–12 nm nanoparticles formed from this reaction, including their size distributions as a function of time and relative humidity, as well as their size-resolved chemical composition. For comparison, some data for the reaction of MSA with methylamine (MA), which is known to efficiently form particles,[102,103,105,106] is also reported. It is shown that MEA is even more effective in forming new nanometer-sized particles than MA but surprisingly, is not very sensitive to the presence of water vapor. Such ultrafine particles are of particular concern as they can be deposited deep into the respiratory tract and even cross cellular membranes to reach other organs.[131–136] Thus, this study has important implications for the potential impacts of CCS on climate,[128,129] visibility[137–140] and health.[131,132,136,141]

Experimental methods

Flow reactor description

Particles were produced from the reaction of gas phase MSA with gas phase MEA (or MA) in the presence or absence of water vapor in a 1-m long borosilicate glass flow reactor[142] described in the ESI† (Fig. S1). Clean, dry air was provided by a purge air generator (Parker-Balston; model 75-62), and further purified by passing through carbon/alumina media (PermaPure, LLC) and a 0.01 μm inline filter (Parker Balston, BQ). Most of the air was supplied at the front end of the flow reactor through the perforated ring inlets as indicated in Fig. S1 (ESI†) (rings A, B and C). In experiments where water vapor was present, one or two bubblers filled with nanopure water (18.2 MΩ cm; Barnstead, Thermo Scientific) were used to humidify a fraction of the air introduced into the ring inlets. The bubblers were kept in a water bath to maintain a constant temperature of 22 °C (295 K). Experiments were carried out at relative humidities (RH) up to ∼60% as indicated by a humidity probe (Vaisala; model HMT 838) located at the end of the flow reactor. The reactants (MSA and MEA or MA) were introduced through the spoke inlets (spoke 2 and 3 respectively) located 60 cm downstream of the last ring inlet. The flow reactor was cleaned regularly with nanopure water and dried with clean hot air overnight (T = 343 K). After cleaning, the flow reactor was conditioned with gas-phase MSA for a least two days prior to an experiment. All experiments presented in this work were performed at 1 atm and at room temperature (T = 297 K).

Reactants

Liquid monoethanolamine ($NH_2CH_2CH_2OH$, Sigma Aldrich, >99.5%) was contained in a small 2-mL glass vial with a septum cap. Approximately ∼1 cm of PEEK tubing (1.59 mm O. D. × 0.18 mm I. D.) was inserted into the septum so that the MEA from the headspace diffused slowly into a stream of air. For comparison, parallel experiments were performed using MA (CH_3NH_2) with a commercial permeation tube (VICI Metronics). The amine vial (or permeation tube) was inserted into separate *U*-shaped glass tubes immersed into a water bath maintained at room temperature (T = 295 K). Glass beads were placed in the upstream arm of the *U*-shaped glass tubes to provide high surface area to keep the gas flow at a constant temperature. Air flowed through each tube at a rate of 215 cm^3 min^{-1} for MEA and 93 or 211 cm^3 min^{-1} for MA. For MSA, air (53 to 216 cm^3 min^{-1}) flowed directly over the pure liquid (Sigma Aldrich, >99.0%) contained in a glass trap which was maintained at room temperature using a water bath. Further details regarding the sampling, analysis and quantification of the gas phase reactants are given in the ESI† (Text S1 and Fig. S2). The initial concentrations of the reactants after dilution in the flow reactor were (1.7–6.8) × 10^{10} molecules cm^{-3} for MSA (0.7–2.8 ppb), (3.7–8.1) × 10^{10} molecules cm^{-3} for MEA (1.5–3.3 ppb) and (11.8–26.6) × 10^{10} molecules cm^{-3} for MA (4.8–10.8 ppb). Note that these concentrations represent upper limits as they do not account for potential wall losses.

Particle size distribution measurements

Particle size distributions were continuously measured using a moveable stainless steel sampling line (0.64 cm O. D. × 0.46 cm I. D.) located inside the flow reactor along the centerline and placed at distances ranging from 3 to 43 cm away from spoke 2 (*i.e.*, the MSA addition port). All particle size distributions reported in this study are number size distributions, unless stated otherwise. These distances correspond to reaction times

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in the reactor ranging from 0.3 to 4.5 s (total flow rate 23.4 L min^{-1}) or 0.5 to 7.7 s (total flow rate 10.7 L min^{-1}) based on a conversion factor determined in previous studies.[99] Note that the amine addition port is introducing the reactant backward into the flow stream so that the reaction of MSA with MEA (MA) is occurring in between spoke 2 and 3, and we chose the MSA addition port as our $t = 0$ reaction time. It is expected that the residual reactants present in the stream exiting the flow reactor are lost to the walls of the small (I.D. 0.46 cm) sampling line. Therefore, the reaction times reported are those in the flow reactor, but these could be underestimated if the reaction continues in the sampling line (residence time ~0.3–0.4 s) and the connection to the SMPS (residence time ~0.8 s). Particle losses through the sampling lines to the SMPS were accounted for as described in the ESI† (Text S2 and Fig. S3). The shortest reaction time accessible (*i.e.* 0.3 s or 0.5 s depending on the total flow in the flow tube, that was 23.4 or 10.7 L min^{-1} respectively) is expected to be the most vulnerable to residence time artefacts. This was tested by sampling at different flow rates through the sampling line (2.4 to 4.8 L min^{-1}), for a given experiment conducted at 0.5 s. Results presented in Fig. S4 (ESI†) show no change in the size distribution measured at all flow rates and suggest that reaction in the sampling line is not significant.

Size distributions were measured using a scanning mobility particle sizer (SMPS) consisting of a ^{210}Po radioactive source (10 mCi; NRD LLC; model P-2021), an electrostatic classifier (model 3080; TSI Inc.) equipped with a nano-differential mobility analyzer (nano-DMA; model 3085; TSI, Inc.), and a butanol-based ultrafine condensation particle counter (UCPC; model 3776; TSI, Inc.). To prevent buildup of the reactants in the SMPS during sampling, the sheath air inside the DMA was not recirculated, but instead air was provided by the purge air generator (15 L min^{-1}) and a vacuum pump connected to the sheath air flow pulled the sheath air out of the DMA. The aerosol flow was set to 1.5 L min^{-1}, which provided measurements of the size distributions over a mobility diameter range of 2.5 to 64 nm. The software AIM v9 (TSI, Inc.) was used to record and process the data. Particles were observed to be stable for long periods of time (Fig. S5, ESI†), allowing for size-resolved measurements that took up to 20 min per scan to yield enough mass for mass spectrometric analysis.

Size-resolved chemical composition measurements

Nanoparticles with diameters ranging from 4 to 12 nm were sampled using a thermal desorption chemical ionization mass spectrometer (TDCIMS)[105,143–146] which was connected to the same sampling line as the SMPS. The particle stream was sampled through two inlets, each equipped with a ^{210}Po unipolar charger (UPC)[143,147] to generate negatively charged particles. At each inlet, particles were subsequently size-selected using a radial nano-DMA (rDMA) running in either high resolution mode with a sheath flow of 10 L min^{-1} and an aerosol flow of 1.0 L min^{-1} through each nano-rDMA, or low resolution mode with a sheath air flow of 5.0 L min^{-1} and an aerosol flow rate of 1.6 L min^{-1} through each nano rDMA.[148] For both conditions, instead of recirculating the sheath gas within the nano-DMA, gaseous N_2 produced from the headspace of a liquid N_2 dewar was used as the sheath flow to prevent the accumulation of gas-phase MSA or MEA, and a vacuum pump was used at the DMA sheath flow outlet. The particles were collected on the tip of a Pt filament by electrostatic precipitation (applied high voltage of +3.5 kV). The filament was continuously flushed with an additional 1.25 L min^{-1} flow of N_2 to minimize sampling artifacts from gas-phase species. To select particles with a defined mobility diameter, the voltage on each rDMA was varied from 30 to 325 V. Note that the use of two separate inlets, which merged at the collection wire region, increases the flux and mass of particles that are collected on the wire without sacrificing the rDMA resolution.

The TDCIMS was run in positive ion mode to measure MEA with $(H_2O)_nH^+$ as the reagent ions (n = 0–3), and in negative ion mode to measure MSA with $(H_2O)_nO_2^-$ as the reagent ions from the presence of trace amounts of H_2O and O_2, respectively, in the carrier N_2 gas. Monoethanolamine was detected as two major ions in the mass spectra, the parent $[M + H]^+$ ion (m/z 62) and a fragment ion corresponding to $[M + H–H_2O]^+$ (m/z 44). The fragmentation of the parent $[M + H]^+$ ion of MEA is consistent with early experimental and theoretical studies[149,150] showing that although the amino group is the favored protonation site due to its higher proton affinity compared to the alcohol group,[151] rearrangement and the loss of H_2O dominates over the loss of NH_3. The corresponding fragment ion associated with the loss of NH_3 (m/z 45) was not observed in any of the mass spectra. MSA was detected in negative ion mode as the parent deprotonated $[M - H]^-$ ion (m/z 95) followed by a major fragment ion at m/z 80 (SO_3^-), with additional minor ions at m/z 64 (SO_2^-), m/z 96 (SO_4^-), m/z 97 $(HSO_4)^-$ and m/z 112 (SO_5^-). Both positive and negative mass spectra are presented in Fig. S6 (ESI†). From the desorption profiles presented in Fig. S7 (ESI†), it is evident that MEA (and MA; data not shown) desorbs first from the filament followed by MSA, consistent with the differences in their respective saturation vapor pressures (P_{sat}) at 298 K: P_{sat}(MEA) = 3.4 × 10^{-4} atm[152] and P_{sat}(MSA) = 7.4 × 10^{-7} atm.[153] Additional details on the TDCIMS analysis are described in the ESI† (Text S3–S5 and Fig. S6–S11).

Results and discussion

Fig. 1 represents the size distributions of particles from the MSA + MEA reaction under dry conditions, with each panel (A–F) representing a different reactant concentration condition. Varying reactant concentrations were achieved by either increasing or decreasing the flow of the reactant that was introduced into the flow tube, or by changing the total flow rate in the flow tube (23.4 L min^{-1} for panels (A–C); 10.7 L min^{-1} for panels (D–F)). Clearly, mixing gas phase MSA and MEA at low ppb levels results in rapid formation of particles. Corresponding plots of the evolution of the total number concentration as well as the geometric diameter as a function of the reaction time are

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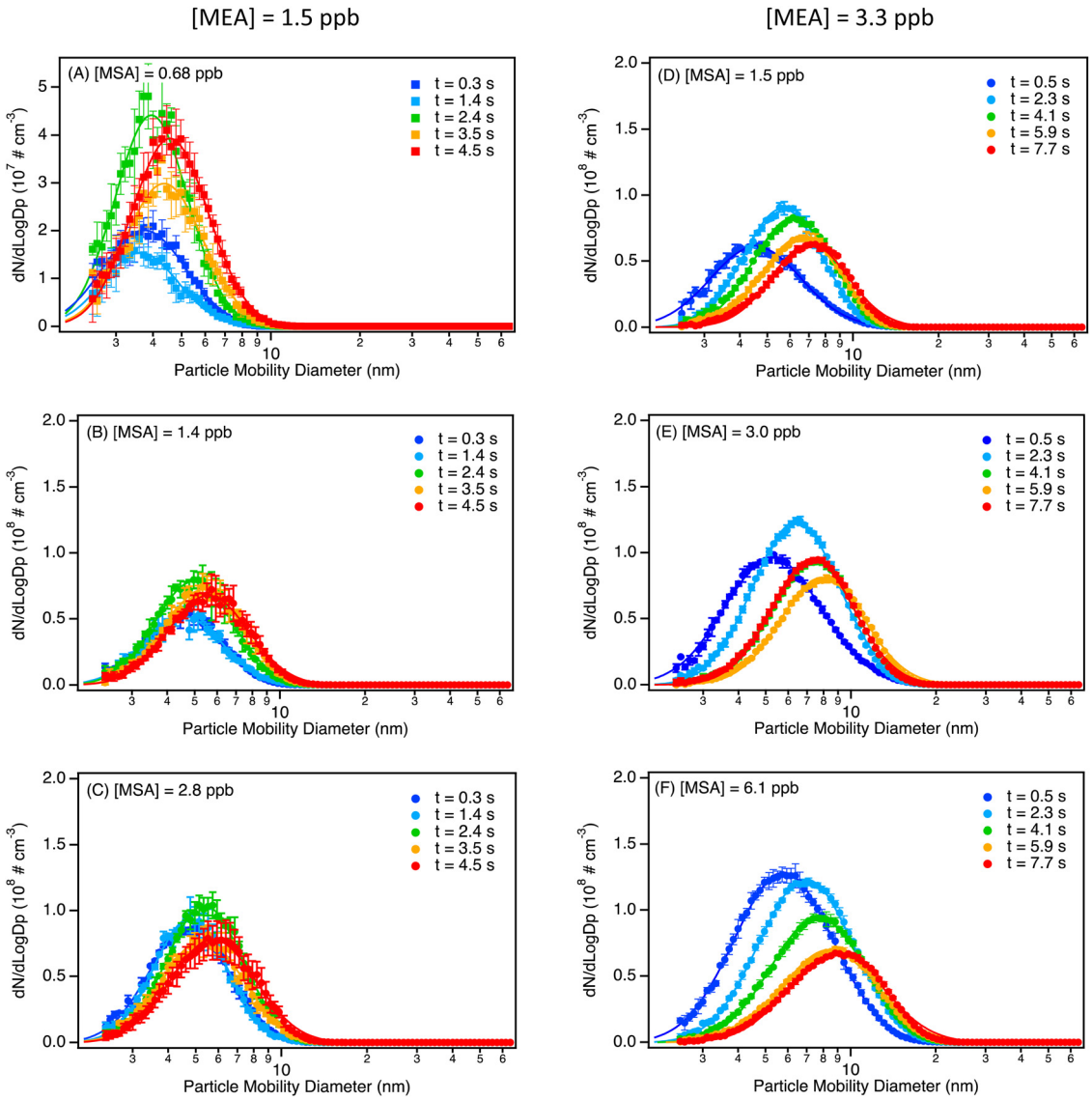

Fig. 1 Size distributions of particles from MEA (1.5 ppb) reacting with (A) 0.68 ppb MSA, (B) 1.4 ppb MSA and (C) 2.8 ppb MSA, and size distribution from MEA (3.3 ppb) reacting with (D) 1.5 ppb MSA, (E) 3.0 ppb MSA and (F) 6.1 ppb MSA. Measurements were conducted at the same sampling ports distributed equally along the length of the flow tube, but experiments displayed in panel (A)–(C) were performed with a total flow rate of 23.4 L min^{-1} (resulting in reaction times between 0.3 and 4.5 s), while experiments displayed in panel (D)–(F) were performed with a total flow rate of 10.7 L min^{-1} (resulting in reaction times between 0.5 and 7.7s). All experiments were performed under dry conditions, and size distributions are the average of 3 to 8 replicates (error bars correspond to one standard deviation) for each reaction time. All size distributions were corrected for particle losses through the sampling lines. Total particle concentrations and geometric mean diameters as a function of reaction times are given in Fig. S12 (ESI†).

presented in Fig. S12 (ESI†). Even at the smallest reactant concentrations (Fig. 1(A), 1.5 ppb MEA, 0.68 ppb MSA), particles measured at the shortest reaction time (t = 0.3 s; total flow rate 23.4 L min^{-1}) are formed at a number concentration of 6.3×10^6 particles cm^{-3} with a geometric mean mobility diameter (GMD) of ~ 4 nm. At 2.4 s, the number concentration increases by a factor of two with little change in size. At longer times, there is no further increase in the particle number concentration while the particles continue to grow to a GMD of ~4.6 nm, suggesting that under these conditions there is a balance between nucleation, growth by addition of the reactants onto particles, and coagulation. Particle losses inside the flow tube were estimated using the particle loss calculator tool developed by von der Weinder *et al.*[154] (using a density of 1 g cm^{-3}), and was found to be small for all diameters (*e.g.* for a particle diameter of 2.5 nm, particle transmission is predicted to be 92 or 95% for a total flow rate inside the flow tube of 10.7 or 23.4 L min^{-1}).

Similar behavior is seen as the initial MSA concentration is increased, but with larger total particle number concentrations formed (Fig. 1(B), (C) and Fig. S12A, B, ESI†). In this case, at longer reaction times the particle number concentrations start to decrease and the GMD increases due to coagulation (Fig. 1(C)). Similar, but more pronounced, trends are seen at an initial MEA concentration of 3.3 ppb and increasing MSA

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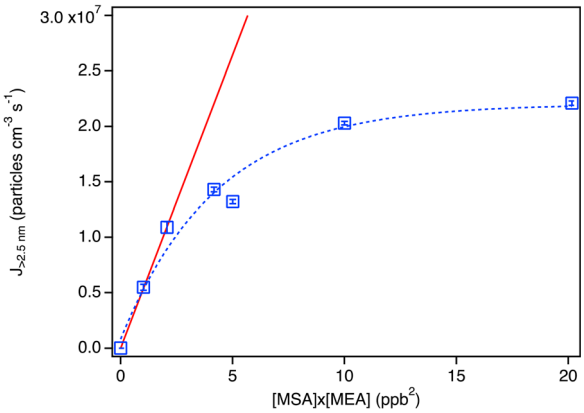

Fig. 2 Particle formation rate ($J_{>2.5\,nm}$) for the MSA + MEA system under dry conditions as a function of the product of the MSA and MEA mixing ratios in ppb. Each data point represents an average over 3 to 8 individual SMPS scans taken at 2.3–2.4 s reaction time, with error bars representing one standard deviation, and corrected for particle losses through the sampling lines. The red line is a linear fit to the data ([MSA] × [MEA] ≤ 2 ppb^2) with a slope of (5.3 ± 0.03) × 10^6 particles cm^{-3} ppb^2.

concentrations (Fig. 1(D)–(F)). For approximately the same MSA concentration (Fig. 1(B), (D) and Fig. 1(C), (E)), doubling the concentration of MEA leads to an increase in total number concentration of a factor of ∼1.2–1.4 at 2.3–2.4 s reaction time, with an increase in diameter from 4.9 to 5.6 nm (MSA = 1.4–1.5 ppb) and from 5.3 to 6.3 nm (MSA = 2.8–3.0 ppb).

For the low concentration series, the formation of approximately half of the peak particle concentration at the first measurement time implies that the rate-determining step is fast. There is some uncertainty in the exact reaction time for this first data point since it does not take into account possible continued reaction in the sampling lines. However, a half-life of ∼0.5 s for the reaction of MSA with excess MEA at 1.5 ppb (Fig. 1(A)), is consistent with a gas phase bimolecular reaction rate constant for MEA with MSA of approximately 4×10^{-11} cm^3 molecules^{-1} s^{-1}.

The particle formation rate ($J_{>2.5nm}$) was estimated using the total concentration of particles measured at ∼2.4 s (peak concentration) for all conditions, and dividing by the reaction time in seconds. Fig. 2 shows the resulting $J_{>2.5nm}$ values as a function of the product of the MEA and MSA initial concentrations. There is an initial rapid increase which is approximately linear out to [MEA] × [MSA] ∼ 2 ppb^2, suggesting that the initial 1 : 1 cluster formation is the rate-determining step. The drop-off at higher concentrations reflects coagulation. This is consistent with the TDCIMS measurements (Fig. 3), which show that the acid/base molar ratios in the particles from 4–12 nm remains within experimental error of one. All measurements were performed at 4.5 s reaction time and at an initial concentration of [MEA] of 1.5 ppb. There were no significant differences in the measured molar ratio across these experiments performed with MSA concentrations ranging from 0.68 to 2.8 ppb and the data obtained for all MSA concentrations was averaged together.

MSA concentrations in air can be as high as 10^7 molecules cm^{-3} (∼0.4 ppt)[60,61,66,68] and MEA in the low ppb range has been recorded outside a CCS facility.[7] The slope of the line in Fig. 2 at the lowest reactant concentrations is (5.3 ± 0.03) × 10^6 particles cm^{-3} ppb^{-2} so a NPF rate from the upper limit atmospheric concentrations of MEA (10 ppb) and MSA (0.4 ppt) of as much as ∼21 200 particles cm^{-3} is predicted. This can be compared to a range of formation rates of particles >3 nm diameter (J_3) from sulfuric acid of 0.001–10^5 cm^{-3} observed in different environments around the world.[155] In short, even for conditions where MEA and MSA concentrations are less than the reported maxima, this single reaction system may contribute significantly to NPF and its importance may increase as MEA use in CCS increases, and MSA increases due to a warming climate.

Efficient particle formation from MEA and MSA is consistent with the excellent stability at room temperature and low vapor pressure of the MSA–MEA salt synthesized by Greaves and co-workers.[156] Furthermore, MEA–MSA has been reported to have properties of a protic ionic liquid, even though it remains a solid at room temperature.[156–159] Its properties include a glass transition of −44 °C, melting point of about 100 °C, and a thermal stability up to 286–323 °C for the fused salt.[156]

Tropospheric air contains significant amounts of water vapor, hence the impact of relative humidity (RH) on particle formation from MEA + MSA was also examined. Surprisingly,

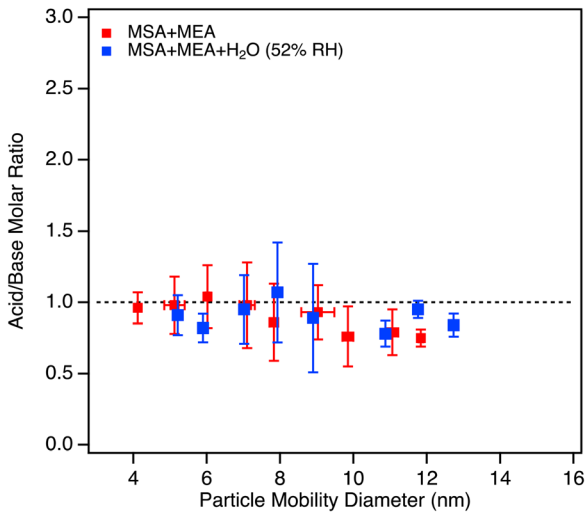

Fig. 3 Acid/base molar ratios measured by the TDCIMS for the MSA + MEA system, under dry conditions (red data points) and at 52% RH (blue data points) collected at 4.5 s reaction time. MEA was measured in POS ion mode while MSA was measured in NEG ion mode, and the ion distributions in the MS spectra were similar at all reactant concentrations (Fig. S6, ESI†). Text S5 provides more detailed information on how the acid/base molar ratios were estimated. All measurements were performed with initial MEA concentration of 1.5 ppb. No significant difference was observed in the measured molar ratio across for experiments performed with [MSA] = 0.68 ppb, [MSA] = 1.4 ppb or [MSA] = 2.8 ppb, in either dry or humid conditions; thus the data points represent average values across the [MSA] concentrations range for each RH condition. For each data point, the error bars represent one standard deviation. The dashed line corresponds to an acid/base molar ratio of unity for reference.

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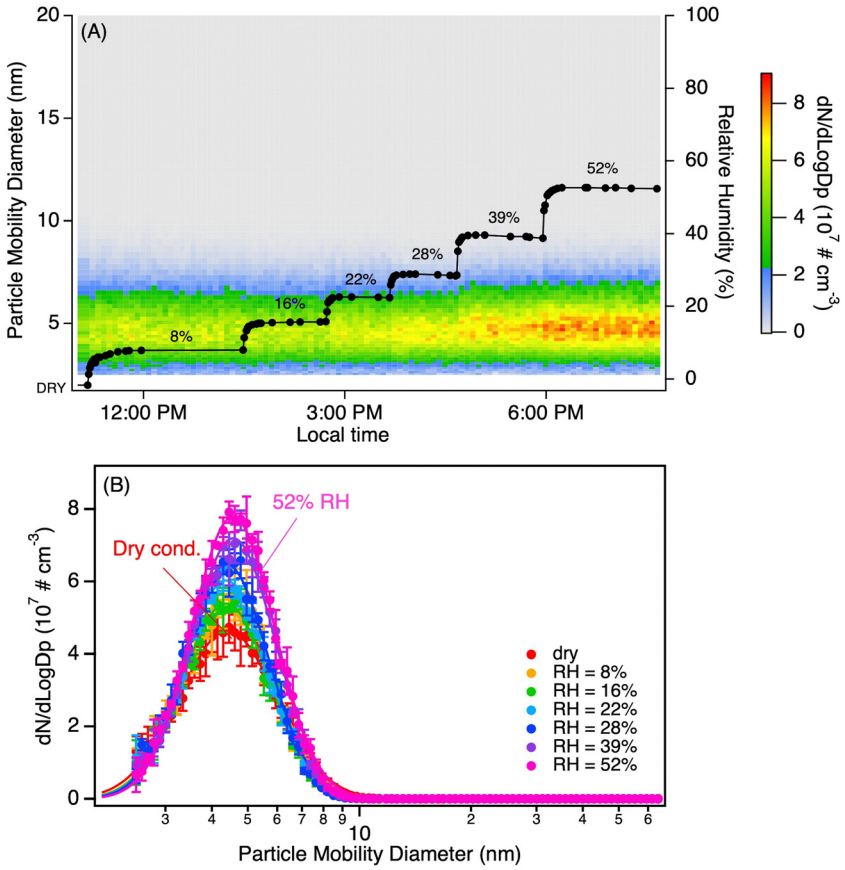

Fig. 4 Evolution of the particle size distributions as a function of relative humidity (RH) from the reaction of MSA (0.7 ppb) with MEA (1.4 ppb). Panel (A) represents the evolution as a function of time while panel (B) represents a snapshot of the size distributions at a given RH (each distribution is an average over three SMPS scans with the error bars representing one standard variation). All measurements were performed at 4.5 s reaction time, and particle size distributions were corrected for particle loss through the sampling lines.

and in contrast to previous results obtained for small alkylamines, the addition of water vapor to the MSA + MEA system did not significantly increase the number concentration at RH below ~20% as indicated in Fig. 4. Fig. 5(A) and (B) shows the evolution of the particle size distributions as a function of time at an RH of ~50% for two different sets of precursor concentrations corresponding to the dry conditions presented in Fig. 1(A) and (C) respectively. The evolution of the size distributions as a function of time in the flow reactor is similar to that observed under dry conditions. To better compare the dry *versus* humid case, total particle concentrations and geometric mean diameters measured at 4.5 s over several repeated experiments were averaged and are shown in Fig. S13 (ESI†). The addition of water vapor increased the total number concentration by only a factor of 1.3–1.5 as indicated by the bars. Note that the enhancement factor (EF) measured at 4.5 s for the high MSA, high RH case is an underestimate as it already includes coagulation (Fig. 5(C)). At the peak particle concentration (t = 1.4 s reaction time), EF = 1.9. There is only a small increase in size (red squares) at the highest MSA concentrations.

Classical nucleation theory predicts that the number of water molecules in the critical cluster can, under some conditions, be obtained from the slope of a log–log plot of the formation rate of new particles *versus* the gas phase water concentration.[160] However, this is highly dependent on a number of assumptions.[161] As seen in Fig. 6, there is no significant correlation with H_2O concentration. This could indicate that water is not a central ingredient in the critical cluster formed from MEA and MSA. Alternatively, it could be due to the absence of an energy barrier in the reaction so the slope simply reflects a lack of particle formation rate on the water concentration.[161] Furthermore, no change in the acid/base molar ratio was observed in the TDCIMS measurements in the presence of water compared to the dry case (Fig. 3; blue data points) indicating that the particles remained neutral. This lack of dependence on water is in contrast to previous results obtained for the small alkylamines,[102] where a slope of 1.3–2.3 in the log–log plot was observed.

Shen *et al.*[108] carried out computational studies of cluster formation from MEA and MSA, They showed that the 1 : 1 cluster was the least stable and hence formation of this cluster is the rate-determining step. This is consistent with the measured rates of particle formation depending on the product of the MEA and MSA concentrations and the 1 : 1 acid/base ratio of the particles. They demonstrated that the binding of MEA and MSA was determined by a combination of proton transfer from

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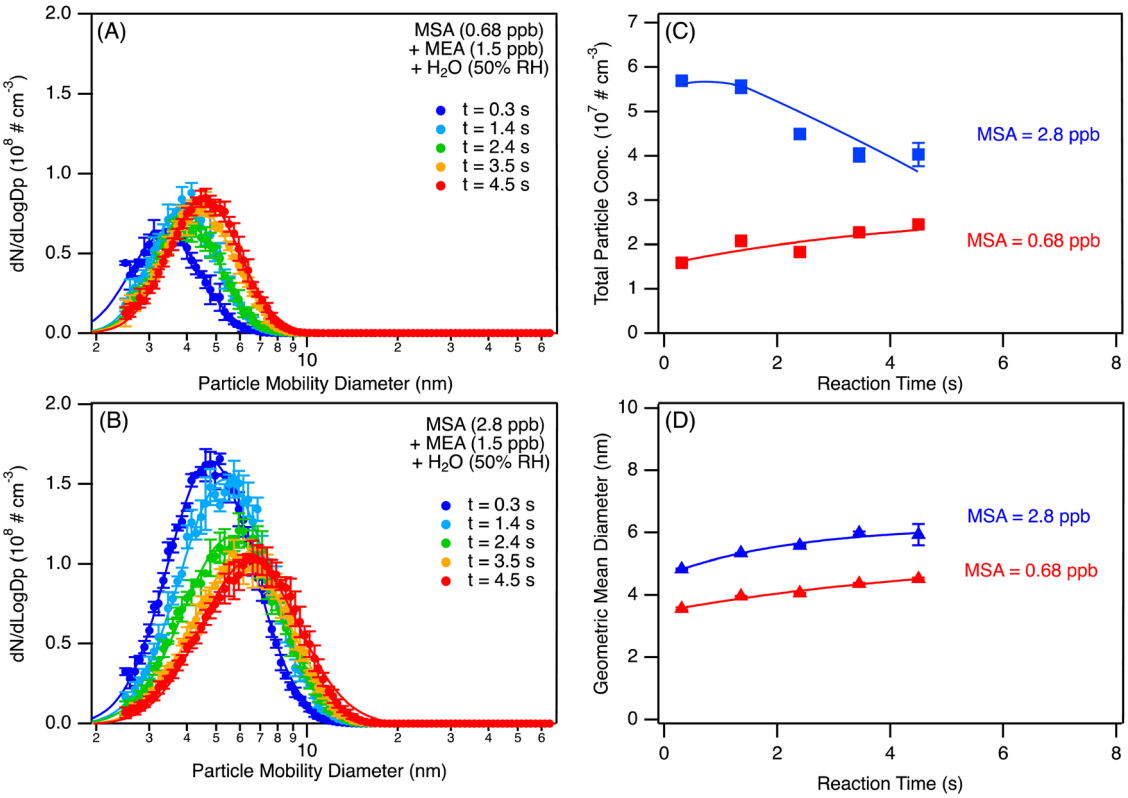

Fig. 5 Size distributions (A) and (B) and evolution of the particle total concentrations and geometric mean diameters measured as a function of the reaction time (C) and (D) in the flow reactor for the MSA + MEA reaction system at 50% RH. All lines in panels C and D are guides to the eye. All data originate from replicate scans (n = 5) and are displayed with one standard deviation. All size distributions were corrected for particle losses through the sampling lines.

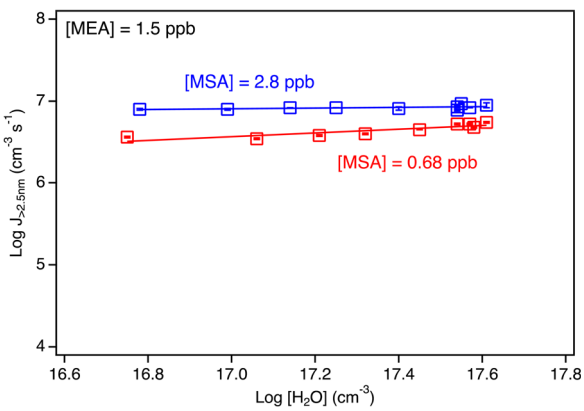

Fig. 6 Logarithm of the particle formation rate ($J_{>2.5\ nm}$) for the MSA + MEA system under humid conditions (RH ranging from 8 to 56%) as a function of the log of the water concentration (in molecules cm^{-3}). Each data point represents an average over 3 to 6 individual SMPS scans taken at 4.5 s reaction time, with error bars representing one standard deviation. All data points were corrected for particle loss through the sampling line. Red data are for [MSA] = 0.68 ppb and [MEA] = 1.5 ppb while the blue data are for [MSA] = 2.8 ppb and [MEA] = 1.5 ppb. The slopes of the lines are 0.04 for 2.8 ppb MSA and 0.2 for 0.68 ppb MSA.

the acid MSA to the nitrogen of the MEA base, along with hydrogen bonding. MEA differs from simple amines in that it has both the $-NH_2$ group as well as the –OH group, providing more than one hydrogen-bonding opportunity to MSA. Indeed, in all acid–base clusters, MSA acted as a H-bond donor and in many of the clusters, the –OH group of MEA acted as a H-bond donor to MSA. This results in strongly bound clusters held together by both electrostatic forces and a network of H-bonds, as illustrated in Fig. S14 (ESI†). It is interesting that the resulting structures have the $-CH_3$ group of MSA on the edge of the cluster, making the cluster somewhat hydrophobic. The hydrate distribution reported by Shen *et al.*[108] predicted that each cluster was predominantly hydrated by only one water molecule even at relatively high RH (80%). They also predicted that if water is present during cluster formation, it will enhance particle formation by about an order of magnitude at 50% RH due to a decrease in the evaporation rate of the initially formed 1 : 1 cluster. This predicted increase is significantly greater than the factor of 1.5–1.6 measured in these experiments.

In previous studies of NPF from MSA and amines, methylamine (MA) was shown to be the most efficient of the simple alkylamines in forming particles.[102,103,105,106] Fig. 7 compares the size distributions of particles formed from the reactions of 1.4 ppb MSA with 1.5 ppb MEA or 4.8 ppb MA under dry conditions. Even with three times the amine concentration, the total concentration of particles formed from MA is 17 times smaller than from MEA. This is consistent with previously

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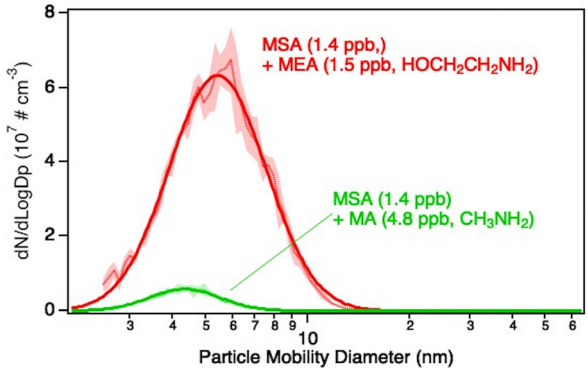

Fig. 7 Representative averaged size distribution (red trace) from the reaction of MSA (1.4 ppb) with MEA (1.5 ppb). For comparison, a size distribution for MSA (1.4 ppb) reacting with MA (4.8 ppb) is also shown (green trace). Both size distributions were taken at ∼4 s reaction time. Each size distribution was averaged over five consecutive scans and the shaded area corresponds to one standard deviation uncertainty. The thick line corresponds to a log normal fit to the averaged data. Both size distributions have been corrected for particle losses through the sampling lines.

reported theoretical calculations[108,114,162] which predict a greater stability of the clusters with the increased H-bonding capability of MEA and, as a consequence, particle formation rates that are orders of magnitude higher for MSA + MEA compared to that for MSA + MA at similar concentrations. The gas phase basicity[151] of MEA (896.8 kJ mol^{-1}) compared to MA (864.5 kJ mol^{-1}) also favors particle formation from MEA, along with the increased H-bonding opportunities.

In previous experimental studies, water had a dramatic effect on NPF from MSA reacting with small alkylamines,[102,104–106,163] quite different from MEA. In the case of MA, the presence of water during particle formation led to a large increase in both number concentration and size starting at RH < 10% (Fig. S15, ESI†). Calculations indicated that the 4MSA-4MEA cluster with one water molecule, for example, resulted in a structure that had many potential hydrogen bonding sites available, allowing the cluster to grow *via* H-bonding with other species.[163] For MEA, however, the clusters already have strongly hydrogen-bonded internal networks so that opportunities for further interactions with water molecules are reduced.

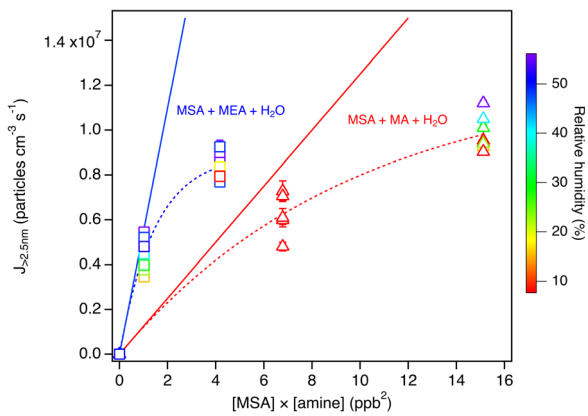

Fig. 8 Comparison between particle formation rate ($J_{>2.5\ nm}$) for the MSA + MEA and the MSA + MA systems under humid conditions (RH ranging from 8 to 56%) as a function of the product of the MSA and the amine mixing ratios in ppb. Each data point represents an average over 3 to 6 individual SMPS scans taken at 4.5 s reaction time, with error bars representing one standard deviations. The dashed lines are exponential fits to the data and the solid lines are the tangent to the fits with slopes of 5.5 × 10^6 and 1.2 × 10^6 for the MSA + MEA and MSA + MA systems respectively. All data points were corrected for particle loss through the sampling lines.

To compare the relative importance of the MEA and MA reactions with MSA for particle formation under atmospheric conditions, measurements under 10–50% RH were carried out with MA (Fig. S15, ESI†). Fig. 8 shows the NPF rate ($J_{>2.5\mathrm{nm}}$) for MEA compared to that of MA as a function of the product of the reactant concentrations. The slope of the linear fit through the data for the MEA reaction is more than four times that of the MA reaction. Thus, although NPF from MA + MSA is greatly enhanced in the presence of water, the MEA reaction is still more efficient under similar conditions. This highlights the significance of alkanolamines in NPF at low concentrations and points to H-bonding as a driver for NPF with MSA.

Conclusions

This study shows that the acid/base interaction of MSA with a short alkanolamine widely used in CCS is quite strong and produces sub-10 nm particles extremely well compared to a simple primary alkylamine, methylamine. Water vapor has a limited impact on NPF rates as MEA has OH− groups that already promote strong H-bonding network within the clusters. This is in contrast with previous work on alkylamines where water had a large impact on nucleation and growth of new particles. The particle composition from 4–12 nm showed an acid/base molar ratio close to unity, whereas those from the MA reaction contained more acid at the smaller diameters. These findings highlight that there is not a one-size-fits-all when it comes to treating amine interactions with MSA in atmospheric models.

The overall contribution of MSA-initiated aerosol chemistry may become increasingly more important in the future.[164] For example, there is a reduction of sea-ice coverage at the poles, leading to an increase in DMS emissions[94,96–98] with an associated increase in MSA. At the same time, there has been a decline in anthropogenic SO_2 emissions over few the past decades,[165–170] with a related reduction in particulate sulfate in ambient particles in the Northern part of the globe.[167,168,171,172] Thus, MSA acid–base mediated NPF will become increasingly more important in air in the near future.

Lastly, alkanolamines are being widely deployed in CCS technology which may lead to an increase in their abundance in the atmosphere. Thus, assessing and understanding the impacts of this acid–base driven chemistry on new particle formation in air is more important than ever.

Conflicts of interest

There are no conflicts to declare.

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