Clusteromics III: Acid Synergy in Sulfuric Acid–Methanesulfonic Acid–Base Cluster Formation

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1. INTRODUCTION

Aerosol particles are important for our global climate due to their direct interaction with solar radiation and their potential to act as a nucleus for cloud droplet formation. Clustering of low volatile acid molecules with atmospheric base molecules is the prime driver of atmospheric new particle formation (NPF). Newly formed atmospheric particles provide the required surface to initiate cloud droplet formation, and modeling studies have shown that NPF can explain roughly half the global number concentration of cloud condensation nuclei (CCN). However, the compounds involved in the formation and growth of atmospheric aerosols are highly uncertain, leading to a large uncertainty in global climate estimation. Over the open oceans and at coastal regions, the emission of dimethyl sulfide (DMS) is believed to be an important source of atmospheric aerosol particles. DMS reacts with oxidants in the atmosphere via long oxidation chains, and over time, DMS is transformed into the low volatile acids sulfuric acid (SA) and methanesulfonic acid (MSA). SA clustering with atmospheric base molecules is well-established as a main driver for inland NPF. In contrast, the role of MSA in NPF is much more uncertain. Recent measurements have been performed in marine environments across the globe identifying typical concentrations of SA and MSA in the range of 10^5–10^7 molecules cm^-3 depending on location and season. However, simultaneous gas-phase measurements of SA and MSA remain scarce, leading to limited information about the combined role of the two compounds in NPF.

Quantum chemical calculations of thermochemical parameters can be used as input to cluster kinetics modeling, yielding detailed insight into the exact role of various chemical species. Both SA–base and MSA–base clusters have extensively been studied using quantum chemical methods. However, studies involving clusters containing both SA and MSA remain extremely scarce. Bork et al. studied SA–MSA–DMA clusters using quantum chemical methods. It was found that in marine environments MSA could enhance cluster formation between SA and dimethylamine up to a factor of 3 at 258.15 K. Applying a combination of flowtube experiments and quantum chemical calculations, Wen et al. demonstrated that adding MSA to newly formed SA–water particles led to a dual particle distribution, while adding SA to newly formed MSA–water particles did not show this behavior. In both cases, mixed SA–MSA–water particles emerged, but with highly different number concentrations and size distributions.
Recently, an increased interest has also led to investigation of the potential synergistic effect between two different base molecules such as ammonia and dimethylamine as well as different amines such as mono-/di-/trimethylamine. This concept was recently extended to tribase synergy between three base molecules in (SA)_2(base) clusters. However, genuine multicomponent clusters simultaneously consisting of multiple acid molecules and multiple base molecules have not yet been studied.

Studying acid–base clusters using quantum chemical methods is extremely time-consuming. We recently introduced the clusteromics approach, which involves the comprehensive screening of small multicomponent molecular clusters, thereby providing direct insight into which chemical species are potentially involved in the initial cluster formation and growth. While giving insight into the species involved in cluster formation, the clusteromics approach also aids in constructing high-quality thermochemical data sets that can be applied to train quantum machine learning (QML) models. As a proof-of-concept, we recently reported the application of a kernel ridge regression ML model with the FCHL representation for studying sulfuric acid–water cluster formation. It was shown that it was possible to train an ML model to accurately predict the binding energies of sulfuric acid–water clusters with mean absolute errors below 0.5 kcal mol⁻¹.

In our first two clusteromics papers, we studied SA–base and MSA–base clustering. Depending on the basicity of the clustering base, SA–base clusters can rapidly form and grow. On the contrary, MSA–base clusters where unable to form in any appreciably amounts by themselves, thereby requiring an additional clustering species. This is caused by the lack of hydrogen bond donors available in the MSA molecule, which hinders the growth beyond the (acid)(base)₂ cluster systems. Exchanging one MSA molecule with an SA molecule in the clusters will increase the hydrogen-bonding capacity, thereby potentially alleviating this deficiency. This work is the third installment in the clusteromics series of papers that sets out to study the thermochemistry and cluster kinetics of mixed (SA)₂(base)₃ clusters with the bases ammonia (A), methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and ethylenediamine (EDA). To the best of our knowledge, this is the first study that investigates SA–MSA–base clusters with two different base molecules.

2. COMPUTATIONAL DETAILS

Density functional theory and semiempirical PM7 geometry optimizations and vibrational frequency calculations were carried out with Gaussian 16. The Gaussian 09 default convergence criteria were used to allow comparison with the data in the Atmospheric Cluster Database (ACDB). We used the ORCA 4.2.1 program to carry out the Domain based Local Pair Natural Orbital DLPNO–CCSD(T)/aug-cc-pVTZ calculations on top of the DFT geometries.

Herein, we also study clusters that consist of two different acids and thereby extend the concept of base synergy to the acids SA and MSA via the acid synergy factor 𝜋SA,MSA:

\[ \pi_{SA,MSA} = \Delta G_{bind,i...j,k,...} - \left( \frac{\Delta G_{bind,i...j,...} + \Delta G_{bind,j...k,...}}{2} \right) \]

This formulation will allow us to easily identify for which systems it is favorable to exchange a SA molecule with a MSA molecule.

2.2. ACDC. The calculated thermochemical parameters (ΔH and ΔS) are used as input for cluster kinetics simulations using the Atmospheric Cluster Dynamics Code (ACDC) to simulate the cluster formation potentials (Γpotential). The original ACDC code was downloaded from the ACDC repository and modified. We used default values for coagulation losses corresponding to typical values in the boundary layer (cr_exp = −1.6 and cs_ref = 1 × 10⁻⁷). The simulations were performed at 3000 as the population size (SN = 3000), a maximum of 200 generations (g_max = 200), and a maximum of 4 scout bees (g_sim = 4). A total of 1000 local minima were saved for each cluster.
278.15 K as this corresponds to conditions where nucleation bursts are frequently observed in pristine environments. Similar to our previous studies, clusters consisting of \((\text{acid})_2(\text{base})_{-3}\) were allowed to leave the simulation box and contribute to the cluster formation potential. The \((\text{acid})_2(\text{base})_3\) base clusters were not allowed to contribute to the \(I_{\text{potential}}\) value, as clusters that contain more bases than acids are usually unstable in electrically neutral acid–base cluster systems.5,76

3. RESULTS AND DISCUSSION

3.1. Cluster Structures. Applying the workflow described above, we identified a total of 3418 unique \((\text{SA})_1(\text{MSA})_1(\text{base})_3\) cluster structures. All the cluster structures have been added to the Atmopheric Cluster DataBase (ACDB).\(^5\) The identified lowest free energy clusters are displayed in Figure 1, presenting the studied largest \((\text{SA})_1(\text{MSA})_1(\text{base})_3\) clusters that contain two different base molecules. The cluster structures were calculated at the DLPNO–CCSD\((T_0)/\text{aug-cc-pVTZ}///\text{B97X-D/6-31++G(d,p)}\) level of theory using the quasi-harmonic approximation and at 298.15K, 1 atm.

The identified cluster structures bear high resemblance to the previously studied corresponding SA–base cluster structures.\(^5\) While the MSA–base clusters,\(^5\) for most systems, adopt a “symmetric” shape similar to the \((\text{SA})_1(\text{MSA})_1(\text{A})_1(\text{MA})_1\) cluster in Figure 1, this is not the case for the majority of the SA–base or SA–MSA–base clusters. The most striking difference between SA–base–base clusters and the corresponding SA–base clusters is the lack of vacant S–OH bonds. In the SA–base clusters vacant S–OH bonds were present in most clusters that contained weaker bases such as ammonia (A) and/or methyleneamine (MA). For the SA–MSA–base cluster systems a vacant S–OH bond is only present in the \((\text{SA})_1(\text{MSA})_1(\text{A})_1(\text{MA})_1\) cluster. In the remaining clusters, the S–OH bond from the sulfuric acid molecule interacts with the MSA molecule, forming strong acid–acid interactions. Previously, we identified that the SA–TMA system had a high cluster formation potential\(^5\) while the corresponding MSA–TMA system effectively formed zero clusters.\(^5\) This effect was attributed to the emergence of weak S=O–H–C noncovalent interactions due to MSA and TMA only having one donor–acceptor pair available for hydrogen bonding. However, the observed interactions between the SA and MSA molecules in the SA–MSA–base clusters in Figure 1 will likely mitigate the low cluster formation potential observed in the MSA–TMA system.

3.2. Thermochemistry. The calculated free energies (at 298.15K and 1 atm) of the studied SA–MSA–base clusters are presented in Table 1. The calculations are performed at the DLPNO–CCSD\((T_0)/\text{aug-cc-pVTZ}///\text{B97X-D/6-31++G(d,p)}\) level of theory using the quasi-harmonic approximation.

![Figure 1](image1)

**Figure 1.** Calculated lowest free energy (298.15 K, 1 atm) cluster structures at the DLPNO-CCSD\((T_0)/\text{aug-cc-pVTZ}///\text{B97X-D/6-31++G(d,p)}\) level of theory using the quasi-harmonic approximation.

| Cluster Structure | Free Energy (kcal/mol) |
|-------------------|------------------------|
| \((\text{SA})_2\) | \(-5.5\) |
| \((\text{MSA})_2\) | \(-5.4\) |
| \((\text{MSA})_1(\text{SA})_1\) | \(-5.1\) |
| \((\text{SA})_1(\text{MA})_1\) | \(-20.5\) |
| \((\text{MA})_2\) | \(-31.5\) |
| \((\text{DMA})_2\) | \(-36.6\) |
| \((\text{TMA})_2\) | \(-34.4\) |
| \((\text{EDA})_2\) | \(-34.4\) |

**Table 1.** Calculated Binding Free Energies (in kcal/mol, at 298.15 K, 1 atm) of the SA–MSA–Base Clusters at the DLPNO-CCSD\((T_0)/\text{aug-cc-pVTZ}///\text{B97X-D/6-31++G(d,p)}\) Level of Theory Using the Quasi-harmonic Approximation

\(^a\) The base strength classifications are divided into: \(w = \text{weak}, m = \text{medium}, \) and \(s = \text{strong}\). \(^b\) Data taken from ref 50 and 51, respectively.
(d,p) level of theory using the quasi-harmonic approximation. The corresponding data for the SA–base\textsuperscript{50} and MSA–base\textsuperscript{51} systems are presented as a comparison. On the basis of the gas-phase basicity of the base molecules,\textsuperscript{79} they are divided into classifications (weak, medium, strong).

The acid homo- and heterodimers show very similar thermochemistry with values of $-5.5$, $-5.4$, and $-5.1$ kcal/mol for the (SA)$_2$, (MSA)$_2$, and (SA)(MSA)$_1$ dimer clusters, respectively. It has previously been shown that for weakly bound cluster systems, such as the sulfuric acid–ammonia system,\textsuperscript{56} the acid dimer can be an important initial step in cluster formation. The formation of these dimer clusters will depend on the concentrations of SA and MSA. Because of their similar thermochemistry, having one acid in high excess will perturb the equilibrium concentration of each of the acid dimers. For instance, in the case where MSA is in high excess, the (MSA)$_2$ and (SA)$_1$(MSA)$_1$ dimer clusters will be formed predominantly.

The (SA)$_1$(MSA)$_1$(base)$_1$ clusters show the following trend in stability (in kcal mol$^{-1}$), with more negative free energies representing more stable clusters: (A)$_1$ ($-18.3$) < (MA)$_1$ ($-24.2$) < (TMA)$_1$ ($-24.9$) < (EDA)$_1$ ($-26.7$) < (DMA)$_1$ ($-28.2$). This is consistent with the previously observed trend in the corresponding (SA)$_2$(base)$_2$ clusters.\textsuperscript{56} In case of the (MSA)$_2$(base)$_2$ clusters, the stability ranking is slightly different, with the DMA- and TMA-containing clusters being less stable than the EDA-containing clusters. This is caused by the bulky methyl substituents having unfavorable interactions with the methyl group in MSA. Hence, exchanging one MSA molecule with an SA molecule alleviates some of the steric hindrance.

For the (SA)$_1$(MSA)$_1$(base)$_2$ clusters, with a single base type, we observe the following stability ranking (in kcal mol$^{-1}$), with more negative free energies representing more stable clusters: (A)$_2$ ($-23.6$) < (TMA)$_2$ ($-31.9$) < (MA)$_2$ ($-33.8$) < (EDA)$_2$ ($-39.1$) < (DMA)$_2$ ($-41.8$). This is consistent with the corresponding (MSA)$_2$(base)$_2$ clusters. However, the mixed (SA)(MSA)$_1$(TMA)$_2$ and (SA)(MSA)$_1$(MA)$_2$ clusters are closer in free energy ($-31.9$ and $-33.8$ kcal/mol, respectively) compared to the (MSA)$_2$(TMA)$_2$ and (MSA)$_2$(MA)$_2$ clusters ($-25.6$ and $-31.5$ kcal/mol, respectively). Again, this implies that exchanging one MSA molecule with one SA molecule will relieve some of the deficiencies observed in the MSA-TMA cluster system. In contrast, for the (SA)$_2$(base)$_2$ clusters, the stability of the (SA)$_2$(TMA)$_2$ clusters is significantly higher than the stability of the (SA)$_2$(MA)$_2$ clusters.

For the (SA)$_1$(MSA)$_1$(base)$_2$ clusters with two different bases, we observe a $m_1m_2/s < m_1s < s,s$ pattern based on the base classifications. Hence, the cluster stability to some extent follows the basicity of the base molecules. The only exception is the (SA)$_1$(MSA)$_1$(EDA)$_1$ cluster, which ranks lower in stability than the $m,s$ clusters. This pattern can be understood from the number of bulky methyl group substituents in the (SA)$_1$(MSA)$_1$(TMA)$_1$(EDA)$_1$ cluster. This trend is quite similar to the (SA)$_2$(base)$_2$ clusters with two different bases. However, this differs from the (MSA)$_2$(base)$_2$ clusters, where clusters containing MA rank significantly higher despite their lower basicity. This is consistent with previous studies on SA–base clusters:\textsuperscript{56,78} that have demonstrated that this is caused by an intricate combination of hydrogen bond capacity, basicity of the base, and steric hindrance.

Overall, the stability of the clusters follows (MSA)$_2$(base)$_1$$_2$ < (SA)$_1$(MSA)$_1$(base)$_1$$_2$ < (SA)$_2$(base)$_1$$_2$. Hence, the stability of the mixed (SA)$_1$(MSA)$_1$(base)$_1$$_2$ clusters is seen to be in between that of the (SA)$_2$(base)$_1$$_2$ and (MSA)$_2$(base)$_1$$_2$ clusters. However, inspecting the thermochemistry in Table 1, it is clear that the thermochemistry of the mixed clusters more closely resembles that of the corresponding SA–base clusters, especially for the larger clusters. To look further into this trend we can inspect the cluster synergy factors.

### 3.3. Synergy Factors

The synergy factors, as defined in section 2.1, correspond to the binding free energy difference between a cluster that consists of the components $j,k$ and the average of the corresponding clusters that consist of $j,j$ and $k,k$. Hence, a negative synergy factor indicates a synergistic effect between the components $j,k$ corresponding to a lowering of the average binding free energy. On the contrary, a positive synergy factor corresponds to an increase in the average binding free energy leading to a dysynergy between the components. Table 2 presents the calculated base synergy factors at the DLPNO-

| base synergy | (SA)$_2$(MSA)$_2$ | (SA)$_2$(TMA)$_2$ | (SA)$_2$(EDM)$_2$ | (MSA)$_2$(TMA)$_2$ | (MSA)$_2$(EDM)$_2$ |
|--------------|-----------------|-----------------|---------------|-----------------|---------------|
| $\Gamma_{SA}$ | $-0.4$ | $-0.9$ | $-0.6$ | $-1.7$ | $-0.3$ |
| $\Gamma_{MA}$ | $-0.3$ | $-1.9$ | $-2.8$ | $-0.3$ | $-0.1$ |
| $\Gamma_{EDM}$ | $-0.3$ | $-1.9$ | $-2.8$ | $-0.3$ | $-0.1$ |
| $\Gamma_{TMA}$ | $-0.9$ | $-1.7$ | $-0.3$ | $-0.1$ | $-0.1$ |

In all cases, we observe a slight base synergy, as all the calculated synergy factors are negative. This implies that the mixed base system is more thermodynamically stable compared to the average of the two isolated base systems. We observe large negative values of $-1.9$, $-2.8$, and $-1.7$ kcal/mol for $\Gamma_{SA,TMA}$, $\Gamma_{MA,TMA}$, and $\Gamma_{DMA,TMA}$, respectively. This is caused by the fact that the MSA-TMA clusters are quite unstable, and thus, the exchange of one TMA molecule with either A, MA, or DMA leads to a large increase in stability. From the discussion of the cluster structures in section 3.1 and the calculated thermochemistry in Table 1, it is clear that there is some synergy between the two acids SA and MSA in the SA–MSA–base clusters. Table 3 presents the calculated acid synergy factors ($\Gamma_{SA,MSA}$) at the DLPNO-CCSD(T$\omega$)/aug-cc-pVTZ//ωB97X-D/6-311++G(d,p) level of theory using the quasi-harmonic approximation at 298.15 K and 1 atm.

For the clusters with two identical bases, the acid synergy factors ($\Gamma_{SA,MSA}$) are favorable for the (SA)$_1$(MSA)$_1$(DMA)$_2$ and (SA)$_1$(MSA)$_1$(EDA)$_2$ clusters. This implies that exchanging one MSA molecule with one SA molecule in the (SA)$_1$(MSA)$_1$(DMA)$_2$ and (SA)$_1$(MSA)$_1$(EDA)$_2$ clusters does not come with a large thermodynamic penalty. In contrast, the acid synergy factor for (SA)$_1$(MSA)$_1$(TMA)$_2$ is positive, which implies that exchanging one MSA molecule with one SA molecule is not sufficient to overcome the low stability of the (MSA)$_2$(TMA)$_2$ clusters. For the clusters with two different bases, only the
(SA)\textsubscript{1}(MSA)\textsubscript{1}(A)\textsubscript{1}(MA)\textsubscript{1} and (SA)\textsubscript{1}(MSA)\textsubscript{1}(TMA)\textsubscript{1}(EDA)\textsubscript{1} clusters present positive synergy factors.

3.4. Cluster Formation Potential. The previous sections have presented the calculated cluster thermochemistry, which is essential for the stability of the clusters and, hence, their ability to grow into larger sizes. However, the abundance of each of the clustering species is also important to consider. We have simulated the cluster formation potential ($P_{\text{potential}}$) of the studied systems using ACDC. We kept the SA concentration fixed at $1 \times 10^6$ molecules cm$^{-3}$ and studied MSA concentrations of $1 \times 10^5$, $1 \times 10^6$, and $1 \times 10^7$ molecules cm$^{-3}$. This allows us to investigate three different MSA:SA concentration ratios which correspond to the scenarios where MSA is limited (1:10), MSA is equal to SA (1:1), and MSA is in excess (10:1). We studied the following atmospherically relevant ratios of the bases: ammonia ($10 \text{ ppt to } 10 \text{ ppb}$), methylamine ($1 \text{ ppt to } 100 \text{ ppt}$), dimethylamine ($1 \text{ ppt } 10 \text{ ppt}$), trimethylamine ($1 \text{ ppt } 10 \text{ ppt}$), and ethylenediamine ($1 \text{ ppt } 10 \text{ ppt}$). Table 3 presents the simulated cluster formation potentials in the studied lower and upper limits of the bases.

Unsurprisingly, it is observed that the cluster formation potential for each of the studied systems increases with increasing MSA concentration. This is simply caused by the fact that increased concentrations of clustering acids are available. Hence, even though MSA is a worse clustering species than SA, bases are generally in excess, and thus, increased concentration of the acids will increase the cluster formation potential.

The simulated cluster formation potential of the SA–MSA–A clusters is quite low. Even when considering a high load of up to $10 \text{ ppb}$ of ammonia and [MSA] = $10^7$ molecules cm$^{-3}$, the cluster formation potential remains $1.48 \times 10^{-3}$ clusters cm$^{-3}$ s$^{-1}$ or below. The clusters are growing out exclusively via collisions with the (SA)\textsubscript{2}(A)\textsubscript{2} clusters even when considering [MSA] up to $10^7$ molecules cm$^{-3}$. This is caused by the fact that both the MSA–A and SA–MSA–A cluster systems have significantly higher binding free energies than the corresponding SA–A cluster systems.

The cluster formation potential of the SA–MSA–MA cluster system is also observed to be low, with a maximum cluster formation potential of $0.345$ clusters cm$^{-3}$ s$^{-1}$ at $100 \text{ ppt}$ of MA and [MSA] = $10^7$ molecules cm$^{-3}$. At [MSA] = $10^6$ molecules cm$^{-3}$ or below, the clusters are exclusively growing out by collisions with the (SA)\textsubscript{2}(MA)\textsubscript{2} clusters, but at $100 \text{ ppt}$ of MA and [MSA] = $10^7$ molecules cm$^{-3}$, $12\%$ of the clusters are leaving the system as mixed (SA)\textsubscript{1}(MSA)\textsubscript{1}(MA)\textsubscript{2} clusters via collisions with MSA molecules.

In contrast to the SA–MSA–A and SA–MSA–MA systems, the cluster formation potential of the SA–MSA–DMA clusters is significantly higher, indicating that these clusters will definitely be formed and grow under realistic atmospheric conditions. Even at $1 \text{ ppt}$ of DMA and [MSA] = $10^6$ molecules cm$^{-3}$, the cluster formation potential is $0.568$ clusters cm$^{-3}$ s$^{-1}$. At $10 \text{ ppt}$ of DMA and [MSA] = $10^6$ molecules cm$^{-3}$, $P_{\text{potential}}$ is found to be $140$ clusters cm$^{-3}$ s$^{-1}$. At $1 \text{ ppt}$ of DMA and [MSA] = $10^7$ molecules cm$^{-3}$, $67\%$ of the clusters are growing out via collisions with mixed (SA)\textsubscript{1}(MSA)\textsubscript{1}(DMA)\textsubscript{2} clusters. At $10 \text{ ppt}$ of DMA and [MSA] = $10^7$ molecules cm$^{-3}$, this is increased to $87\%$. Hence, the mixed SA–MSA–DMA clusters have a pivotal role in the formation and growth pathways of the system.

The SA–MSA–TMA cluster system is also observed to have a high cluster formation potential. However, the clusters exclusively grow out as clusters that contain SA and TMA. This is caused by the high instability of the MSA–TMA clusters. The SA–MSA–TMA cluster formation potential appears to be less sensitive to the MSA concentration compared to the SA–MSA–DMA system. In contrast, the SA–MSA–TMA system is seen to be very dependent on the TMA concentration. This is because the (SA)\textsubscript{1}(TMA)\textsubscript{1} dimer cluster is important for the cluster formation pathways. For instance, at $1 \text{ ppt}$ of TMA and [MSA] = $10^6$ molecules cm$^{-3}$, $9\%$ of the collisions out of the system is due to collisions with the (SA)\textsubscript{1}(TMA)\textsubscript{1} dimer cluster. At $10 \text{ ppt}$ of TMA and [MSA] = $10^6$ molecules cm$^{-3}$ this is increased to $26\%$.

Table 3. Calculated Acid Synergy Factors ($\Gamma_{\text{SA,MSA}}$) for the Mixed Sulfuric Acid–Methanesulfonic Acid Clusters Containing a Single Type of Base\textsuperscript{a}

| cluster system | lower limit | upper limit |
|----------------|-------------|-------------|
| SA–MSA–A [MSA] | $10^6$ | $10^7$ |
| [MSA] = 1 ppt | $10^6$ | $10^7$ |
| [MSA] = 10 ppt | $10^6$ | $10^7$ |
| [MSA] = 100 ppt | $10^6$ | $10^7$ |

\textsuperscript{a}The sulfuric acid concentration was fixed at $1 \times 10^6$ molecules cm$^{-3}$. The [MSA] concentration is given in molecules cm$^{-3}$, and the $P_{\text{potential}}$ values are in clusters cm$^{-3}$ s$^{-1}$. The simulations were performed at 278.15 K.
The SA–MSA–EDA cluster system is seen to be quite dependent on the available MSA concentration. At 10 ppt of EDA and \([\text{MSA}] = 10^7\) molecules cm\(^{-3}\) we obtain a high cluster formation potential of 19.5 clusters cm\(^{-3}\) s\(^{-1}\). The high sensitivity to the MSA concentration is caused by the mixed SA–MSA–EDA clusters being important in the cluster formation pathways. At 1 ppt of EDA and \([\text{MSA}] = 10^7\) molecules cm\(^{-3}\), 24% of collisions leading out of the system occurs via collisions with the \((\text{SA})_1(\text{MSA})_1(\text{EDA})_2\) clusters. Increasing the EDA concentration to 10 ppt, 69% of the collisions out of the system occurs via the \((\text{SA})_1(\text{MSA})_1(\text{EDA})_2\) clusters.

Based on the upper concentration limits of the bases, we find that the cluster formation potentials of the SA–MSA–base clusters to follow the trend \(A < \text{MA} < \text{EDA} < \text{TMA} < \text{DMA}\). This differs substantially from the corresponding SA–base clusters\(^{50}\) \(A < \text{MA} < \text{EDA} < \text{TMA} < \text{DMA}\). This implies that the cluster formation potential of the SA–MSA–base clusters follows the base classifications with \(w < m < s\). Hence, by exchanging a single acid, the SA–MSA–TMA clusters are again near the top of the cluster formation potential. This clearly demonstrates the high sensitivity of the exact molecular composition of the clusters.

### 3.5. Enhancement in \(R_{\text{potential}}\) Potential

The simulated SA–MSA–base cluster formation potentials can be compared to the pure SA–base cluster formation potentials to elucidate the enhancing effect of having MSA present in the clusters. The enhancement is calculated using the upper limits of the base concentrations and relative to the pure SA–base cluster formation potentials (data taken from ref \(^{50}\)). Hence, we calculate \(R_{\text{MSA}}\) as

\[
R_{\text{MSA}} = \frac{f_{\text{potential}}(\text{SA} - \text{MSA} - \text{base})}{f_{\text{potential}}(\text{SA} - \text{base})}
\]

| cluster system          | \([\text{MSA}]\) | \(R_{\text{MSA}}\) |
|-------------------------|------------------|------------------|
| SA–MSA–A                | \(10^6\)         | 0.110            |
|                         | \(10^7\)         | 0.204            |
|                         | \(10^8\)         | 1.17             |
| SA–MSA–MA               | \(10^6\)         | 1.12             |
|                         | \(10^7\)         | 2.25             |
|                         | \(10^8\)         | 16.4             |
| SA–MSA–DMA              | \(10^6\)         | 1.14             |
|                         | \(10^7\)         | 2.60             |
|                         | \(10^8\)         | 20.9             |
| SA–MSA–TMA              | \(10^6\)         | 1.06             |
|                         | \(10^7\)         | 1.54             |
|                         | \(10^8\)         | 2.98             |
| SA–MSA–EDA              | \(10^6\)         | 1.11             |
|                         | \(10^7\)         | 2.21             |

\(R_{\text{MSA}}\) is the sulfuric acid concentration was fixed at \(1 \times 10^6\) molecules cm\(^{-3}\), and the simulations were performed at 278.15 K.

Table 5 presents the calculated enhancement in cluster formation potentials of the studied clusters.

At \([\text{MSA}] = 1 \times 10^6\) molecules cm\(^{-3}\), the enhancement is relatively low with a maximum enhancement of 1.14 for the SA–MSA–DMA system. Interestingly, for the SA–MSA–A cluster system there is observed an inhibiting effect for MSA concentrations of \(\geq 1 \times 10^8\) molecules cm\(^{-3}\) or below. This is most likely caused by the fact that the SA–A, SA–MSA–A, and MSA–A cluster systems all bind very weakly. Hence, there will be a build-up of smaller clusters distributed over more systems that cannot grow. We see that the enhancement in cluster formation potential is quite limited for the SA–MSA–TMA system and not very sensitive to the MSA concentration, with a maximum enhancement of a factor of 2.98. This is caused by the fact that the MSA–TMA clusters bind very weakly. The SA–MSA–MA/DMA/EDA cluster systems show similar \(R_{\text{MSA}}\) values with enhancements up to a factor of around 20 at \([\text{MSA}] = 1 \times 10^8\) molecules cm\(^{-3}\). It should be mentioned that in the high MSA concentration limit more collisions with MSA molecules will lead out of the system. This also implies that we are intrinsically assuming that the formed \((\text{SA})_1(\text{MSA})_1(\text{base})_2\) clusters can be also considered stable, which presently remains unknown. Thus, the best estimate of the enhancing potential of having MSA present in the clusters is the situation when \([\text{SA}] = [\text{MSA}] = 10^8\) molecules cm\(^{-3}\). However, this still implies that having MSA present can lead to an enhancement in cluster formation potential around a factor of 2. This clearly demonstrates that MSA shows great synergy in SA–MSA–base cluster systems, and in marine environments.

### 4. CONCLUSIONS

Using computational methods, we have screened the cluster formation potential of small multicomponent \((\text{SA})_1(\text{MSA})_1(\text{base})_2\) clusters with the bases being ammonia (A), methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and ethylenediamine (EDA). The cluster thermochromy has been calculated at the DLPNO-CCSD(T)_ω/aug-cc-pVTZ/ωB97X-D/6-31++G(d,p) level of theory using the quasi-harmonic approximation. We find that the mixed SA–MSA–base clusters more closely resemble the structures and thermochromy of the SA–base clusters as opposed to the MSA–base clusters. We find that the inability of the MSA–TMA system in forming clusters is alleviated by exchanging one of the MSA molecules with an SA molecule. Cluster kinetics simulations reveal that the cluster formation potential of the mixed SA–MSA–base clusters are enhanced by up to a factor of 20 compared to the corresponding SA–base clusters. Studying the cluster formation potential, we find that the SA–MSA–DMA clusters have the highest cluster formation potential of the studied systems. Hence, these clusters should be extended to larger sizes in future work.

As there is a clear positive interaction between the acid components in the clusters, we will in the following manuscripts...
in the series look into other, more abundant acid molecules that might be relevant for stabilizing the initial cluster formation. For instance, nitric acid has recently been demonstrated to be important in the initial steps of SA–DMA cluster formation as well as for the particle growth in polluted regions. In a similar manner, because of its high abundance, formic acid was recently shown to be the most efficient organic acid in enhancing MSA–MA cluster formation. Furthermore, by studying small clusters consisting of sulfuric acid, formic acid, ammonia, and water, Harold et al. recently showed that formic acid is just as effective as ammonia in stabilizing the clusters. Hence, further studies on the role of nitric acid and formic acid in cluster formation is warranted.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01396.

xyz files of the five lowest free energy cluster structures for each studied system at the B97X-D/6-31+G(d,p) levels of theory (ZIP)

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Notes

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