

# Potential Enhancement in Atmospheric New Particle Formation by Amine-Assisted Nitric Acid Condensation at Room Temperature

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Key points:

- Nitric acid can condense on nanoparticles with amines at a comparable or higher temperature than with ammonia
- Amines with additional hydrogen bonding ability can condense with nitric acid at room temperature
- Particles condensed with amines and nitric acid may absorb water at low relative humidity to influence their subsequent atmospheric aging

Abstract

Atmospheric aerosol contributes significantly to public health and plays a critical role in global climate. Recent laboratory experiments showed that new particle formation is significantly enhanced by rapid condensation of nitric acid and ammonia at low temperatures. Amines are derivatives of ammonia with a significant presence in the atmosphere. Using thermodynamic simulations, the condensation of amines and nitric acid under various temperatures was systematically evaluated. Monoamines condense with nitric acid at a temperature comparable to ammonia, while amines with additional hydrogen bonds (such as monoethanolamine and piperazine) condense with nitric acid at room temperature. The condensed amines and nitric acid also lower the aerosol deliquescence point, which may alter its subsequent atmospheric transformations. Our results suggest the potentially critical role of amines in new particle formation via condensation with nitric acid to rapidly grow newly formed clusters over their critical size in a wide temperature range.

### Plain Language Summary

The collection of microscopic liquid and solid nanoparticles suspended in the air is commonly referred as aerosol or particulate matters. It is important for us to understand how these nanoparticles are formed and grow in the atmosphere, because aerosol plays critical roles in public health and the global climate. Ammonia and amines are air pollutants emitted into the air in large quantities. Recently, ammonia and nitric acid are found to facilitate the grow of newly formed aerosol particles at low temperature. Due to the similarities between ammonia and amines, amines and nitric acid may also assist in the growth of ambient nanoparticles. Our hypothesis was evaluated using thermodynamic simulations on a mixture of ammonia, amines, nitric acid and sulfuric acid under various temperature and relative humidity conditions. Similar to ammonia, simple amines may enhance particle growth at low temperature with nitric acid. Notably, nitric acid and amines with the ability to form additional hydrogen bonds may facilitate particle growth at room temperature. The resulting aerosol may absorb water even at low relative humidity, leading to distinctively different particle properties and climate effects. Our results indicate that amines and nitric acid could contribute significantly to ambient particle growth at various temperatures.

## 1. Introduction

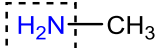
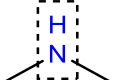
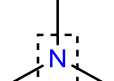
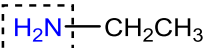
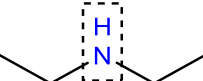
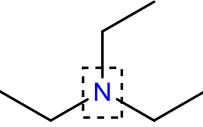
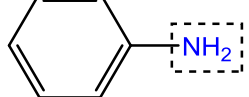
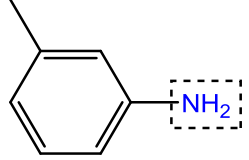
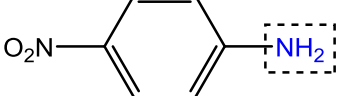
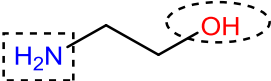
Aerosol, microscopic nanoparticles suspended in the atmosphere, contributes significantly to air quality, human health, regional weather and the global climate [Seinfeld and Pandis, 2016]. For example, aerosol particles can directly absorb and/or scatter solar radiation, and serve as cloud condensation nuclei (CCNs) to influence the cloud formation, the Earth's hydrological cycle and the radiative forcing [Stocker et al., 2013]. Therefore, it is important to understand the formation and transformation of ambient aerosol, especially in the troposphere of metropolitan centers.

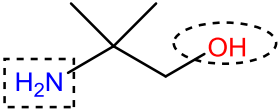
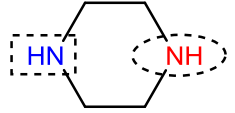
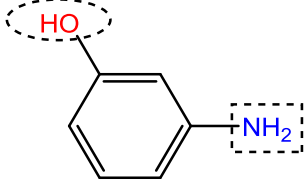
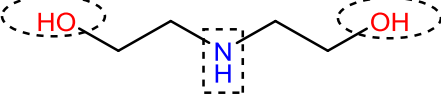
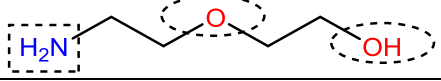
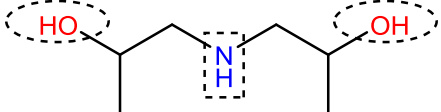
New particle formation (NPF) events significantly increase the ambient aerosol number concentration in a short period of time but our understanding of NPF is limited, especially in urban areas with complex emission inventories of chemicals from various natural and anthropogenic sources [Zhang et al., 2012]. It is generally believed that gaseous sulfuric acid (SA) leads to the NPF by forming freshly nucleated clusters (FNCs), often with the contributions from other chemicals, including ammonia, nitric acid (NA) [Liu et al., 2018; Wang et al., 2020], oxidized organics [Zhang et al., 2004; Wang et al., 2010; Fang et al., 2020], and amines [Almeida et al., 2013; Yao et al 2018]. These small clusters need to grow quickly into a critical diameter (of several nanometers) to avoid being scavenged by coagulation with other particles [Smith et al. 2020]. Therefore, the growth of FNCs are critical in understanding the formation and transformation of aerosol.

Ammonia and NA are generally several orders of magnitude more concentrated than SA in the atmosphere. Wang et al [2020] recently reported rapid ammonia and NA condensation on FNCs at or below 278 K (+5 °C) in laboratory experiments using SA, NA and ammonia concentrations comparable to those commonly found in the urban atmosphere. This significant new result offers new insights into the potential contribution of ammonia and NA condensation to NPF under cold weather conditions.

Amines are emitted into the atmosphere in large amounts from nature sources (e.g., water bodies) and human activities (e.g., agriculture, animal husbandry, sewage and chemical manufacturing) [Cape et al., 2011; Ge et al., 2011a; Qiu and Zhang, 2013]. Some amines are primarily emitted as industrial chemicals: monoethanolamine (MEA) and piperazine (PZ) are widely used in Carbon Capture and Storage (CCS) technology in the post combustion of fossil fuels [Nielsen et al., 2012]. The concentrations of amines in the atmosphere vary significantly; in some extreme cases, amine concentrations at the proximity of their emission sources can be comparable to that of ammonia [SEPA, 2015]. However, ambient amine concentrations are generally at least 1–2 orders of magnitude lower than that of ammonia [Yli-Juuti et al., 2013]. Ammonia and amines are collectively referred as reduced nitrogen compounds (RNCs) in this study (see Table 1 for their structures and abbreviations).

Table 1. The chemical structures and properties of reduced nitrogen compounds (RNCs) involved in this study.

RNC name	Abbreviation	Chemical Structure	$p_{sat}^a$	$GB^b$	$K_b^c$	$K_p^d$	$T_c^e$	Group <sup>f</sup>
Ammonia	NH <sub>3</sub>	NH <sub>3</sub>	$9.94 \times 10^5$	819.0	$1.76 \times 10^{-5}$	$4.48 \times 10^{-7}$	$273.4_{-10}^{+4.6}$	I
Methylamine	MA		$9.75 \times 10^4 \dagger$	864.5	$4.57 \times 10^{-4}$	$4.54 \times 10^{-8}$	$274.1_{-3.6}^{+15}$	I
Dimethylamine	DMA		$5.37 \times 10^4 \dagger$	896.5	$5.38 \times 10^{-4}$	$6.27 \times 10^{-8}$	$270.6_{-3.0}^{+17}$	I
Trimethylamine	TMA		$2.31 \times 10^5$	918.1	$6.33 \times 10^{-5}$	$1.65 \times 10^{-6}$	$274.8_{-5.5}^{+5.8}$	I
Ethylamine	EA		$1.39 \times 10^5 \ddagger$	878.0	$4.46 \times 10^{-4}$	$2.83 \times 10^{-8}$	$272.7_{-0.8}^{+15}$	I
Diethylamine	DEA		$3.00 \times 10^4 \ddagger$	919.4	$6.90 \times 10^{-4}$	$7.01 \times 10^{-9}$	$263.9_{-7.7}^{+24}$	I
Triethylamine	TEA		$9.03 \times 10^3$	951	$5.62 \times 10^{-4}$	$9.39 \times 10^{-8*}$	$273.8_{-10}^{+10}$	I
Aniline	AN		$8.52 \times 10^1$	850.6	$7.41 \times 10^{-10}$	$1.01 \times 10^{-4}$	$256.6_{-2.8}^{+2.8}$	I
3-Methylaniline	AN-M		$1.07 \times 10^1$	864.0	$5.13 \times 10^{-10}$	-	$256.6_{-4.4}^{+4.4}$	I
p-Nitroaniline	AN-N		$6.79 \times 10^{-2} \ddagger$	834.2	$1.05 \times 10^{-13}$	-	$256.6_{-0.1}^{+0.1}$	I
Monoethanol amine	MEA		$6.51 \times 10^1$	896.8	$3.16 \times 10^{-5}$	$1.41 \times 10^{-12*}$	$304.5_{-4.9}^{+5.2}$	II

Isobutanol amine	IBA		$7.48 \times 10^1$	-	$7.25 \times 10^{-5}$	-	$307.0^{+7.1}_{-7.1}$	II
Piperazine	PZ		$5.32 \times 10^2$	914.7	$5.38 \times 10^{-5}$	-	$302.4^{+4.8}_{-5.1}$	II
3-Aminophenol	AN-O		$3.80 \times 10^{-3}$	866.9	$2.34 \times 10^{-10}$	-	$289.0^{+4.6}_{-4.9}$	II
Diethanol amine	DAE		$6.87 \times 10^{-2}$	920	$9.77 \times 10^{-6}$	$9.14 \times 10^{-13*}$	$323.5^{+4.9}_{-4.9}$	II
Diglycol amine	DGA		$1.54 \times 10^{-1}$	-	$5.01 \times 10^{-6}$	-	$323.7^{+6.8}_{-6.5}$	II
Diisopropanol amine	DIPA		$5.67 \times 10^{-1}$	-	$9.12 \times 10^{-6}$	-	$313.5^{+6.6}_{-6.6}$	II

<sup>a</sup> The saturation vapor pressure (in Pa) of the amine at 298 K [Ge et al., 2011b; Linstrom and Mallard, 2018].

<sup>b</sup> The gaseous basicity (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) at 298 K [Hunter and Lias, 1998].

<sup>c</sup> The aqueous base hydrolysis constant (in  $\text{mol}\cdot\text{kg}^{-1}$ ) of the amine at 298.15 K [Ge et al., 2011b].

<sup>d</sup> The solid/gas equilibrium dissociation constant (in  $\text{Pa}^2$ ) of the nitrate salt of the amine at 298.15 K [Ge et al., 2011b].

<sup>e</sup> The transitional temperature (in K) of nitric acid condensation, defined as the temperature at which the moles of total nitrate in the condensed phases equals to 5% of the initial moles of nitric acid and determined in this study. Details on uncertainty estimations are in the Supporting Information (Table S1).

<sup>f</sup> classified based on the  $T_c$  of the amine: Group I amines with  $T_c \leq 278$  K and Group II with  $T_c > 288$  K.

<sup>†</sup> At 266 K; <sup>‡</sup> Extrapolated to 298 K based on the Antoine Equation [Linstrom and Mallard, 2018]; \* At 293 K.

Since the salts of amines with NA [Salo et al., 2011] showed comparable or lower saturation vapor pressure than that of ammonium nitrate, it is conceivable that the cluster growth in the ASN nucleation system can be enhanced by amines due to the condensation of amines and NA, at least at low temperature. Amines may, therefore, contribute to both the formation and growth of FNCs. Also, due to the various amines observed in the atmosphere, it is uncertain how their chemical structures may play a role in their contribution to the ASN nucleation system. Furthermore, since ambient amines are typically much lower in concentrations than ammonia, investigation on the effect of excess ammonia on the possible condensation of amines and NA under ambient conditions is also warranted.

In this study, the contribution of amines to the condensation of NA on nanoparticles was investigated using Extended Aerosol Inorganics Models (E-AIM) [Wexler and Clegg, 2002; Ge et al., 2011b] under conditions that closely resemble typical ambient conditions, especially those found in an urban environment. Our results showed that monoamines and NA can condense at comparable temperature to ammonia. Much to our surprises, significant condensation of NA was observed, at room temperature, with amines that can form additional hydrogen bonds. Such process seems to enhance the water uptake by nanoparticles at lower relative humidity (RH) and unaffected by the presence of excess ammonia. Our results suggest that RNCs may facilitate the NPF by co-condensing with NA on nanoparticles at a wide range of temperatures. Our results may be important in regions commonly polluted with amine emissions, such as megacities, agricultural lands and heavily industrialized areas.

## 2. Method

E-AIM employs thermodynamic state equations that consider phase and chemical equilibria of chemicals in solid, liquid and gas states under given initial conditions [Wexler and Clegg, 2002]. E-AIM solves these equations numerically and predicts all possible phases (gas, aqueous solution, organic solution, and solid) as well as the distributions of a chemical in each phase. We used E-AIM to evaluate the equilibrium state of a chemical system involving SA, NA, ammonia and amines under various conditions, including temperature, RH, and the initial moles of the chemicals. Detailed descriptions and justifications on the default parameters used in our simulations are included in the Supporting Information. Several chemicals in this study have multiple forms in condensed phases. For example, ammonia may exist in an aqueous solution as dissolved free ammonia (base form) and protonated ammonium cation (acid form). Since the primary interest of this study is the distribution of a chemical in gas and condensed phases, to simplify the analysis of the simulation results, the total moles of all forms of a chemical in all condensed phases were aggregated together. For example, the moles of nitrate as ammonium nitrate solid and aqueous nitrate anion were reported together as the moles of condensed nitrate,  $n_{cond.}(\text{NO}_3^-)$ .

The typical temperature and RH ranges used in our simulations were 260 K to 330 K ( $-13\text{ }^{\circ}\text{C}$  to  $57\text{ }^{\circ}\text{C}$ ) and 10% to 90%, respectively, while the total pressure and volume were fixed at 101,325 Pa and  $1\text{ m}^3$ , respectively. The typical initial moles of an RNC, SA and NA were  $1.11151\times 10^{-9}$ ,  $2.03777\times 10^{-11}$  and  $8.86895\times 10^{-8}$ , respectively, corresponding to a mixing ratio of 1915 pptv RNC, 0.44 pptv SA and 24 pptv NA at 60 % RH, 263.15 K, and 101,325 Pa. These values were chosen to represent typical atmospheric conditions in polluted megacities as suggested by Wang et. al. [2020]. Cases where ammonia was partially replaced with amines were also explored with the initial moles of all RNCs fixed at  $8.86895\times 10^{-8}$  and the mol ratio of amine and ammonia varied. The initial moles of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and RNCs were fixed when the temperature

or RH input was changed to provide a consistent basis of comparison.

### 3. Results and Discussion

As expected, our E-AIM simulation on ammonia and SA binary system without any NA showed the complete condensation of the sulfate into the solid phase as ammonium sulfate. The focus was then moved to a ternary RNC-SA-NA system, since NA is in general always in large excess than SA in the atmosphere. Figure 1a (black curve) shows that ammonia and NA, which were generally considered to be unstable in the particles in the atmosphere at room temperature, can thermodynamically condense into particle phase in the ternary system when the temperature is low enough (below 273 K). As the temperature decreases, more and more condensed ammonia and NA will exist in condensed phases, facilitating the growth of ammonium sulfate FNCs. This observation is consistent with the experimental findings by Wang et al. [2020], where they identified that ammonia and NA in such ternary system could only condense at or below 278 K, but above 263 K.

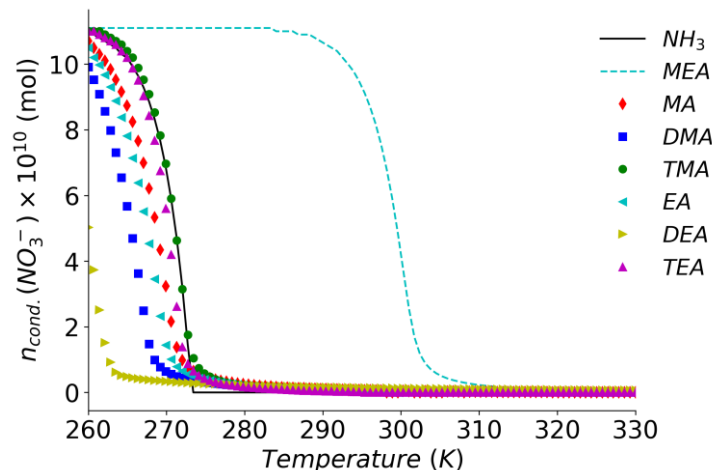
Our simulations revealed the different temperature-dependence of the condensation of NA in the presence of varying RNCs other than ammonia. The most commonly observed organic amines in the atmosphere are monoamines with methyl groups, MA, DMA and TMA (Table 1). It was clear that these monoamines may all contribute to the condensation of NA on particles at low temperature (Figure 1a). For example, TMA and TEA showed very similar effects on the NA condensation as ammonia. Considering the potential high concentrations of these alkylamines in some urban and coastal environment, it is possible that both ammonia and amines can contribute to the growth of FNCs under cold weather conditions by facilitating the condensation of available gaseous NA on the freshly formed particles.

To our surprise, alcohol amines, such as MEA, can condense with NA even at room temperature and higher (Figure 1a, blue dash line). Since ammonia is not likely to contribute to the NA condensation at these temperatures [Liu et al., 2018; Wang et al., 2020], our findings suggest that an environment polluted with MEA and NA may experience rapid new particle growth due to the condensation of NA facilitated by MEA. Further investigations on several other amines with additional  $\text{-NH}_2$  or  $\text{-OH}$  group(s) (labeled in red in Table 1) also showed significant condensation with NA at room temperature (Figure 1b).

To further quantitatively describe the influences of ammonia and different amines on the condensation of NA, the transitional temperature of NA condensation ( $T_c$ ), which is defined as the temperature at which the moles of total nitrate in the condensed phases equals to 5% of the initial moles of NA, was identified and summarized in Table 1, along with the estimated uncertainties (details in Supporting Information, Figure S1 and Table S1).

Common monoamines, including MA, DMA, TMA, EA, DEA and TEA, all showed  $T_c$  values ranging from 263 K to 275 K, similar to that of ammonia. It implies the limited contribution of alkyl groups in enhancing NA condensation. Group I RNCs is hereby defined as those that will only condense with NA at or below 278 K. Other RNCs with  $T_c$  values at or above 288 K are collectively referred as Group II RNCs in this study. Our results indicate that the existence of Group II amines (e.g., MEA and PZ) in the atmosphere may greatly facilitate the condensation of NA at room temperature and enhance the new particle formation process by growing the critical clusters over the “valley of death” with excessive particle savaging.

(a)



(b)

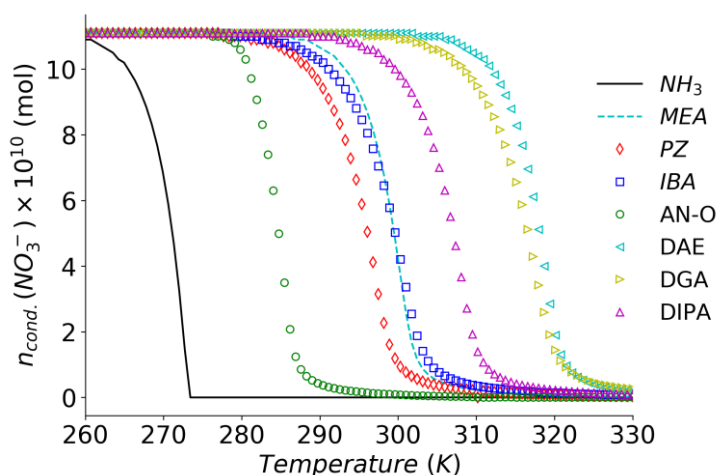


Figure 1. The moles of condensed nitrate against temperature in a ternary system of RNC-sulfuric acid-nitric acid at fixed initial water vapor of 0.07848 mol (equivalent to 60% RH at 263.15 K and 101325 Pa in 1 m<sup>3</sup>). All curves have the same initial moles of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and the RNC as  $1.11151 \times 10^{-9}$ ,  $2.03777 \times 10^{-11}$  and  $8.86895 \times 10^{-8}$ , respectively. The legend on the right indicates which RNC is present in each trace. (a) includes all RNCs in Group I (defined in Table 1) and MEA (as comparison) and (b) includes all RNCs in Group II and ammonia (as comparison).

To further elucidate the reason for such significant difference in  $T_c$  values among amines, the properties of several amines with distinctively different functional groups were compared (Table 1). Neither gaseous basicity (GB), aqueous basicity ( $K_b$ ) or the volatility of an RNC or its nitrate salt ( $p_{sat}$  and  $K_p$ , respectively) seems to directly determine the  $T_c$  of an RNC. For example, DMA and MEA have similar GB values yet distinctively different  $T_c$ . When compared with PZ, TMA have a similar  $K_b$  yet a  $T_c$  that is  $\sim 28$  K lower. PZ has a much higher GB than MEA but their  $T_c$  values are comparable. AN and MEA have similar saturation vapor pressures at room temperature yet distinctive different  $T_c$ , ruling out any direct contribution on  $T_c$  from the volatility of the amine. The solid/gas dissociation constants of the nitrates of alkylamines are about 10 times lower than that of ammonium nitrate yet they exhibit comparable  $T_c$ , suggesting that saturation condensation of nitrate salts alone may not explain the difference in  $T_c$  for Group I and II RNCs. Furthermore, the molar mass of IBA is about 50% more than that of MEA, but their  $T_c$  values are essentially the same, suggesting



that Van der Waals forces do not contribute significantly here. It appears that the electron affinity of the functional groups on the amines has little effect on the  $T_c$ . For example, the nitro group in AN-N and the methyl group in AN-M are electron withdrawing and electron donating groups, respectively. However, both RNCs showed little contribution to NA condensation at above 260 K.

One distinctive observation is that amines with only alkyl (e.g., MA) or aromatic (e.g., AN) substitutions showed much lower  $T_c$  than those with hydroxyl (–OH) groups (e.g., MEA). Furthermore, IBA and PZ, showed  $T_c$  values comparable to that of MEA, with the former having a similar chemical structure as MEA, while the latter having a second amine group (–NH–) in the ring (Table 1). Since MEA and PZ do not share the same functional groups, their high  $T_c$  values could not be explained alone by the presence of –OH groups in the chemical structure.

Based on these observations, it is proposed that the ability of RNCs to form additional hydrogen bonds plays a critical role on how RNCs may facilitate the condensation of NA on nanoparticles. Generally, the  $T_c$  value will increase significantly when a RNC can form more hydrogen bonds. MEA, PZ and IBA, with one additional hydroxyl or amine group than monoamines, have  $T_c$  values of  $\sim 300$  K. DAE, DGA and DIPA with two additional hydrogen bonds, showed  $T_c$  values as high as 323 K (Table 1), allowing NA to condense above room temperature.

Another factor that may affect the  $T_c$  is hydrophobicity. AN and AN-M both contain an aromatic ring which is more hydrophobic than a methyl group. The decreasing solubility of amines in water results in less NA condensed and dissolved in the particle, greatly diminishing the condensation of NA compared with MA. In the case of AN-O, the –OH attached to the aromatic ring can form additional hydrogen bonds, which seems to offset the negative effect of the non-polar aromatic ring and increase the  $T_c$  to 289K (+15 °C).

To evaluate the Kelvin curvature effect [Zhang et al, 2012] on the condensation of RNC and NA, the saturation vapor pressure  $p_{sat}$  of MEA was increased by factors of 10 and  $10^2$ ; the corresponding  $T_c$  values decreased to 296 K and 288 K, respectively. This analysis suggests the significant impact of particle size on the condensation of NA in the presence of RNCs.

Although Figure 1 and Table 1 well demonstrate the enhancement of NA condensation by the presence of amines, ambient concentration of amines is normally much lower than 1900 pptv, nor would amines exist in the atmosphere without a relatively high concentration of ammonia. In reality, the ambient concentration of amines is usually 1–2 orders of magnitude lower than that of ammonia, although the amine:ammonia mol ratio could be higher near industries emitting amines, such as near a power-plant using CCS technology. As a result, a chemical system of ammonia, MEA, SA and NA with varying MEA:ammonia mol ratios was investigated. Figure 2a illustrates the change of the  $T_c$  value of an ASN system with varying amount of the ammonia replaced with MEA. The enhancement of the NA condensation by MEA is noticeable even at as low as 0.1 mol % ( $\sim 2$  pptv). It appears that as the mole fraction of MEA increases, the  $T_c$  increases following an excellent linear relationship ( $R^2 = 0.99$  and Figure S2):

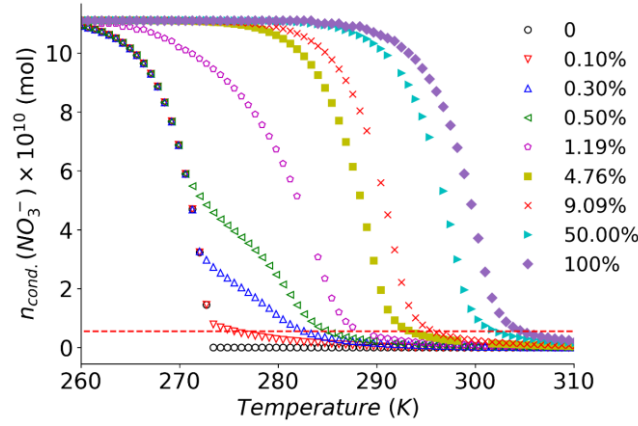
$$T_c = 9.1615 \times [-\log(\text{MEA}\%)] + 305.33 \quad (1)$$

where MEA% is the MEA mole fraction in total RNCs (mol %).

In addition to the structures and concentrations of amines, amount of total water is another factor that may impact the condensation of NA. Our further investigation (Figure S3) suggested that increase in the total water vapor in the system leads to an increase in  $T_c$  of the system, hence facilitating the condensation of NA. However, the

enhancement is not as strong as other effects such as additional hydrogen bonding or hydrophobicity. A similar trend was observed by Chee et al. [2019] when they studied the nanoparticle formation and growth in a DMA-NA system.

(a)



(b)

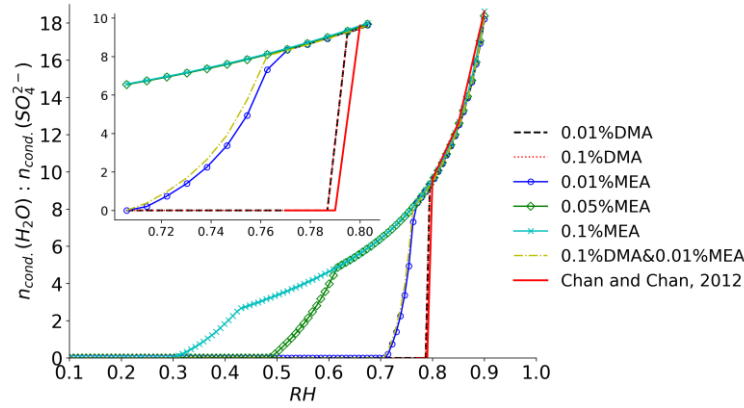


Figure 2. NA condensation and hygroscopicity of a chemical system of RNCs-sulfuric acid-nitric acid. (a) The moles of condensed nitrate against temperature with varying mol fraction of MEA at fixed initial water vapor of 0.07848 mol (equivalent to 60% RH at 263.15 K and 101,325 Pa in 1 m<sup>3</sup>). (b) the mole ratio of water and sulfate in the condensed phases at different RH with varying amine:ammonia mole ratios at 298K. The reference curve (red solid line) only has ammonium sulfate [Chan and Chan, 2012]. All curves have the same total moles of RNCs as  $8.86895 \times 10^{-8}$  and the same initial moles of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as  $1.11151 \times 10^{-9}$  and  $2.03777 \times 10^{-11}$ , respectively. The percentage in the legends refers to the initial mole fraction (mol %) of the amine(s) in the total RNCs.

In addition to  $T_c$ , deliquescence relative humidity (DRH) may also play an important role in the nucleation and growth of particles. The RH at a transition point, at which the water starts to condense on the particles, is referred as DRH. Generally, dry ammonium sulfate particles have a DRH  $\sim 79\%$ . While ammonium nitrate may uptake water vapor at much lower temperature, the condensation of ammonia and NA is likely hindered at room temperature [Wang et. al., 2020]. Figure 2b shows the water uptake by the condensed phases at 298 K in an ASN system with additional amines (DMA and MEA representing Group I and II RNCs, respectively). The chemical compositions of the RNCs and varying amine:ammonia mol ratios relevant to the atmosphere were investigated. In all cases, the sulfate all condensed as ammonium sulfate; therefore, the mol ratio of aqueous water to sulfate is directly proportional to the level of water uptake by the condensed phases. Since ammonia and NA do not

condense at 298 K in the system of ammonia-SA-NA, the DRH of the ASN system without amines is expected to be 79 % (the DRH of ammonium sulfate) [Chan and Chan, 2012]. Adding 0.01 % or 0.1 % mole fraction of DMA to the system only lowered the DRH by  $\sim 1$  %. However, the presence of only 0.01 mol % MEA can lower the DRH of the condensed phases to  $\sim 71$  % (Figure 2b, insert).

In contrast to the limited effects of DMA on particle DRH, MEA plays a significant role in lowering the DRH at high concentrations. For example, 0.1 mol % MEA can lower the DRH to 30 %, helping the particles absorb water in a relatively dry environment. These observations are consistent with the hygroscopic behavior of aminium cations in aqueous solutions [Qiu and Zhang, 2012; Clegg et al., 2013; Rovelli et al., 2017]. As shown in the Figure 2b insert, the system with 0.01 % MEA and 0.1 % DMA shows somewhat enhanced water uptake by the condensed phase than the cases with only 0.01 % MEA or 0.1 % DMA; however, the effect is limited and the presence of 0.01 % MEA was the main contributor to the lowered DRH. It seems that the effects of amines on the hygroscopicity of particles formed in the RNCs-SA-NA system are additive and dominated by Group II RNCs.

#### 4. Atmospheric Implications

Thermodynamic models are useful to evaluate how a chemical may condense on a particle since the feasibility of such process in the atmosphere is governed by the final physical and chemical equilibria of the system. To accurately estimate the impact of amine-assisted NA condensation during NPF, it would be ideal to use kinetic information on how fast amine and NA can condense on FNCs, which unfortunately is currently lacking for many of the amines in this study. However, several kinetic studies involving Density Function Theory (DFT) and Atmospheric Clusters Dynamic Code (ACDC) [Elm et al., 2020] have suggested that: (1) An 1:1 DMA-NA cluster appears to have a slightly lower kinetic energy barrier to form than that of ammonia and NA [Liu et al., 2018; Chee et al., 2019], suggesting that it will be faster to form DMA-NA clusters than the ammonium nitrate ones. Since recent laboratory experiments [Wang et al. 2020] demonstrated rapid ammonia and NA condensation at  $+5$  °C, it is reasonable to assume that DMA can also quickly condense with NA at a similar temperature. (2) MEA and PZ may form FNCs at a kinetic rate that is comparable or faster than that of DMA with SA [Xie et al., 2017; Ma et al., 2019]. Theoretical studies showed that gas-phase NA will undergo proton transfer reaction with hydroxyl radicals  $\sim 1000$  times faster than gaseous SA [Gonzalez and Anglada, 2010; Long et al., 2011], suggesting that the reactions between amines and NA (which will likely be a proton transfer reaction) will probably proceed no slower than those between amines and SA. Therefore, it is likely that MEA and PZ could condense with NA at a rate comparable to or faster than that of DMA with NA.

Our thermodynamic simulations suggest that there are two distinct groups of amines (Table 1): Group I with a low  $T_c$  of  $+5$  °C or below and Group II with a  $T_c$  of  $+15$  °C or above. Both groups may assist condensation of NA on nanoparticles under various ambient conditions and play an important role in the NPF, especially in polluted urban, agricultural and industrial areas.

At relatively low ambient temperatures ( $\sim -10$  °C to  $0$  °C), monoamines will likely condense with NA on particles, suggesting that the contribution of amines to NPF may be underestimated without the consideration of monoaminium nitrates. Considering the high ambient concentrations of monoamines, especially in some metropolitan centers, it is likely that monoamines will further contribute to NPF by facilitating the NA condensation at low temperature (e.g., during winter or near the top of the planetary

boundary layers) in addition to their assistance in forming FNCs. Low-temperature amines and NA condensation could be an additional pathway to consider when evaluating the lifetime of monoamines in the atmosphere.

In warmer weather conditions, on the other hand, all Group II amines may facilitate the growth of FNCs by assisting in the NA condensation regardless of their ambient concentrations, because such NA condensation did not appear to be affected by gaseous ammonia concentration in our simulations. This could be particularly important in heavily industrialized areas with significant manufacturing and/or applications of these amines (e.g., a power plant using MEA based CCS technology). Our results indicated that it is possible to consider all Group II amines together with one total concentration, which can then be used in Equation 1 in order to estimate their impact on NPF under specific atmospheric conditions for field and modeling studies.

When the temperature in the atmosphere changes relatively quickly in a short period of time, the contribution of Group II RNCs to NA condensation becomes more significant. Furthermore, our simulation results suggest that even at very low concentration, the condensed MEA and NA may facilitate the formation of a thin layer of solution at the particle surface [Hsiao et al., 2016]. Such modification to particle surface may change critical properties of the particles, including the viscosity [Shiraiwa et al., 2011], surface tension [Ovadnevaite et al., 2017] and Kelvin curvature effect [Zhang et al., 2012], surface uptake and heterogenous reactions [Kolb et al., 2011; Rossignol et al., 2016], hygroscopicity and CCN potentials [Lavi et al., 2013].

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