

Potential Enhancement in Atmospheric Nanoparticles Growth by Amine-Assisted Nitrate 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

The formation and aging of atmospheric aerosol are of critical importance in public health and the global climate. Recently laboratory experiments suggested rapid condensation of nitrate and ammonia during new particle formation events at low temperature. Amines are emitted into the atmosphere in large quantities from natural and anthropogenic sources. Using thermodynamic simulations, the contribution of amines to nitrate condensation into ambient nanoparticles at various temperature and relative humidity conditions was systematically evaluated. It is observed that monoamines will facilitate nitrate condensation at a low temperature comparable to ammonia, while those with additional hydrogen bonds (such as monoethanolamine and piperazine) showed the potential to condense nitrate at room temperature. The condensation of amines and nitrate could also lower the aerosol deliquescence point, possibly altering particle properties and aging. Our results suggest the potentially critical role of amines in ambient aerosol growth via nitrate condensation at a wide temperature range.

Plain Language Summary

There are many tiny liquid or solid nanoparticles suspended in the air and they are commonly referred as aerosol or particulate matters. It is important for us to know 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 is found to participate in the rapid condensation of nitrate salts and facilitate the formation of new aerosol particles at low temperature. Due to the similarities between ammonia and amines, we used thermodynamic simulations to investigate the contribution of amines to nitrate condensation into ambient nanoparticles at various temperature and relative humidity conditions. Simple amines may also enhance nitrate condensation just like ammonia at low temperature. Notably, amines with the ability to form additional hydrogen bonds may condense nitrate at room temperature. Aerosol condensed with amines and nitrate may absorb water even at low relative humidity, which may lead to distinctively different particle properties and climate effects. Our results indicate that amines could contribute significantly to ambient particle growth.

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 radiations, and serve the role 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 nanoparticles 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 on 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 leads to the NPF by forming freshly nucleated clusters (FNCs), often with the contributions from other chemicals, including ammonia, nitric acid [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 excessive particle coagulations with other particles [Smith et al. 2020]. Therefore, the growth mechanisms of FNCs are critical in understanding the formation and transformation of aerosol.

Ammonia and nitric acid are generally several orders of magnitude more concentrated than sulfuric acid in the atmosphere. Wang et al [2020] recently reported rapid ammonium nitrate condensation on FNCs at or below 278 K (+5 °C) in laboratory experiments using sulfuric acid, nitric acid and ammonia concentrations comparable to those commonly found in the urban atmosphere. This significant new result offers new insights into the potential contribution of a ternary ammonia-sulfuric acid-nitric acid (ASN) nucleation system 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 [Neilsen 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 ^f
Ammonia	NH ₃	NH ₃	$\times 10^5$		$\times 10^{-5}$	$\times 10^{-7}$		I
Methylaniline	MA		$\times 10^4 \ddagger$		$\times 10^{-4}$	$\times 10^{-8}$		I
Dimethylaniline	DMA		$\times 10^4 \ddagger$		$\times 10^{-4}$	$\times 10^{-8}$		I
Trimethylaniline	TMA		$\times 10^5$		$\times 10^{-5}$	$\times 10^{-6}$		I
Ethylamine	EA		$\times 10^5$		$\times 10^{-4}$	$\times 10^{-8}$		I
Diethylamine	DEA		$\times 10^4 \ddagger$		$\times 10^{-4}$	$\times 10^{-9}$		I
Triethylamine	TEA		$\times 10^3$		$\times 10^{-4}$	$\times 10^{-8*}$		I
Aniline	AN		$\times 10^1$		$\times 10^{-10}$	$\times 10^{-4}$		I
-	AN-		$\times 10^1$		$\times 10^{-10}$	-		I
Methylaniline	MA		$\times 10^1$		$\times 10^{-13}$	-		I
p-Nitroaniline	AN-N		$\times 10^{-2} \ddagger$		$\times 10^{-5}$	$\times 10^{-12*}$		II
Monoethanolamine	MEA		$\times 10^1$		$\times 10^{-5}$	-		II
Isobutanolamine	IBA		$\times 10^1$	-	$\times 10^{-5}$	-		II
Piperazine	PZ		$\times 10^2$		$\times 10^{-5}$	-		II

RNC name	Abbreviation	Chemical Structure	p_{sat}^a	GB^b	K_b^c	K_p^d	T_c^e	Group ^f
-	AN-O		×		×	-		II
Aminophenol			10^{-3}		10^{-10}			
Diethanoamine	DAE		×		×	×		II
Diglycol amine	DGA		10^{-2}		10^{-6}	10^{-13*}		
Diglycol amine			×	-	×	-		II
Diisopropylamine	DIPA		10^{-1}		10^{-6}			
Diisopropylamine			×	-	×	-		II
			10^{-1}		10^{-6}			

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

^b The gaseous basicity (in kJ mol⁻¹) at 298 K [Hunter and Lias, 1998].

^c The aqueous base hydrolysis constant (in mol kg⁻¹) of the amine at 298.15 K [Ge et al., 2011b].

^d The solid/gas equilibrium dissociation constant (in Pa²) of the nitrate salt of the amine at 298.15 K [Ge et al., 2011b].

^e The transitional temperature (in K) of nitrate condensation assisted with the amine, defined as the temperature at which the moles of condensed nitrate in the condensed phases equals to 5% of the initial moles of nitrate and determined in this study.

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

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

Since the salts of amines with nitric acid [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 aminium nitrates, at least at low temperature. Amines may, therefore, contribute to both the formation and growth of FNCs. Also, due to the complex chemical structures of amines observed in the atmosphere, it is uncertain whether the amine structures may play a significant 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 aminium nitrates under ambient conditions is also warranted.

In this study, the possible contribution of amines to the condensation of nitrate into 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 can condense nitrate at comparable temperature to ammonia. Much to our surprises, significant condensation of nitrate was observed, at room temperature, for amines that can form additional hydrogen bonding. 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 nitric acid into nanoparticles at a wide range of temperatures. Our results may be important in areas 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 between chemicals in solid, liquid and gas states under given initial boundary 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 each chemical. We used E-AIM models to evaluate the equilibrium state of a chemical system involving sulfuric acid, nitric acid, ammonia and amines under various conditions, including temperature, RH, and the amounts of the chemicals. 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 phase were aggregated together. For example, the moles of nitrate as ammonium nitrate solid and aqueous nitrate anion were reported together as the mole 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 was fixed at 101,325 Pa (1 atm). The typical initial moles of an RNC, sulfuric acid and nitric acid were 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} mol, respectively, corresponding to a mixing ratio of 1915 pptv RNC, 0.44 pptv sulfuric acid and 24 pptv nitric acid 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 8.86895×10^{-8} mol and the mol ratio of amine and ammonia varied. The initial moles of HNO_3 , H_2SO_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 sulfuric acid binary system

without any nitric acid showed the complete condensation of the sulfate into the solid phase as ammonium sulfate. The focus was then moved to a ternary RNC-sulfuric acid-nitric acid system, since nitric acid is in general always in large excess than sulfuric acid in the atmosphere. Figure 1a (black curve) shows that the ammonium nitrate, which was 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 ammonium nitrate 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 ammonium nitrate in such ternary system could only condense at or below 278 K.

Our simulations revealed the different temperature-dependence of the condensation of nitrate 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 nitrate into particle phase at low temperature (Figure 1a). For example, TMA and TEA showed very similar effects on the nitrate 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 nitric acid into the freshly formed particle phase.

To our surprise, amines with more complex functional groups, such as MEA, can facilitate the nitrate condensation process even at room temperature and higher (Figure 1a, open diamonds). Since ammonia is not likely to contribute to the nitrate condensation at these temperatures [Liu et al., 2018; Wang et al., 2020], our findings suggest that an environment polluted with MEA and nitric acid may experience particle growth due to the nitrate condensation facilitated by MEA. Further investigations on several other amines with additional $-\text{NH}_2$ or $-\text{OH}$ group(s) also showed significant nitrate condensation at room temperature (Figure 1b).

To further quantitatively describe the influences of ammonia and different amines on the condensation of nitrate, the transitional temperature of nitrate condensation (T_c), which is defined as the temperature at which the moles of nitrate in the condensed phases equals to 5% of the initial moles of nitrate, was identified and summarized in Table 1.

(a)

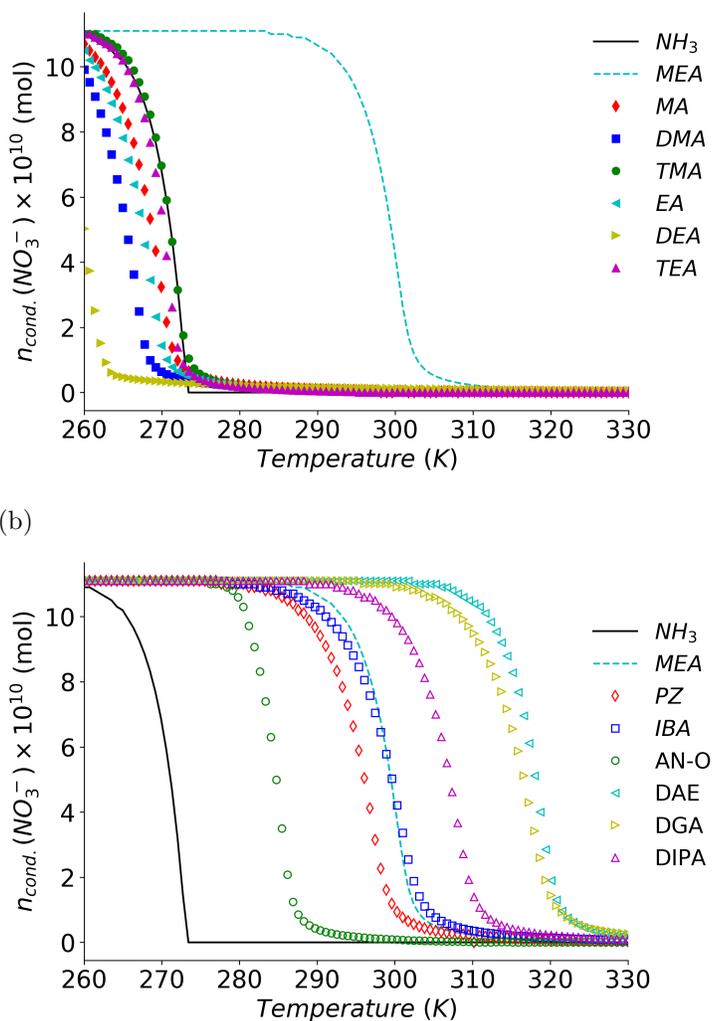


Figure 1. The moles of condensed nitrate against temperature in a ternary system of RNC-sulfuric acid-nitric acid at fixed initial mole of water vapor of 0.07848 mol (equivalent to 60% RH at 263.15 K and 101325 Pa in 1 m^3). All curves have the same initial moles of HNO_3 , H_2SO_4 and the RNC as 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} mol, 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).

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 stabilizing aminium nitrates in the condensed phase. Group I RNCs is hereby defined as those that will only

condense nitrate 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 nitrate at room temperature and enhance the new particle formation process by growing the critical clusters over the “valley of death” with excessive particle savaging.

To evaluate the Kelvin curvature effect [Zhang et al, 2012] on the condensation of RNC and nitrate, 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 nitrates in the presence of RNCs.

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) seem 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 ~ 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 the intermolecular 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 nitrate 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 by the presence of $-OH$ groups in the chemical structure.

Based on these observations, it is proposed that the chemical structures of RNCs, especially their ability to form additional hydrogen bonds, play a critical role on how RNCs may facilitate the condensation of nitrate on nanoparticles. Generally, the T_c value will increase significantly when a RNC can form more hydro-

gen bonds. MEA, PZ and IBA, with one additional hydroxyl or amine group than monoamines, have T_c values of ~ 300 K. DAE, DGA and DIPA with two additional hydrogen bonds, showed T_c values as high as 323 K (Table 1), allowing nitrate to condense at even higher 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 nitrate condensed and dissolved in the particle, greatly diminishing the condensation of nitrate 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).

Although Figure 1 and Table 1 well demonstrate the different effects of amines on the condensation of nitrate in an RNC-sulfuric acid- nitric acid ternary system, such high concentration of amines is not normally observed in the atmosphere, 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, sulfuric acid and nitric acid 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 condensation of nitrate by MEA is noticeable even at as low as 0.1 mol % (~ 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 S1):

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

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

In addition to the structures and concentrations of amines, amount of total water vapor is also another factor that may impact the condensation of nitrate. Our further investigation (Figure S2) suggested that increase in the total water vapor in the system will likely lead to an increase in T_c of the RNCs in the system, hence facilitating the condensation of nitrate. However, the enhancement is not as strong as other effects such as additional hydrogen bonding or hydrophobicity. Similar trend was observed by Chee et al. [2019] when they studied the nanoparticle formation and growth in a DMA and nitric acid system.

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 nitrate 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 nitrate does not condense at 298 K in the system of ammonia-sulfuric acid-nitric acid, 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 ~ 1 %. However, the presence of only 0.01 mol % MEA can lower the DRH of the condensed phases to ~ 71 % (Figure 2b, insert).

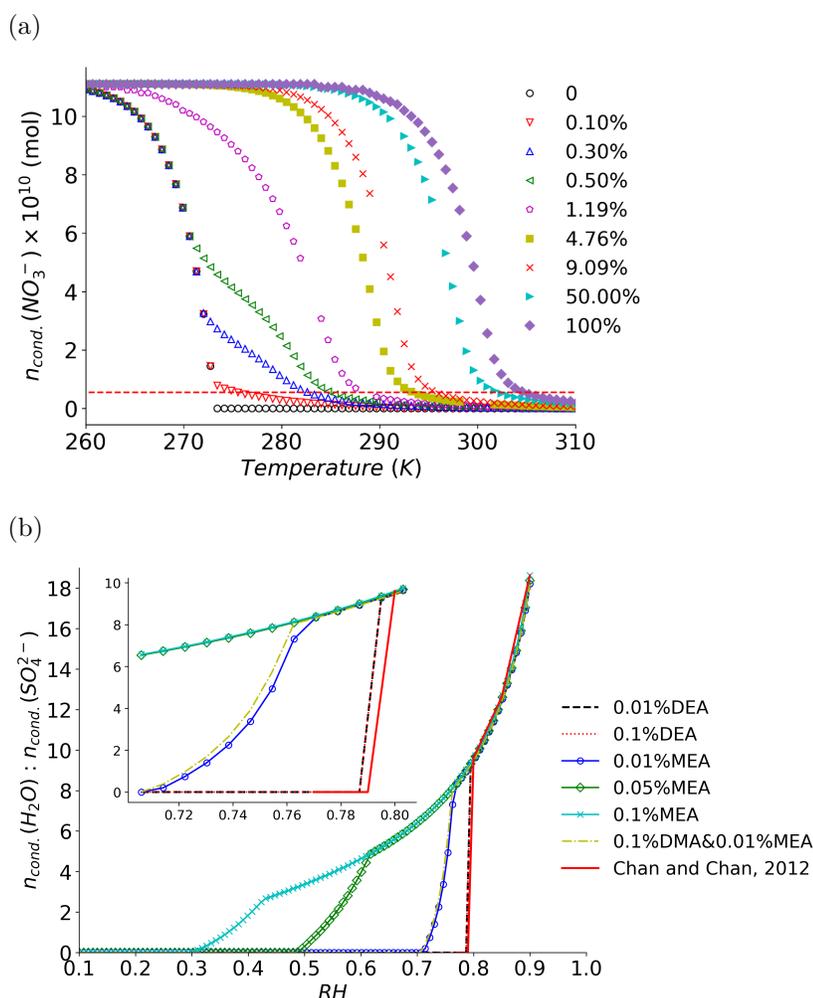


Figure 2. Nitrate condensation and hygroscopicity of a chemical system of RNCs-sulfuric acid-nitric acid. (a) The moles of condensed nitrate against temperature

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 m³). (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 8.86895×10^{-8} and the same initial moles of HNO₃ and H₂SO₄ as 1.11151×10^{-9} and 2.03777×10^{-11} , respectively. The percentage in the legends refers to the initial mole fraction (mol %) of the amine(s) in the total RNCs.

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 behaviors 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 showed somewhat enhanced water uptake by the condensed phase when compared to the individual amines; 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-sulfuric acid-nitric acid system are combinative and dominated by Group II RNCs.

4. Atmospheric Implications

Thermodynamic models are useful to evaluate the results of condensation into particle phase 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 nitrate condensation during NPF, it would be ideal to use kinetic information on how fast amine and nitric acid 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-nitric acid cluster appears to have a slightly lower kinetic energy barrier to form than that of ammonia and nitric acid [Liu et al., 2018; Chee et al., 2019], suggesting that DMA-NA clusters will likely be formed faster than the ammonium nitrate ones. Since recent laboratory experiments [Wang et al. 2020] demonstrated rapid condensation of ammonium nitrate at +5 °C, it is reasonable to assume that DMA can also quickly condense with nitric acid 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 sulfuric acid [Xie et al., 2017; Ma et al., 2019]. Theoretical studies showed that gas-phase nitric acid will undergo proton transfer reaction with hydroxyl radicals ~1000 times faster than gaseous sulfuric acid [Gonzalez and Anglada, 2010; Long et al., 2011], suggesting that the reactions between amines and nitric acid (which will likely be a proton transfer reaction) will probably proceed no slower than those between amines and sulfuric acid. Therefore, it is likely that MEA and PZ could condense with nitric acid at a rate comparable to or faster than that

of DMA with nitric acid.

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 nitrate into 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 (~ -10 °C to 0 °C), monoamines will likely condense with nitric acid into particle phase, 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 nitrate 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 nitrate 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 nitrate condensation regardless of their ambient concentrations, because such nitrate 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 as a single collective 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.

The complex weather conditions in the atmosphere may include scenarios when the temperature changes relatively quickly in a short period of time, in which the contribution of Group II RNCs to nitrate condensation will become more significant. Furthermore, our simulation results suggest that even at very low concentration, the condensed MEA and nitrate 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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models are openly available at <http://www.aim.env.uea.ac.uk/aim/aim.php>. The original data used for the table and figures in the study are available at Harvard Dataverse via <https://doi.org/10.7910/DVN/WZJBHU> with CC0 license.

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