

Removal of Atmospheric Monoethanolamine and Piperazine by Nitric Acid Assisted Condensation at Room Temperature

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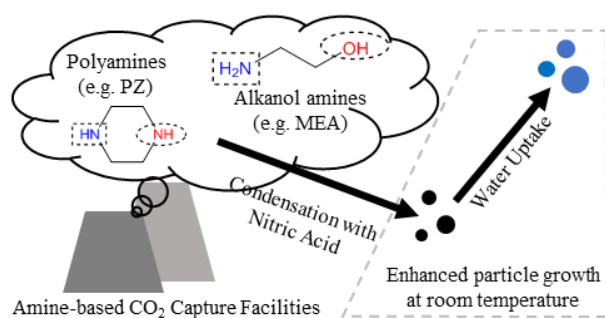
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Abstract

Monoethanolamine (MEA) and piperazine (PZ) are widely used industrial solvents for Post-Combustion Carbon Capture (PCCC) technology and their emissions into the atmosphere may increase significantly when amine-based PCCC units are implemented on a large, global scale. Recent laboratory experiments showed that ammonia may condense rapidly with nitric acid on freshly formed new clusters at low temperatures. Using thermodynamic simulations, the condensation of alkylamines, MEA and PZ with nitric acid at various temperatures was systematically evaluated. Alkylamines appeared to condense with nitric acid at temperatures comparable to that of ammonia. However, with an additional hydrogen bonding group than ammonia, MEA and PZ condensed with nitric acid at room temperature, suggesting a new potential pathway to remove these amines from the atmosphere, especially since such removal process appeared to be independent of the ambient ammonia concentration. Our results suggest the potentially critical role of MEA and PZ in the atmospheric new particle formation via condensation with nitric acid to rapidly grow freshly nucleated clusters over their critical size at a higher temperature than ammonia. The condensed amines and nitric acid can also facilitate water uptake at low relative humidity by aerosol particles, which may alter their subsequent atmospheric transformations.

Graphic for Table of Contents (TOC)/Abstract Art (3.25 by 1.75 in)



Keywords and Synopsis

- Nitric acid can condense on nanoparticles with amines with additional hydrogen bonding ability, such as monoethanolamine (MEA) and piperazine (PZ) at room temperature, much higher than with ammonia
- Alkylamines will condense with nitric acid near 273 K, comparable to ammonia.
- Particles condensed with amines and nitric acid may absorb water at low relative humidity to influence their subsequent atmospheric aging

The abstract, figure captions, TOC art, acknowledgments, and references are not included in the word count.

Appendix 2: Preparing Graphics

Resolution

Digital graphics pasted into manuscripts should have the following minimum resolutions:

Black and white line art, 1200 dpi

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Size

Graphics must fit a one- or two-column format. Single-column graphics can be sized up to 240 points wide (3.33 in.) and double-column graphics must be sized between 300 and 504 points (4.167 in. and 7 in.). The maximum depth for all graphics is 660 points (9.167 in.) including the caption (allow 12 pts. For each line of caption text). Lettering should be no smaller than 4.5 points in the final published format. The text should be legible when the graphic is viewed full-size. Helvetica or Arial fonts work well for lettering. Lines should be no thinner than 0.5 point.

Introduction

Amines are emitted into the atmosphere in large quantities from nature sources and anthropogenic activities.^{1–3} Ambient amine concentrations are generally at a parts per trillion (ppt) level and at least 1–2 orders of magnitude lower than that of ammonia;⁴ Methylamine (MA) and Dimethylamine (DMA) are two representative alkylamines commonly found in ambient gas and particle phases.² Ammonia and amines are hereby collectively referred as reduced nitrogen compounds (RNCs) and their properties are summarized in Table S1.

A significant source of anthropogenic amines is chemical absorption Post-Combustion Carbon Capture (PCCC) technology using monoethanolamine (MEA), piperazine (PZ) and other alkanolamines.⁵ While a large-scale application of amine-based PCCC units can effectively mitigate the raising ambient CO₂ level and the trends in climate change,⁶ such industrial application of amines will inevitably increase their emissions into the atmosphere.⁷ It is estimated that 80 tons of gaseous MEA will be emitted into the atmosphere by a PCCC plant removing one million tons of CO₂ annually.⁸ In some extreme cases, the near-source ambient MEA concentrations can be comparable to that of ammonia⁹ and reach to parts per million (ppm) level.¹⁰

Previous studies suggested several possible pathways for the removal of anthropogenic amines such as MEA and PZ, including gas-phase oxidation¹¹ that may lead to potentially hazardous products of nitramine and nitrosamine,¹² new particle formation (NPF) and growth events involving sulfuric acid (SA),^{13–15} and heterogenous uptake by the acidic constituents in atmospheric aerosol.^{10,16,17}

Recent laboratory experiments reported rapid ammonia and nitric acid (NA) condensation on freshly nucleated clusters (FNCs) at or below 278 K (+5 °C) using ammonia, SA and NA concentrations comparable to those commonly found in the urban atmosphere, offering new insights into a ternary RNC, SA and NA nucleation system under cold weather conditions.¹⁸ Since the nitrates of alkylamines and MEA showed better thermal stability than that of ammonium nitrate,¹⁹ it is conceivable that the cluster growth in a ternary amine-SA-NA system can be enhanced by amine and NA condensation. Anthropogenic amines such as MEA and PZ may, therefore, be removed by gas-phase NA, especially near their emission sources (such as PCCC units).

In this study, the condensation removal of amines with NA on nanoparticles was investigated using Extended Aerosol Inorganics Models (E-AIM)^{20,21} under conditions that are typically found in the atmosphere, especially in an urban environment. Our results showed that alkylamines can condense with NA at a comparable temperature to ammonia. Interestingly, significant condensation of MEA and PZ with NA was observed at room temperature, as well as other industrial alkanolamines that can form additional hydrogen bonds. Such process seems to be unaffected by the presence of excess ammonia. Our results suggest that amines may be removed from the atmosphere by co-condensing with NA on nanoparticles in a wide range of temperatures. Such condensation may contribute to NPF by assisting the growth of FNCs into a critical diameter (of several nanometers) to avoid being scavenged by coagulation with other particles.²² Our results may be important in regions commonly polluted with amine emissions, such as megacities, agricultural lands and heavily industrialized areas.

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. E-AIM solves these equations numerically and predicts all possible phases (gas, aqueous and organic solutions, and solid) and distributions of a chemical in these phases (Text

S1). We used E-AIM to evaluate the equilibrium state of a chemical system involving SA, NA, ammonia and amines under varying temperatures (260 K to 330 K, or $-13\text{ }^{\circ}\text{C}$ to $57\text{ }^{\circ}\text{C}$), relative humidity (RH, 10% to 90%), and initial moles of the chemicals. The total pressure and volume were fixed at 101,325 Pa and 1 m^3 , respectively. The typical initial moles of NA, SA and an RNC were 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} , respectively, corresponding to a mixing ratio of 24 pptv NA, 0.44 pptv SA and 1915 pptv RNC at 60 % RH, 263.15 K, and 101,325 Pa. These values were chosen to represent typical atmospheric compositions in polluted megacities.¹⁸

Detailed descriptions and justifications of the simulation parameters can be found in Text S2–S5. Several chemicals in this study have multiple forms in condensed phases. For example, NA may exist in an aqueous solution as a free acid and a nitrate anion. Since the primary interest of this study is the distribution of a chemical in gas and condensed phases, the moles of all forms of a chemical in all condensed phases were aggregated together. For example, the total moles of NA as free acid and nitrate were reported together as the moles of condensed NA, $n_{\text{cond.}}(\text{NO}_3^-)$.

Results and Discussion

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. In a ternary system of ammonia-SA-NA, ammonia and NA (Figure 1a) can condense into particle phase when the temperature is low enough (below $\sim 273\text{ K}$). As the temperature decreases, more and more condensed ammonia and NA will exist in condensed phase. This prediction is consistent with experimental findings¹⁸ that ammonia and NA in such ternary system could only condense at or below 278 K.

Our simulations on a ternary system of alkylamine, SA and NA suggested that alkylamines such as MA and DMA condensed with NA at about 270 K, similar to that of ammonia (Figures 1a and S1a). The concentrations of alkylamines can be significant in urban and coastal environment from anthropogenic and biogenic emissions and may therefore contribute to NPF events in cold weather by facilitating the condensation of available gaseous NA on the FNCs.

Interestingly, alkanolamines such as MEA can condense with NA at room temperature (Figures 1a and S1b), suggesting its potential contribution to NPF under warmer weather conditions. Since ammonia is not likely to contribute to the NA condensation at room temperature,^{18,23} our findings suggest that gaseous MEA may contribute to NPF and be effectively removed by NA even in the presence of ammonia, especially at room temperature. Such observation is not limited to alkanolamines: PZ with two amine groups can also condense with NA at room temperature (Figure 1a).

In our simulations, the limiting reagents of the condensation process are the acids in the system. The moles of condensed RNC did not exceed those of condensed sulfate (fixed in all cases) and nitrate. Therefore, condensed nitrate directly reflects the amount of condensed RNC in the particle phase. To quantitatively describe the condensation of RNCs, the transitional temperature of 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 S1, along with the estimated uncertainties (Text S6, Figure S2 and Table S2).

Alkylamines commonly found in the atmosphere all showed T_c values ranging from 263 K to 275 K, similar to that of ammonia and implying the limited contribution of alkyl groups in the condensation of alkylamines with NA. 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 NA-assisted condensation may serve as a potentially significant removal process for Group II RNCs (e.g., MEA and PZ), especially in warmer weather. Group II amines in the atmosphere may also greatly facilitate the NPF by condensing with NA at room temperature to grow the critical clusters over the “valley of death” with excessive particle savaging.

Further analysis between the T_c and the physical and chemical properties (Table S1) of RNCs in this study suggested that the T_c of an RNC is not significantly influenced by the gaseous basicity (GB) or aqueous basicity (K_b) of the RNC, the volatility of the RNC or its nitrate salt (p_{sat} and K_p , respectively), Van der Waals forces, the electron affinity or the hydrophobicity of the functional groups on the RNC (Text S7).

One distinctive observation is that Group I RNCs can form only one hydrogen bond while Group II RNCs can form two or more (Table S1), suggesting that additional hydrogen bonding can significantly increase the temperature at which an RNC may condense with NA. For example, MEA and PZ can form two hydrogen bonds and have T_c values of ~ 300 K. Alkanolamines that can form three hydrogen bonds, commonly used as industrial chemicals, showed T_c values as high as 323 K (Table S1), allowing condensation with NA above room temperature.

To evaluate the Kelvin curvature effect¹⁵ 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 RNCs and NA.

Although Figure 1a well demonstrated the condensation of amines and NA in a wide range of temperatures, ambient amine concentrations vary significantly with the constant presence of ammonia. The ambient concentration of amines is usually 1–2 orders of magnitude lower than that of ammonia, but the amine:ammonia mol ratio could be as high as 1:1 near a power-plant using PCCC technology. As a result, a chemical system of ammonia, MEA, SA and NA with varying MEA:ammonia mol ratios was investigated. Figure 1b illustrated the additional condensation of nitrate as a result of added MEA. The enhancement in NA condensation was noticeable with as low as 0.1 mol % added MEA (~ 2 pptv). It appeared that as the mole fraction of MEA increases, the T_c increases following an excellent linear relationship (Figure S3):

$$T_c = -10.872 \times \log(\text{MEA}\%) + 308.74 \quad (1)$$

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

In addition to the structures and concentrations of amines, amount of total water is another factor that may impact the condensation of amines and NA. The condensation of DMA and NA was enhanced by the presence of water in a recent DMA-NA nucleation study.²⁴ Our further investigation suggested that an increase in the total water vapor in the RNC-SA-NA system led to an increase in T_c , hence facilitating the condensation of amine and NA at a higher temperature (Figure S4). However, the enhancement was not as strong as additional hydrogen bonding.

In addition to T_c , the onset RH at which aerosol starts to uptake water vapor may also play an important role in the formation and growth of nanoparticles. While ammonium nitrate may uptake water vapor at low RH, the condensation of ammonia and NA is likely hindered at room temperature.¹⁸ Therefore, an ammonia-SA-NA system without amines is expected to start absorbing water vapor at about 79% RH like ammonium sulfate.²⁵ The onset RH of water uptake by the condensed phases at 298 K was systematically evaluated in an ammonia-SA-NA system with additional DMA and MEA (representing Group I and II RNCs, respectively) and varying amine:ammonia mole ratios (Figure 2). In all cases, all the sulfate condensed as ammonium sulfate; therefore, the mol ratio of condensed water to sulfate is directly proportional to the

moles of condensed water.

Adding 0.01 or 0.1 mol % of DMA (in the total moles of all RNCs) to the system only promoted water uptake at a slightly lower RH (~78.5%). In contrast, MEA played a significant role in lowering the onset RH of water uptake by the condensed phases. For example, the presence of 0.01 and 0.1 mol % of MEA lowered the onset RH to ~71 % and 30 %, respectively (Figure 2), facilitating the water uptake by the condensed phases in a dry environment. These observations are consistent with the hygroscopic behavior of aminium (especially MEA) cations in aqueous solutions.^{10,26–28} The system with 0.01 mol % MEA and 0.1 mol % DMA showed somewhat enhanced water uptake by the condensed phases than the cases with only MEA or DMA (Figure 2, insert); however, the effect was limited and the presence of MEA was the main contributor to the lowered onset RH. It seems that the enhancement of particle hygroscopicity in an RNCs-SA-NA system is additive of the contributions from the RNCs in the system and dominated by Group II RNCs.

Atmospheric Implications

Thermodynamic models are useful to evaluate how anthropogenic amines such as MEA and PZ may condense with NA on atmospheric particles since the feasibility of such process in the atmosphere is governed by the final physical and chemical equilibria of the system. Our simulations suggest that there are two distinct groups of amines (Table S1): Group I with a 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 contribute to NPF in addition to their assistance in forming FNCs,^{13–15} especially in polluted urban, agricultural and industrial areas.

Several kinetic studies involving Density Function Theory (DFT) and Atmospheric Clusters Dynamic Code (ACDC)²⁹ showed that: (1) DMA and NA will form a 1:1 cluster at a slightly lower kinetic energy barrier than that of ammonia and NA,^{23,24} suggesting that DMA-NA clusters will form faster than ammonia-NA ones. Since recent laboratory experiments demonstrated rapid ammonia and NA condensation at +5 °C,¹⁸ it is reasonable to assume that DMA and NA can condense with a similar kinetic rate at a comparable temperature. (2) MEA and PZ may form clusters with SA at a kinetic rate that is comparable or faster than that of DMA,^{30,31} suggesting that the condensation of MEA or PZ with NA will probably proceed no slower than that between DMA and NA. Such deduction is further supported by the substantially lower saturation vapor pressure of MEA nitrate compared to that of ammonium nitrate. We can therefore estimate the removal of MEA by condensation with NA to be 0.6–60 times that of oxidation by hydroxyl radical (Text S8), suggesting an alternative explanation to some field observations of unexpected abundant MEA in ambient nanoparticles.^{32,33}

Our estimations suggest a potentially significant removal pathway of Group II amines by condensation with NA in the atmosphere at room temperature regardless of ambient ammonia concentration. Since most amines in Group II are anthropogenic alkanol amines (MEA) and polyamines (PZ), our results offer an additional pathway to consider when evaluating the ambient lifetime of industrial amines, especially under warmer weather conditions. This could be particularly important in areas with PCCC units using MEA or PZ. Our results also indicated that it is possible to aggregate the quantities of all Group II amines into a single mole fraction parameter to identify their maximum condensation temperature with NA for field and modeling applications.

Furthermore, our results suggest that even at very low concentrations, the condensed MEA and NA may facilitate the water uptake by aerosol to form a thin layer of solution at the particle surface.³⁴ Such modification to the particle surface may

change critical properties of aerosol, including the viscosity,³⁵ surface tension³⁶ and Kelvin curvature effect,¹⁵ surface uptake and heterogeneous reactions,^{37,38} hygroscopicity^{10,28} and CCN potentials.³⁹

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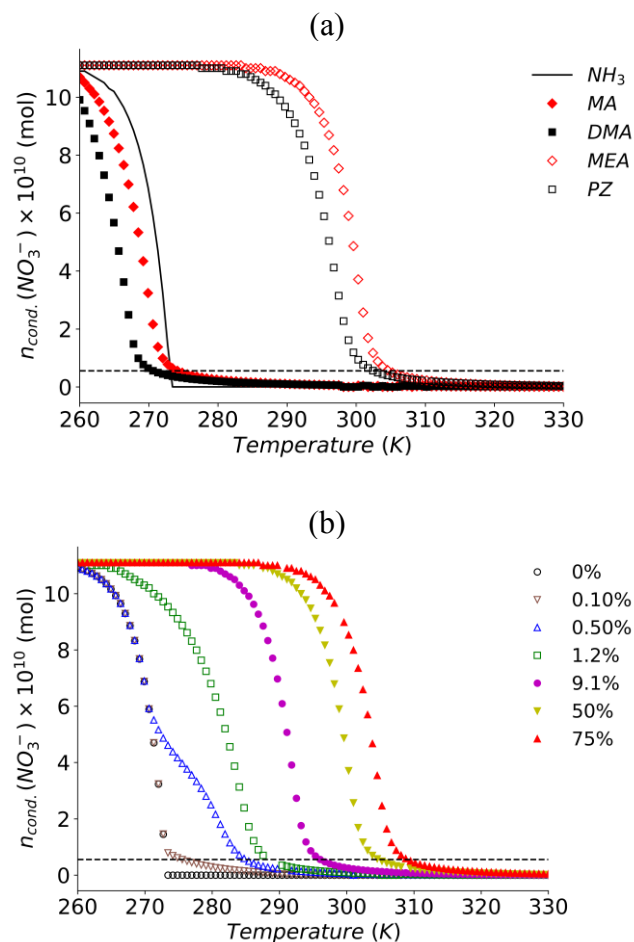


Figure 1. (a) The moles of condensed nitrate against temperature in a ternary system of RNC-sulfuric acid-nitric acid. All curves have the same initial moles of HNO_3 , H_2SO_4 and the RNC as 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} , respectively. The legend indicates which RNC is present in each trace. (b) The moles of condensed nitrate against temperature in an ammonia-MEA-sulfuric acid-nitric acid chemical system with varying mole ratios of ammonia and MEA. All curves have the same initial moles of HNO_3 , H_2SO_4 and ammonia as 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} , respectively. The legend indicates the initial mole fraction (mol %) of the MEA in the total moles of RNCs in each trace. In both panels, the initial water vapor was fixed at 0.07848 mol (equivalent to 60% RH at 263.15 K and 101,325 Pa in 1 m^3).

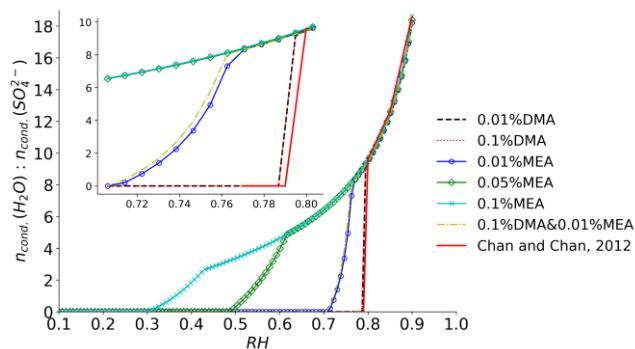


Figure 2. Hygroscopicity of a chemical system of RNCs-sulfuric acid-nitric acid at 298 K. The y-axis is the mole ratio of water and sulfate in the condensed phases. Difference traces represent the varying initial amine:ammonia mole ratios. All curves have the same total moles of RNCs as 8.86895×10^{-8} and the same initial moles of HNO_3 and H_2SO_4 as 1.11151×10^{-9} and 2.03777×10^{-11} , respectively. The reference curve (red solid line based on Ref. 25) only has ammonium sulfate. The legend indicates the initial mole fraction (mol %) of the amine(s) in the total RNCs in each trace.