Potential Enhancement in Atmospheric Nanoparticles Growth by Amine-Assisted Nitrate Condensation at Room Temperature

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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.

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

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Abstract Atmospheric aerosol plays a critical role in global climate and public health. Recent 18 19 laboratory experiments showed that new particle formation is significantly enhanced by rapid condensation of nitric acid and ammonia at low temperatures. Amines are 20 derivatives of ammonia with a significant presence in the atmosphere. For example, the 21 22 wide implementation of amine-based Post-Combustion Carbon Capture (PCCC) units may significantly increase the ambient alkanolamine and polyamine levels. Using 23 thermodynamic simulations, the condensation of alkylamines, alkanolamines and 24 polyamines with nitric acid at various temperatures was systematically evaluated. 25 Alkylamines will condense with nitric acid at temperatures comparable to that of 26 ammonia. However, with additional hydrogen bonding groups, alkanolamines and 27 polyamines may condense with nitric acid at room temperature, suggesting a new 28 potential pathway to remove these amines from the atmosphere. Our results suggest the 29 potentially critical role of amines in the atmospheric new particle formation via 30 condensation with nitric acid to rapidly grow freshly nucleated clusters over their 31 critical size at a higher temperature than ammonia. The condensed amines and nitric 32 acid can also facilitate water uptake by aerosol particles at low relative humidity, which 33 may alter their subsequent atmospheric transformations. 34

35 Highlights:

- Nitric acid can condense on nanoparticles with amines at a comparable or higher 36 • 37 temperature than with ammonia Amines with additional hydrogen bonding ability can condense with nitric acid 38 ٠ 39 at room temperature Condensation of nitric acid and amines can grow freshly nucleated clusters 40 ٠ significantly to facilitate new particle formation at various temperatures 41 Condensation with nitric acid can be a significant removal pathway for amines, 42 •
 - Condensation with nitric acid can be a significant removal pathway for amines, especially those with two or more hydrogen bonds
- Particles condensed with amines and nitric acid may absorb water at low relative
 humidity to influence their subsequent atmospheric aging
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48 **Graphics Abstract Art**

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53 Keywords:

new particle formation, atmospheric cluster growth, room-temperature nitrate condensation, atmospheric amines, amine-based post-combustion carbon capture,

56 aerosol hygroscopicity

57 **1. Introduction**

Amines are emitted into the atmosphere in large quantities from natural sources 58 and anthropogenic activities (Qiu and Zhang, 2013; Cape et al., 2011; Ge et al., 2011a). 59 Ambient amine concentrations are generally at a parts per trillion (ppt) level and at least 60 1-2 orders of magnitude lower than that of ammonia (Yli-Juuti et al., 2013); 61 Methylamine (MA) and Dimethylamine (DMA) are two representative alkylamines 62 commonly found in ambient gas and particle phases (Cape et al., 2011). A significant 63 source of anthropogenic amines is chemical absorption Post-Combustion Carbon 64 Capture (PCCC) technology using alkanolamines (e.g. monoethanolamine, MEA) and 65 polyamines (e.g. piperazine, PZ) (Chao et al., 2021). While a large-scale application of 66 amine-based PCCC units can effectively mitigate the raising ambient CO₂ level and the 67 trends in climate change (Nielsen et al, 2012), such industrial application of amines will 68 69 inevitably increase their emissions into the atmosphere (Reynolds et al. 2012). It is estimated that 80 tons of gaseous MEA will be emitted into the atmosphere by a PCCC 70 unit removing one million tons of CO₂ annually (Sharma et al, 2014). In some extreme 71 cases, the near-source ambient MEA concentrations can be comparable to that of 72 73 ammonia (Scottish EPA, 2015) and reach to parts per million (ppm) level (Tian et al., 2022). Previous studies suggested several possible pathways for the removal of 74 atmospheric amines, including gas-phase oxidation (Møller et al, 2020) that may lead 75 76 to potentially hazardous products of nitramine and nitrosamine (Nielsen et al., 2011), new particle formation (NPF) and growth events involving sulfuric acid (SA) (Kürten 77 et al., 2019; Yao et al., 2018; Almeida et al., 2013; Zhang et al., 2012), and heterogenous 78 79 uptake by the acidic constituents in atmospheric aerosol (Tian et al., 2022; Qiu et al., 2011; Wang et al., 2010). Ammonia and amines related to this study are collectively 80 referred as reduced nitrogen compounds (RNCs) and their properties are summarized 81 82 in Table 1.

Nitric acid (NA), directly emitted from natural and anthropogenic sources and 83 produced from gas-phase photochemical processes (Mezuman et al., 2016; Fairlie et al., 84 2010; Brown et al., 2006), has a significant presence in the atmosphere as high as 10^{12} 85 cm⁻³ (Kumar et al., 2018b; Acker et al., 2005; Aloiso and Francisco et al., 1999) in 86 some polluted areas (Ding et al., 2019; Zhang et al., 2018). Recent laboratory 87 experiments reported rapid ammonia and nitric acid (NA) condensation on freshly 88 nucleated clusters (FNCs) at or below 278 K (+5 °C) using ammonia, SA and NA 89 concentrations comparable to those commonly found in the urban atmosphere, offering 90 new insights into a ternary RNC, SA and NA nucleation system under cold weather 91 92 conditions (Wang et al., 2020).

Since the nitrates of alkylamines and MEA showed better thermal stability than 93 that of ammonium nitrate (Salo et al., 2011), it is conceivable that the cluster growth in 94 a ternary amine-SA-NA system can be enhanced by amine and NA condensation. The 95 reaction kinetics between several RNCs and NA were investigated in the gas phase 96 (Chee et al., 2019; Kumar et al., 2018a) using the Density Function Theory (DFT) and 97 Atmospheric Clusters Dynamic Code (ACDC) (Elm et al., 2020). Several pathways for 98 the RNC and NA to co-condense and facilitate cluster growth were discovered and they 99 are thermodynamically preferred at lower temperature (The formation equilibrium 100 constants of 1:1 RNC-NA cluster at 270 K were 8-15 times higher than those at 298 K) 101 and depend strongly on the RH of the system. Theoretical simulations on the 102 condensation of RNCs and NA at the air-water interface (Kumar et al., 2018a) 103 104 suggested an interesting contribution of the hydrogen bond between the RNC and water to facilitate the cluster formation at the interface. Liu et al. (2021) demonstrated that 105

adding the pathway of FNC growth due to DMA and NA co-condensation to the current
 simulation model can bring closure between theoretical prediction involving only the
 DMA-SA nucleation and field measurement results in polluted areas in the winter time
 (~280 K). Anthropogenic alkanolamines and polyamines from industrial processes,
 such as MEA and PZ widely used in PCCC, may, therefore, also be removed by gas phase NA and contribute to the growth of FNCs and ambient nanoparticles, especially
 near their emission sources (such as PCCC units).

In this study, the condensation removal of amines with NA on nanoparticles was 113 investigated using Extended Aerosol Inorganics Models (E-AIM) (Ge et al., 2011b; 114 Wexler and Clegg, 2002) under conditions that are typically found in the atmosphere, 115 especially in an urban environment. Our results showed that alkylamines can condense 116 with NA at a comparable temperature (~273 K) to ammonia. Interestingly, significant 117 118 condensation of MEA and PZ with NA was observed at room temperature (298 K), as well as other industrial alkanolamines that can form two or more hydrogen bonds. Such 119 process seems to be unaffected by the presence of excess ammonia. Our results suggest 120 that amines may be removed from the atmosphere by co-condensing with NA on 121 122 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) 123 to avoid being scavenged by coagulation with other particles (Smith et al., 2020). Our 124 125 results may be important in regions commonly polluted with amine emissions, such as megacities, agricultural lands and heavily industrialized areas. 126

127128 2. Method

129 **2.1 Overview.**

The Extended-Aerosol Inorganics Model (E-AIM) considers the partitions of a particular chemical in four phases: gas (g), solid (s, including its salts), aqueous solution (aq) and hydrophobic organic solution (org) at any given relative humidity and temperature in a fixed total volume of 1 m³ and at a fixed total pressure of 101,325 Pa. The E-AIM model (http://www.aim.env.uea.ac.uk/aim/aim.php) allows the users to specify the initial concentration of the chemical (as moles in 1 m³), as well as instructions regarding the properties and activity of the chemical.

In this study, for example, the following series of state equations are possible for
 MEA (with its conjugated acid labeled as MEAH⁺):

139
$$MEA(g) \rightleftharpoons MEA(aq)$$
 Eq. 1

140
$$MEA(aq) + H^+(aq) \rightleftharpoons MEAH^+(aq)$$
 Eq. 2

141
$$MEAH^+(aq) + NO_3^-(aq) \rightleftharpoons MEA \cdot HNO_3(s)$$
 Eq. 3

142
$$MEA \cdot HNO_3(s) \rightleftharpoons MEA(g) + HNO_3(g)$$
 Eq. 4

143
$$2MEAH^+(aq) + SO_4^{2-}(aq) \rightleftharpoons 2MEA \cdot H_2SO_4(s) \qquad \text{Eq. 5}$$

144
$$2MEA \cdot H_2SO_4(s) \rightleftharpoons MEA(g) + H_2SO_4(g)$$
 Eq. 6

Each of the equation above involves an equilibrium constant *K* that is temperature dependent and may have been determined experimentally or can be derived using other thermodynamic properties of MEA.

149 **2.2 Application of E-AIM on RNC–SA–NA System.**

We used E-AIM to evaluate the equilibrium state of a chemical system involving 150 SA, NA, ammonia and amines under varying temperatures (260 K to 330 K, or -13 °C 151 to 57 °C), relative humidity (RH, 10% to 90%), and initial moles of the chemicals. The 152 total pressure and volume were fixed at 101,325 Pa and 1 m³, respectively. The typical 153 initial moles of NA, SA and an RNC were 1.11151×10⁻⁹, 2.03777×10⁻¹¹ and 154 8.86895×10^{-8} , respectively, corresponding to a mixing ratio of 24 pptv NA, 0.44 pptv 155 SA and 1915 pptv RNC at 60 % RH, 263.15 K, and 101,325 Pa. These values were 156 chosen to represent typical atmospheric compositions in polluted megacities (Wang et 157 158 al., 2020).

All possible states for water (g, aq and s) are considered by the E-AIM. However, 159 160 in this study, low temperatures at which the water may start to freeze were avoided. The 161 autoprotolysis of water and both hydrolysis equilibria of the inorganic diacid H_2SO_4 are also considered to include H⁺, HSO₄⁻ and OH⁻ concentrations in the calculations. The 162 protonation of ammonia and the formation of ammonium nitrate and sulfate solids are 163 164 considered in our simulations to represent the partition of ammonia in aqueous solution and solid phases as accurately as possible. Since NH_4^+ , SO_4^{2-} and NO_3^- are the 165 primarily inorganic ions of consideration, E-AIM Model II was used throughout our 166 study. Thermodynamic data on ammonia and its nitrate and sulfate salts have been 167 extensively studied and their thermodynamic properties and constants are relatively 168 well established (Wexler and Clegg, 2002) Therefore, default inputs (including the 169 methods to estimate activities) in the existing E-AIM Model II on ammonia, sulfuric 170 acid and nitric acid are used without further modification. Detailed descriptions and 171 justifications of the simulation parameters can be found in Section 4.1. 172

173 Several chemicals in this study have multiple forms in condensed phases. For 174 example, NA may exist in an aqueous solution as a free acid and a nitrate anion. Since 175 the primary interest of this study is the distribution of a chemical in gas and condensed 176 phases, the moles of all forms of a chemical in all condensed phases were aggregated 177 together. For example, the total moles of NA as free acid and nitrate were reported 178 together as the moles of condensed NA, n_{cond} (NO₃⁻).

179180 3. Results

Our E-AIM simulation on ammonia and SA binary system showed the complete 181 condensation of the sulfate into the solid phase as ammonium sulfate. In a ternary 182 183 system of ammonia-SA-NA, ammonia and NA (Figure 1a) can condense into particle phase when the temperature is low enough (273 K and below). Wang et al. (2020) 184 identified that ammonia and nitric acid in the ammonia-sulfuric acid-nitric acid ternary 185 system could only condense at or below 278 K, but above 263 K, suggesting that our 186 simulation results on the ammonia-SA-NA ternary system should have an uncertainty 187 within the range of -3.8% to +1.7%. 188

Our simulations used initial ammonia, SA and NA concentrations significantly exceeding the saturation vapor pressure of ammonium sulfate and nitrate (Wang et al., 2020; Liu et al., 2018; Ge et al., 2011b). As the temperature decreases, more and more condensed ammonia and NA will exist in condensed phase. This prediction is consistent with experimental findings that ammonia and NA in such ternary system could only condense at or below 278 K (Wang et al., 2020).

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Figure 1. The moles of condensed nitrate against temperature in a ternary system of RNCsulfuric 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 m³). All curves have the same initial moles of HNO₃, H₂SO₄ and the RNC as 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-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).

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). 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 215 temperature (Figures 1b), suggesting its potential contribution to NPF under warmer 216 weather conditions. Since ammonia is not likely to contribute to the NA condensation 217 218 at room temperature (Wang et al., 2020; Liu et al., 2018), our findings suggest that 219 gaseous MEA may contribute to NPF and be effectively removed by NA even in the 220 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 221 222 temperature (Figure 1b).

In our simulations, the initial amines and NA concentrations should significantly exceed the saturation vapor pressures of aminium nitrate which are expected to be no

more than that of ammonium nitrate (Salo et al., 2011). It is also noted that in our 225 simulations the limiting reagents of the condensation process are the acids in the system. 226 The moles of condensed RNC did not exceed those of condensed sulfate (fixed in all 227 cases) and nitrate. Therefore, condensed nitrate directly reflects the amount of 228 condensed RNC in the particle phase. To quantitatively describe the condensation of 229 RNCs and nitrate, the transitional temperature of condensation (T_c) , which is defined 230 as the temperature at which the moles of total nitrate in the condensed phases equal to 231 5% of the initial moles of NA, was identified and summarized in Table 1, along with 232 the estimated uncertainties. Our methods to estimate these uncertainties are presented 233 in Section 4.1, Figure 2 and Table 2. 234

236 4. Discussion

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237 **4.1 Estimation of Uncertainties.**

238 4.1.1 Effects of the Saturation Vapor Pressure of Amines.

Data on the saturation vapor pressure (p^0) of an amine at various temperatures are 239 needed to accurately describe its distribution between gaseous and condensed phases. 240 However, comprehensive and high-quality experimental data on p^0 of amines are not 241 always available. Ge et al. (2011b) systematically evaluated the available experimental 242 data and several theoretical vapor pressure calculation models for amines and 243 concluded that the method by Moller et al. (2008) provides the best estimations. 244 Alkanolamines, such as MEA, showed the largest difference in calculated and measured 245 vapor pressure values (up to a factor of 3.56 times). Such discrepancy was much smaller 246 among monoamines with alkyl groups (a factor of 1.06). The default p^0 values for 247 amines in the E-AIM models were experimental data and only when these data were 248 missing, the calculation method by Moller et al. (2008) was used, with the exception of 249 250 MA, DMA, EA, DEA and AN-N (discussed in Section 4.1.2). In our study, to provide the most conservative estimation of the uncertainties caused by errors in p^0 of amines. 251 the vapor pressure of each amine was increased and decreased by a factor of 3.56, 252 representing the maximum uncertainty range by the method of Moller et al. (2008), 253 while the rest of the conditions remained the same (initial moles of nitric acid, sulfuric 254 acid and an amine at 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} , respectively, 255 initial mole of water at 0.07848 that corresponds to 60 % RH at 263.15 K and 101,325 256 Pa). Figure 2(a) illustrates the results of such error analysis using PZ as an example. 257 The corresponding T_c values are summarized in Table 2 and the relative uncertainties 258 were generally small $(\pm 3\%)$. 259



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2€ 265 Figure 2. (a) The uncertainties in T_c of PZ (gray area) resulting from the uncertainties in its saturation vapor pressure p^0 . The dash line represents the results using p^0 values recommended 266 by Ge et al (2011b). The lower and upper boundaries of the gray area were derived by increasing 267 268 and decreasing the vapor pressure by a factor of 3.56, respectively. (b) The differences in T_c for MA, DMA, EA and DEA when using Henry's law constant K_H (hallow markers) and the 269 extrapolated vapor pressure p^{0} at 298 K (solid markers). The extrapolated vapor pressures were 270 271 based on their Antoine Equations at low temperatures (Linstrom and Mallard, 2018). (c) The 272 uncertainties in T_c of DMA (gray area) resulting from the uncertainties in its Henry's law constant K_H at 298 K. The dash line represents the results using the K_H at 298 K value 273 recommended by Linstrom and Mallard (2018). The lower and upper boundaries of the gray 274 area were derived by using the minimum and maximum K_H at 298 K values (with clearly stated 275 276 methods of determination) in Sander (2015), respectively. (d) The comparison in T_c values of 277 PZ using different activity estimation methods. The black solid line was calculated with the UNIFAC method and the red dash line was based on Raoult's law. 278 279

280 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 10 281 (9 nm particle diameter) and 10^2 (4.5 nm particle diameter). This p_{sat} range was 282 estimated based on the 0.050 J m⁻² surface free energy value for the nitrates of MEA 283 (Greaves et al. 2006) and a calculated molar volume of 259 mol cm^{-3} (Salo et al. 2011). 284 The corresponding T_c values decreased to 296 K and 288 K, respectively. This analysis 285 suggests the significant impact of particle size on the condensation of RNCs and NA. 286 However, a systematic evaluation of uncertainties from the Kelvin effect was not 287 conducted due to the limited available information on the physical properties of the 288 289 nitrate salts of amines.

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4.1.2 Effects of the Henry's Law constant of monoamines 291

292 MA, DMA, EA and DEA are monoamines with small alkyl group(s) and their measured p^{0} ranges (described by the Antoine equation parameters) are generally well 293 below 298 K (Linstrom and Mallard, 2018). Opposite to these small alkylamines, AN-294 N has extremely low p^0 at 298 K and therefore has an Antoine equation applicable only 295 at 415–609 K (Linstrom and Mallard, 2018). It is therefore difficult to use p^0 to study 296 these amines, without introducing unknown levels of uncertainties by extrapolating 297 their Antonie equations to 298 K. Alternatively, Henry's Law constant K_H for these 298 amines can be used to describe their partition between gas and aqueous solution and 299 has been determined on these amines previously (Linstrom and Mallard, 2018; Sander, 300 2015). The values recommended by Ge et al. (2011b) were considered the default input 301

302 parameters in our study (corresponding results reported in Table 1).

Additional simulations were carried out using the extrapolated p^0 for each of the 303 five monoamines with initial moles of the nitric acid, sulfuric acid and amine at 304 1.11151×10^{-9} , 2.03777×10^{-11} and 8.86895×10^{-8} , respectively, and a fixed initial mole 305 of water at 0.07848 (corresponding to 60 % RH at 263.15 K and 101,325 Pa). The 306 results were plotted in Figure 2(b), except for AN-N which showed negligible 307 difference (< 0.05%). While the results for the four alkylamines using the K_H and the 308 extrapolated p^0 appeared to be very different, it is important to note that in all four cases 309 the T_c values calculated using the extrapolated p^0 values are higher than those calculated 310 using the K_H values, suggesting that the reported T_c values in our Table 2 are the lower 311 bound estimation of the transitional temperature at which the amines can condense with 312 nitric acid. Numerically, the choice to use K_H or extrapolated p^0 for our simulations will 313 314 cause a change in T_c values by 6% or less.

Due to the potentially large errors in extrapolating the p^0 values, the variability in 315 the T_c of DMA associated with its extrapolated p^0 was further tested by increasing and 316 decreasing its extrapolated p^0 at 298 K by a factor of 4.8 (limited by the maximum 317 allowed p^0 value of 10 atm in E-AIM). In the case of AN-N, the extrapolated p^0 value 318 at 298 K from Antoine equation was lower by 30 times based on another vapor pressure 319 estimation method, EPI Suite v 4.11 (US EPA, 2019). The corresponding relative 320 uncertainties in T_c caused by these drastic changes in extrapolated p^0 values were within 321 322 2%.

It is also important to note the complications in applying the K_H values from 323 literatures in our thermodynamic simulations. The K_H values at 298 K for the five 324 amines vary significantly in literatures (Sander, 2015). In our simulations, the K_H values 325 recommended by Linstrom and Mallard (2018) were used as default input values 326 (corresponding results reported in Table S1). When applicable, the largest and smallest 327 K_H values of an amine (with clearly stated method of determination) at 298 K 328 summarized by Sander (2015) were used to estimate the possible uncertainties caused 329 by the variability in K_H at 298 K. Figure 2(c) illustrated such uncertainty estimation on 330 DMA as an example. The T_c values after varying the K_H values at 298 K for the four 331 amines are included in Table 2. 332

Note that among available data, there are also significant uncertainties in the temperature dependence of K_H for amines. A systematic uncertainty analysis was difficult due to the lack of such literature data for most of the amines in our study, which could be a potential issue in the accurate determination of T_c values. However, for the five amines with available alternative temperature dependence coefficients of K_H (Sander, 2015), the uncertainties in T_c values caused by the alternative coefficients are within 3%.

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341 **4.1.3 Effects of the Activity of amines**

It is possible to carry out thermodynamic simulations with or without considering 342 343 the activities of the chemicals in the aqueous solution, including the ammonium and aminium cations, the nitrate and sulfate anions and the dissolved amines. The scenario 344 where activities of all chemical species are considered to be one is referred as the 345 Raoult's law method, which is likely applicable at high relative humidity due to the 346 much-diluted ion concentrations. However, at a higher temperature or lower relative 347 humidity, water condensation on the particle may be limited and the formed aqueous 348 349 solution may have a very high ionic strength (Pye et. al., 2020). Therefore, it is important to evaluate the uncertainties caused by the methods used for activity estimations in our simulations.

The activities of the anions involved in our simulations were relatively well studied (Wexler and Ge, 2002). Ge et al. (2011b) showed that it is reasonable to assume the activities of the aminium cations to be the same as that of ammonium cation. As highly polar molecules, the activities of amines dissolved in an aqueous solution may be described using the UNIFAC method (Fredenslund, 1977).

Our T_c values reported in Table 1 were based on simulations using the UNIFAC 357 method as default to estimate the activities of the amines. Ge et al. (2011b) showed that 358 the estimation of activities of amines using UNIFAC method will generally lead to 359 satisfactory results yet the dataset for comparison was far from comprehensive. 360 Therefore, additional simulations were carried out using the Raoult's law method for 361 362 all the amines. One example comparing the results between Raoult's law and UNIFAC methods is shown in Figure 2(d). The relative difference in T_c using the two activity 363 estimation methods for amines in our study was generally below 2.5%. 364

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366 4.1.4 Effects of the Solubility of the Nitrate Salts of Amines

One last potential complication in our thermodynamic simulations is the possible formation of the solid aminium nitrate salts. Only a handful of the nitrates of alkylamines (such as MA, DMA, TMA), AN and MEA were studied for their solubility properties. The general trend is that the nitrate salts of alkylamines and alcohol amines are highly soluble in water, which consequentially makes no impact on the thermodynamic modeling results.

In the case of AN, its nitrate salt has low solubility. Additional simulation using E-AIM while specifying the solubility of AN nitrate showed that no solid of AN nitrate may form under our simulation conditions. It is therefore reasonable to assume that the water solubility of the aminium nitrate salts had no impact on our T_c results.

377378 4.1.5 Overall uncertainty estimations

379 As discussed previously, it is assumed that the overall uncertainties of our simulation were determined by errors in p^0 (or K_H) estimations and the discrepancies in 380 the activity estimation methods (assuming that the true value lies in the middle of the 381 two methods), and the two sources were independent from each other. The uncertainties 382 in the temperature dependence of K_H were not considered in our error estimations due 383 to the large variability in the data in the literature. Instead, the values suggested by 384 385 Linstrom and Mallard (2018) were used as the default values for the temperature dependence of K_{H} . 386

The overall uncertainty for the T_c value of each amine was therefore the square root of the square sum of the two independent sources (summarized in Table 2).

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4.2 Temperature Dependence of Amine and Nitric Acid Co-condensation.

391 Our simulation results strongly suggest that amines can co-condense with nitric acid onto FNCs and nanoparticles in the atmosphere and the process depends on the 392 temperature. For example, alkylamines commonly found in the atmosphere all showed 393 394 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 395 I RNCs is hereby defined as those that will only condense with NA at or below 278 K. 396 397 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 398

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.

It is worth noting that typically the uncertainty of the upper boundary for the T_c value is larger than that of the lower boundary. This is particularly pronounced in DEA and may bring its T_c value up to the 280 K range. While the uncertainty analysis presented in Table 2 could move some of the amines from Group I to Group II, it doesn't change our conclusion that amines may contribute significantly to nitric acid condensations in the presence of high ammonia concentration, especially at higher temperature where ammonia and nitric acid are not likely to condense.

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4.3 Structural Dependence of Amine and Nitric Acid Co-condensation.

To further elucidate the reason for the variance in T_c of the amines in the two groups. the properties of amines with distinctively different functional groups (Table 1) were compared to identify possible factors contributing to the significant difference in T_c values among amines.

Neither gaseous basicity (GB), aqueous basicity (K_b) or the volatility of an RNC (K_p) 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 has 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.

To our surprises, the solid/gas dissociation constants of the nitrates of alkylamines 423 are about 10 times lower than that of ammonium nitrate yet they exhibit comparable T_c , 424 suggesting that saturation condensation of nitrate salts alone may not explain the 425 difference in T_c for Group I and II RNCs. As discussed later in Section 4.5, water 426 condensation was frequently observed even at low RH in our simulations involving 427 amines and NA. Previous studies have suggested a strong stabilization effect of particle 428 water content on the condensed aminium nitrates (Chee et al., 2019; Kumar et al., 429 430 2018a).

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.

It is therefore deducted that additional hydrogen bonding can significantly increase
the temperature at which an RNC may condense with NA, since Group I RNCs can
form only one hydrogen bond while Group II RNCs can form two or more (Table 1).

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 1), allowing condensation with NA above room temperature.

Another factor that may affect the T_c is hydrophobic functional groups of RNCs as 452 there was a noticeable decrease in T_c value from MA to AN and AN-M. AN and AN-M 453 both contain an aromatic ring which is more hydrophobic than a methyl group. As 454 suggested by other theoretical analysis (Chee et al., 2019; Kumar et al., 2018a), it is 455 hypothesized that any hydrophobic functional group of an RNC may hinder the 456 formation of hydrogen bond between the nitrate of the RNC and water, resulting in less 457 nitrate condensation. For example, in the case of AN-O, the -OH attached to the 458 aromatic ring can form one additional hydrogen bond, which seems to offset the 459 460 negative effect of the non-polar aromatic ring and increase the T_c to 289K (+15 °C).

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462 4.4 Effects of Excess Ammonia on Amine and Nitric Acid Co-condensation.

Although Figure 1 well demonstrated the condensation of amines and NA in a wide 463 464 range of temperatures, ambient amine concentrations vary significantly with the constant presence of ammonia. The ambient concentration of amines is usually 1-2465 orders of magnitude lower than that of ammonia, but the amine: ammonia mol ratio 466 could be as high as 1:1 near a power-plant using PCCC technology. As a result, a 467 chemical system of ammonia, MEA, SA and NA with varying MEA:ammonia mol 468 ratios was investigated. Figure 3(a) illustrated the additional condensation of nitrate as 469 a result of added MEA. 470

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Figure 3. (a) The moles of condensed nitrate against temperature in an ammonia-MEA-sulfuric 474 acid-nitric acid chemical system with varying mole ratios of ammonia and MEA. The legend 475 indicates the initial mole fraction (mol %) of the MEA in the total moles of RNCs in each trace. 476 (b) Linear relationships between the transitional temperature of nitric acid condensation $(T_c,$ 477 defined as the temperature at which the moles of total nitrate in the condensed phases equals to 478 479 5% of the initial moles of nitric acid and determined in this study.) and logarithm of MEA mole fraction (mol %) in total moles of RNCs (ammonia and MEA) in the system at 298K. All 480 simulations have the same total moles of ammonia as 8.86895×10^{-8} and the same initial moles 481 of HNO₃ and H₂SO₄ as 1.11151×10^{-9} and 2.03777×10^{-11} , respectively. The system has a fixed 482 initial moles of water vapor as 0.07848 (equivalent to 60% RH at 263.15 K and 101,325 Pa in 483 1 m^3). 484

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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 3b):

 $T_c = -10.872 \times log(MEA\%) + 308.74$ Eq. 7

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

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492 **4.5 RH Dependence of Amine and Nitric Acid Co-condensation.**

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 (Chee et al., 2019). 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 4a). However, the enhancement was not as strong as additional hydrogen bonding.

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504 Figure 4. (a) The moles of condensed nitric acid against temperature with 1.2 mol % of MEA 505 506 in total RNCs at fixed total water (TW) or fixed relative humidity (RH) in a chemical system of ammonia, MEA, sulfuric acid and nitric acid. Both curves have the initial moles of ammonia 507 and MEA as 8.86895×10^{-8} and 1.06427×10^{-9} , respectively. The percentage refers to the mol % 508 of MEA in moles of all RNCs (ammonia and MEA) in the system. For open square curve, the 509 initial TW of the system was fixed at 0.07848 mol (equivalent to 60% RH at 263.15 K and 510 101,325 Pa in 1 m³). For solid square curve, the initial RH of the system was fixed at 60%. The 511 black line is the T_c threshold. When the initial RH of the system was fixed in each simulation, 512 as the temperature increased, the corresponding TW of the system also increased. (b) 513 Hygroscopicity of a chemical system of RNCs-sulfuric acid-nitric acid at 298 K. The y-axis is 514 515 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 516 517 8.86895×10^{-8} . The reference curve (red solid line based on Ref. Chan and Chan, 2012) only has ammonium sulfate. The legend indicates the initial mole fraction (mol %) of the amine(s) 518

in the total RNCs in each trace. Both panels have the same initial moles of HNO₃ and H_2SO_4 as 1.11151×10^{-9} and 2.03777×10^{-11} , respectively.

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522 **4.6 Hygroscopicity of Aerosol after Amine and Nitric Acid Co-condensation.**

In addition to T_c , the onset RH at which aerosol starts to uptake water vapor may 523 524 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 525 and NA is likely hindered at room temperature (Wang, 2020). Therefore, an ammonia-526 527 SA-NA system without amines is expected to start absorbing water vapor at about 79% RH like ammonium sulfate (Chan and Chan, 2012). The onset RH of water uptake by 528 the condensed phases at 298 K was systematically evaluated in an ammonia-SA-NA 529 530 system with additional DMA and MEA (representing Group I and II RNCs, respectively) and varying amine: ammonia mole ratios (Figure 4b). In all cases, all the sulfate 531 532 condensed as ammonium sulfate; therefore, the mol ratio of condensed water to sulfate 533 is directly proportional to the moles of condensed water. Water update at 65% RH by a mixture of ammonium nitrate-ammonium sulfate (Lee et al., 2008) was not observed in 534 535 our simulations, probably because of the anticipated lack of condensation of ammonium 536 nitrate at 298 K (Figure 1).

Adding 0.01 or 0.1 mol % of DMA (in the total moles of all RNCs) to the system 537 only promoted water update at a slightly lower RH (~78.5%). In contrast, MEA played 538 a significant role in lowering the onset RH of water uptake by the condensed phases. 539 For example, the presence of 0.01 and 0.1 mol % of MEA lowered the onset RH to \sim 71 % 540 and 30 %, respectively (Figure 4b), facilitating the water uptake by the condensed 541 phases in a dry environment. These observations are consistent with the hygroscopic 542 543 behavior of aminium (especially MEA) cations in aqueous solutions (Tian et al., 2022; Rovelli et al., 2017; Chu et al., 2015; Clegg et al., 2013; Qiu and Zhang, 2012). The 544 system with 0.01 mol % MEA and 0.1 mol % DMA showed somewhat enhanced water 545 546 uptake by the condensed phases than the cases with only MEA or DMA (Figure 4b, 547 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 548 549 hygroscopicity in an RNCs-SA-NA system is additive of the contributions from the RNCs in the system and dominated by Group II RNCs. 550

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4.7. Atmospheric Implications

Thermodynamic models are useful to evaluate how anthropogenic amines such as 553 MEA and PZ may condense with NA on atmospheric particles since the feasibility of 554 555 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 556 (Table 1): Group I with a T_c of +5 °C or below and Group II with a T_c of +15 °C or 557 above. Both groups may assist condensation of NA on nanoparticles under various 558 ambient conditions and contribute to NPF in addition to their assistance in forming 559 FNCs (Yao et al., 2018; Almeida et al., 2013; Zhang et al., 2012), especially in polluted 560 urban, agricultural and industrial areas. However, since the growth of FNCs is largely 561 562 governed by the kinetics of the system, a careful evaluation of the reaction kinetics of amine-nitric acid condensation is warranted. 563

The reaction rate constant of ammonia-NA condensation can be estimated based on the lab experiments (Wang et al., 2020), which showed that ammonia and NA can condense on clusters (with core diameters of 5–10 nm and primarily consisted of ammonium sulfate) at a rate of \sim 45 nm per hour. In 45 minutes, the clusters grew into

nanoparticles with diameters of 39–44 nm and a number concentration of $\sim 10^5$ cm⁻³. 568 Assuming the net increase in particle size was solely from the condensation of 569 ammonium nitrate with a material density of 1.72 g cm^{-3} , we estimated that the 570 condensation flux of ammonium nitrate on nanoparticles was $1.4-2.1 \times 10^7$ cm⁻³ s⁻¹. 571 Since the experiments were conducted with 1915 pptv ammonia and 24 pptv NA at 1 572 atm and 278 K, the concentrations of ammonia and NA were estimated to be 5×10^{10} 573 574 and 6×10^8 cm⁻³, respectively. The observed condensation rate of ammonia and nitrate at 278 K is therefore estimated as $4.5-6.5 \times 10^{-13}$ cm³ s⁻¹. 575

Several kinetic studies involving DFT and ACDC showed that DMA and NA 576 condense at a faster rate (Liu et al., 2021; Chee et al., 2019; Kumar et al., 2018a) than 577 that of ammonia and NA (Liu et al., 2018) on FNCs in the RNC-NA or RNC-NA-SA 578 nucleation systems. It is reasonable to assume that alkanolamines such as MEA will 579 580 condense with NA at a rate no slower than that of DMA. This assumption is based on 581 the observation that MEA and PZ may form clusters with SA at a kinetic rate that is comparable or faster than that of DMA (Ma et al., 2019; Xie et al., 2017), suggesting 582 that the condensation of MEA or PZ with NA will probably proceed no slower than that 583 584 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. 585

Since the nitrate of MEA has a molar mass of 124.10 and material density of 1.26 586 587 g cm⁻³ (Salo, 2011), its molar volume is estimated to be twice as that of ammonium nitrate. Assuming the same condensation rate of ammonia and NA, a ppm level of 588 ambient MEA near a PCCC unit may lead to particle growth due to the MEA and NA 589 590 (of 24 pptv) condensation at a rate as high as 57.8 nm per hour. Therefore, atmospheric clusters and nanoparticles may experience a significant growth near a PCCC unit due 591 to MEA and NA condensation at room temperature. However, the particle growth will 592 593 be significantly slower as moving away from the emission source of MEA.

Our estimations suggest a potentially significant removal pathway of Group II 594 amines by condensation with NA in the atmosphere at room temperature regardless of 595 ambient ammonia concentration and offer an alternative explanation to some field 596 observations of unexpectedly abundant MEA in ambient nanoparticles (Huang et al., 597 2016; Zhang and Anastasio, 2003). Typically, at 278 K, MEA will react with hydroxyl 598 radicals \cdot OH (with a typical ambient concentration of $c_{\text{OH}} = 10^6 \text{ cm}^{-3}$) at a rate of k_{OH} 599 = 8 × 10⁻¹¹ cm³ s⁻¹ (Xie et al., 2014). If MEA will condense with NA at a rate of k_{NA} = 600 5×10^{-13} cm³ s⁻¹ at 278 K as estimated above and the ambient concentration of NA is 601 $c_{\rm NA} = 10^8 - 10^{10}$ cm⁻³, the relative contribution of NA to the condensation removal of 602 603 MEA in the atmosphere can be estimated as: $k_{\text{NA}} \cdot c_{\text{NA}}/(k_{\text{OH}} \cdot c_{\text{OH}}) = 0.6 - 60$, suggesting that the contribution of NA assisted condensation removal of MEA in the atmosphere 604 can be as significant as gas-phase oxidations. Since most amines in Group II are 605 anthropogenic alkanolamines (MEA) and polyamines (PZ), our results offer an 606 additional pathway to consider when evaluating the ambient lifetime of industrial 607 amines, especially under warmer weather conditions. This could be particularly 608 important in areas with PCCC units using MEA or PZ. Our results also indicated that it 609 is possible to aggregate the quantities of all Group II amines into a single mole fraction 610 parameter to identify their maximum condensation temperature with NA for field and 611 modeling applications. 612

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 (Hsiao et al., 2016). Such modification to the particle surface may change critical properties of aerosol, including the viscosity (Shiraiwa et al., 2010), surface tension (Ovadnevaite et al., 2017) and Kelvin curvature effect (Zhang
et al., 2012), redox reactivities (Kong et al., 2021), surface uptake and heterogeneous
reactions (Rossignol et al., 2016; Kolb et al., 2011), hygroscopicity (Tian et al., 2022;
Qiu and Zhang, 2012) and CCN potentials (Lavi et al., 2013).

622 **5.** Conclusions

Systematic thermodynamic simulations were conducted to evaluate the potential 623 contribution of the condensation of atmospheric amines and nitric acid on the growth 624 of atmospheric clusters and nanoparticles under various temperature and relative 625 humidity conditions. Our results indicated two distinctly different groups of amines: 626 Group I amines (e.g., MA and DMA) can only form one hydrogen bond and can 627 condense with nitric acid under cold weather conditions, similar to ammonia; Group II 628 629 amines (e.g. MEA and PZ) can form two or more hydrogen bonds and may condense with nitric acid near room temperature, independent of the ambient ammonia 630 631 concentration. The condensed amines and nitric acid are likely to promote particle water uptake from the gas phase, which may facilitate further atmospheric transformation of 632 633 the aerosol. Our findings also suggested an alternative removal pathway for atmospheric amines, especially those from industrial processes (e.g. PCCC technology). 634

635636 Data Availability

E-AIM 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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RNC name	Abbreviation	Chemical Structure	psat ^a	GB^b	K_b^c	K_p^{-d}	T_c^{e}	Group ^f
Ammonia	NH ₃	NH ₃	9.94×10^{5}	819.0	1.76×10^{-5}	4.48×10^{-7}	$273.4^{+4.6}_{-10}$	Ι
Methylamine	MA	H ₂ N+CH ₃	$9.75 imes10^{4\dagger}$	864.5	4.57×10^{-4}	4.54×10^{-8}	$274.1^{+15}_{-3.6}$	Ι
Dimethylamine	DMA	H Z	$5.37 imes10^{4}$ †	896.5	5.38×10^{-4}	6.27×10^{-8}	$270.6^{+17}_{-3.0}$	Ι
Trimethylamine	TMA	N	$2.31 imes 10^5$	918.1	6.33×10^{-5}	1.65×10^{-6}	$274.8^{+5.8}_{-5.5}$	Ι
Ethylamine	EA	H ₂ N+CH ₂ CH ₃	1.39×10^{5} [‡]	878.0	4.46×10^{-4}	$2.83 imes 10^{-8}$	$272.7^{+15}_{-0.8}$	Ι
Diethylamine	DEA		$3.00 imes 10^4$ ‡	919.4	6.90×10^{-4}	7.01 × 10 ⁻⁹	263.9 ⁺²⁴	Ι
Triethylamine	TEA		$9.03 imes 10^3$	951	5.62×10^{-4}	$9.39 imes 10^{-8*}$	273.8 ⁺¹⁰ ₋₁₀	Ι
Aniline	AN		$8.52 imes 10^1$	850.6	7.41×10^{-10}	1.01×10^{-4}	256.6 ^{+2.8}	Ι
3-Methylaniline	AN-M	NH ₂	$1.07 imes 10^1$	864.0	5.13 × 10 ⁻¹⁰	-	256.6 ^{+4.4}	Ι
p-Nitroaniline	AN-N	O ₂ N	$6.79 imes 10^{-2}$ ‡	834.2	1.05×10^{-13}	-	256.6 ^{+0.1}	Ι
Monoethanol amine	MEA	H ₂ N	6.51×10^{1}	896.8	3.16×10^{-5}	$1.41 \times 10^{-12*}$	$304.5^{+5.2}_{-4.9}$	II

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

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

^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 Pa^2) of the nitrate salt of the amine at 298.15 K (Ge et al., 2011b).

^e 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 Table 2.

^f classified based on the T_c of the amine: Group I amines with $T_c \le 278$ 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.

	$T_c{}^{\mathrm{a}}$	Unner limit of T	Lower limit of T	Difference in T _c	Overall	Overall
RNC		due to n^{θ} (298 K) ^b	due to n^{θ} (298 K) ^b	due to activity ^c	uncertainty in T_c ,	uncertainty in T_c ,
		uuc to p (270 K)	uut to p (290 K)		upper limit ^d	lower limit ^d
NH3	273.4	-	-	-	+ 1.7%**	- 3.8%**
MA	274.1	288.4*	274.1*	-2.5% [†]	+ 5.4%	- 1.3%
DMA	270.6	287.3*	270.6*	-2.2% [†]	+ 6.3%	- 1.1%
TMA	274.8	279.6	270.6	-2.4%	+ 2.1%	- 2.0%
EA	272.7	288.0^{*}	272.0*	-0.2%†	+ 5.6%	- 0.3%
DEA	263.9	287.4*	257.9*	3.5%†	+ 9.1%	- 2.9%
TEA	273.8	278.4	269.7	6.7%	+ 3.8%	- 3.7%
AN	256.6	256.6	256.6	2.2%	+ 1.1%	- 1.1%
AN-M	256.6	256.6	256.6	3.6%	+ 1.7%	- 1.7%
AN-N	256.6	256.5*	256.7*	< 0.05%‡	<+0.05%#	<- 0.05%#
MEA	304.5	309.6	299.9	-0.9%	+ 1.7%	- 1.6%
IBA	307.0	314.0	300.0	-1.1%	+ 2.3%	- 2.3%
PZ	302.4	308.8	296.5	-2.5%	+ 2.5%	- 2.3%
AN-O	289.0	293.0	284.7	1.7%	+ 1.6%	- 1.7%
DAE	323.5	328.5	318.6	-0.2%	+ 1.5%	- 1.5%
DGA	323.7	330.6	317.3	0.1%	+ 2.1%	- 2.0%
DIPA	313.5	319.5	307.5	1.9%	+2.1%	-2.1%

Table 2. Uncertainty estimations of the T_c values for the reduced- nitrogen compounds (RNCs) in this study.

The transitional temperature (in K) of nitric acid condensation assisted with the amine by using default E-AIM input parameters.

^b The limits of the T_c (in K) resulting from the uncertainties in vapor pressure p^0 at 298 K of the amine (unless noted otherwise). The upper and lower limits of T_c were obtained by decreasing and increasing p^0 at 298 K of the amine by a factor of 3.56, respectively.

^c The relative difference in T_c between the UNIFAC and the Raoult's law methods to determine activities of the amine in an aqueous solution.

^d It is assumed that the uncertainty in T_c was caused mainly by the uncertainties of the p^{θ} (or K_H when applicable) and activity estimations.

[†] This uncertainty was within $\pm 0.05\%$ when the Henry's law constant K_H of the amine was used. It was then conservatively estimated by using the extrapolated vapor pressure at 298 K based on the Antoine Equation of the amine.⁵ The enthalpy change at 298 K was extrapolated based on

compiled data by Linstrom and Mallard (2018). The heat capacity was assumed to be the same as that of TMA, $-90 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

[‡] Both enthalpy change values of 70.0 kJ/mol and 77.9 kJ/mol⁵ produced similar results (<0.05% difference).

^{*} The limits of the T_c (in K) resulting from the uncertainties in the Henry's law constant K_H at 298 K. The upper and lower limits of T_c were obtained by choosing the maximum and minimum K_H values at 298 K from available literature values with stated method of determination in Sander (2015). The temperature dependence of the Henry's law constants was based on the values recommended by Linstrom and Mallard (2018).

** The relative uncertainties were estimated by comparing with the experimental observations (263 – 278 K) by Wang et al (2020).

[#] The relative uncertainties were less than 0.05%.