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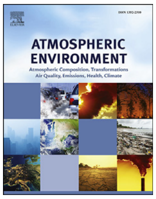

Short communication

Phase considerations in the gas/particle partitioning of organic amines in the atmosphere

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HIGHLIGHTS

- Amines in the atmosphere can be found in different phases in atmospheric particulate matter (PM).
- Phases of interest include liquid water, organic PM, and solid salt solutions.
- Protonation of an amine Am to form AmH^+ can greatly increase partitioning to water and OPM phases.

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ABSTRACT

Amines in the atmosphere are of interest because of their likely role in new particle formation, and because of anthropogenic emissions of amines at post-combustion carbon capture (PCCC) facilities. A conceptual framework for considering the partitioning of a monobasic amine (Am = unprotonated, "free-base form") from the gas phase to atmospheric particulate matter (PM) is presented for cases when the PM may be composed of multiple liquid phases. Three types of liquid phases are considered as being individually or simultaneously possible for absorptive uptake of atmospheric amines: w) a mostly water phase; α) a mostly (by mass) organic phase that has at least some polarity (*e.g.*, predominantly secondary organic aerosol (SOA), may contain significant water on a mole fraction basis); and β) a mostly organic phase that is less polar than an α phase (*e.g.*, predominantly primary organic aerosol (POA), containing little water). That one or more salts may contain the aminium ion AmH^+ (formed by protonation of Am) is subject to the fact that the trace levels of individual amines in the atmosphere make formation of a pure solid such as $AmHHSO_{4(s)}$ exceedingly unlikely: when solid salts of AmH^+ are indeed present, by far the most likely form is as a solid solution, *e.g.*, $(NH_4^+)_{1-y}(AmH^+)_y HSO^-_{4(s)}$ where $y << 1$. Neglecting dissolution in solid salts, and considering only partitioning to liquid phases, the overall gas/particle partitioning constant is $K_{p,tot}(m^3\ \mu g^{-1}) = c_{p,tot}/c_g = \sum_\theta f^\theta K^\theta_{p,fb}/\alpha^\theta_{fb}$. The quantity $c_{p,tot}$ ($\mu g\ \mu g^{-1}$) is the total Am concentration ($Am + AmH^+$) in the PM as summed over all phases using the index θ ($= w, \alpha, \beta$); c_g is the gas-phase concentration of Am; f^θ is the mass fraction of the total PM that is the θ phase; $K^\theta_{p,fb}$ is the gas/particle partitioning constant for the free-base (Am) form to the θ phase; and $0 < \alpha^\theta_{fb} < 1$ is the fraction of the amine in the θ phase that is in the free-base form. To date, most treatments of the partitioning of amines to PM have only considered contributions to $K_{p,tot}$ from absorption into a mostly water phase, according to the term $f^w K^w_{p,fb}/\alpha^w_{fb}$. However, unless the PM contains little or no organic-phase material, the α and/or β terms are likely to also be relevant. The Am form of a low MW amine will in general have reasonable affinities for both α and β type phases, so in general $K^w_{p,fb}$, $K^\alpha_{p,fb}$, and $K^\beta_{p,fb}$ will all be roughly similar in magnitude. And, with significant water uptake into an α phase certain to occur at moderate to high RH values, solvation of ions will often be possible in an α phase. This will assist protonation of Am to AmH^+ (as is known to occur for nicotine in tobacco smoke PM). The overall result is that to a first approximation, α^w_{fb} and α^α_{fb} can be similar in magnitude, making $K^\alpha_{p,fb}/\alpha^\alpha_{fb}$ likely to be generally comparable to $K^w_{p,fb}/\alpha^w_{fb}$. In a β phase, ion solvation will not be as good, so that for acidic aerosol α^β_{fb} will generally be closer to one than the other two α_{fb} values, making $K^\beta_{p,fb}/\alpha^\beta_{fb}$ smaller than both

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$K^{w}_{p,fb}/\alpha^{w}_{fb}$ and $K^{\alpha}_{p,fb}/\alpha^{\alpha}_{fb}$. Overall, modeling of amine behavior in the atmosphere should include consideration of partitioning into organic PM. Unfortunately, this will be more difficult than water-phase only modeling because prediction of α_{fb} values in multiphase PM will be greatly complicated by the needs to: 1) have estimated values of acidity constants in mostly organic phases of variable composition; and 2) allow distribution of chemicals over multiple liquid phases.

Nomenclature

Roman	
A	concentration (μg m^{-3}) of the amine in the gas phase (only free-base form is volatile);
Am	free-base form of an amine;
AmH^{+}	monoprotonated form of an amine;
$c^{\theta}_{p,fb}$	concentration (μg μg^{-1}) of the free-base form of an amine in liquid phase θ;
$c^{\theta}_{p,tot}$	concentration (μg μg^{-1}) of total (free-base + protonated) amine in liquid phase θ;
c_{g}	concentration (μg m^{-3}) of the amine in the gas phase (only free-base form is volatile);
f^{θ}	weight fraction of the PM that is the absorbing liquid phase θ;
F^{θ}_{fb}	particle-phase associated concentration (μg m^{-3}) of the free-base form of an amine in liquid phase θ;
F^{θ}_{tot}	particle-phase associated concentration (μg m^{-3}) of the total (free-base + protonated) amine in liquid phase θ;
K_{a}	acidity constant on molal scale, using solution phase activities; referenced to infinite dilution in water;
$^{c}K_{a}$	acidity constant on molal scale, using solution phase concentrations; value depends on the composition of the medium;
$K^{w}_{H,fb}$	Henry's gas law constant (m atm^{-1}) for partitioning to a mostly-aqueous phase, with molal activity for the dissolved species; referenced to infinite dilution in water;
$^{c}K^{w}_{H,fb}$	Henry's gas law partitioning constant (m atm^{-1}) for partitioning of the free-base Am to water, with molal concentration for the dissolved species; value depends on the composition of the solution;
$K^{\theta}_{p,fb}$	gas/particle partitioning constant (m^{3} μg^{-1}) for the free-base form of an amine to liquid phase θ;
$K^{\theta}_{p,tot}$	gas/particle partitioning constant (m^{3} μg^{-1}) for total (free-base + protonated) amine to liquid phase θ;
M^{θ}	mass concentration (μg m^{-3}) of absorbing liquid phase θ;
M_{tot}	total mass concentration (μg m^{-3}) of PM;
$\overline{\mathrm{MW}}^{\theta}$	mean molecular weight (g mol^{-1}) of an absorbing liquid PM phase θ;
$\overline{\mathrm{MW}}^{w}$	mean molecular weight (g mol^{-1}) of an absorbing, mostly water liquid PM phase;
MW	molecular weight (g mol^{-1});
OPM	organic particulate matter;
p	gas-phase pressure (atm);
$p^{o}_{L,Am}$	vapor-pressure (atm) at temperature T of pure liquid amine (sub-cooled if necessary);
$\mathrm{pH}^{\theta}_{eff}$	the pH that in dilute water that would give the same α_{fb} as exists in liquid phase θ;
PM	particulate matter (μg m^{-3});
R	gas constant (8.2 × 10^{-5} m^{3} atm mol^{-1} K^{-1});
SOA	secondary organic aerosol;
T	temperature (K);
x^{θ}	mole-fraction-scale concentration of compound in the liquid phase θ;
Greek	
α	phase α – *e.g.*, a mostly SOA phase; a phase that is mostly organic by mass, is at least somewhat polar, and is more polar than a β phase;
α_{fb}	fraction of amine in the free-base form in liquid phase θ;
β	phase β – *e.g.*, a mostly hydrophobic POA phase; a phase that is mostly organic by mass, and is less polar than an α phase;
γ^{θ}	molal scale activity coefficient (dimensionless) of a compound in liquid phase θ;
ζ^{θ}	mole-fraction-scale activity coefficient (dimensionless) of a compound in liquid phase θ.

1. Introduction

The behavior of amines in the atmosphere is of increasing interest. The nucleation of new particles in the ambient atmosphere has been discussed as involving molecular-scale clusters that include natural amines (Barsanti et al., 2009; Smith et al., 2010; Bzdek et al., 2011a,b; Yli-Juuti et al., 2013; Bzdek et al., 2014). Amines such as monoethanol amine (MEA) (Rochelle, 2009), diethanol amine (DEA), and methyldiethanolamine (MDEA) (Reynolds et al., 2012) are being considered for use in post-combustion carbon capture (PCCC) of CO_2 at fossil fuel energy plants. Measurements of amines in the ambient environment are the focus of recent study (*e.g.*, Zheng et al., 2015).

The unprotonated, "free-base" form of an amine is represented herein as Am, which is assumed to be monobasic; protonated Am is represented as AmH^{+}. By analogy with ammonia, which forms solid salts of NH_4^+ such as $NH_4HSO_{4(s)}$ and is very soluble in water, Ge et al. (2011) argue that: 1) solid salts of AmH^{+} may form in the atmosphere with bisulfate (*e.g.*, as $\mathrm{AmH^{+}HSO^{-}_{4(s)}}$), sulfate, or nitrate; and 2) strong partitioning of low-MW amines can occur into a particle phase that is largely water (by mass), especially under low-pH conditions so that the reaction $\mathrm{Am + H^{+} \rightarrow AmH^{+}}$ can be important. However, as regards formation of salts, trace levels of AmH^{+} will not be present as pure solid salt(s). Rather, since ionic