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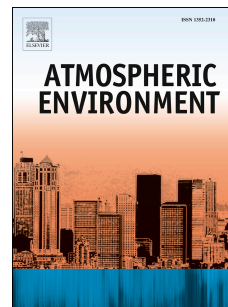
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6 - TECHNICAL NOTE -
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11 Organic Amines in the Atmosphere
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43 **Abstract**

44 Amines in the atmosphere are of interest because of their likely role in new particle for-
 45 mation, and because of anthropogenic emissions of amines at post-combustion carbon capture
 46 (PCCC) facilities. A conceptual framework for considering the partitioning of a monobasic amine
 47 (Am = unprotonated “free-base form) from the gas phase to atmospheric particulate matter (PM) is
 48 presented for cases when the PM may be composed of multiple liquid phases. Three types of liquid
 49 phases are considered as being individually or simultaneously possible for absorptive uptake of
 50 atmospheric amines: w) a mostly water phase; α) a mostly (by mass) organic phase that has at least
 51 some polarity (*e.g.*, predominantly secondary organic aerosol (SOA), and may contain significant
 52 water on a mole fraction basis); and β) a mostly organic phase that is less polar than an α phase
 53 (*e.g.*, predominantly primary organic aerosol (POA), containing little water). That one or more salts
 54 may contain the aminium ion AmH^+ (formed by protonation of Am) is subject to the fact that the
 55 trace levels of individual amines in the atmosphere make formation of pure solid such as
 56 $\text{AmHHSO}_{4(s)}$ exceedingly unlikely: when solid salts of AmH^+ are indeed present, by far the most
 57 likely form is as a solid solution, *e.g.*, $(\text{NH}_4^+)_{1-y}(\text{AmH}^+)_y\text{HSO}_4^-$ where $y \ll 1$.

58 Neglecting dissolution in solid salts, and considering only partitioning to liquid phases, the
 59 overall gas/particle partitioning constant is $K_{p,\text{tot}} (\text{m}^3 \mu\text{g}^{-1}) = c_{p,\text{tot}} / c_g = \sum_{\theta} f^{\theta} K_{p,\text{fb}}^{\theta} / \alpha_{\text{fb}}^{\theta}$. The
 60 quantity $c_{p,\text{tot}} (\mu\text{g} \mu\text{g}^{-1})$ is the total Am concentration (Am+AmH⁺) in the PM as summed over all
 61 phases using the index θ (= w, α , β); c_g is the gas phase concentration of Am; f^{θ} is the mass
 62 fraction of the total PM that is the θ phase; $K_{p,\text{fb}}^{\theta}$ is the gas/particle partitioning constant for the free-
 63 base (Am) form to the θ phase; and $0 < \alpha_{\text{fb}}^{\theta} < 1$ is the fraction of the amine in the θ phase that is in
 64 the free-base form.

65 To date, the partitioning of amines to PM have only considered contributions to $K_{p,\text{tot}}$ from
 66 absorption into a mostly water phase, according to the term $f^w K_{p,\text{fb}}^w / \alpha_{\text{fb}}^w$. However, unless the PM
 67 contains little or no organic phase material, the α and/or β terms are likely to also be relevant. The
 68 Am form of a low MW amine will in general have reasonable affinities for both α and β type

69 phases, so in general $K_{p,fb}^w$, $K_{p,fb}^\alpha$, and $K_{p,fb}^\beta$ will all be roughly similar in magnitude. And, with
70 significant water uptake into an α phase certain to occur at moderate to high RH values, good
71 solvation of ions will often be possible in an α phase. This will assist protonation of Am to AmH^+
72 (as is known to occur for nicotine in tobacco smoke PM). The overall result is that to a first
73 approximation, α_{fb}^w and α_{fb}^α can be similar in magnitude, making $K_{p,fb}^\alpha / \alpha_{fb}^\alpha$ likely to be generally
74 comparable to $K_{p,fb}^w / \alpha_{fb}^w$. In a β phase, ion solvation will not be as good, so that for acidic aerosol
75 α_{fb}^β will generally be closer to one than the other two α_{fb} values, making $K_{p,fb}^\beta / \alpha_{fb}^\beta$ smaller than both
76 $K_{p,fb}^w / \alpha_{fb}^w$ and $K_{p,fb}^\alpha / \alpha_{fb}^\alpha$. Overall, modeling of amine behavior in the atmosphere should include
77 consideration of partitioning organic PM. Unfortunately, this will be more difficult than water-
78 phase only modeling because prediction of α_{fb} values in multiphase PM will be greatly complicated
79 by the needs to: 1) have estimated values of acidity constants in mostly organic phases of variable
80 composition; and 2) allow distribution of chemicals over multiple liquid phases.

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85 **Keywords:** amines, free-base, organic particulate matter, OPM, secondary organic aerosol, SOA.

*(no line numbers for table)***Nomenclature****Roman**

A	concentration ($\mu\text{g m}^{-3}$) 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;
$c_{\text{p,fb}}$	concentration ($\mu\text{g } \mu\text{g}^{-1}$) of the free-base form of an amine in some liquid phase θ ;
$c_{\text{p,tot}}$	concentration ($\mu\text{g } \mu\text{g}^{-1}$) of total (free-base + protonated) amine in some liquid phase θ ;
c_{g}	concentration ($\mu\text{g m}^{-3}$) 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_{fb}	particle-phase associated concentration ($\mu\text{g m}^{-3}$) of the free-base form of an amine in some liquid phase θ ;
F_{tot}	particle-phase associated concentration ($\mu\text{g m}^{-3}$) of the total (free-base+protonated) amine in some liquid phase θ ;
K_{a}	acidity constant on molal scale, using solution phase activities; referenced to infinite dilution in water;
${}^{\text{c}}K_{\text{a}}$	acidity constant on molal scale, using solution phase concentrations; value depends on the composition of the medium;
$K_{\text{H,fb}}^{\text{w}}$	Henry's gas law constant ($m \text{ atm}^{-1}$) for partitioning to a mostly phase, with molal activity for the dissolved species; referenced to infinite dilution in water;
${}^{\text{c}}K_{\text{H,fb}}^{\text{w}}$	Henry's gas law partitioning constant ($m \text{ atm}^{-1}$) with molal concentration for the dissolved species; value depends on the composition of the medium;
$K_{\text{p,fb}}$	gas/particle partitioning constant ($\text{m}^3 \mu\text{g}^{-1}$) for the free-base form of an amine to some liquid phase θ ;
$K_{\text{p,tot}}$	gas/particle partitioning constant ($\text{m}^3 \mu\text{g}^{-1}$) for total (free-base + protonated) amine to some liquid phase θ ;
M^{θ}	mass concentration ($\mu\text{g m}^{-3}$) of absorbing liquid phase θ ;
M_{tot}	total mass concentration ($\mu\text{g m}^{-3}$) of PM;
$\overline{\text{MW}}$	mean molecular weight (g mol^{-1}) of an absorbing liquid PM phase θ ;
$\overline{\text{MW}}^{\text{w}}$	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);
$p_{\text{L,Am}}^{\circ}$	vapor-pressure (atm) at temperature T of pure liquid amine (sub-cooled if necessary);
pH_{eff}	the pH that in dilute water that would give the same α_{fb} as in liquid phase θ ;
PM	particulate matter ($\mu\text{g m}^{-3}$);
R	gas constant ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$);
SOA	secondary organic aerosol;
T	temperature (K);
x	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
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	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	molal scale activity coefficient (dimensionless) of a compound in liquid phase θ ;
ζ	mole-fraction-scale activity coefficient (dimensionless) of a compound in liquid phase θ .

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88 1. Introduction

89 The behavior of amines in the atmosphere is of increasing interest. The nucleation of new
90 particles in the ambient atmosphere has been discussed as involving molecular-scale clusters that
91 include natural amines (Barsanti et al., 2009; Smith et al., 2010; Bzdek et al., 2011a,b; Yli-Juuti et
92 al., 2013; Bzdek et al., 2014). Amines such as monoethanol amine (MEA) (Rochelle, 2009),
93 diethanol amine (DEA), and methyldiethanolamine (MDEA) (Reynolds et al., 2012) are being
94 considered for use in post-combustion carbon capture (PCCC) of CO₂ at fossil fuel energy plants.
95 Measurements of amines in the ambient environment continue to be the focus of recent study (e.g.,
96 Zheng et al., 2015).

97 The unprotonated, “free-base” form of an amine is represented herein as Am, which is
98 assumed to be monobasic; protonated Am is represented AmH⁺. By analogy with ammonia, which
99 forms solid salts of NH₄⁺ such as NH₄HSO_{4(s)} and is enormously soluble in water, Ge et al. (2011)
100 discuss that: 1) solid salts of AmH⁺ may form in the atmosphere with bisulfate (e.g., as
101 AmH⁺HSO_{4(s)}⁻), sulfate, or nitrate; and 2) strong partitioning of low-MW amines can occur into a
102 particle phase that is largely water (by mass), especially under low-pH conditions so that the
103 reaction Am + H⁺ → AmH⁺ can occur. However, as regards formation of salts, trace levels of
104 AmH⁺ will not be present as pure solid salt(s). Rather, since ionic solid solutions are very well
105 known, including solid solutions involving salts of ammonium and sulfate (e.g., Smith, 1992), it is
106 certain that when present in ionic solids ammonium ions will be present as dilute ionic solid
107 solution(s). Evidence for such formation can be found in the study by Chan and Chan (2013)
108 wherein reactions of ammonia gas with solid ammonium salts were considered.

109 With ammonium bisulfate, the result would be (NH₄⁺)_{1-y}(AmH⁺)_yHSO_{4(s)}⁻ where y << 1. Second, as
110 regards absorptive partitioning, in addition to uptake into a mostly aqueous particulate matter (PM),

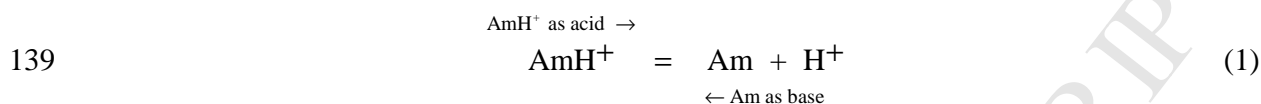
111 in the general case it will also be necessary to consider absorption into mostly organic particulate
112 matter (OPM), especially when there is appreciable water in the OPM. Guo et al. (2014) used
113 indirect aerosol measurements to estimate that significant levels of water were present within OPM
114 at ground-level in the southeast United States during May to November, 2012. Those results are
115 supported by “molecular view” (MV) chemical transport modeling of water uptake into OPM in
116 that region by Pankow et al. (2015) and Jathar et al. (2015). The results of Guo et al. (2014),
117 Pankow et al. (2015), and Jathar et al. (2015) all support the view that in the southeast United
118 States, particle water within SOA OPM can currently reach a third or more of the total water+OPM
119 mass loading. If the MW of the organic portion is $\sim 200 \text{ g mol}^{-1}$, with the MW of water only 18 g
120 mol^{-1} , then $\frac{1}{3}$ by mass water corresponds to mole fraction values of $x_w = 0.85$ and $x_o = 0.15$. If it is
121 assumed that the condensed SOA OPM resembles an aliphatic C_{10} diacid (MW = 202), for dilute
122 MEA and DEA in a solution within $x_w \approx 0.85$ and $x_o \approx 0.15$, the UNIFAC algorithm for mole-
123 fraction scale activity coefficients (Fredunslund *et al.*, 1977) predicts the Am-form activity
124 coefficients are $\zeta_{\text{MEA}} = 0.33$ and $\zeta_{\text{DEA}} = 0.20$. For a mostly water phase with ($x_w \approx 1$), the predicted
125 values are $\zeta_{\text{MEA}} = 0.37$ and $\zeta_{\text{DEA}} = 0.55$, so that an OPM phase containing appreciable water can be
126 expected to be at least as favored for uptake of low MW amines as $x_w \approx 1$. Moreover, water in
127 OPM can solvate AmH^+ ions: when aerosol acidity increases, uptake of an amine will increase not
128 only in particle water but also in the OPM. (It is well-known that tobacco smoke OPM is usually
129 sufficiently acidic to greatly increase the partitioning of nicotine from the gas phase (Liang and
130 Pankow, 1996; Pankow et al., 1997; Pankow, 2001)). Further, when a mostly water ($x_w \approx 1$) phase
131 contains high concentrations of dissolved salts, “salting-out” effects can reduced the comfort level
132 of the Am in the salty-water phase relative to an organic-rich phase (Zuend and Seinfeld, 2012).

133 2. Equations

134 2.1. Effects of Protonation of Amines in Absorptive Partitioning

135 In the gas phase, the neutral “free-base” Am is the only form present: AmH⁺ is essentially
 136 completely non-volatile. Within a given condensed liquid PM phase, only a fraction of the total
 137 amine in the phase is ever in the Am form: AmH⁺ is always present to some extent.

138 Am and AmH⁺ are conjugate opposites:



140 In a condensed solution phase, the acidity constant for AmH⁺ is

$$141 \quad K_a = \frac{\{\text{Am}\}\{\text{H}^+\}}{\{\text{AmH}^+\}} = \frac{\gamma_{\text{Am}}[\text{Am}]\gamma_{\text{H}^+}[\text{H}^+]}{\gamma_{\text{AmH}^+}[\text{AmH}^+]} \quad (2)$$

142 The concentration scale for both the terms in braces and brackets is the molal scale, so the γ values
 143 are molal-scale activity coefficients. K_a values are most commonly tabulated for the condition of
 144 “infinitely dilute” water in which $\gamma_{\text{Am}} = \gamma_{\text{H}^+} = \gamma_{\text{AmH}^+} \equiv 1$.

145 For a given constant composition of the liquid phase in which the equilibrium is being
 146 attained, as usual $\text{p}K_a \equiv -\log K_a$, and $\text{p}^c K_a \equiv -\log {}^c K_a$ with

$$147 \quad {}^c K_a \equiv \frac{[\text{Am}][\text{H}^+]}{[\text{AmH}^+]} = K_a \frac{\gamma_{\text{AmH}^+}}{\gamma_{\text{Am}}\gamma_{\text{H}^+}} \quad (3)$$

148 The γ values depend on the composition of the medium, so that ${}^c K_a$ values for a given acid can be
 149 very different in different media. For example, the group $\gamma_{\text{AmH}^+}/(\gamma_{\text{Am}}\gamma_{\text{H}^+})$ will be very different in
 150 dilute water *vs.* in a phase in which $x_w = 0.25$ and some $x_o = 0.75$. In fact, for two different acids
 151 (including AmH⁺ ions), it can easily be the case that the $\text{p}^c K_a$ order is reversed between one phase
 152 *vs.* another.

153 The fraction of the free base in a liquid phase is denoted α_{fb} (Liang and Pankow, 1996), with
 154 $0 \leq \alpha_{\text{fb}} \leq 1$. When is mono-basic, then within the phase the fraction of AmH⁺ is $1 - \alpha_{\text{fb}}$ and

$$\alpha_{fb} \equiv \frac{[Am]}{[Am] + [AmH^+]} \quad 1 - \alpha_{fb} = \frac{[AmH^+]}{[Am] + [AmH^+]} \quad (4)$$

156 For absorptive partitioning to a given liquid phase (Liang and Pankow, 1996; Pankow et al., 2003)

$$157 \quad K_{p,fb} \text{ (m}^3 \text{ } \mu\text{g}^{-1}\text{)} = \frac{c_{p,fb}}{c_g} = \frac{c_{p,fb}}{A} \quad (5)$$

158 where $c_{p,fb}$ ($\mu\text{g } \mu\text{g}^{-1}$) is the PM-phase concentration of the Am portion, and c_g ($\mu\text{g m}^{-3}$) $\equiv A$ ($\mu\text{g m}^{-3}$)
 159 is concentration of Am in the gas-phase. The counterpart to A is F ($\mu\text{g m}^{-3}$), which is the PM-
 160 associated concentration for the aerosol system.

161 As with the uptake of ammonia into particle water, Eq.(5) is an incomplete treatment of Am
 162 partitioning into PM because increasing $\{H^+\}$ in a liquid PM phase (*i.e.*, decreasing the pH
 163 conditions) will decrease α_{fb} . Since it is Am that is in direct gas/particle exchange with the gas
 164 phase, more total Am can be present in the PM at low pH than at high pH (Pankow et al., 1997;
 165 2003; Ge et al., 2011).

166 It is common in the atmosphere that the PM contains more than one absorptive liquid phase.
 167 You et al. (2014) discuss liquid-liquid phase separation in systems involving laboratory produced
 168 secondary organic material and aqueous salt solution, and Zuend and Seinfeld (2012) discuss
 169 predictions of phase separation in such systems. Erdakos and Pankow (2004) discuss cases when
 170 relatively polar SOA compounds and non-polar primary organic aerosol (POA) compounds are
 171 jointly present at similar mass concentrations with some water. The cases considered resulted in
 172 phase separation into two mostly organic phases, one phase (α) being more polar and containing
 173 more water than the other (β). Since a mostly aqueous phase is possible (You et al., 2014; Zuend
 174 and Seinfeld, 2012), it can be concluded that atmospheric PM with three liquid phases is possible.

175 The mass concentration of the θ phase portion of the PM is denoted M^θ ($\mu\text{g m}^{-3}$)

$$176 \quad c_{p,fb}^\theta \text{ (}\mu\text{g } \mu\text{g}^{-1}\text{)} \equiv \frac{F_{fb}^\theta}{M^\theta} \quad c_{p,tot}^\theta \text{ (}\mu\text{g } \mu\text{g}^{-1}\text{)} \equiv \frac{F_{tot}^\theta}{M^\theta} \quad (6)$$

$$177 \quad K_{p,fb}^{\theta} (\text{m}^3 \mu\text{g}^{-1}) = \frac{F_{fb}^{\theta} / M^{\theta}}{c_g} = \frac{F_{fb}^{\theta} / M^{\theta}}{A} \quad K_{p,tot}^{\theta} (\text{m}^3 \mu\text{g}^{-1}) = \frac{F_{tot}^{\theta} / M^{\theta}}{c_g} = \frac{F_{tot}^{\theta} / M^{\theta}}{A} \quad (7)$$

178 where $c_{p,tot}^{\theta} (\mu\text{g} \mu\text{g}^{-1}) \equiv F_{tot}^{\theta} / M^{\theta}$ is the total (*i.e.*, Am + AmH⁺) θ -phase mass concentration of the
179 amine (computed as Am). With α_{fb}^{θ} defined for each phase θ according to Eq.(4), then

$$180 \quad c_{p,fb}^{\theta} = \alpha_{fb}^{\theta} c_{p,tot}^{\theta} \quad (8)$$

$$181 \quad F_{fb}^{\theta} = \alpha_{fb}^{\theta} F_{tot}^{\theta} \quad (9)$$

$$182 \quad K_{p,fb}^{\theta} (\text{m}^3 \mu\text{g}^{-1}) = \frac{\alpha_{fb}^{\theta} c_{p,tot}^{\theta}}{c_g} = \frac{\alpha_{fb}^{\theta} F_{tot}^{\theta} / M_{\theta}}{c_g} \quad (10)$$

$$183 \quad \frac{F_{tot}^{\theta} / M_{\theta}}{c_g} = \frac{c_{p,tot}^{\theta}}{c_g} = \frac{K_{p,fb}^{\theta}}{\alpha_{fb}^{\theta}} \quad (11)$$

$$184 \quad \boxed{K_{p,tot}^{\theta} = \frac{K_{p,fb}^{\theta}}{\alpha_{fb}^{\theta}}} \quad (12)$$

185 Partitioning of an amine to a phase θ is greatly enhanced when the phase is acidic because then α_{fb}^{θ}
186 $\ll 1$, and $K_{p,tot}^{\theta} \gg K_{p,fb}^{\theta}$ (Pankow *et al.* 1997).

187 $K_{p,fb}^{\theta}$ for an amine in the θ phase depends on: a) the liquid vapor pressure $p_L^{\circ}(T)$ of the
188 amine; and b) how its structural characteristics compare to those comprising the major components
189 of the θ phase (and thus set the value of ζ_{Am}^{θ}). The value of α_{fb}^{θ} and thus the overall partitioning
190 constant $K_{p,tot}^{\theta}$ depend on: a) the basicity of the amine in the θ phase; and b) the effective pH
191 conditions in the θ phase. Different liquids always exhibit different equilibrium solvation
192 properties, so that when comparing phases in a multi-phase PM, no two $K_{p,fb}^{\theta}$ and no two α_{fb}^{θ} values
193 will ever be exactly equal.

194 Summing over all phases, the total mass concentration in the PM is

$$195 \quad F_{\text{tot}} = \sum_{\theta} F_{\text{tot}}^{\theta} = \sum_{\theta} c_{\text{p,tot}}^{\theta} M^{\theta} \quad (13)$$

$$196 \quad = \sum_{\theta} c_{\text{p,fb}}^{\theta} M^{\theta} / \alpha_{\text{fb}}^{\theta} = \sum_{\theta} AK_{\text{p,fb}}^{\theta} M^{\theta} / \alpha_{\text{fb}}^{\theta} \quad (14)$$

197 f^{θ} gives the mass fraction of the total PM that is the θ phase:

$$198 \quad M^{\theta} = f^{\theta} M_{\text{tot}} \quad (15)$$

199 The overall K_{p} for total amine in the PM is

$$200 \quad K_{\text{p,tot}} = \frac{F_{\text{tot}} / M_{\text{tot}}}{A} = \sum_{\theta} f^{\theta} K_{\text{p,fb}}^{\theta} / \alpha_{\text{fb}}^{\theta} \quad (16)$$

201 By analogy with the case for a non-ionizing compound, for the aerosol system the fraction
202 of the total amine (free-base + protonated) in the PM phase is given by (Liang and Pankow, 1996)

$$203 \quad f_{\text{p}} = \frac{F_{\text{tot}}}{F_{\text{tot}} + A} \quad (17)$$

204 From Eq.(16), $F_{\text{tot}} / A = K_{\text{p,tot}} M_{\text{tot}}$,

$$205 \quad f_{\text{p}} = \frac{K_{\text{p,tot}} M_{\text{tot}}}{K_{\text{p,tot}} M_{\text{tot}} + 1} = \frac{M_{\text{tot}} \sum_{\theta} f^{\theta} K_{\text{p,fb}}^{\theta} / \alpha_{\text{fb}}^{\theta}}{M_{\text{tot}} \sum_{\theta} f^{\theta} K_{\text{p,fb}}^{\theta} / \alpha_{\text{fb}}^{\theta} + 1} \quad (18)$$

206 The value of f_{p} increases towards 1 with: increasing M_{tot} ; each increasing $K_{\text{p,fb}}^{\theta}$; and each
207 decreasing $\alpha_{\text{p,fb}}^{\theta}$. Increasingly acidic conditions will generally cause all $\alpha_{\text{fb}}^{\theta}$ to decrease, and vice
208 versa. If in addition to absorptive partitioning some precipitation as a salt occurs, then the
209 expression for f_{p} will be more complicated than Eq.(18).

210 2.2. Partitioning to a Particular Phase

211 From Pankow (1994), for the free-base form we can write

$$212 \quad K_{\text{p,fb}}^{\theta} = \frac{c_{\text{p,fb}}^{\theta} (\mu\text{g } \mu\text{g}^{-1})}{c_{\text{g}} (\mu\text{g } \text{m}^{-3})} = \frac{RT}{10^6 \overline{\text{MW}}^{\theta} \zeta_{\text{Am}}^{\theta} P_{\text{L,Am}}^{\theta}} \quad (19)$$

213 where R is the gas constant ($= 8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$); T (K) is temperature; $\overline{\text{MW}}^{\theta}$ (g mol^{-1}) is

214 the mean molecular weight of the θ phase; ζ_{Am}^0 is the mole-fraction scale activity coefficient of Am
 215 in the θ phase; and $p_{\text{L,Am}}^0$ (atm) is the vapor-pressure at temperature T of pure Am as a liquid (sub-
 216 cooled if necessary). Equilibrium partitioning of a gaseous fb amine to a w phase is often
 217 parameterized in terms of the activity-based Henry's Law constant K_{H} for water

$$218 \quad K_{\text{H,fb}}^{\text{w}} \text{ (molality atm}^{-1}\text{)} = \frac{\{\text{Am}\}^{\text{w}}}{p_{\text{Am}}} = \frac{[\text{Am}]^{\text{w}} \gamma_{\text{Am}}^{\text{w}}}{p_{\text{Am}}} \quad (20)$$

219 where we add the subscript fb for clarity, and p (atm) is the gas-phase pressure. In dilute water,
 220 $\gamma_{\text{Am}}^{\text{w}} = 1$. $K_{\text{p,fb}}^{\text{w}}$ ($\mu\text{g } \mu\text{g}^{-1}$ per $\mu\text{g m}^{-3}$) is an activity-based partitioning constant. The corresponding
 221 concentration-based partitioning constant is

$$222 \quad {}^{\text{c}}K_{\text{H,fb}}^{\text{w}} \equiv \frac{[\text{Am}]^{\text{w}}}{p_{\text{Am}}} = \frac{K_{\text{H,fb}}^{\text{w}}}{\gamma_{\text{Am}}^{\text{w}}} \quad (21)$$

223 ${}^{\text{c}}K_{\text{H,fb}}^{\text{w}}$ and $K_{\text{p,fb}}^{\text{w}}$ are both gas/water partition coefficients that use concentration in the w phase. By
 224 means of the Ideal Gas Law and unit conversions,

$$225 \quad K_{\text{p,fb}}^{\text{w}} = \frac{{}^{\text{c}}K_{\text{H,fb}}^{\text{w}} \left(\frac{\text{mol}}{\text{kg-atm}} \right) RT \left(\frac{\text{m}^3\text{-atm}}{\text{mol-K}} \right)}{10^9 \left(\frac{\mu\text{g}}{\text{kg}} \right)} = \frac{K_{\text{H,fb}}^{\text{w}} RT}{10^9 \gamma_{\text{Am}}^{\text{w}}} \quad (22)$$

226 2.3. pH_{eff} Values in Multi-Phase PM

227 A schematic representation of amine partitioning is provided in Figure 1, which assumes the
 228 presence of three liquid phase types and one solid salt phase. Table 1 summarizes other possible
 229 combinations. "Liquid" refers to any phase that, regardless of viscosity, is characterizable
 230 thermodynamically as a liquid because it has little or no long-range order/crystallinity.

231 If present, for the w phase,

$$232 \quad \alpha_{fb}^w = \frac{[Am]^w}{[Am]^w + [AmH^+]^w} = \frac{1}{1 + [AmH^+]^w / [Am]^w} \quad (23)$$

233 In dilute water, all $\gamma = 1$ and $pH^w = -\log[H^+]$, and Eqs.(2) and (19) give

$$234 \quad \alpha_{fb}^w = \frac{1}{1 + \frac{[H^+]^w}{K_a}} = \frac{1}{1 + \frac{10^{-pH^w}}{10^{-pK_a}}} = \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH^w}} \quad (24)$$

235 Eq.(24) relates three quantities for dilute water: 1) α_{fb} ; 2) the basicity of the amine (pK_a); and 3)
236 the basicity of the solution (pH).

237 For a liquid phase θ in which the $\gamma \neq 1$ (including water), then it is useful to invoke the
238 concept of pH_{eff}^{θ} (effective pH) by which all the needed activity corrections are bundled as
239 (Pankow, 2001):

$$240 \quad pH_{eff}^{\theta} \equiv -\log \frac{\gamma_{Am}^{\theta} [H^+]^{\theta} \gamma_{H^+}^{\theta}}{\gamma_{AmH^+}^{\theta}} \quad (25)$$

241 (For dilute water, $pH_{eff}^{\theta} = pH$.) By Eq.(2),

$$242 \quad \frac{[AmH^+]^{\theta}}{[Am]^{\theta}} = \frac{1}{K_a} \frac{\gamma_{Am}^{\theta} [H^+]^{\theta} \gamma_{H^+}^{\theta}}{\gamma_{AmH^+}^{\theta}} \quad (26)$$

$$243 \quad = \frac{1}{10^{-pK_a}} 10^{-pH_{eff}^{\theta}} \quad (27)$$

244 Thus, even when we do not know any of the relevant γ values, we can still always write for any
245 particular amine in any liquid phase that

$$246 \quad \alpha_{fb}^{\theta} = \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH_{eff}^{\theta}}} \quad (28)$$

247 For monoethanol amine, $pK_a = 8.06$ at $20^{\circ}C$ (Gonzalez et al., 1980). Thus, if at $25^{\circ}C$ the value of
248 α_{fb}^{θ} in the θ phase of some PM was 0.50, then by definition $pH_{eff}^{\theta} = 8.06$: the composition of the
249 phase is such that the values of $[H^+]$ and all the activity coefficients give $\alpha_{fb} = 0.5$, the same as for

250 dilute water at 20 °C with pH = 8.06. As suggested above, if w, α , and β phases are all present, then
 251 differences in the activity coefficient values will certainly cause the three pH_{eff} values to be
 252 different:

$$253 \quad \text{pH}_{\text{eff}}^{\text{w}} \neq \text{pH}_{\text{eff}}^{\alpha} \neq \text{pH}_{\text{eff}}^{\beta} \neq \text{pH}_{\text{eff}}^{\text{w}} \quad \alpha_{\text{fb}}^{\text{w}} \neq \alpha_{\text{fb}}^{\alpha} \neq \alpha_{\text{fb}}^{\beta} \neq \alpha_{\text{fb}}^{\text{w}} \quad (29)$$

254

255 3. Summary

256 The Am form of a low MW amine will in general have reasonable affinities for both α and β type
 257 phases, so consideration of Eq.(22) indicates that $K_{\text{p,fb}}^{\text{w}}$, $K_{\text{p,fb}}^{\alpha}$, and $K_{\text{p,fb}}^{\beta}$ will all be roughly similar
 258 in magnitude: for all three phase types, the $\zeta_{\text{Am}}^{\theta}$ values will generally be similar, as will the $\overline{\text{MW}}^{\theta}$
 259 values (though $\overline{\text{MW}}^{\text{w}}$ will be smaller than $\overline{\text{MW}}^{\alpha}$ and $\overline{\text{MW}}^{\beta}$). And, with significant water
 260 uptake into an α phase certain to occur at moderate to high RH values, good solvation of ions will
 261 often be possible in an α phase. This will assist protonation of Am to AmH^+ in such a phase (as is
 262 known to occur for nicotine in tobacco smoke PM). The overall result is that to a first
 263 approximation, $\alpha_{\text{fb}}^{\text{w}}$ and $\alpha_{\text{fb}}^{\alpha}$ can be similar in magnitude, making $K_{\text{p,fb}}^{\alpha} / \alpha_{\text{fb}}^{\alpha}$ likely to be generally
 264 comparable to $K_{\text{p,fb}}^{\text{w}} / \alpha_{\text{fb}}^{\text{w}}$. In a β phase, ion solvation will not be as good, so that for acidic aerosol
 265 $\alpha_{\text{fb}}^{\beta}$ will generally be closer to one than the other two α_{fb} values, making $K_{\text{p,fb}}^{\beta} / \alpha_{\text{fb}}^{\beta}$ smaller than both
 266 $K_{\text{p,fb}}^{\text{w}} / \alpha_{\text{fb}}^{\text{w}}$ and $K_{\text{p,fb}}^{\alpha} / \alpha_{\text{fb}}^{\alpha}$. Overall, modeling of amine behavior in the atmosphere should include
 267 consideration of partitioning organic PM. Unfortunately, this will be more difficult than water-
 268 phase only modeling because prediction of α_{fb} values in multiphase PM will be greatly complicated
 269 by the needs to: 1) have estimated values of acidity constants in mostly organic phases of variable
 270 composition; and 2) allow distribution of chemicals over multiple liquid phases.

271

272

273

274 **Acknowledgment**

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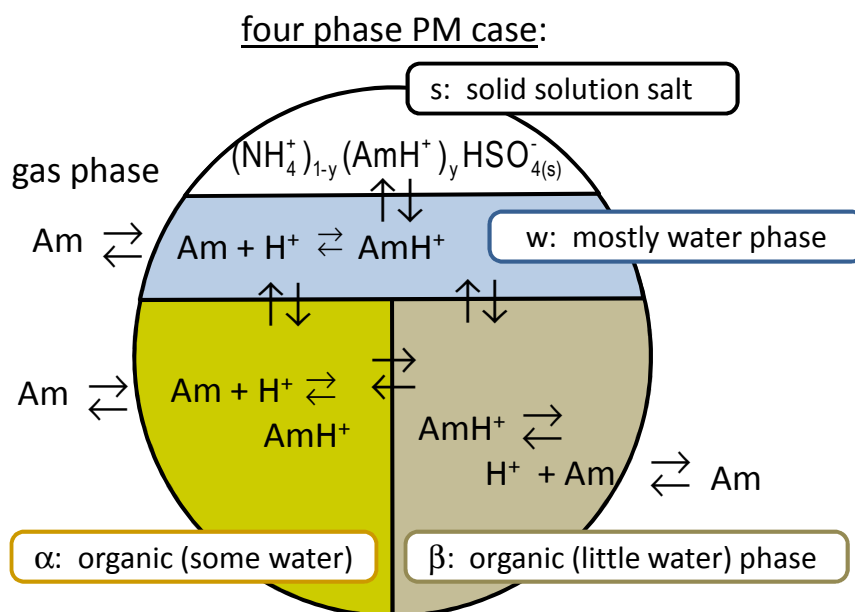
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Table 1. Possible phase combinations involving four phase types:

- α** somewhat polar liquid, mostly organic by mass;
 β non polar liquid, mostly organic by mass;
w mostly water phase by mass, presence favored by high RH conditions; and
s solid salt, presence favored by low RH conditions.

<u>phase(s)</u>	<u>dominant component(s)</u>
α	SOA
β	POA
w	water
s	solid salt
α, w	SOA, water
β, w	POA, water
α, s	SOA, solid salt
β, s	POA, solid salt
α, w, s	SOA, water, solid salt
β, w, s	POA, water, solid salt
α, β	SOA, POA
α, β, w	SOA, POA, water
α, β, s	SOA, POA, solid salt
α, β, w, s	SOA, POA, water, solid salt (Fig.1)

Figure 1. Schematic diagram of multiple-phase particulate matter with three liquid phases and one solid salt phase that is a dilute solid solution of an aminium bisulfate in ammonium bisulfate.



HIGHLIGHTS

- Amines in the atmosphere can be found in different phases in atmospheric particulate matter (PM).
- Phase 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.