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Phase Considerations in the Gas/Particle Partitioning of Organic Amines in the Atmosphere

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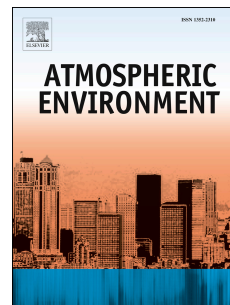*Portland State University*, pankowj@pdx.edu

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6 **- TECHNICAL NOTE -**
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9 Phase Considerations in the Gas/Particle Partitioning of
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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 $AmHHSO_{4(s)}$ exceedingly unlikely: when solid salts of AmH^+ are indeed present, by far the most

57 likely form is as a solid solution, *e.g.*, $(NH_4^+)_{1-y}(AmH^+)_y HSO_{4(s)}^-$ 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 $K_{p,tot} (m^3 \, \mu g^{-1}) = c_{p,tot} / c_g = \sum_\theta f^\theta K_{p,fb}^\theta / \alpha_{fb}^\theta$. The

60 quantity $c_{p,tot}$ ($\mu g \, \mu g^{-1}$) is the total Am concentration ($Am+AmH^+$) in the PM as summed over all

61 phases using the index θ ($= w, \alpha, \beta$); 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; $K_{p,fb}^\theta$ is the gas/particle partitioning constant for the free-

63 base (Am) form to the θ phase; and $0 < \alpha_{fb}^\theta < 1$ 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 $K_{p,tot}$ from

66 absorption into a mostly water phase, according to the term $f^w K_{p,fb}^w / \alpha_{fb}^w$. 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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(no line numbers for table)

Nomenclature	
Roman	
A	concentration ($\mu g\ m^{-3}$) 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;
$c_{p,fb}$	concentration ($\mu g\ \mu g^{-1}$) of the free-base form of an amine in some liquid phase θ;
$c_{p,tot}$	concentration ($\mu g\ \mu g^{-1}$) of total (free-base + protonated) amine in some liquid phase θ;
c_g	concentration ($\mu g\ m^{-3}$) 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 ($\mu g\ m^{-3}$) of the free-base form of an amine in some liquid phase θ;
F_{tot}	particle-phase associated concentration ($\mu g\ m^{-3}$) 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;
^cK_a	acidity constant on molal scale, using solution phase concentrations; value depends on the composition of the medium;
$K_{H,fb}^w$	Henry's gas law constant ($m\ atm^{-1}$) for partitioning to a mostly phase, with molal activity for the dissolved species; referenced to infinite dilution in water;
$^cK_{H,fb}^w$	Henry's gas law partitioning constant ($m\ atm^{-1}$) with molal concentration for the dissolved species; value depends on the composition of the medium;
$K_{p,fb}$	gas/particle partitioning constant ($m^3\ \mu g^{-1}$) for the free-base form of an amine to some liquid phase θ;
$K_{p,tot}$	gas/particle partitioning constant ($m^3\ \mu g^{-1}$) for total (free-base + protonated) amine to some liquid phase θ;
M^θ	mass concentration ($\mu g\ m^{-3}$) of absorbing liquid phase θ;
M_{tot}	total mass concentration ($\mu g\ m^{-3}$) of PM;
$\overline{MW}$	mean molecular weight ($g\ mol^{-1}$) of an absorbing liquid PM phase θ;
$\overline{MW}^w$	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);
$p_{L,Am}^o$	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 ($\mu g\ m^{-3}$);
R	gas constant ($8.2 \times 10^{-5}\ m^3\ atm\ mol^{-1}\ K^{-1}$);
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

		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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87

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 CO_2 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 NH_4^+ such as $NH_4HSO_{4(s)}$ 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 $Am + H^+ \rightarrow AmH^+$ 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 aminium 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 $(NH_4^+)_{1-y}(AmH^+)_y HSO_{4(s)}^-$ where $y \ll 1$. Second, as

110 regards absorptive partitioning, in addition to uptake into a mostly aqueous particulate matter (PM),
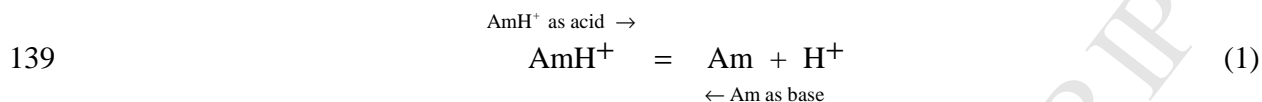
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111 in the general case it will also be necessary to consider absorption into mostly organic particulate

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 ~200 g mol^{-1}, with the MW of water only 18 g

120 mol^{-1}, then ⅓ 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 $\zeta_{MEA} = 0.33$ and $\zeta_{DEA} = 0.20$. For a mostly water phase with ($x_w \approx 1$), the predicted

125 values are $\zeta_{MEA} = 0.37$ and $\zeta_{DEA} = 0.55$, 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:

139
$$
\begin{array}{c}
\text{AmH}^+ \text{ as acid } \rightarrow \\
\text{AmH}^+ \quad = \quad \text{Am} + \text{H}^+ \\
\leftarrow \text{Am as base}
\end{array}
\qquad (1)
$$

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

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

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 $\gamma_{Am} = \gamma_{H^+} = \gamma_{AmH^+} \equiv 1$.

145   For a given constant composition of the liquid phase in which the equilibrium is being

146   attained, as usual $pK_a \equiv -\log K_a$, and $p^cK_a \equiv -\log{}^cK_a$ with

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

148   The γ values depend on the composition of the medium, so that ${}^cK_a$ values for a given acid can be

149   very different in different media. For example, the group $\gamma_{AmH^+}/(\gamma_{Am}\gamma_{H^+})$ 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 p^cK_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    $0 \le \alpha_{fb} \le 1$. When is mono-basic, then within the phase the fraction of AmH^+ is $1\text{-}\alpha_{fb}$ and

5

155
$$\alpha_{\mathrm{fb}} \quad \equiv \quad \frac{[\mathrm{Am}]}{[\mathrm{Am}] + [\mathrm{AmH}^+]} \qquad 1 - \alpha_{\mathrm{fb}} \quad = \quad \frac{[\mathrm{AmH}^+]}{[\mathrm{Am}] + [\mathrm{AmH}^+]} \qquad (4)$$

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

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

158 where $c_{\mathrm{p,fb}}$ ($\mu\mathrm{g} \; \mu\mathrm{g}^{-1}$) is the PM-phase concentration of the Am portion, and c_{g} ($\mu\mathrm{g} \; \mathrm{m}^{-3}$) $\equiv A$ ($\mu\mathrm{g} \; \mathrm{m}^{-3}$)

159 is concentration of Am in the gas-phase. The counterpart to A is F ($\mu\mathrm{g} \; \mathrm{m}^{-3}$), 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 $\{\mathrm{H}^+\}$ 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 ($\mu\mathrm{g} \; \mathrm{m}^{-3}$)

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

177 $\qquad K_{\mathrm{p,fb}}^{\theta}\ (\mathrm{m}^3\ \mu\mathrm{g}^{-1})\ =\ \dfrac{F_{\mathrm{fb}}^{\theta}/M^{\theta}}{c_{\mathrm{g}}}=\dfrac{F_{\mathrm{fb}}^{\theta}/M^{\theta}}{A}\qquad K_{\mathrm{p,tot}}^{\theta}\ (\mathrm{m}^3\ \mu\mathrm{g}^{-1})\ =\ \dfrac{F_{\mathrm{tot}}^{\theta}/M^{\theta}}{c_{\mathrm{g}}}=\dfrac{F_{\mathrm{tot}}^{\theta}/M^{\theta}}{A}$ (7)

178 where $c_{\mathrm{p,tot}}^{\theta}\ (\mu\mathrm{g}\ \mu\mathrm{g}^{-1})\ \equiv\ F_{\mathrm{tot}}^{\theta}/M^{\theta}$ is the total (*i.e.*, Am + AmH$^+$) θ-phase mass concentration of the

179 amine (computed as Am). With $\alpha_{\mathrm{fb}}^{\theta}$ defined for each phase θ according to Eq.(4), then

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

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

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

183 $$\dfrac{F_{\mathrm{tot}}^{\theta}/M_{\theta}}{c_{\mathrm{g}}}\ =\ \dfrac{c_{\mathrm{p,tot}}^{\theta}}{c_{\mathrm{g}}}\ =\ \dfrac{K_{\mathrm{p,fb}}^{\theta}}{\alpha_{\mathrm{fb}}^{\theta}}$$ (11)

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

185 Partitioning of an amine to a phase θ is greatly enhanced when the phase is acidic because then $\alpha_{\mathrm{fb}}^{\theta}$

186 $\ll 1$, and $K_{\mathrm{p,tot}}^{\theta} \gg K_{\mathrm{p,fb}}^{\theta}$ (Pankow *et al.* 1997).

187 $\qquad K_{\mathrm{p,fb}}^{\theta}$ for an amine in the θ phase depends on: a) the liquid vapor pressure $p_{\mathrm{L}}^{o}(T)$ 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 $\zeta_{\mathrm{Am}}^{\theta}$). The value of $\alpha_{\mathrm{fb}}^{\theta}$ and thus the overall partitioning

190 constant $K_{\mathrm{p,tot}}^{\theta}$ 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 $K_{\mathrm{p,fb}}^{\theta}$ and no two $\alpha_{\mathrm{fb}}^{\theta}$ values

193 will ever be exactly equal.

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

7

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

196
$$= \quad \sum\nolimits_{\theta} c_{\text{p,fb}}^{\theta} M^{\theta} / \alpha_{\text{fb}}^{\theta} \quad = \quad \sum\nolimits_{\theta} A K_{\text{p,fb}}^{\theta} M^{\theta} / \alpha_{\text{fb}}^{\theta} \qquad (14)$$

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

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

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

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

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

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

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

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

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

8

214 the mean molecular weight of the θ phase; ζ_{Am}^{θ} is the mole-fraction scale activity coefficient of Am

215 in the θ phase; and $p_{L,Am}^{o}$ (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 $$K_{H,fb}^{w} \text{ (molality atm}^{-1}) = \frac{\{Am\}^{w}}{p_{Am}} = \frac{[Am]^{w} \gamma_{Am}^{w}}{p_{Am}} \qquad (20)$$

219 where we add the subscript fb for clarity, and p (atm) is the gas-phase pressure. In dilute water,

220 $\gamma_{Am}^{w} = 1$. $K_{p,fb}^{w}$ (μg μg^{-1} per μg m^{-3}) is an activity-based partitioning constant. The corresponding

221 concentration-based partitioning constant is

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

223 $^{c}K_{H,fb}^{w}$ and $K_{p,fb}^{w}$ 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 $$K_{p,fb}^{w} = \frac{^{c}K_{H,fb}^{w}\left(\dfrac{mol}{kg\text{-}atm}\right) RT \left(\dfrac{m^{3}\text{-}atm}{mol\text{-}K} K\right)}{10^{9}\left(\dfrac{\mu g}{kg}\right)} = \frac{\dfrac{K_{H,fb}^{w}}{\gamma_{Am}^{w}} RT}{10^{9}} \qquad (22)$$

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

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

234
$$\alpha_{fb}^{w} = \frac{1}{1 + \dfrac{[H^{+}]^{w}}{K_{a}}} = \frac{1}{1 + \dfrac{10^{-pH^{w}}}{10^{-pK_{a}}}} = \frac{10^{-pK_{a}}}{10^{-pK_{a}} + 10^{-pH^{w}}} \qquad (24)$$

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} (effective pH) by which all the needed activity corrections are bundled as

239 (Pankow, 2001):

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

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

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

243
$$= \frac{1}{10^{-pK_{a}}} 10^{-pH_{eff}^{\theta}} \qquad (27)$$

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
$$\alpha_{fb}^{\theta} = \frac{10^{-pK_{a}}}{10^{-pK_{a}} + 10^{-pH_{eff}^{\theta}}} \qquad (28)$$

247 For monoethanol amine, $pK_{a} = 8.06$ at 20 ^{o}C (Gonzalez et al., 1980). Thus, if at 25 ^{o}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 $^{\circ}$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   $$\mathrm{pH}_{\mathrm{eff}}^{\mathrm{w}} \neq \mathrm{pH}_{\mathrm{eff}}^{\alpha} \neq \mathrm{pH}_{\mathrm{eff}}^{\beta} \neq \mathrm{pH}_{\mathrm{eff}}^{\mathrm{w}} \qquad \alpha_{\mathrm{fb}}^{\mathrm{w}} \neq \alpha_{\mathrm{fb}}^{\alpha} \neq \alpha_{\mathrm{fb}}^{\beta} \neq \alpha_{\mathrm{fb}}^{\mathrm{w}} \qquad (29)$$

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 $K_{\mathrm{p,fb}}^{\mathrm{w}}$, $K_{\mathrm{p,fb}}^{\alpha}$, and $K_{\mathrm{p,fb}}^{\beta}$ will all be roughly similar

258   in magnitude: for all three phase types, the $\zeta_{\mathrm{Am}}^{\theta}$ values will generally be similar, as will the $\overline{\mathrm{MW}}^{\theta}$

259   values (though $\overline{\mathrm{MW}}^{\mathrm{w}}$ will be smaller than $\overline{\mathrm{MW}}^{\alpha}$ and $\overline{\mathrm{MW}}^{\beta}$). 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, $\alpha_{\mathrm{fb}}^{\mathrm{w}}$ and $\alpha_{\mathrm{fb}}^{\alpha}$ can be similar in magnitude, making $K_{\mathrm{p,fb}}^{\alpha} / \alpha_{\mathrm{fb}}^{\alpha}$ likely to be generally

264   comparable to $K_{\mathrm{p,fb}}^{\mathrm{w}} / \alpha_{\mathrm{fb}}^{\mathrm{w}}$. In a β phase, ion solvation will not be as good, so that for acidic aerosol

265   $\alpha_{\mathrm{fb}}^{\beta}$ will generally be closer to one than the other two α_{fb} values, making $K_{\mathrm{p,fb}}^{\beta} / \alpha_{\mathrm{fb}}^{\beta}$ smaller than both

266   $K_{\mathrm{p,fb}}^{\mathrm{w}} / \alpha_{\mathrm{fb}}^{\mathrm{w}}$ and $K_{\mathrm{p,fb}}^{\alpha} / \alpha_{\mathrm{fb}}^{\alpha}$. 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

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273

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277   **References**

278   Barsanti, K., McMurry, P., Smith, J. 2009. The potential contribution of organic salts to new

279   particle formation.   Atmospheric Chemistry and Physics 8, 2949-2957.

280   Bzdek, B. R., Ridge, D. P., Johnston, M. V. 2011a. Amine reactivity with charged sulfuric acid

281   clusters. Atmospheric Chemistry and Physics 11, 8735-8743.

282   Bzdek, B.R., Zordan, C.A., Luther, G.W., Johnston, M.V. 2011b. Nanoparticle chemical

283   composition during new particle formation. Aerosol Science and Technology 45, 1041-1048

284   Bzdek, B.R., Lawler, M.J., Horan, A.J., Pennington, M.R., DePalma, J.W., Zhao, J., Smith, J.N.,

285   Johnston, M.V. 2014. Molecular constraints on particle growth during new particle

286   formation. Geophysical Research Letters 41, 6045-6054.

287   Chan, L.P., Chan, C.K. 2013. Role of the aerosol phase state in ammonia/amines exchange

288   reactions. Environmental Science & Technology 47, 5755–5762.

289   Erdakos, G.B., Pankow, J.F. (2004) Gas/particle partitioning of neutral and ionizing compounds to

290   single and multi-phase aerosol particles. 2. Phase separation in liquid particulate matter

291   containing both polar and low-polarity organic compounds.   Atmospheric Environment 38,

292   1005-1013.

293   Fredenslund, A., Gmehling, J., Rasmussen, P., 1977. *Vapor–Liquid Equilibria Using UNIFAC: A*

294   *Group Contribution Method*. Elsevier, Amsterdam, 380 pp.

295   Ge, G., Wexler, A.S., Clegg, S.L. 2011. Atmospheric amines - Part II. Thermodynamic properties

296   and gas/particle partitioning. Atmospheric Environment 45, 561-577.

297   Gonzalez, E., Monge, C., and Whittembury, J. 1980. Ionization constants of 5,5'-dimethyl-2,4-

298   oxazolidinedione (DMO) and nicotine at temperatures and NaCl concentrations of biological

299   interest. Acta Cientifica Venezolana 31, 128-130.

300   Guo, H., Xu, L., Bougiatioti, A., Cerully, K.M., Capps, S.L., Hite, J.R., Carlton, A.G., Lee, S.-H.,

301   Bergin, M.H., Ng, N.L., Nenes, A., Weber, R.J., 2014. Particle water and pH in the

302   southeastern United States. Atmospheric Chemistry and Physics Discussion 14, 27143–

303   27193.

304   Jathar, S.H., Mahmud, A., Barsanti, K.C., Asher, W.E., Pankow, J.F., Kleeman, M.J. (2015) Water

305   uptake and its influence on gas/particle partitioning of secondary organic aerosol in the

306   United States. Submitted to Atmospheric Environment.

307   Liang, C., Pankow, J.F. (1996) Gas/particle partitioning of organic compounds to environmental

308   tobacco smoke: partition coefficient measurements by desorption and comparison to urban

309   particulate material. Environmental Science & Technology 30, 2800-2805.

310   Pankow, J.F. 1994 An absorption model of gas/particle partitioning in the atmosphere. Atmospheric

311   Environment, 28, 185-188.

312   Pankow, J.F., Mader, B.T., Isabelle, L.M., Luo, W., Pavlick, A., Liang, C. 1997. Conversion of

313   nicotine in tobacco smoke to its volatile and available free-base form through the action of

314   gaseous ammonia. Environmental Science & Technology 31, 2428-2433. See also Errata,

315   Environmental Science & Technology 33, 1320.

316   Pankow, J.F. 2001. A consideration of the role of gas/particle partitioning in the deposition of

317   nicotine and other tobacco smoke compounds in the respiratory tract. Chemical Research in

318   Toxicology 14, 1465-1481.

319 Pankow, J.F., Tavakoli, A.D., Luo, W., Isabelle, L.M. (2003) percent free-base nicotine in the

320   tobacco smoke particulate matter of selected commercial and reference cigarettes. Chemical

321   Research in Toxicology 16, 1014-1018.

322 Pankow, J.F., Marks, M.C., Barsanti, K.C., Mahmud, A., Asher, W.E., Li, J., Ying, Q., Jathar, S.H.,

323   Kleeman, M.J. 2015, Molecular view modeling of atmospheric organic particulate matter:

324   Incorporating molecular structure and co-condensation of water. Submitted to Atmospheric

325   Environment.

326 Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E., Feron, F. 2012. Towards

327   commercial scale postcombustion capture of CO_2 with monoethanolamine solvent: key

328   considerations for solvent management and environmental impacts. Environmental Science

329   & Technology 46, 3643-3654.

330 Rochelle, G.T. 2009. Amine scrubbing for CO_2 capture. Science 325, 1652-1654.

331 Smith, N.O. 1992. Thermodynamics of ionic solid solutions. A new treatment of existing

332   distribution data. Journal of Solution Chemistry, 1992, 21, 1051-1068.

333 Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H.,

334   Williams, B. J., McMurry, P. H. 2010. Observations of aminium salts in atmospheric

335   nanoparticles and possible climatic implications. Proceedings of the National Academy of

336   Sciences 107, 6634–6639.

337 Yli-Juuti, T., Barsanti, K., Ruiz, L., Kulmala, M., Riipinen, I. 2013. Model for acid-base chemistry

338   in nanoparticle growth. Atmospheric Chemistry and Physics, 2013, 13: 12507-12524.

339 Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A.F., Yao, L., Wang, Z., Wang, X.,

340   Chen, L. 2015. Measurement of atmospheric amines and ammonia using the high resolution

341   time-of-flight chemical ionization mass spectrometry. Atmospheric Environment 102, 249-

342   259.

14

343   Zuend, A., Seinfeld, J.H., 2012. Modeling the gas-particle partitioning of secondary organic

344   aerosol: the importance of liquid-liquid phase separation. Atmospheric Chemistry and

345   Physics 12, 3857–3882.

346

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.

phase(s)	dominant component(s)
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.
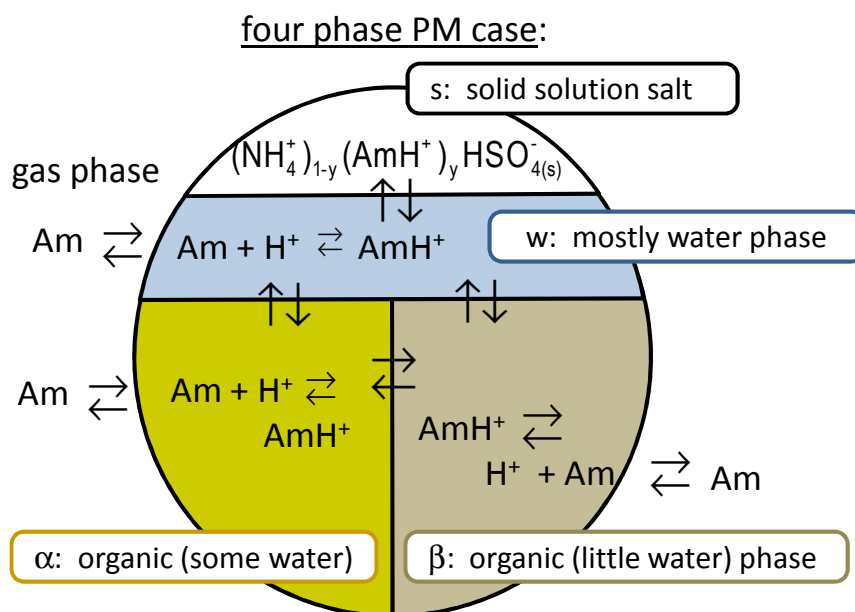
HIGHLIGHTS

- 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.