

Supplementary Information for

Assessing pH- and Temperature-dependence in the Aqueous Phase Partitioning of Organic Acids and Bases in the Atmosphere

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Partitioning Space Equations

Definition of Variables:

H_{eff} : effective Henry's Law constant of a compound of interest, accounting for the difference between the pH of the aqueous system and said compound's pK_a (temperature-dependent)

H : a compound of interest's intrinsic Henry's Law constant, $\text{mol L}^{-1} \text{atm}^{-1}$ (temperature-dependent)

K_p : gas-particle partition coefficient, $\text{m}^3 \mu\text{g}^{-1}$ (adapted from Pankow, 1994)¹

f_{WIOM} : weight fraction that is the absorbing phase for K_p (water-insoluble organic matter, WIOM)

MW_{WIOM} : average or surrogate molecular weight for absorbing organic phase, g mol^{-1}

p_L^0 : compound of interest's pure-liquid vapor pressure, atm (temperature-dependent)

$K_{W/G}$: aqueous-gas partition coefficient, L L^{-1} (adapted from Wania et al., 2015)²

R : ideal gas constant, $0.08206 \text{ L atm mol}^{-1} \text{K}^{-1}$

T : temperature, K

$K_{WIOM/G}$: WIOM-gas partition coefficient, $\text{m}^3 \text{m}^{-3}$ (as defined by Wania et al., 2015)²

δ_{WIOM} : density of WIOM phase, g m^{-3}

φ_W : fraction of the total amount of a compound of interest that is in the aqueous phase (as opposed to gas and WIOM)

V_G, V_W, V_{WIOM} : volume of each phase, m³

Equations used in this work:

$$H_{eff} = H(1 + 10^{pH-pK_a}) \dots\dots\dots (S1)$$

$$K_p = \frac{RTf_{WIOM}}{10^6 MW_{WIOM} p_L^0} \dots\dots\dots (S2)$$

$$K_{W/G} = H_{eff} RT \dots\dots\dots (S3)$$

$$K_{WIOM/G} = K_p \delta_{WIOM} \frac{10^6 \mu g}{g} \dots\dots\dots (S4)$$

$$\varphi_W = 1 / (1 + K_{G/W} \frac{V_G}{V_W} + K_{WIOM/W} \frac{V_{WIOM}}{V_W}) \dots\dots\dots (S5)$$

$$pH - pK_a = \log \left(\frac{\frac{\varphi_W V_G}{RT V_W} + \frac{\varphi_W f_{WIOM} \delta_{WIOM} V_{WIOM}}{p_L^0 MW_{WIOM} V_W}}{H(1 - \varphi_W)} - 1 \right) \dots\dots\dots (S6)$$

Table S1: pK _a values determined for this work, each using a single temperature-controlled potentiometric titration. Ninety-five percent confidence intervals for the linear regression estimations of the pK _a values are reported. Experimental details outlined in main text.		
Compound	T (°C)	pK _a
ammonia	15	9.598 ± 0.003
	22	9.470 ± 0.002
	41	8.877 ± 0.005
	55	8.447 ± 0.005
methylamine	16	10.93 ± 0.01
	20.	10.860 ± 0.006
	32	10.51 ± 0.01
	43	10.146 ± 0.007
monoethanolamine	2	10.09 ± 0.01
	20.	9.675 ± 0.005
	32	9.347 ± 0.005
	40.	9.110 ± 0.003
<i>cis</i> -pinonic acid	8	4.528 ± 0.004
	19	4.580 ± 0.004
	24	4.604 ± 0.005
	39	4.655 ± 0.006
2-hydroxyisobutyric acid	13	3.93 ± 0.03
	22	3.945 ± 0.006

	33	3.872 ± 0.005
	40	3.898 ± 0.005

References

- (1) Pankow, J. F. *AN ABSORPTION MODEL OF GAS/PARTICLE PARTITIONING OF ORGANIC COMPOUNDS IN THE ATMOSPHERE*; 1994; Vol. 28.
- (2) Wania, F.; Lei, Y. D.; Wang, C.; Abbatt, J. P. D.; Goss, K. U. Using the Chemical Equilibrium Partitioning Space to Explore Factors Influencing the Phase Distribution of Compounds Involved in Secondary Organic Aerosol Formation. *Atmos Chem Phys* **2015**, 15 (6), 3395–3412. <https://doi.org/10.5194/acp-15-3395-2015>.