Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supplemental Material: Equilibration times in viscous and viscoelastic aerosol particles

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1 Contents of Supplemental Material

In this document, we provide parameters for aqueous sucrose calculations (Section 2), parameters for aqueous oxidized α-pinene calculations (Section 3), the modelled global relative humidity (Section 4), and the modelled global relative temperature (Section 5). Provided as separate files are the output of from AIOMFAC-VISC calculations for aqueous sucrose and aqueous oxidized α-pinene.

2 Aqueous sucrose

2.1 Diffusivity

For aqueous sucrose, the binary (Fickian) diffusivity from Zobrist et al. was used in all calculations.[1] The activity- and temperature-dependent diffusivity, $D_{\mathrm{w}}(a_{\mathrm{w}}, T)$, is

$$\log_{10} D_{\mathrm{w}}(a_{\mathrm{w}}, T) = -\left(A(a_{\mathrm{w}}) + \frac{B(a_{\mathrm{w}})}{T - T_0(a_{\mathrm{w}})} \right), \tag{S1}$$

where T is the temperature, a_{w} is the activity of water, and the three parameters A, B, and T_0, are

$$A(a_{\mathrm{w}}) = 7 + 0.175(1 - 46.46(1 - a_{\mathrm{w}})), \tag{S2}$$

$$B(a_{\mathrm{w}}) = 262.867(1 + 10.53(1 - a_{\mathrm{w}}) - 0.3(1 - a_{\mathrm{w}})^2), \tag{S3}$$

$$T_0(a_{\mathrm{w}}) = 127.9(1 + 0.4514(1 - a_{\mathrm{w}}) - 0.5(1 - a_{\mathrm{w}})^{1.7}). \tag{S4}$$

2.2 Activity

The parameterization for a_{w} from Zobrist et al. was used here.[1] It is

$$a_{\mathrm{w}}(T, w_{\mathrm{s}}) = \frac{1 + a w_{\mathrm{s}}}{1 + b w_{\mathrm{s}} + c w_{\mathrm{s}}^2} + (T - T^{\theta})(d w_{\mathrm{s}} + e w_{\mathrm{s}}^2 + f w_{\mathrm{s}}^3 + g w_{\mathrm{s}}^4), \tag{S5}$$

where w_s is mass fraction of sucrose in solution, $T^\theta = 298.15$ K and a to g are fit parameters: $a = -1$, $b = -0.99721$, $c = 0.13599$, $d = 0.001688$, $e = -0.005151$, $f = 0.009607$, and $g = -0.006142$.

2.3 Density

The density was calculated using the partial specific volumes 0.001 m^3/kg for water and 0.000632 m^3/kg for sucrose.

2.4 Young's Modulus

Measured values of the elastic modulus for sucrose crystals at room temperature range from 32.3 to 38.2±0.4 GPa.[2,3] We used 33 GPa in all calculations, which is representative of these reported measurements.

2.5 Viscosity

AIOMFAC-VISC was used to calculate the activity- and temperature-dependent viscosity of aqueous sucrose. Datasets were generated in steps of 10 K from 200 to 310 K. This set of output is provided as separate files in the supplementary material. Two-dimensional interpolation of this output was used for all activity- and temperature-dependent viscosity calculations.

3 Aqueous oxidized α-pinene

3.1 Diffusivity (Lienhard et al. parameterization)

The binary (Fickian) diffusivity for aqueous oxidized α-pinene was calculated using functions and parameters in Lienhard et al.[4] and additional functions provided by the authors of that

work. The diffusivity is

$$D_{\mathrm{w}}(a_{\mathrm{w}}, T) = D_{\mathrm{w}}(0, T)^{1-x_{\mathrm{w}}\alpha} D_{\mathrm{w}}(1, T)^{x_{\mathrm{w}}\alpha}, \tag{S6}$$

where x_{w} is the mole fraction of water,

$$\ln \alpha = (1-x_{\mathrm{w}})^2[A(T)+3B(T)-4(1-x_{\mathrm{w}})B(T)], \tag{S7}$$

$$A(T) = \begin{cases} a_1+a_2T, & T \leq T_a \\ a_1+a_2T_a, & T > T_a, \end{cases} \tag{S8}$$

$a_1 = -18.31$, $a_2 = 0.063$ K^{-1}, $T_a = 273$ K,

$$B(T) = \begin{cases} b_1+b_2T, & T \leq T_b \\ b_1+b_2T_b, & T > T_b, \end{cases} \tag{S9}$$

$b_1 = -10.65$, $b_2 = 0.039$ K^{-1}, $T_b = 273$ K,

$$D_{\mathrm{w}}(1, T) = D_0 \exp[-E_{\mathrm{act,w}}/(T-T_{0,\mathrm{w}})], \tag{S10}$$

$D_0 = 0.00306$ cm^2/s, $E_{\mathrm{act,w}} = 892$ K, $T_{0,\mathrm{w}} = 118$ K,

$$D_{\mathrm{w}}(0, T) = \exp(\zeta_{\mathrm{A}}), \tag{S11}$$

$$\zeta_{\mathrm{A}} = \zeta_{\mathrm{A}}^{\circ} - \frac{E_{\mathrm{act}}}{RT} \tag{S12}$$

$E_{\mathrm{act}} = 65.5$ kJ/mol, $R = 8.3145$ J/(mol K),

$$\zeta_{\mathrm{A}}^{\circ} = \ln[D_{\mathrm{w}}(0, T_g)/(\mathrm{cm}^2\ \mathrm{s}^{-1})] + \frac{E_{\mathrm{act}}}{RT_g}, \tag{S13}$$

$T_g = 270$ K, and $\ln[D_{\mathrm{w}}(0, T_g)/(\mathrm{cm}^2\ \mathrm{s}^{-1})] = -26.60$.

Additionally, to convert between water activity, mass fraction, and mole fraction we use a molar mass of 150 g/mol for oxidized α-pinene and the function

$$a_{\mathrm{w}} = \frac{(1-w_{\mathrm{s}})^{0.49099}}{1-0.21245w_{\mathrm{s}}^2-0.35w_{\mathrm{s}}}, \tag{S14}$$

where w_s is the mass fraction of the oxidized α-pinene. Note that this activity function is only used for calculations involving Eq. S6. A different activity function (Eq. S16) is used in all other calculations involving the activity.

3.2 Diffusivity (fit to Price et al. measurements)

The measurements from Price et al.[5] were fitted using a quadratic polynomial. The best-fit was

$$\log_{10} D_w(a_w) = -13.08 + 0.9280 a_w + 1.717 a_w^2. \tag{S15}$$

3.3 Activity

For calculations involving activity, mass fraction, and mole fraction not connected to Eq. S6, the function

$$w_s = \left(1 + \frac{0.02202 a_w}{1 - a_w}\right)^{-3}, \tag{S16}$$

was used. Although Eq. S16 is different than Eq. A9 in Ref. 4, it exactly reproduces the red curve in Fig. A4b of that paper.

3.4 Density

The density was calculated using the partial specific volumes 0.001 m^3/kg for water and 0.000716 m^3/kg for oxidized α-pinene. Although these parameters have no temperature-dependence, the resulting density will still closely match Eq. A10 in Ref. 4 for any temperature of interest in the current work (i.e. 200 to 310 K).

3.5 Viscosity

AIOMFAC-VISC was used to calculate the activity- and temperature-dependent viscosity of aqueous oxidized α-pinene, where the oxidized α-pinene was characterized with a system of 15 SOA surrogate components. Datasets were generated in steps of 10 K from 200 to 310 K. This set of output is provided as separate files in the supplementary material. Two-dimensional interpolation of this output was used for all activity- and temperature-dependent viscosity calculations.

4 Global relative humidity

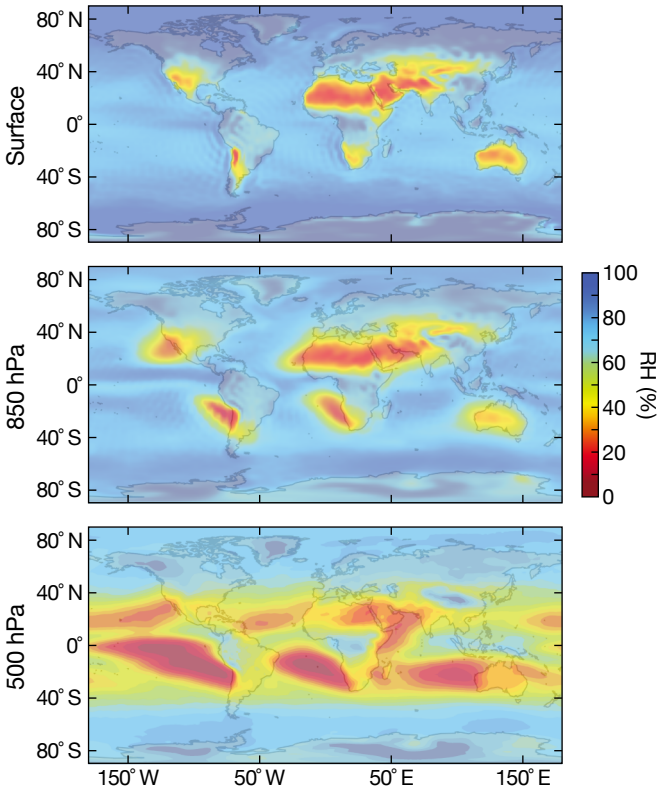

Figure S1: Relative humidity (RH) from the global chemistry climate model EMAC[6] that was used in calculations in the main text. The RH shown here is identical to that used in Ref. 7.

5 Global temperature

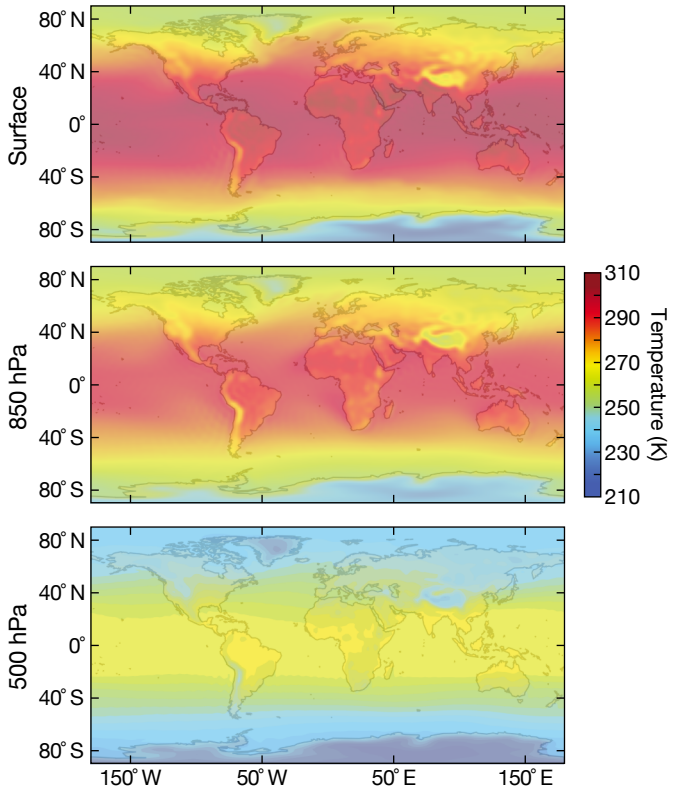

Figure S2: Temperature from the global chemistry climate model EMAC[6] that was used in calculations in the main text. The RH shown here is identical to that used in Ref. 7.

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