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*Supplement of*

## **Viscosities, diffusion coefficients, and mixing times of intrinsic fluorescent organic molecules in brown limonene secondary organic aerosol and tests of the Stokes–Einstein equation**

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## Supplement

### S1. Conditioning times with the surrounding relative humidity.

The time needed to condition the brown LSOA particles to a controlled RH was calculated using the following equation (Seinfeld and Pandis, 2006; Shiraiwa et al., 2011):

$$\tau_{diff,water} = \frac{R_{droplet}^2}{\pi^2 D_{H2O}} \quad (S1)$$

where  $\tau_{diff,water}$  is the characteristic time for mixing of water by molecular diffusion within a droplet,  $R_{droplet}$  is the radius of the droplet, and  $D_{H2O}$  is the diffusion coefficient of water molecules in the brown LSOA. Equation S1 corresponds to the time, at which the concentration of water at the centre of the droplet deviates by less than  $1/e$  from the equilibrium concentration. To calculate  $\tau_{diff,water}$ , we used the diffusion coefficients of water within sucrose-water mixtures from Price et al. (2014) evaluated at the same water activity as in the brown LSOA particles. Since the viscosity of sucrose-water mixtures are higher than the viscosity of brown LSOA evaluated at the same water activity (compare Fig. 3 in Powers et al. (2013) with Fig. 5 in Hinks et al. (2016) (Hinks et al., 2016; Power et al., 2013)), this assumption most likely leads to an overestimation of the time needed for conditioning the particles to the controlled RH. As an illustration, at a water activity of 0.3, the viscosity of brown LSOA is between  $2.2 \cdot 10^2$  to  $1.4 \cdot 10^4$  Pa·s (Hinks et al. (2016)), while the viscosity of sucrose-water mixtures is approximately  $3 \cdot 10^8$  Pa·s (Power et al. (2013)). Shown in Table S1 are the experimental times used to condition the brown LSOA particles ( $t_{exp}$ ) for the rFRAP experiments as well as the corresponding calculated  $\tau_{diff,water}$  values.

For the bead mobility experiments, which were carried out at  $\geq 70$  % RH, the size of the particles were 5 to 50  $\mu\text{m}$  in diameter. These particles were left to equilibrate for 20 min prior to each measurement. For comparison, the calculated conditioning time for a 50  $\mu\text{m}$  diameter droplet at 70 % RH based on the method described above is 44 s. Shown in Table S2 are results from the bead-mobility experiments.

### S2. Relationship between fluorescence signal and concentration of intrinsic fluorophores in brown LSOA.

The fluorescence intensity  $F$  of a sample depends on the intensity of the incoming light,  $I_0$ , the intensity of the outgoing light,  $I$ , and the rate constant,  $k_f$ , that takes the ability of a molecule to fluoresce into account :

$$F = k_f(I_0 - I). \quad (S2)$$

By combining Equation S2 with the Beer-Lambert Law, the following equation can be obtained:

$$F = k_f I_0 (1 - 10^{-\epsilon l c}), \quad (S3)$$

where  $\epsilon$  is the absorption coefficient,  $l$  is the distance the light travels through the fluorescent medium and  $c$  is the concentration of the fluorescent dye. Equation S3 can be used to derive the following equation:

$$\frac{F(t)}{F_0} = \frac{1 - 10^{-\epsilon l c(t)}}{1 - 10^{-\epsilon l c_0}}, \quad (S4)$$

where  $F(t)$  is the fluorescence intensity at time  $t$  after photobleaching,  $F_0$  is the fluorescence intensity prior to photobleaching,  $c(t)$  is the concentration at time  $t$  after photobleaching, and  $c_0$  is the concentration prior to photobleaching.

The transmittance prior to photobleaching,  $T_0$ , can be described by the following equation:

$$T_0 = 10^{-\epsilon l c_0}. \quad (S5)$$

Combining Eq. S4 and Eq. S5 gives the following equation:

$$\frac{F(t)}{F_0} = \frac{1 - 10^{-\epsilon l c(t)}}{1 - T_0}. \quad (S6)$$

Equation S6 and S5 can be used to derive the following relationship between the normalized concentration of the intrinsic fluorescent dye and the normalized fluorescence signal:

$$\frac{c(t)}{c_0} = \frac{\log\left[1 - (1 - T_0) \frac{F(t)}{F_0}\right]}{\log(T_0)}. \quad (S7)$$

## Tables

**Table S 1: Selected parameters used in rFRAP experiments as well as the measured diffusion coefficients (D).  $\tau_{diff,water}$  is the calculated characteristic time for molecular diffusion of water within the studied droplets.  $t_{exp}$  is the time used for conditioning the droplets to a known relative humidity.**

$a_w$	Slide #	Droplet radius ( $\mu\text{m}$ )	$\tau_{diff,water}$	$t_{exp}$	Measured D value ( $\mu\text{m}^2/\text{s}$ )
0.90	1	200	23 s	17 min	0.39
	2	175	17 s	17 min	0.64
	3	160	15 s	22 min	0.55
	4	200	23 s	22 min	0.66
0.80	1	175	2.2 min	22 min	0.049
	2	175	2.2 min	18 min	0.051
	3	175	2.2 min	18 min	0.052
0.70	1	160	11.3 min	1.5 h	0.014
	2	160	11.3 min	3 h	0.019
	3	125	7 min	3 h	0.017
0.60	1	190	1.5 h	8 h	0.010
	2	225	2.2 h	8 h	0.010
	3	175	1.3 h	7 h	0.0084
0.49	1	150	6.6 h	38 d	0.0020
	2	185	10 h	38 d	0.0017
	3	150	6.6 h	38 d	0.0016
0.38	1	200	7.6 d	47 d	2.04E-4
	2	100	2 d	47 d	3.21E-4
	3	200	7.6 d	35 d	1.90E-4
0.33	1	57	2.4 d	10 d	9.54E-5
	2	57	2.4 d	10 d	3.79E-5

**Table S 2: Measured viscosities at various water activities ( $a_w$ ) using the bead mobility technique.**

Sample	$a_w$	Average bead speed ( $\mu\text{m}/\text{ms}$ )	Average viscosity (Pa s)	Highest viscosity measured (Pa s)	Lowest viscosity measured (Pa s)
1	0.92	1.12E-04	1.02	1.65	0.60
	0.79	1.13E-05	10.13	20.38	6.41
	0.71	4.26E-06	25.00	37.51	17.18
2	0.92	8.93E-05	1.42	2.34	0.75
	0.77	4.17E-06	25.74	33.58	18.13
	0.72	1.90E-06	48.94	57.19	37.81
3	0.89	1.98E-04	0.61	0.82	0.19
	0.80	3.32E-05	3.26	4.63	2.41
	0.70	6.14E-06	17.08	20.93	11.16

Figures

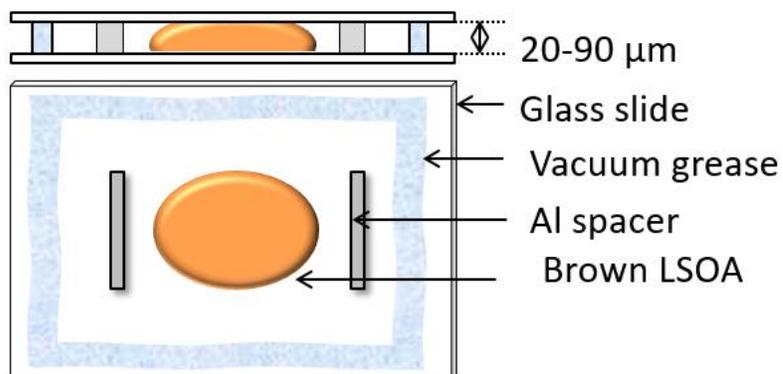


Fig. S1. Schematic of a thin film of brown LSOA used in the diffusion coefficient measurements.

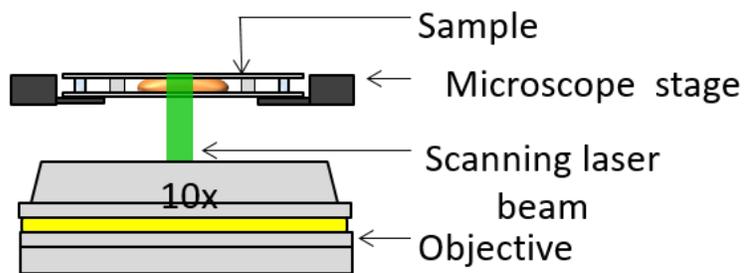


Fig. S2. Simplified schematic of the setup used to carry out the rFRAP measurements.

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