S1. Calculation of equilibration times

The time required for droplets to come to equilibrium with the surrounding water activity (a_w) was calculated using the following equation (Seinfeld and Pandis, 2006; Shiraiwa et al., 2011):

$$\tau_{diff,H20} = \frac{dp^2}{4\pi^2 D_{H2O}} \tag{S1}$$

where $\tau_{\mathrm{diff,\,H2O}}$ is the characteristic mixing time of water due to molecular diffusion, d_p is the diameter of the droplet, and D_{H2O} is the diffusion coefficient of water in the matrix. A discussion of the values used for D_{H2O} in organic-water droplets follows. Diffusion coefficients of water in the organic matrices studied here are assumed to equal the diffusion coefficients of water in a sucrose matrix when the viscosity of the two matrices are equal. Diffusion coefficients for water in a sucrose matrix at a given viscosity were calculated using a parametrization for diffusion coefficients as a function of a_w from Price et al. (2016) and a parameterization for sucrose viscosity as a function of a_w from Grayson et al. (2017). Those diffusion coefficients were used as an estimate for diffusion coefficients of water in citric acid, sorbitol, and sucrose-citric acid at that same viscosity. The expected viscosity of citric acid, sorbitol, and sucrose-citric acid matrices at each a_w was calculated using viscosity-a_w parameterizations from Rovelli et al. (n.d.) and Song et al. (2016) (Figs. S7-S9).

S2. Diffusion coefficients and viscosity data from literature sources

Figure 3a in the main text includes log (D) – log (kT/6πR$_H$) plotted as a function of log (η) for organics diffusing in sucrose and brown limonene SOA matrices. The following gives additional details on this data.

S2.1 Sucrose matrices

In Price et al. (2016) and Chenyakin et al. (2017) , diffusion coefficients were reported as a function of a_w. The a_w was converted to viscosity using the viscosity vs. a_w parameterization from Figure S1 in Grayson et al. (2017) for sucrose solutions. The experiments of Chenyakin et al. (2017) were performed at 294.5 K, and the experiments of Price et al. (2016) were performed at 296 K.

The diffusion coefficients of Champion et al. (1997) were reported as a function of experimental temperature (T) minus the glass transition temperature (T_g). Those data were digitized using Origin software. The sucrose mass fraction of the solution used for each measurement was also given. The T_g at each sucrose mass fraction was calculated, using the Gordon-Taylor equation and parameters provided by Champion et al. (1997). Next, the experimental temperature for each measurement was calculated using the reported T-T_g values and the calculated T_g. Only diffusion coefficients measured at temperatures of 292 – 298 K were used. The sucrose mass fraction was converted to a_w using the relation between sucrose mass fraction and a_w

given in Zobrist et al. (2011). Finally, viscosity was calculated using the relation between viscosity and a_w given in Grayson et al. (2017) for sucrose solutions.

Rampp et al. (2000) measured diffusion coefficients of sucrose as a function of temperature, but reported their results for sucrose-water solutions in terms of parameters for the Vogel-Tammann-Fulcher (VTF) equation:

$$D = D_0 e^{\left(-\frac{T_0 C}{T - T_0}\right)} \tag{S2}$$

where D is the diffusion coefficient (m^2/s), and D_0, T_0, and C are free parameters. D_0 represents the expected diffusion at some value T_0, and C is the fragility parameter. The VTF parameters were reported as a function of mass fraction sucrose. Using the VTF equation and the reported VTF parameters, we calculated a diffusion coefficient at a temperature of 295 K for each mass fraction sucrose they studied. Sucrose mass fraction was then converted to viscosity using the relation between sucrose mass fraction and a_w of Zobrist et al. (2011) and the relation between viscosity and a_w in sucrose solutions given in Grayson et al. (2017).

Diffusion coefficients of the fluorescent organic molecule fluorescein in a sucrose matrix have also been measured by Corti et al. (2008) in the temperature range of 292-298 K. However, diffusion coefficients measured by Corti et al. (2008) are not included in Fig. 3 of the main text because Price et al. (2016) has shown that these measurements are inconsistent with other literature measurements of large organics in sucrose matrices.

As mentioned above, the viscosity-a_w parameterization provided in Figure S1 in Grayson et al. (2017) was used to convert water activities to viscosities in sucrose-water matrices. Sucrose-water viscosity data in that parameterization come from several viscosity measurements (Först et al., 2002; Green and Perry, 2007; Haynes, 2015; Lide, 2001; Migliori et al., 2007; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007). All viscosity measurements were made at a temperature of 293 K.

S2.2 Matrices consisting of brown limonene SOA generated in the laboratory

Diffusion coefficients in brown limonene SOA are reported as a function of a_w in Ullmann et al. (2019). The viscosity of brown limonene SOA matrices as a function of a_w were also reported in that work. Both diffusion and viscosity measurements were performed at 294.5 K.

Tables

Table S1. Selected parameters used in preparing droplets containing rhodamine 6G in a citric acid matrix for rFRAP experiments and measured diffusion coefficients. $\tau_{diffusion,\ H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see section S1 and Eq. (S1)). $t_{experimental}$ is the time used for conditioning the droplets at a given relative humidity.

a_w	Max diameter (µm)	$\tau_{diffusion,\ H2O}$ (calculated)	$t_{experimental}$	Log (η, Pa s) [a]	Diffusion coefficient (m^2/s)
0.23 ± 0.025	228	1 hour	4.2 days	2.92 ± 0.61	2.99 E-15 ± 2.55E-15
0.331 ± 0.025	628	2.89 hours	20 hours	1.82 ± 0.56	1.73E-14 ± 7.83 E-15
0.432 ± 0.025	656	0.75 hours	20 hours	0.85 ± 0.54	1.30 E-13 ± 2.53 E-14
0.514 ± 0.025	542	9.1 minutes	15 hours	0.16 ± 0.51	5.53 E-13 ± 1.26E-13
0.571 ± 0.025	828	8.7 minutes	15 hours	-0.30 ± 0.50	1.05 E-12 ± 1.13 E-13
0.732 ± 0.025	914	38 seconds	20 hours	-1.31 ± 0.47	1.07 E-11 ± 1.44 E-12
0.863 ± 0.025	1128	6 seconds	15 hours	-1.89 ± 0.47	3.14 E-11 ± 3.72 E-12

[a] The lower limit of viscosity was calculated using the upper limit of a_w with the lower 95% confidence band in Fig. S7, while upper limit of viscosity was calculated using the lower limit of a_w with the upper 95% confidence band in Fig. S7.

Table S2. Selected parameters used in preparing droplets containing cresyl violet in a citric acid matrix for rFRAP experiments and measured diffusion coefficients. $\tau_{diffusion,\ H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see section S1 and Eq. (S1)). $t_{experimental}$ is the time used for conditioning the droplets at a given relative humidity.

a_w	Max diameter (µm)	$\tau_{diffusion,\ H2O}$ (calculated)	$t_{experimental}$	Log (η, Pa s) [a]	Diffusion coefficient (m^2/s)
0.23 ± 0.025	171	35 minutes	16 days	2.92 ± 0.61	8.59 E-16 ± 3.60 E-16
0.331 ± 0.025	100	246 seconds	17 hours	1.82 ± 0.56	3.80 E-14 ± 1.30 E-14
0.432 ± 0.025	100	62 seconds	17 hours	0.85 ± 0.54	2.63 E-13 ± 1.41 E-13
0.514 ± 0.025	1286	51 minutes	116 hours	0.16 ± 0.51	3.98 E-13 ± 2.87 E-13
0.571 ± 0.025	1170	17 minutes	18 hours	-0.30 ± 0.50	1.10 E-12 ± 6.87 E-13
0.732 ± 0.025	671	20 seconds	15 days	-1.31 ± 0.47	6.17 E-12 ± 3.49 E-12

[a] The lower limit of viscosity was calculated using the upper limit of a_w with the lower 95% confidence band in Fig. S7, while upper limit of viscosity was calculated using the lower limit of a_w with the upper 95% confidence band in Fig. S7.

Table S3. Selected parameters used in preparing droplets containing rhodamine 6G in a sorbitol matrix for rFRAP experiments and measured diffusion coefficients. $\tau_{diffusion,\ H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see section S1 and Eq. (S1)). $t_{experimental}$ is the time used for conditioning the droplets at a given relative humidity.

a_w	Max diameter (µm)	$\tau_{diffusion,\ H2O}$ (calculated)	$t_{experimental}$	Log (η, Pa s) [a]	Diffusion coefficient (µm²/s)
0.23 ± 0.025	742	63.5 hours	8 days	4.24 ± 0.78	1.65 E-17 ± 1.44 E-17
0.331 ± 0.025	770	20.1 hours	7 days	3.31 ± 0.63	9.62 E-17 ± 2.55 E-17
0.432 ± 0.025	828	7.7 hours	4 days	2.36 ± 0.53	1.96 E-14 ± 4.52E-15
0.514 ± 0.025	1142	5.7 hours	4 days	1.61 ± 0.50	1.15 E-13 ± 3.24 E-14
0.571 ± 0.025	1000	2.2 hours	18 hours	1.05 ± 0.51	1.88E-13 + 2.17 E-14

a The lower limit of viscosity was calculated using the upper limit of a_w with the lower 95% confidence band in Fig. S8, while upper limit of viscosity was calculated using the lower limit of a_w with the upper 95% confidence band in Fig. S8.

Table S4. Selected parameters used in preparing droplets containing rhodamine 6G in a sucrose-citric acid matrix for rFRAP experiments and measured diffusion coefficients. $\tau_{diffusion,\ H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see section S1 and Eq. (S1)). $t_{experimental}$ is the time used for conditioning the droplets at a given relative humidity.

a_w	Max diameter (µm)	$\tau_{diffusion,\ H2O}$ (calculated)	$t_{experimental}$	Log (η, Pa s) [a]	Diffusion coefficient (m²/s)
0.14 ± 0.025	243	60 hours	216 hours	6.60 ± 1.15	3.79E-19 ± 2.75 E-19
0.23 ± 0.025	685	60 hours	168 hours	4.92 ± 0.98	1.17 E-18 ± 9.72 E-19
0.26 ± 0.025	257	8.8 hours	72 hours	4.38 ± 0.93	6.23 E-17 ± 5.83 E-17
0.282 ± 0.025	385	13.7 hours	87 hours	4.03 ± 0.89	1.22 E-16 ± 6.49 E-17
0.331 ± 0.025	600	13.4 hours	576 hours	3.26 ± 0.82	4.78 E-16 ± 2.31 E-16
0.432 ± 0.025	571	2.2 hours	601 hours	1.82 ± 0.71	4.08 E-15 ± 1.15 E-15
0.514 ± 0.025	514	28 minutes	19 hours	0.82 ± 0.64	4.84 E-14 ± 1.52 E-14
0.571 ± 0.025	714	20.5 minutes	19 hours	0.16 ± 0.60	1.61 E-13 ± 1.24 E-14
0.732 ± 0.025	657	52 seconds	19 hours	-1.22 ± 0.60	2.85 E-12 ± 3.88 E-13
0.863 ± 0.025	685	13 seconds	19 hours	-1.94 ± 0.67	1.90 E-11 ± 2.00 E-12

[a] The lower limit of viscosity was calculated using the upper limit of a_w with the lower 95% confidence band in Fig. S9, while upper limit of viscosity was calculated using the lower limit of a_w with the upper 95% confidence band in Fig. S9.

Table S5. Hydrodynamic radii of diffusing organic molecules and matrix molecules used in this study.

Diffusing or matrix species	**Organic Molecule**	**Radius (Å)**	**Reference**
Diffusing	Fluorescein	5.02	(Mustafa et al., 1993)
	Rhodamine 6G	5.89	(Müller and Loman, 2008)
	Calcein	7.4	(Tamba et al., 2010)
	Cresyl violet	3.7	Molecular radius calculated using Van der Waals theory of atomic increments (Edward, 1970)
Diffusing and matrix	Sucrose	4.5	Based on the density of amorphous sucrose (Chenyakin et al., 2017)
	Brown limonene SOA components	5.4 ± 0.9	(Ullmann et al., 2019)
Matrix	Citric acid	3.7	(Müller and Stokes, 1956)
	Sorbitol	3.6	(Comper, 1996)

Figures

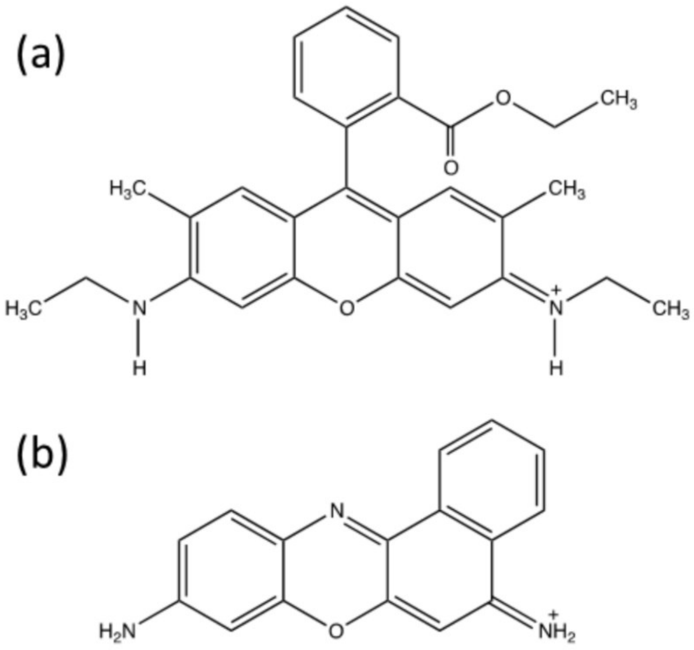

Figure S1. Chemical structures (protonated form) of the fluorescent organic molecules used in this study: A) rhodamine 6G and B) cresyl violet.

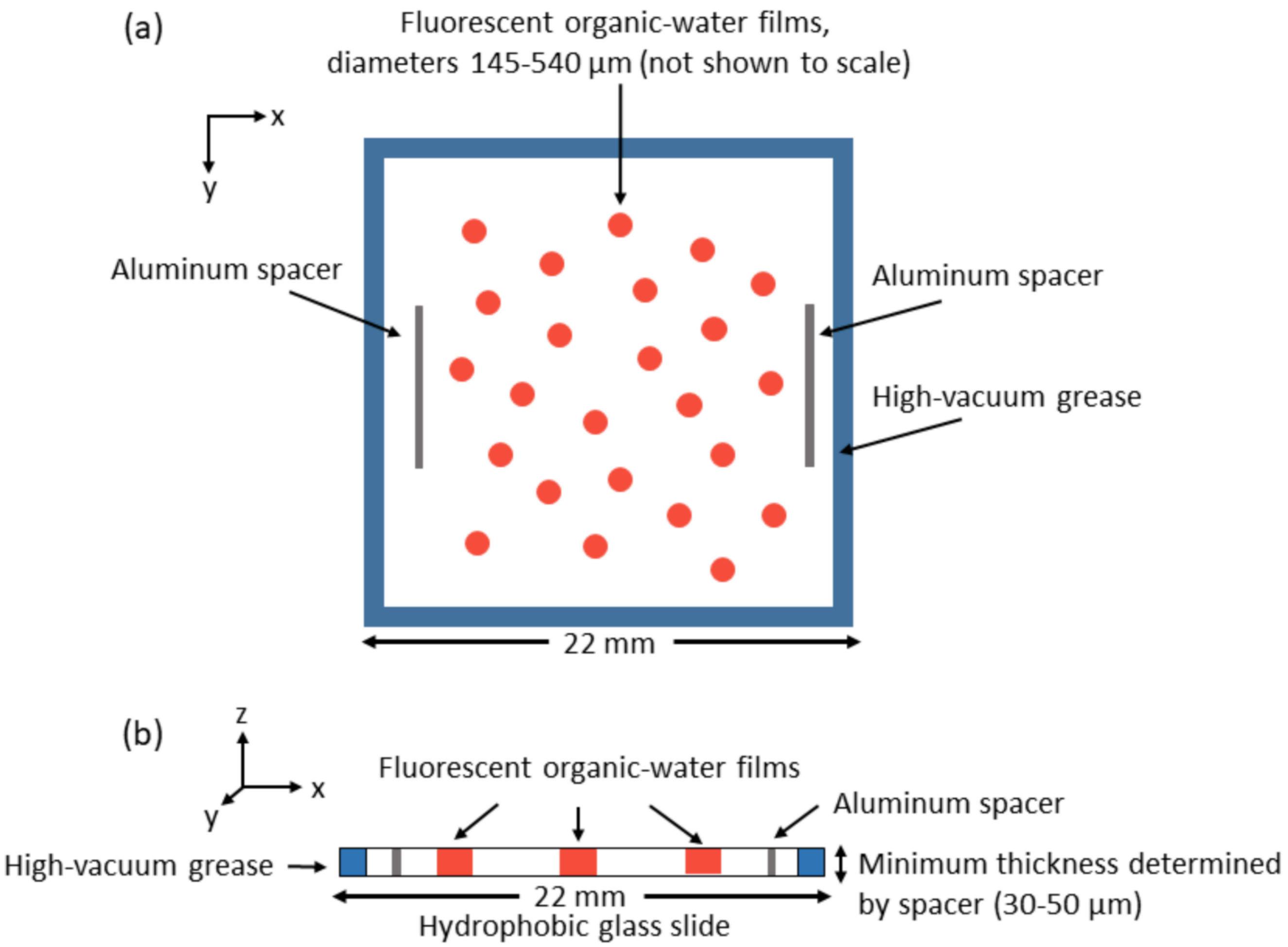

Figure S2. Top view (panel A) and side view (panel B) of a thin film of an organic-water matrix containing trace amounts of the fluorescent organic molecules, sandwiched between two hydrophobic glass slides, for use in rFRAP experiments.

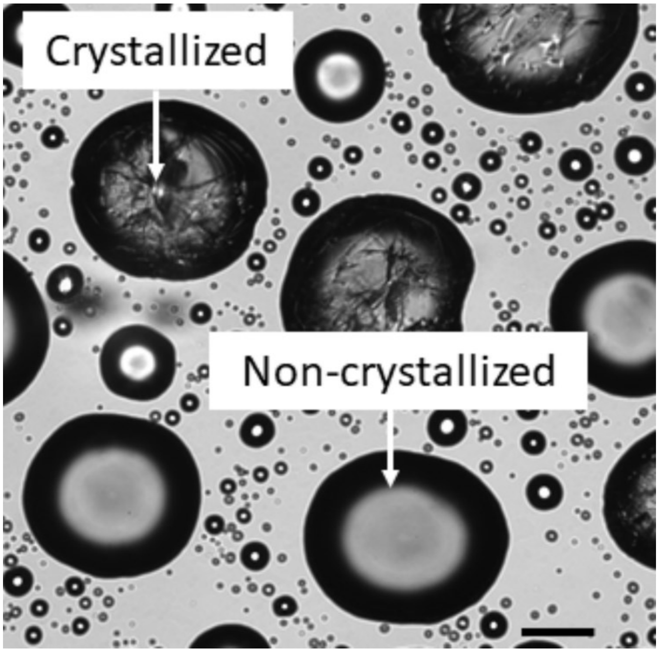

Figure S3. Image showing the difference between crystallized and non-crystallized droplets taken using an optical microscope. The sample was generated using a 0.08 mM solution of cresyl violet in a citric acid matrix, conditioned to $a_w = 0.26$. Slides with crystallized droplets were not used in rFRAP experiments.

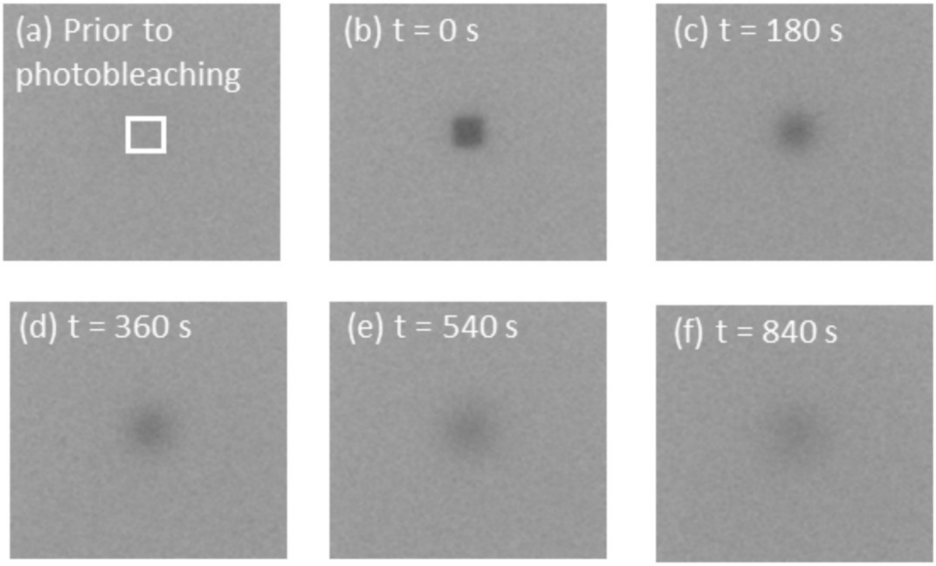

Figure S4. Fluorescence images of films containing rhodamine 6G, citric acid, and water at $a_w = 0.33$, collected using a confocal laser scanning microscope during a rFRAP experiment. Image (a) was taken prior to photobleaching and is used to normalize all images after photobleaching. Image (b) was taken immediately following the photobleaching event and images (c-f) were taken during the recovery period. The white square in panel A represents a 36 μm^2 region for photobleaching, while the size of the imaged region is 3600 μm^2.

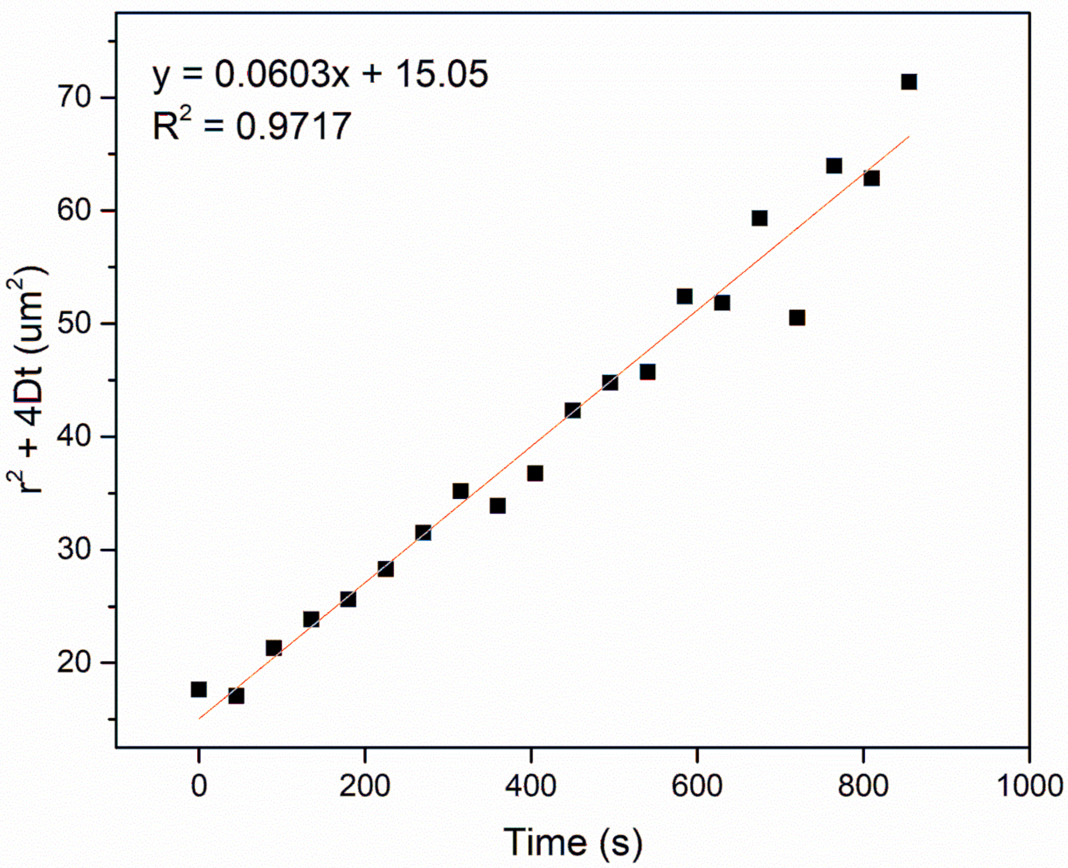

Figure S5. **A plot of *r^2+4Dt* as a function of time after photobleaching in a sample of rhodamine 6G in citric acid matrix at a_w = 0.33. Each black square represents a value of *r^2+4Dt* from the fit of Eq. (2) to an image recorded after photobleaching. The red line is a linear best fit to the data.**

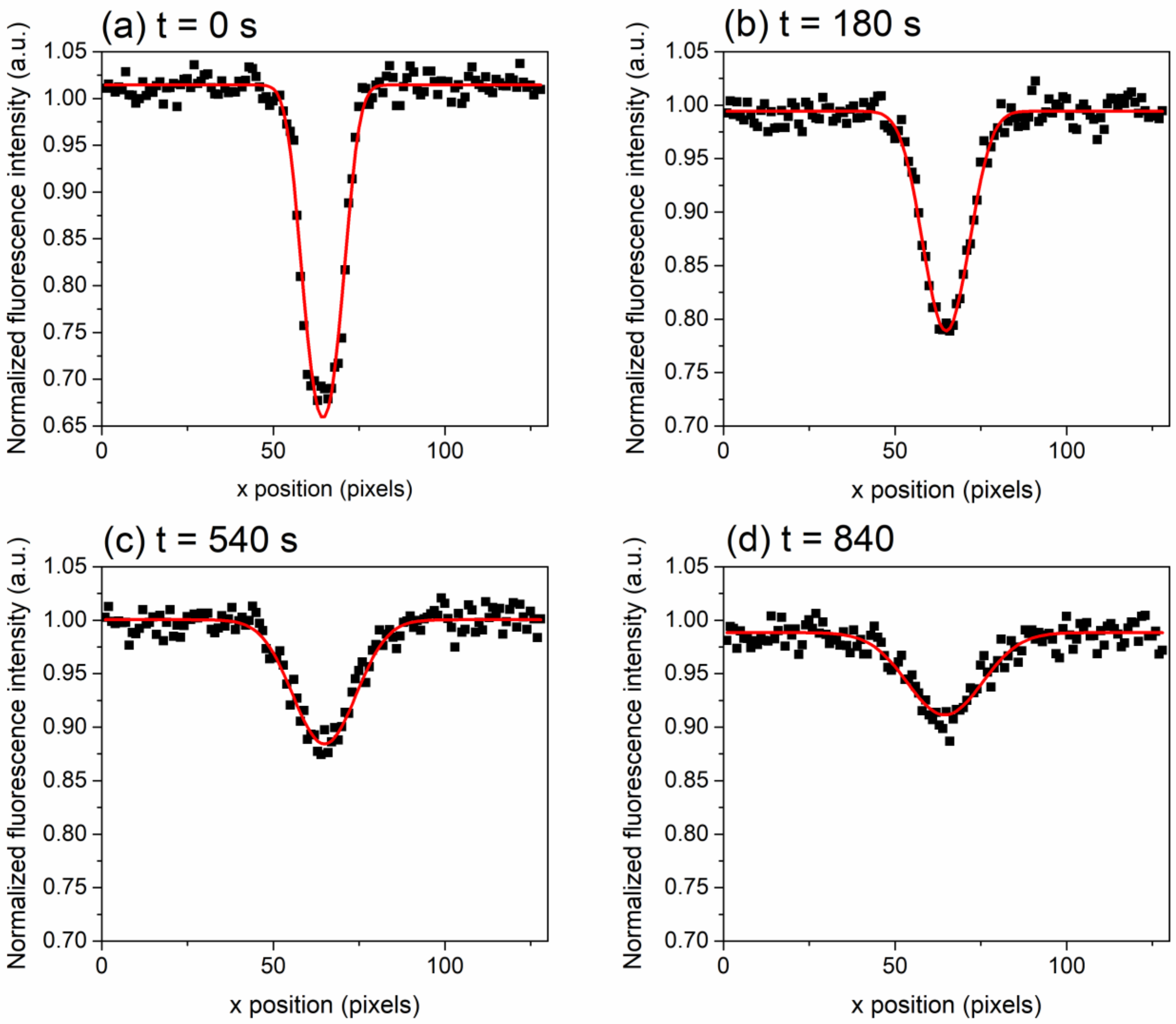

Figure S6. Cross-sectional view of the fluorescence intensity along the *x* direction for the fluorescence images shown in Fig. S4. To generate these plots, at each *x* position the fluorescence intensity is averaged over the width of the photobleached region in the *y* direction. The black squares represent measured fluorescence intensities, while the red line represents the calculated fit to the data. (a) shows the cross-sectional view immediately following the photobleaching event ($t = 0$ s), while (b-d) show the cross-sectional views during fluorescence recovery, at $t = 180$, 540, and 840 s.

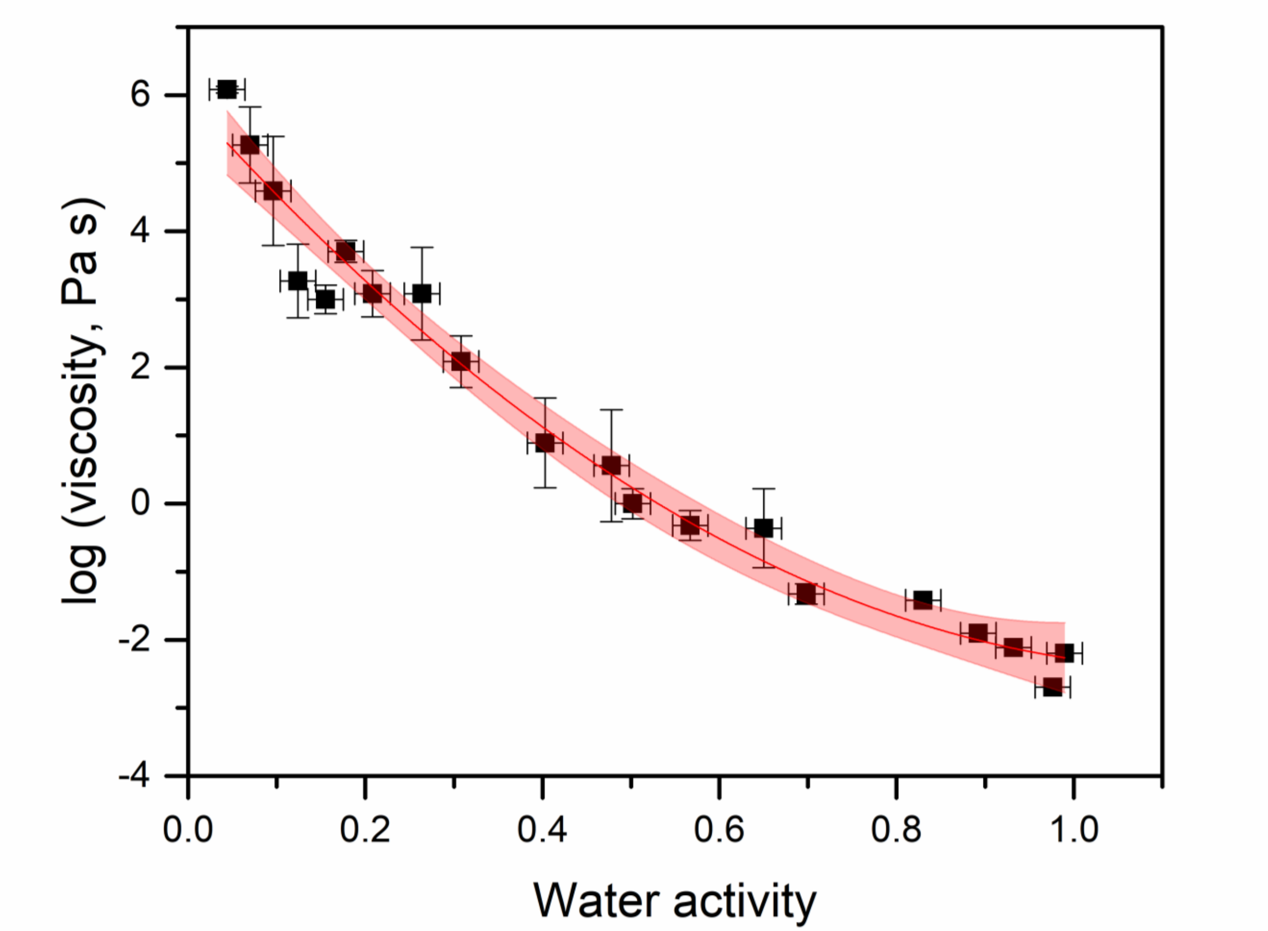

Figure S7. Parameterization between viscosity and water activity for citric acid solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique and measurements in the bulk phase using a rheometer. Measurements were performed at 293 ± 2 K. The equation of the second order polynomial line (red line) is log (η) = 5.9232 ± 0.3772 – 14.508 ± 0.3124(a_w) + 6.30235 ± 0.3605(a_w^2). X-error bars on the data points represent the ± 0.02 a_w and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.

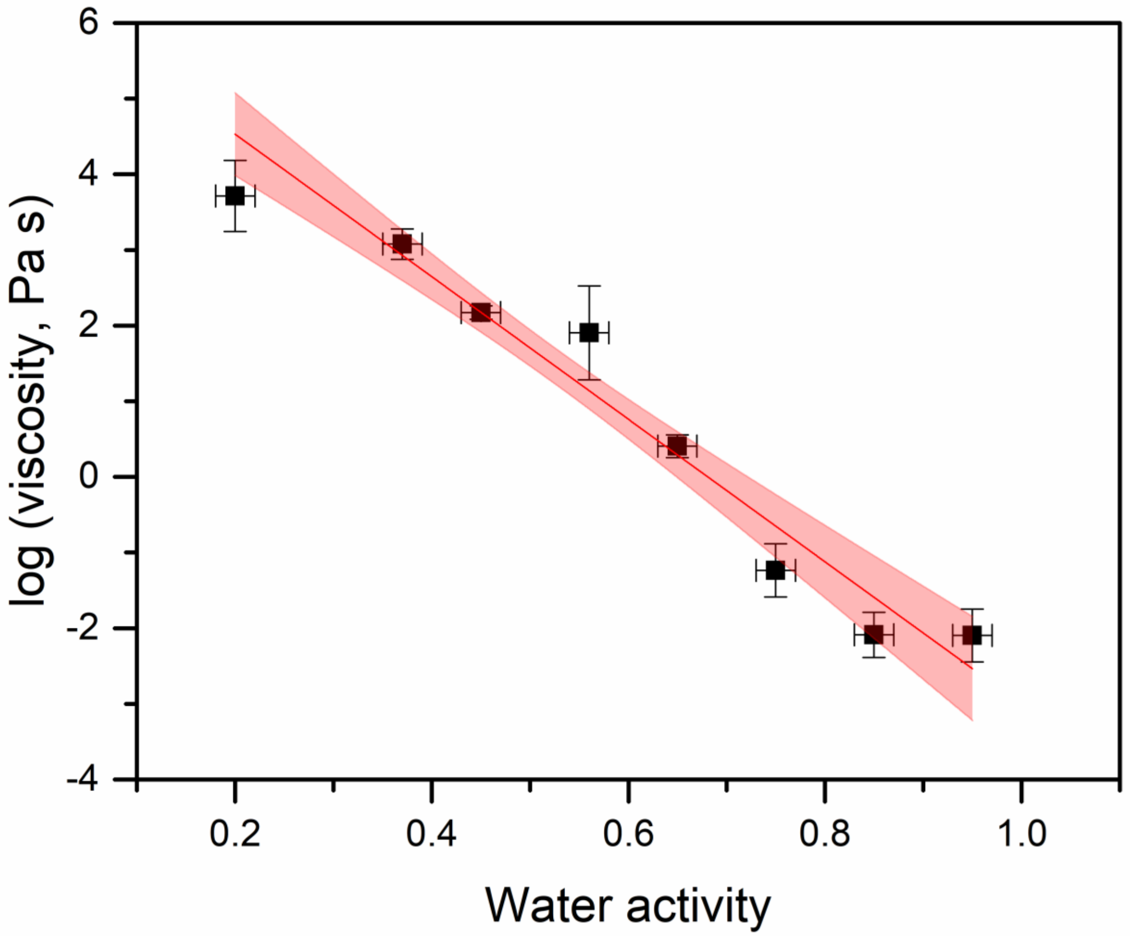

Figure S8. **Parameterization between viscosity and water activity for sorbitol solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique. Measurements were performed at 293 ± 2 K. The equation of the line (red line) is log (η) = 6.4134 ± 1.021 – 9.4175 ± 2.871(a_w) + 0 ± 2.708(a_w^2). X-error bars on the data points represent the ± 0.02 a_w and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.**

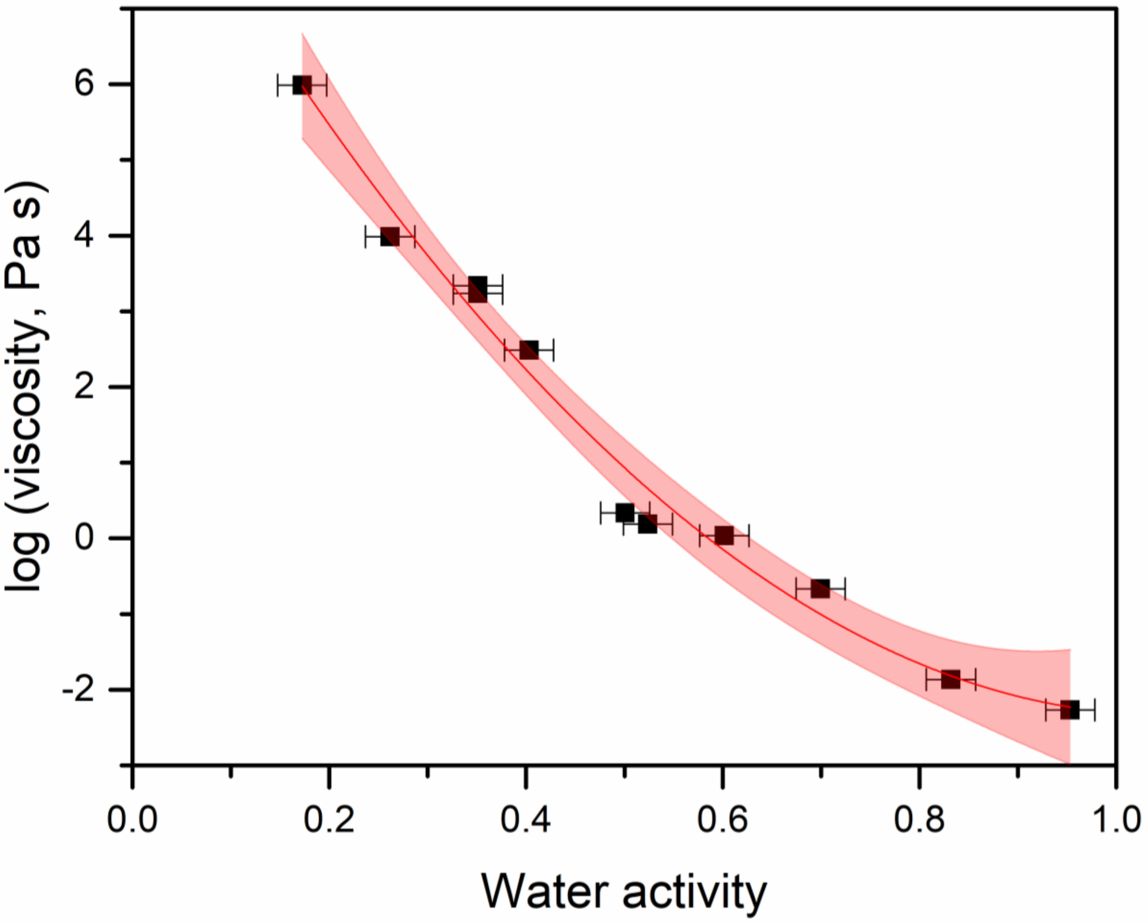

Figure S9. Parameterization between viscosity and water activity for sucrose-citric acid solutions. Data come from Rovelli et al. (n.d.) and only include measurements on particles using the optical tweezers technique. Measurements performed using the poke-and-flow technique were not included due to the larger uncertainty in viscosity measurements using that technique. Measurements were performed at 293 ± 2 K. The equation of the line (red line) is $\log(\eta) = 9.55 \pm 0.857 - 22.62 \pm 1.97(a_w) + 10.76 \pm 1.87(a_w^2)$. X-error bars on the data points represent the ± 0.02 a_w and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.

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