Electronic Supplementary Information

Diffusion across particle-laden interfaces in Pickering droplets

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1. Fluorescent intensity-concentration calibration

The concentration of RhB in heptanol was calibrated against the greyscale values (GV) from the red channel of images, using the correlation $C_{RhB}=aGV^2+bGV$, see **Figure S1(a)**. The calibration was done pixel-by-pixel to account for non-uniform intensity of the excitation light in the field of view. In **Figure S1(b)**, the calibration of RhB in aqueous phase is shown.
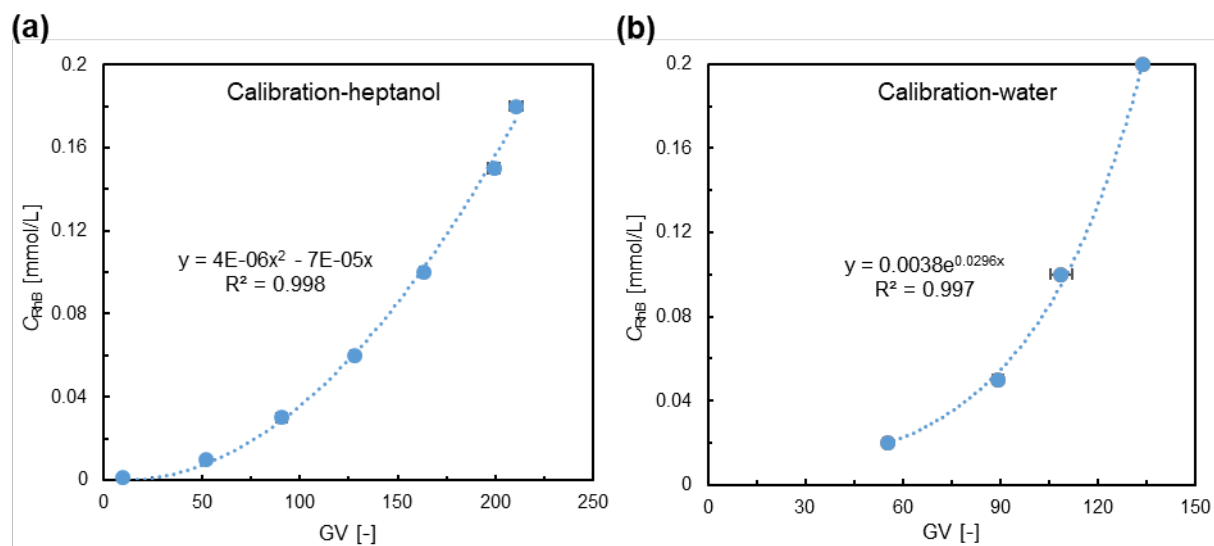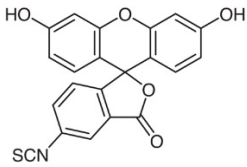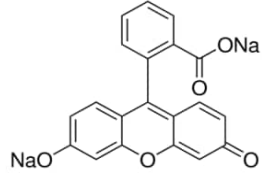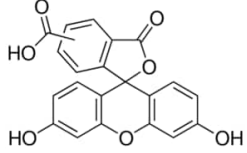

Figure S1. Calibration curve between grey values of captured images and the concentrations of Rhodamine B in **(a)** heptanol and **(b)** water.

2. Control experiments with fluorescein and its derivatives

The table shows the fluorescein derivatives that were tested as alternative to RhB. In the **Results** column, the main observations are listed for each candidate dye. The fluorescence of the dyes in both aqueous and organic phases (v:v=1:1) was tested after equilibrium.

Fluorophore	CAS and structure	Results
Fluorescein 5-Isothiocyanate (isomer I) (FITC- I)	CAS: 3326-32-7 from TCI; $C_{21}H_{11}NO_5S$	Solubility in water <0.025mmol/L water, shows yellow-green color. After equilibrium with heptanol, no color present in organic phase.
Fluorescein sodium salt	CAS: 518-47-8 from Merck; $C_{20}H_{10}Na_2O_5$	For a saturated (1 mg/mL) solution in water, the equilibrium concentration in heptanol is very low, and the corresponding fluorescent intensity in green channel is insufficient.
5(6)-Carboxyfluorescein	CAS: 72088-94-9 from Merck, $C_{21}H_{12}O_7$	Fluorescent intensity in heptanol is insufficient.

3. Desorption of Rhodamine B from nanoparticles in heptanol

Rhodamine B (RhB) adsorbs on the H15 silica nanoparticles during preparation of the water-hexadecane Pickering emulsion, and desorbs from the nanoparticles when the droplet is placed in heptanol. To estimate the amount of desorption from the nanoparticles in heptanol, the nanoparticles were separated from the prepared Pickering emulsion by centrifugation at 14000 rpm. The aggregate of nanoparticles was placed in heptanol and observed with fluorescent microscopy to monitor the desorption of RhB. As shown in **Figure S2**, RhB clearly desorbs from the solid particles from t = 25-200 s. The total mass of desorbed RhB was determined by integrating the concentration over the entire image. Assuming that the nanoparticle aggregate is fully packed, and that its height is same as the height of the spacer (175 µm), the number of nanoparticles in this aggregate was estimated. Then the number of nanoparticles coating a single Pickering droplet was estimated assuming a drop radius of 300 µm, a thickness of the nanoparticle layer of 300 nm and a primary particle radius of 10-15 nm. Assuming that diffusion is sufficiently fast, such that desorption is the rate-limiting step, the desorbed mass of RhB is proportional to the number of nanoparticles. The desorbed mass of RhB from the nanoparticles at the surface of the Pickering droplet is estimated in the range 10^{-12}-10^{-11} mol at t = 25-200 s. This value is to be compared with the mass of RhB diffusing out of a Pickering droplet, typically in the range of 10^{-9}-10^{-8} mol. Thus, the contribution from desorption of RhB is at least of two orders of magnitude lower than that from diffusion from within the droplet.
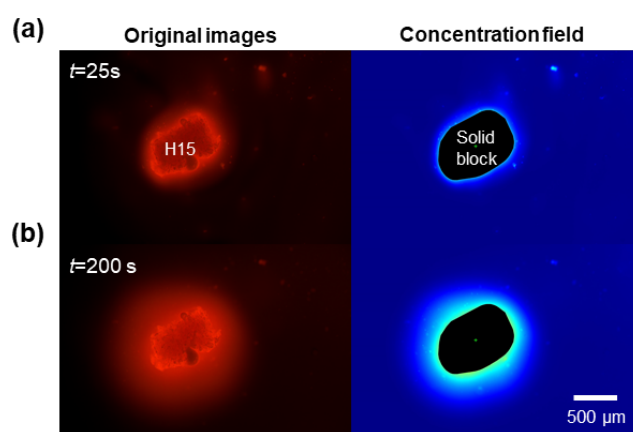

Figure S2. Desorption of Rhodamine B from an aggregate of H15 nanoparticles.

4. Validation of quasi-1D diffusion model

To validate the quasi-1D model (Equations 7-9 in the main text) we compared the concentration profile $C(x)$ at $\tau = 16$ to the average obtained from the $C(x,y,z)$ concentration profile of the full 3D model. The result in **Figure S3** shows that the quasi-1D model correctly reproduces the average concentration profile.
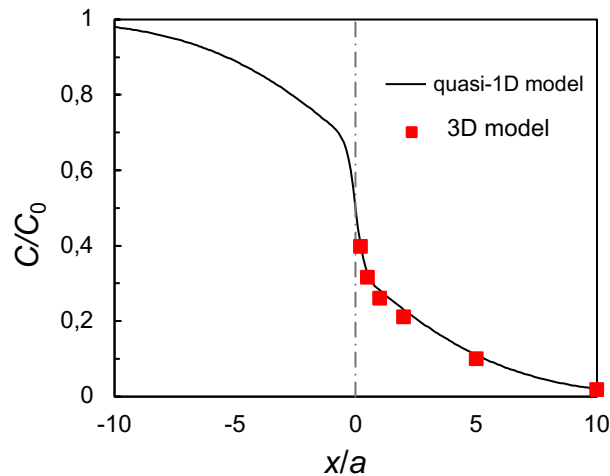

Figure S3. Validation of quasi-1D diffusion model (solid line) against full 3D model (squares).

5. Additional experiments

Additional experiments on different Pickering droplets show reproducibility of the result of Figure 3(b) in the main text.
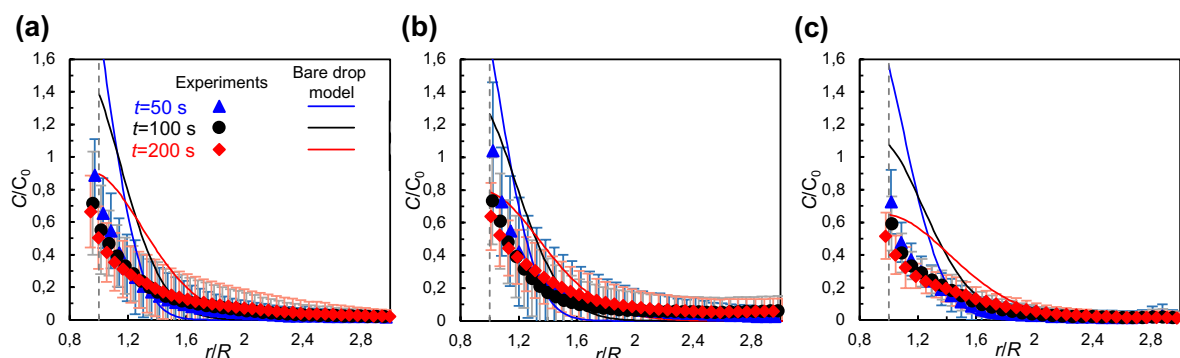

Figure S4. Concentration distribution of RhB diffusing from three independent Pickering droplets with different radius in Hele-Shaw cell at t = 50, 100 and 200 s. The initial concentration in the Pickering droplets is estimated at C_0=0.09 mmol/L (see main text).
The radius of the droplets is **(a)** 360 µm, **(b)** 334 µm, and **(c)** 294 µm.