Supporting information for:

Two modes of phase inversion in a drying emulsion

Huanhuan Feng[*ab], Joris Sprakel[a], Dmitry Ershov[a], Thomas Krebs[c], Martien A. Cohen Stuart[a], Jasper van der Gucht[a]

Emulsion preparation

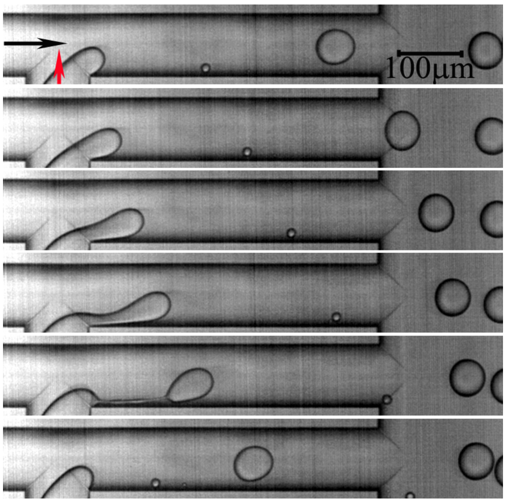

Figure S-1. Production of monodisperse emulsions in a T-junction microfluidic device. Black long arrow shows the flow direction of the continuous phase (10mmol/L SDS). Red short arrow shows the flow direction of the dispersed phase (Nile Red-labelled silicone oil). During droplet pinch-off, small satellite droplets are formed due to the high viscosity ratio. These small satellite droplets were removed by making use of their very small creaming rate: in a sufficiently high container the cream layer that develops consists almost exclusively of the large droplets.

Visualization of emulsions with confocal microscopy

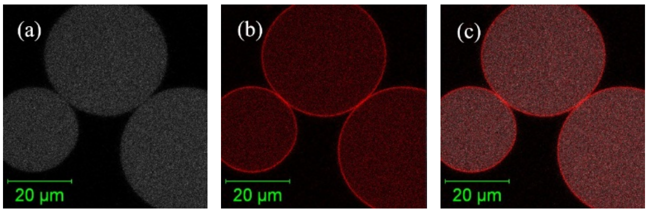

Figure S-2. Confocal microscopy images of a silicone oil in water emulsion with 10mmol/L SDS surfactant, produced by vortexing. (a) Emission between 505 and 530nm colored with gray. (b) Emission for wavelengths larger than 560nm colored with red. (c) Overlap of images (a) and (b) (give a reference here to the original Nile Red interface visualization paper).

Analysis of images to obtain bulk and front coalescence

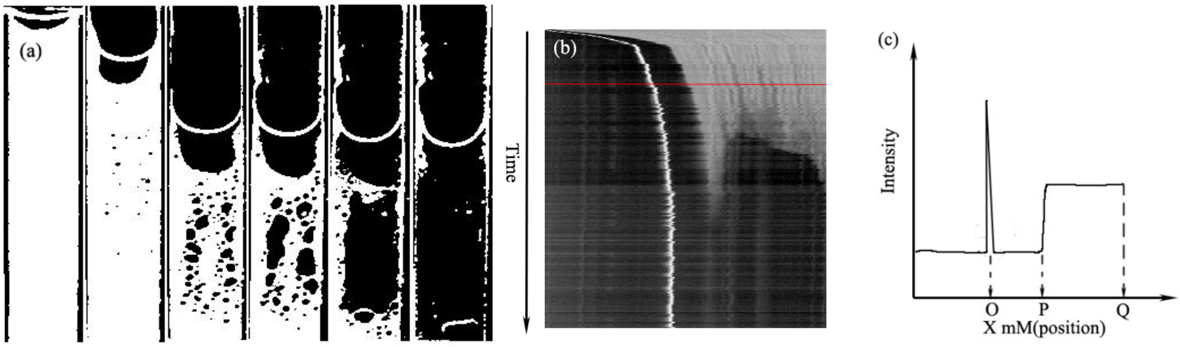

Figure S-3. Analysis of the images of the drying samples. (a) The grayscale images, presented in Figure 3 in the main text, are first converted to binary images using a gray level threshold. In these images, the black pixels below the interface with the air (which is white) represent coalesced emulsion, while the white pixels denote non-coalesced emulsion. (b) From the binary images, we create kymographs (using an ImageJ plugin). In the kymographs, the vertical axis indicates time, while the horizontal axis denotes vertical position (from top to bottom). The pixel intensity indicates the average intensity along a horizontal slice in the binary image. The bright white trace represents the position of the drying front, and the dark regions to the right of it represent coalesced regions. (c) An intensity profile along the sample at one particular time. The point marked with O corresponds to the drying front; the point marked P corresponds to the coalescence front (where continuous oil and emulsion meet). The front contribution to the coalescence is calculated from the distance between O and P, while the bulk contribution is obtained from the average pixel intensity in the region between P and Q.

Measurement of interfacial tension between silicone oil and SDS solution

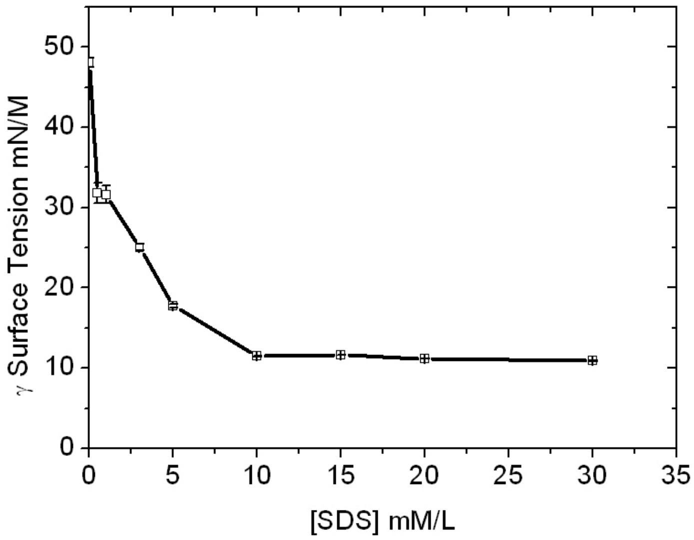

Figure S-4. Interfacial tension between PDMS oil and aqueous SDS solution as a function of SDS concentration. Measurements were done using a pendant drop tensiometer (Sinterface, PAT1) at 298 K.

Hydrodynamic model

Assuming that the water films between droplets are very thin compared to the radius r of the Plateau channels (so that most of the water is found in the channels), the local volume fraction of water can be obtained from the geometry of the channels, $\varepsilon=\alpha(r/R)^2$, with R the droplet size and a parameter of order unity[1]. Flow of water through the channels is driven by a gradient in pressure. According to Poiseuille's law, the velocity of water in the channels is given by

$$v_c = -k\frac{\nabla P r^2}{\eta} \tag{S1}$$

The numerical prefactor k depends on the precise geometry of the channels and on the interfacial viscosity[1]. To obtain the average velocity in the x-direction, we average over the different channel geometries and orientations. This gives an effective value for k of the order of 10^{-3}.

As water evaporates at one end of the sample, water flows towards the dry end. Mass conservation leads to the following continuity equation:

$$\frac{\partial\varepsilon}{\partial t} = -\frac{\partial(\varepsilon v)}{\partial x} \tag{S2}$$

where v is the total velocity of the water at position x. Because the total volume must be filled with either water or oil, a net flow of water towards the dry end through the channels must lead to a counter-flow of emulsion in the opposite direction. By writing a mass balance also for the oil fraction, one obtains that the overall net water velocity is smaller than the velocity in the channels[2]:

$$v = v_c(1 - \varepsilon) \tag{S3}$$

Neglecting contributions of the osmotic pressure, the pressure gradient in equation S1 is equal to the gradient in the Laplace pressure: $\nabla P = (\gamma/r^2)(dr/dx)$. Combining all these equations and writing r in terms of ε, we obtain equation 1 in the main text.

To obtain the boundary condition at the drying end of the sample (denoted $\xi=\xi_1$), we demand that the change of the amount of water in the sample is equal to the amount of water that evaporates:

$$\frac{1}{A}\frac{dV}{dt} = \int_0^{x_1} \frac{\partial \varepsilon}{\partial t}\mathrm{d}x = (1 - \varepsilon)\frac{dx_1}{dt} \tag{S4}$$

with A the cross-section of the sample and V the total volume of water in the sample. Here dx_1/dt denotes the velocity of the air/emulsion interface due to evaporation. After substitution of the drainage equation 1, we obtain boundary condition 3.

1. S.A. Koehler, S. Hilgenfeldt, H.A. Stone, J. Coll. Int. Sci. 2004, 276, 420-438.

2. A. Bhakta and E. Ruckenstein, Advances in Colloid and Interface Science, 1997, **70**, 1-124.