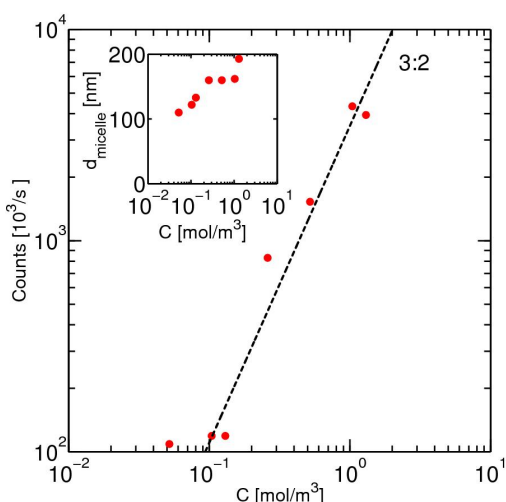


# Microfluidic Dynamic Interfacial Tensiometry ( $\mu$ DIT): Supplementary material

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## DLS measurements of the surfactant



**Fig. 1** DLS measurements for the surfactant between concentrations  $C = 5.2 \times 10^{-3}$  and  $1.3 \text{ mol} \cdot \text{m}^{-3}$ . The solid black line provides a CMC measurement consistent with the pendant drop method. Above the CMC, the scattering signal increases non-linearly. **Inset:** The micellar aggregates present in the solution above the CMC have a typical size of 100 nm. The small variation of the micelle size with the surfactant concentration accounts for the non linear behaviour observed on the scattering intensity beyond CMC.

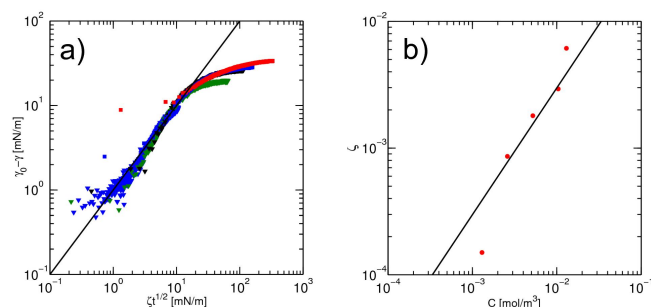
The figure 1 shows the result of Dynamic Light Scattering analysis of the surfactant solutions in HFE. Above the CMC  $C = 1.5 \times 10^{-1} \text{ mol} \cdot \text{m}^{-3}$  the scattering signal is increasing and micelle sizes of 100 nm are found. This measurement is consistent with the pendant drop determination of the CMC, and other measurement performed with similar molecules (Ref. [39] main text).

## Early kinetics of adsorption

The early time kinetics of the surface tension, in diffusive processes is given by (Ref [14] main text):

$$\gamma_0 - \gamma = \zeta \sqrt{t} \quad \text{with} \quad \zeta = 2RTC \sqrt{\frac{D}{\pi}} \quad (1)$$

We fit the experimental dynamics for concentration  $C = 1.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$  to  $C = 2.6 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$  by a  $\zeta t^{1/2}$  power law, and plot  $\zeta$  as a function of the concentration, in order to extract the diffusion coefficient. Figure 1 (a) and (b). We find a linear relation between  $\zeta$  and  $C$  but the value of the diffusion coefficient  $D_{\text{monomer}} = 1 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$  is unphysical. The error is probably due to the contribution of convective currents during droplet production.

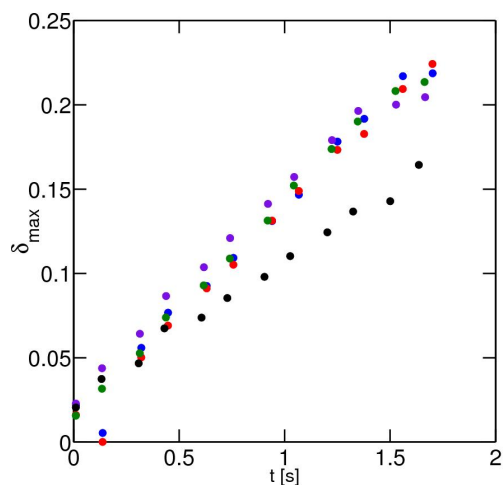


**Fig. 2** (a) Dynamic surface tension rescaled by the prefactor  $\zeta$  for the following surfactant concentrations:  $C = 1.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$  ( $\blacktriangledown$ );  $C = 5.2 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$ , ( $\blacktriangledown$ );  $C = 10.4 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$ , ( $\blacktriangledown$ );  $C = 1.3 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$ , ( $\blacksquare$ );  $C = 2.6 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$ , ( $\blacksquare$ ). All kinetics collapse on a slope power 1 predicted from equation 1. (b) Values of the prefactor  $\zeta$  in function of the surfactant concentration. The solid black line is a fit of equation 1 with parameter  $D_{\text{monomer}} = 1 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$

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## Deformation dependence on the dispersed phase viscosity.

We use a mixture of glycerol/water to achieve a range of viscosity of the disperse phase from  $\eta_{in} = 1 \text{ mPa}\cdot\text{s}$  to  $\eta_{in} = 22.5 \text{ mPa}\cdot\text{s}$  at  $20^\circ\text{C}$ . The kinetics of the droplet deformation with a fixed amount of surfactant, show no dependence on dispersed phase viscosity ranging up to  $\eta_{in} = 10.8 \text{ mPa}\cdot\text{s}$ . Beyond a weak variation is observed, see figure 3.



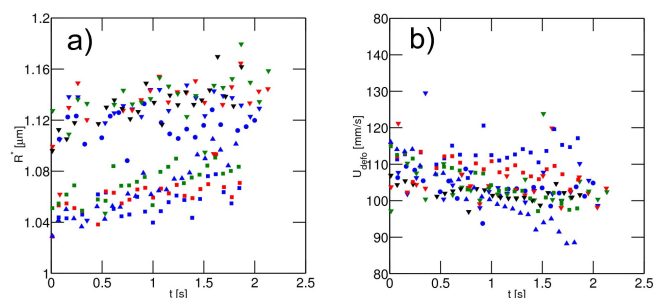
**Fig. 3** Dependence of the droplet maximum deformation on disperse phase viscosity:  $\eta_{in} = 1.00 \text{ mPa}\cdot\text{s}$ , (●);  $\eta_{in} = 1.76 \text{ mPa}\cdot\text{s}$ , (●);  $\eta_{in} = 3.72 \text{ mPa}\cdot\text{s}$ , (●);  $\eta_{in} = 10.8 \text{ mPa}\cdot\text{s}$ , (●);  $\eta_{in} = 22.5 \text{ mPa}\cdot\text{s}$ , (●).

## Changes in droplet size and speed along with surfactant adsorption

Figure 4 shows the droplet speed and size as function of residence time in the channel. The change in size is at most 4%. The change in droplet speed is at most 10%. These small variations are integrating several effects such as the modification of the boundary condition at the interface upon adsorption, a modulation of the channel height by the micrabrication process, a change of the lubrication layer thickness (Bretherton film) and a weak compliance of the NOA. For each measurements, the speed and size of the droplets are determined by image processing to compensate for these experimental variables.

## Measurement at low surface tensions

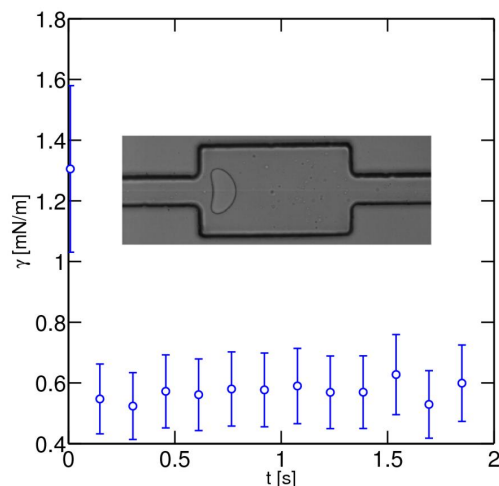
The interface PBS (Phosphate Buffer Saline) 1X and HFE-7500 with a concentration of Krytox FSL, a charged perfluoro-



**Fig. 4** Size (a) and speed (b) of the droplet along a channel during the dynamic measurement of the surface tension, for  $C = 1.3 \times 10^{-3} \text{ mol}\cdot\text{m}^{-3}$ , (●);  $C = 1.3 \times 10^{-2} \text{ mol}\cdot\text{m}^{-3}$ , (▼);  $C = 2.6 \times 10^{-2} \text{ mol}\cdot\text{m}^{-3}$ , (▼);  $C = 5.2 \times 10^{-2} \text{ mol}\cdot\text{m}^{-3}$ , (▼);  $C = 10.4 \times 10^{-2} \text{ mol}\cdot\text{m}^{-3}$ , (▼);  $C = 1.3 \times 10^{-1} \text{ mol}\cdot\text{m}^{-3}$ , (■);  $C = 2.6 \times 10^{-1} \text{ mol}\cdot\text{m}^{-3}$ , (■);  $C = 5.2 \times 10^{-1} \text{ mol}\cdot\text{m}^{-3}$ , (■);  $C = 1.3 \text{ mol}\cdot\text{m}^{-3}$ , (▲).

rosurfactant, around  $C = 0.65 \text{ mol}\cdot\text{m}^{-3}$ , is found to have an equilibrium surface tension.  $\gamma_{eq} < 5 \text{ mN}\cdot\text{m}^{-1}$  in the pendant drop method, but could not be determined precisely.

In microfluidics the deformation for such system is large.  $\delta_{max} = 0.32$  for values of  $R^* = 1$  and  $U_{defo} = 70 \text{ mm}\cdot\text{s}^{-1}$ . This lead to a surface tension of  $\gamma_{eq} = 0.5 \text{ mN}\cdot\text{m}^{-1}$  based on our calibration. Our method can then be used to measure very low surface tension, where the pendant drop method usually fails. Figure 5



**Fig. 5** On chip dynamic tensiometry applied to the system Krytox FSL  $C = 0.65 \text{ mol}\cdot\text{m}^{-3}$  in HFE-7500 and PBS 1X. The surface tension measured are out of the range of the pendant drop method. Inset Micrograph of a droplet at its maximum deformation.