Supplementary information for:

Capillary pressure-based measurement of dynamic interfacial tension in a spontaneous microfluidic sensor

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1. The breakthrough pressure & the lag time

The breakthrough pressure corresponds to the Laplace pressure of the saturated interface. It decreases with increasing SDS concentration and levels off for SDS concentrations above c_{cmc}. In Figure SI 1 A, the breakthrough pressure is plotted against SDS concentration for both bubble (a/w) and droplet (o/w) interfaces. In Figure SI 1 B and C, the lag time is plotted against the applied pressure for two SDS concentrations. In general, as the applied pressure increases, the lag time decreases as an increasingly higher dynamic interfacial tension is needed, requiring less surfactant adsorption. For a given applied pressure (and thus a given dynamic interfacial tension), the lag time decreases as the SDS concentration increases due to faster SDS adsorption.
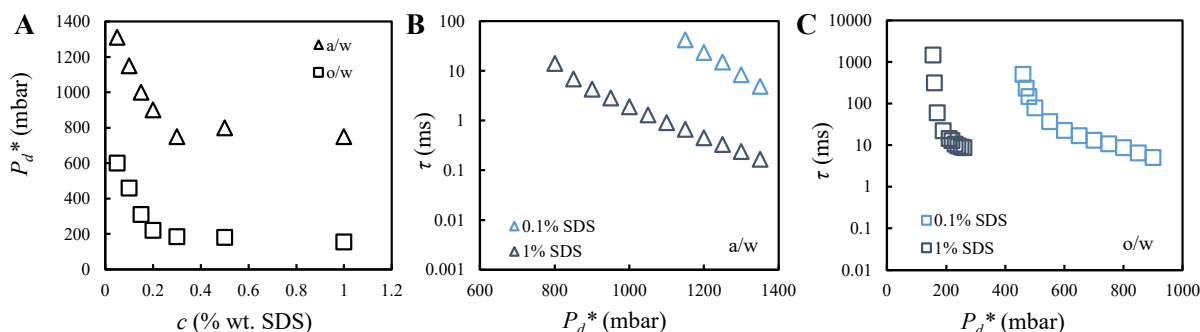

Figure SI 1. A. The breakthrough pressure versus SDS concentration for bubble and droplet formation. The adsorption lag time as function of the applied pressure during the formation of bubble (B) and droplet (C). Two concentrations are shown for comparison, demonstrating the concentration effect on the lag time.

2. Crucial pre-conditions

The time for one bubble formation cycle (τ) can be estimated by $1/f_0$, which includes three consecutive contributions: (1) the time required for surfactant adsorption; (2) the time during which the pore is filled (i.e., forward motion of the meniscus); and (3) the necking time t_n during which the bubble grows and the neck contracts. Both (1) and (2) contributions are included in pore filling time, t_{fill}. For the interfacial tension analysis, the dynamic interfacial tension (γ_d) calculated using the Young-Laplace equation and applied pressure (P^*_d) should

be expressed as function of only the time for surfactant adsorption (i.e., the so-called *adsorption lag time,* τ), namely contribution (1). Below, we demonstrate that this adsorption lag time can be represented by the experimentally easily accessible bubble formation time $1/f_0$.
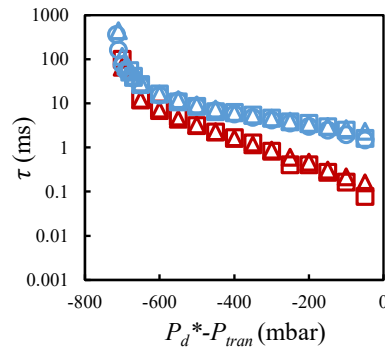

Figure SI 2-1. The adsorption lag time ($\tau \approx 1/f_0$) as function of the normalized applied pressure ($P_d^* - P_{tran}$), measured in the presence of 1% wt. SDS (□△) in a bubble system and 0.3% wt. SDS (□○△) in a droplet system. The hydrodynamic flow resistance of the pore has a ratio of 1:2:4 in microchips with pore length/main plateau length equal to 20/100 (□), 40/200 (○), and 80/400 (△). The negative pressure values indicate that they are in the low-pressure regime, below the transition pressure. The normalized applied pressure $(P_d^* - P_{tran})$ is used to normalize the data sets obtained at different P_{tran} due to variations in working system (droplet vs. bubble), namely 1400 mbar (red symbols) and 900 mbar (blue symbols).

First, we evaluate the pore filling time. An important observation is that the pore filling time is hardly influenced by the hydrodynamic flow resistance of the pore, R_{pore}. We have tested this in devices with varying plateau length to vary the hydrodynamic flow resistance, while keeping necking dynamics (t_n) constant. Figure SI 2-1 shows the results obtained for bubble (red symbols) and droplet (blue symbols) systems in the presence of SDS. The hydrodynamic flow resistance of the tested microchips has a ratio of 1:2:4, and if τ were dominated by the time to fill the pore (i.e., during pore flow), this would result in a time scale that is inversely proportional to R_{pore}. However, all the datasets collapsed, which indicates that τ is dominated by adsorption lag time that is independent of pore length (please note that t_n can be neglected here as $t_{fill} \gg t_n$ as will be discussed in **Figure** SI 2-2). Therefore, these results prove that t_{fill} is mostly determined by the characteristic time scale of dynamic adsorption (of the tested surfactant), while it is hardly influenced by the actual pore flow process.
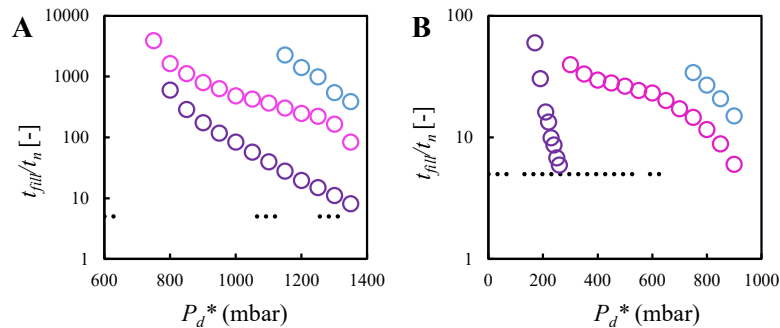

Figure SI 2-2. The relative time scales t_{fill}/t_n in terms of bubble (A) and droplet (B) formation for the effects of SDS concentration: 0.1 (○), 0.3 (○) and 1 (○) % wt. The dashed line represents $t_{fill}/t_n = 5$.

Second, we evaluate the necking time, and the results show that the pore filling time is much larger than the necking time $t_{fill} \gg t_n$ over most of our working range of applied pressures for both bubble and droplet systems. For bubble formation, $t_{fill} \gg t_n$ exists across the full range of applied pressures; only in the presence of 1% wt. SDS, which is the extreme concentration tested here, $t_{fill}/t_n \sim 5$ is observed at the pressure that is only slightly below the P_{tran} (Figure SI 2-2A). For droplet formation, $t_{fill}/t_n \sim 5$ is also only found at the pressure that is just below the transition pressure, illustrated in the presence of 0.3% and 1% wt. SDS (Figure SI 2-2B). $t_{fill} \gg t_n$ proves that τ can be estimated by $1/f_0$ (as shown in Figure SI 2-1).

3. The intermediate steps to obtain $r_d \sim \tau$ plot

In this study, even though we are eventually interested in the interfacial tension as function of time, the experiment itself consists of applying a certain pressure and then measuring the corresponding (droplet or bubble) formation frequency f_0. From the applied pressure γ_d is calculated based on a pressure balance ($\Delta P_{L,pore} = P_d^*$). From the formation frequency, the corresponding formation time $1/f_0$ is calculated, which is (in most cases of negligible necking time) equal to the lag time τ needed for surfactant adsorption to lower the interfacial tension from that of the pure meniscus to the tension in balance with P_d^*.

In Figure SI 3, the time scale is directly plotted against the applied pressure for 0.2% wt. SDS in the case of both droplet (left) and bubble (right) formation. In the manuscript, the axes of Figure SI 3 are inverted and γ_d is calculated; γ_d is then plotted as function of τ.
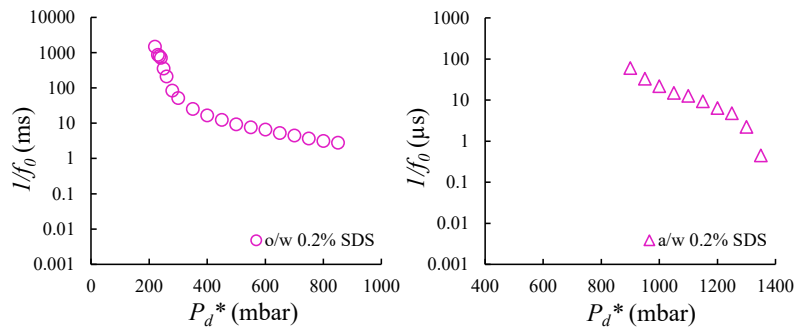

Figure SI 3. The formation time of one droplet (left) and bubble (right) as function of the applied pressure for 0.2% wt. SDS.

4. The reproducible measurement of lag time

The high working stability of the EDGE tensiometer is demonstrated with three repeated experiments for an o/w system in the presence of 0.05% wt. SDS.
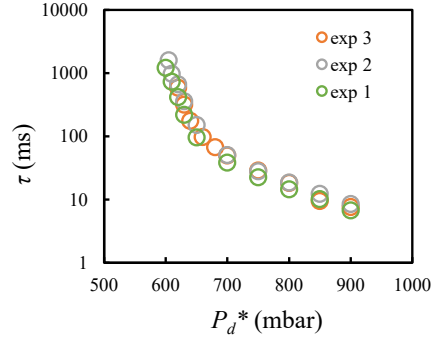
Figure SI 4. Reproducibility tested with 0.05% wt. SDS for droplet interface.
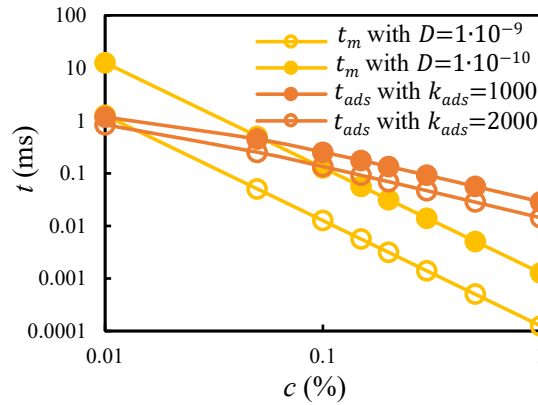
5. Comparison of the characteristic time scales

Figure SI 5. Estimate of the two characteristic time scales. The SDS concentrations vary in the range of 0.05-1% wt.

The relative magnitude of two characteristic time scales determine the mass transfer mechanism of surfactant molecules, namely the diffusion time (t_m) and the adsorption time (t_{ads}). In a stationary flow field, these two time scales can be estimated using equations shown below. The diffusion coefficient (D) is assumed to be in the range $1 \cdot 10^{-10} \sim 1 \cdot 10^{-9} \ m^2/s$; the excess surface concentration (Γ_{eq}) is assumed to be $3.9 \cdot 10^{-7} \ mol/m^2$; the adsorption rate constant (k_{ads}) is presumably in the range of 1000-2000 $m^3/(mol \cdot s)$, and the desorption rate constant (k_{des}) is assumed to be 500 1/s. The bulk SDS concentration (c) varies in the range of 0.01-1% wt. (i.e., 0.35-34.68 mol/m^3).

$$t_m = \frac{h_p^2}{D} \quad \text{(with} \quad h_p \approx \frac{\Gamma_{eq}}{c} \quad \text{the characteristic mass transfer distance of a surfactant)}$$

$$t_{ads} = \frac{1}{k_{ads}c + k_{des}}$$

According to the estimate shown in Figure SI 5, it is clear that 1) for 0.01-0.05% wt., the mass transfer is most likely diffusion-controlled ; 2) for 0.1% wt., the mass transfer is likely mixed or purely kinetic controlled; for > 0.1% wt., the mass transfer is kinetic-controlled.