

Supplementary Information

1. Mass Transport Model

As surfactant adsorbs to an interface, it is removed from the bulk solution. A global mass balance describes the relationship between the initial bulk concentration C_i and the depleted bulk concentration at equilibrium C_{eff} ,

$$C_i V + \Gamma_i A = C_{eff} V + \Gamma_{eff} A \quad (S1)$$

where V is the total solution volume, A is the total surface area available for adsorption, and Γ_i and Γ_{eff} are the initial and equilibrium surface concentrations, respectively. Assuming that the surface is initially surfactant free, $\Gamma_i = 0$, the mass balance simplifies to

$$C_i V = C_{eff} V + \Gamma_{eff} A \quad (S2)$$

At equilibrium, an isotherm model connects the surface concentration and the bulk concentration. For the present study, we consider the Langmuir isotherm model,⁴⁰ as it is the simplest model that includes realistic nonlinear adsorption effects. The Langmuir isotherm is given by

$$\Gamma_{eff}(C_{eff}) = \frac{C_{eff} \Gamma_{\infty}}{C_{eff} + a} \quad (S3)$$

where Γ_{∞} is the maximum packing surface concentration, and $a = \alpha/\beta$ is characteristic concentration composed of the ratio of the desorption rate constant α to the adsorption rate constant β .

When a surfactant solution contacts an interface, surfactant must diffuse to reach the interface. For the spherical interfaces considered in the present study, depicted in Fig. 1 of the manuscript, the time dependent surfactant transport is modeled using Fick's law in spherical coordinates,

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (S4)$$

where C is the local bulk surfactant concentration at a distance r from the center of the sphere and D is the surfactant molecular diffusion coefficient. For diffusion-limited transport, the instantaneous surface concentration is in equilibrium with the instantaneous bulk concentration adjacent to the interface following Eq. (S3), such that

$$\Gamma = \frac{C_s \Gamma_\infty}{C_s + a} \quad (\text{S5})$$

where C_s is the bulk surfactant concentration at the interface, $r = b$, and Γ is the instantaneous surface concentration. One of the boundary conditions corresponding to the partial differential equation given in Eq. (S4) is provided by a flux condition at the interface

$$\frac{\partial \Gamma}{\partial t} = \pm D \frac{\partial C}{\partial r} \Big|_{r=b} \quad (\text{S6})$$

where the positive sign corresponds to the case of surfactant dissolved in the reservoir outside the sphere (Fig. 1a), and the negative sign corresponds to the case of surfactant dissolved inside the sphere (Fig. 1b). The second boundary condition is a Neumann condition. By symmetry, there is no flux at the origin when surfactant is dissolved inside the sphere. When surfactant is dissolved outside the sphere we assume that the outer spherical shell provides an impermeable boundary at $r = R_j$, such that

$$\frac{\partial C}{\partial r} \Big|_{R_j,0} = 0. \quad (\text{S7})$$

We assume that there is no adsorption of surfactant to the impermeable solid boundary, and that there is no partitioning of surfactant across the liquid-fluid interface. Note that the equations governing diffusion within a droplet are equivalent to one of the cases analyzed asymptotically in Ref. 26.

The bulk and surface concentrations are not easy to measure experimentally. Typically, the interfacial tension is measured and related to the surface concentration through an equation of state. The equation of state corresponding to the Langmuir isotherm is given by

$$\gamma = \gamma_0 + RT\Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) \quad (\text{S8})$$

where γ_0 is the clean interfacial tension, R is the gas constant, and T is the temperature.

We solve the governing equations (S4) to (S8) using a spectral analysis method⁴⁵ to obtain the complete time-dependent concentration and interfacial tension profiles for diffusion-limited dynamics, for each of the geometries shown in Fig. 1. The spectral analysis is performed using Chebyshev grid points and an implicit Euler scheme for discretization in time. The details of the method are described elsewhere.^{43, 44}

2. Additional Results – Equilibrium Properties

Other equilibrium properties can be examined in the presence of depletion. Equation (S3) is used to obtain the depleted surface concentration at equilibrium, normalized by the undepleted equilibrium surface concentration $\Gamma_{eq,i}$,

$$\frac{\Gamma_{eff}}{\Gamma_{eq,i}} = \frac{(\zeta + f)(C_{eff}/C_i)}{\left[\zeta + f(C_{eff}/C_i)\right]}. \quad (S9)$$

Fig. S1 presents the normalized depleted surface concentration at equilibrium as a function of ζ^{-1} . Lines in the figure are calculated using Eq. (S9). The influence of depletion on the surface concentration as a function of ζ is qualitatively similar to that of the bulk concentration, approaching asymptotic limits similar to those analyzed for the bulk concentration. For example, the depleted surface concentration approaches $\Gamma_{eff}/\Gamma_{eq,i} \approx 1/f$ when depletion effects are significant, i.e., when $f \gg 1$ and $\zeta^{-1} = 1$. When depletion effects are small in the large concentration limit, i.e., when $\zeta^{-1} \gg f \gg 1$, the surface concentration approaches $\Gamma_{eff} \approx \Gamma_{eq,i}(1 - \zeta^{-2})$. In the small concentration, low surface activity limit, i.e. when $\zeta^{-1} = f = 1$, the surface concentration approaches $\Gamma_{eff} \approx \Gamma_{eq,i}(1 - f)$. The above limits are observed in Fig. S1. When depletion effects are significant, Γ_{eff} does not approach the low concentration limit of $\Gamma_{eff} \approx \Gamma_{eq,i}/f$ as rapidly as C_{eff} approaches its low concentration limit. At intermediate concentrations between $f^{-1} < \zeta^{-1} < 1$, the normalized surface concentration is linearly proportional to the normalized bulk concentration, $\Gamma_{eff}/\Gamma_{eq,i} \approx \zeta^{-1}$.

Equation (S8) is used to determine the depleted interfacial tension at equilibrium, given by

$$\gamma_{eff} = \gamma_0 - RT\Gamma_{\infty} \ln\left(1 + \frac{C_{eff} f}{C_i \zeta}\right). \quad (S10)$$

Equation (S10) can be re-written in terms of a surface pressure $\Pi = \gamma_0 - \gamma$ to eliminate the clean interfacial tension. The resulting surface pressure normalized by its value without depletion is given by

$$\frac{\Pi_{eff}}{\Pi_{eq,i}} = \frac{\gamma_0 - \gamma_{eff}}{\gamma_0 - \gamma_{eq,i}} = \frac{\ln\left(1 + \frac{C_{eff} f}{C_i \zeta}\right)}{\ln\left(1 + \frac{f}{\zeta}\right)}. \quad (S11)$$

Fig. S2 presents the normalized depleted surface pressure at equilibrium as a function of ζ^{-1} . Lines in the figure are calculated using Eq. (S11). The influence of depletion on the surface pressure is qualitatively similar to that of the surface concentration. In the intermediate concentration range, the surface pressure increases more slowly than the bulk concentration with a steep shape change near $\zeta^{-1} \approx 1$. Near $\zeta^{-1} \approx 1$, all three of the quantities shown in Figs. 2, S1, and S2 change so rapidly with ζ that the curves corresponding to different f values cross each other. The specific shapes of the curves in this region arise from the shape of the Langmuir isotherm and the logarithmic form of the equation of state, and do not impact our overall observations regarding depletion effects. Other isotherm models would yield different functional shapes, but the Langmuir model exhibits qualitative behavior that is characteristic of a wide range of surfactant types.

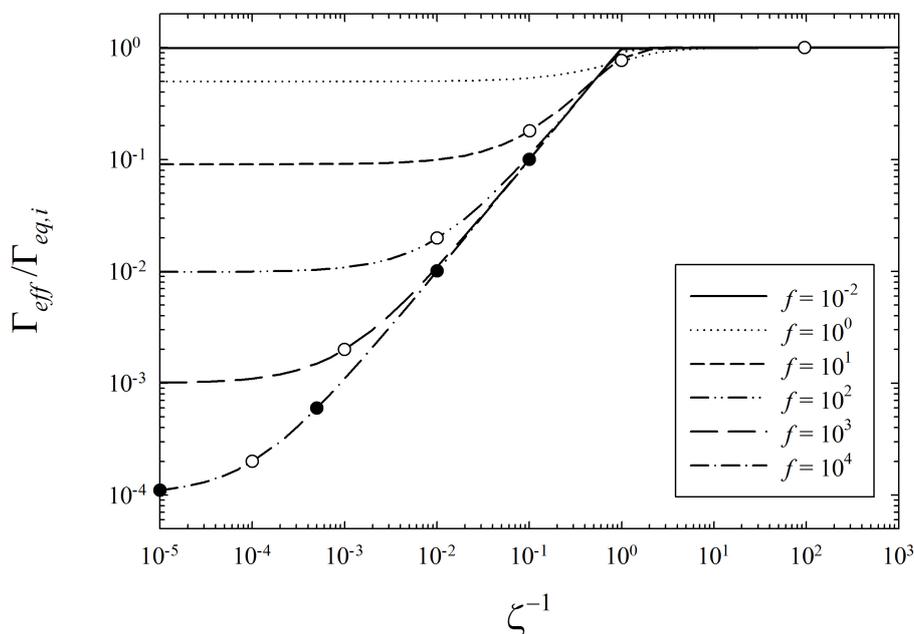


Figure S1

Figure S1. Effective surface concentration normalized by the undepleted equilibrium surface concentration as a function of the maximum potential mass loss parameter ζ . Each line corresponds to a different value of the parameter f , and the symbols represent equilibrium values obtained from numerical simulations of the dynamic surface tension. Filled symbols are obtained from numerical simulations for fixed f , varying ζ . Open symbols are obtained from numerical simulations for fixed C_i/a , varying solution volume.

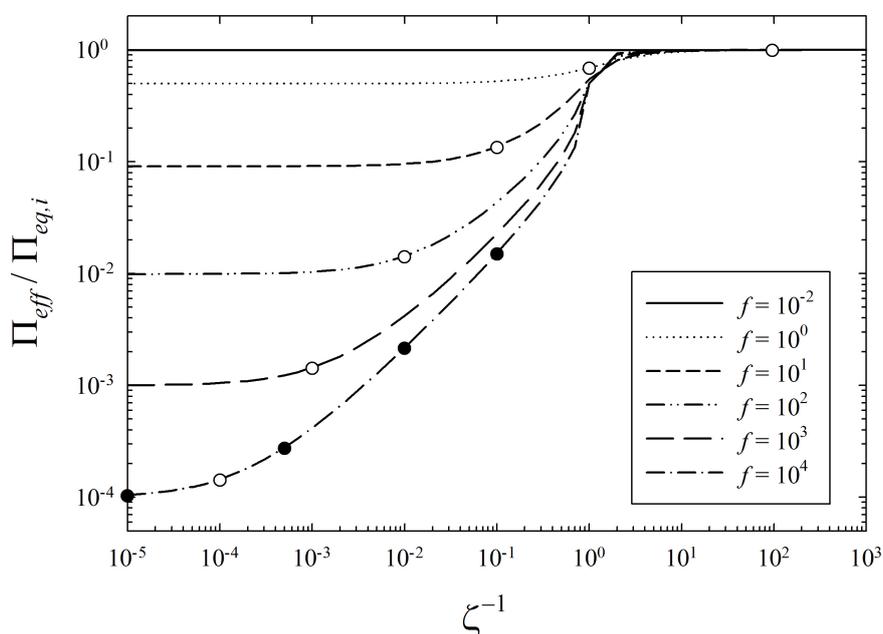


Figure S2

Figure S2. Effective surface pressure normalized by the undepleted value as a function of the maximum potential mass loss parameter ζ . Each line corresponds to a different value of the parameter f , and the symbols represent equilibrium values obtained from numerical simulations of the dynamic surface tension. Filled symbols are obtained from numerical simulations for fixed f , varying ζ . Open symbols are obtained from numerical simulations for fixed C_i/a , varying solution volume.