

# Supporting Information for: The Impact of Micelle Formation on Surfactant Adsorption–Desorption

*Dirk J. Groenendijk\* and Johannes N.M. van Wunnik*

Shell Global Solutions International B.V., Amsterdam, Grasweg 31, 1031 HW Amsterdam, The  
Netherlands

## Different $\text{Ca}^{2+}$ concentrations

Two runs have been performed with  $[\text{Ca}^{2+}]$  concentrations of 0.1 mmol/l and 10 mmol/l. To achieve the correct amount of surfactant adsorption, the value of  $K_{>\text{SurfCa}}$  was changed from  $\log K = -4.95$  to  $\log K = -3.95$ . The input parameters are listed in Table S1.

Parameter	Reference case	Sensitivity case
$K_{\text{SurfCa}^+}$	$\log K = -2.2$	$\log K = -2.2$
$K_{>\text{SurfCa}}$	$\log K = -4.95$	$\log K = -3.95$
$[\text{Surf}_{\text{CMC}}^-]$	0.025 mmol/l	0.025 mmol/l
$[>]^{-0}$	0.05 mol/l	0.05 mol/l
$[\text{Ca}^{2+}]$	0.1 mmol/l	1 mmol/l

Table S1. Parameter values used in the calculations. The second column represent the reference case of Figure S1 and the third column the “sensitivity” case of Figure S2.

Figure S1a shows the resulting profile of  $[>\text{SurfCa}]$  versus the total surfactant concentration, together with the concentration of the surfactants in micelles, the total Ca concentration in solution and the free surfactant monomer concentration. The  $[\text{Surf}^-]$  profile is enlarged in Figure S1b.

The total calcium concentration follows the same pattern as  $[\text{Surf}^-]$  and  $[>\text{SurfCa}]$ . However, the concentration at which it stabilizes depends on the free calcium concentration in solution ( $[\text{Ca}^{2+}]$ ). To illustrate this latter statement, a run has been performed with 10 times larger  $[\text{Ca}^{2+}]$  concentration, i.e., 1.0 instead of 0.1 mmol/l. The results are shown in Figure S2.

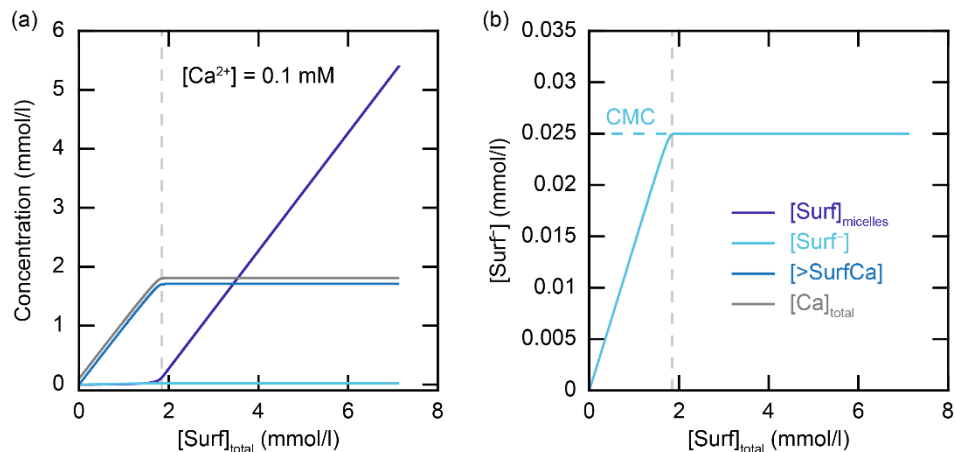


Figure S1. (a)  $[Surf]_{micelles}$ ,  $[Surf^-]$ ,  $[>SurfCa]$  and  $[Ca]_{total}$  versus total surfactant concentration for the case where  $[Ca^{2+}] = 0.1 \text{ mM}$ . (b) Surfactant free monomer concentration versus total surfactant concentration.

The concentration profiles in Figure S2 show the same behavior as in Figure S1, except that the total calcium signal has increased by approximately 1 mmol/l, the value of the imposed free  $[Ca^{2+}]$  in solution.

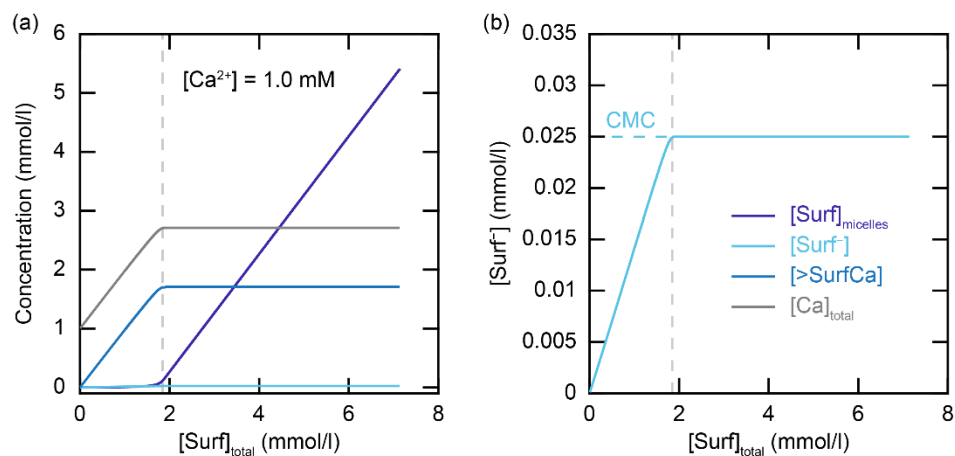


Figure S2. (a)  $[Surf]_{micelles}$ ,  $[Surf^-]$ ,  $[>SurfCa]$  and  $[Ca]_{total}$  versus total surfactant concentration for the case where  $[Ca^{2+}] = 1.0 \text{ mM}$ . (b) Surfactant free monomer concentration versus total surfactant concentration.

## DI water injection

The surfactant monomers are bridged to the surface by  $\text{Ca}^{2+}$ , and therefore the  $\text{Ca}^{2+}$  concentration in solution should also affect the desorption rate. We can model this by injecting DI water into the core, as is shown in Figure S3.

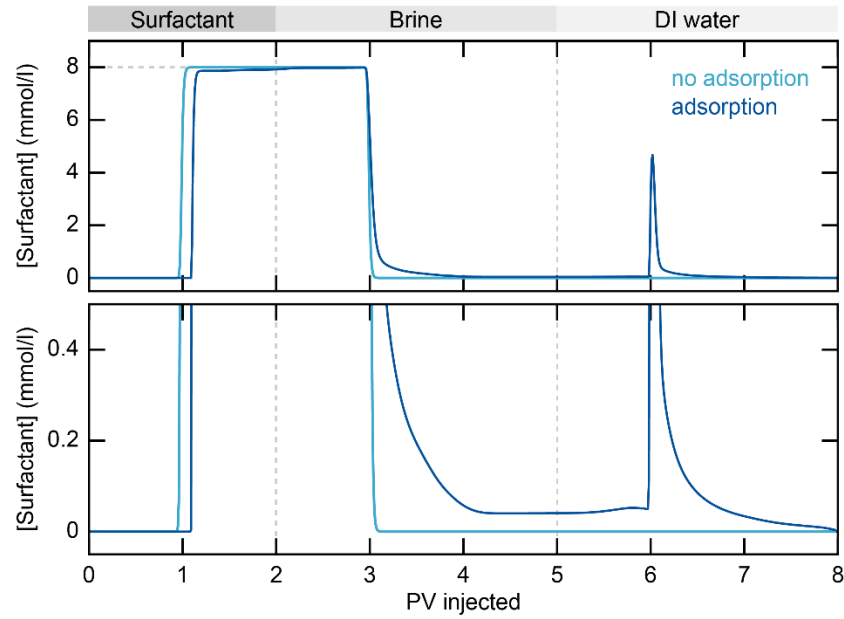


Figure S3. Desorption of a small amount of surfactant upon DI water injection.  $\text{Log } K = -4.0$ .

## Formation of neutral surfactant complexes

The formation of neutral surfactant complexes is given by:



As is assumed that these complexes do not adsorb, this reaction path of equation (1) will reach completion in the solution with relatively little surfactant consumption. In addition, this reaction path is in competition with the actual adsorption path (eq. (2) in the main text) which is likely to overrule (1). This may be different in the presence of oil, as the neutral  $\text{Surf}_2\text{Ca}$  complex can partition into the oil phase. Since we consider single-phase, aqueous systems, reaction path (1) is not further considered in this simplified modelling approach.