

Supporting information:
Cooperative Effects Dominating the
Thermodynamics and Kinetics of Surfactant
Adsorption in Porous Media: From Lateral
Interactions to Surface Aggregation

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1 Quasi Chemical Approximation

Let us consider a solid surface made up of M adsorption sites occupied by N fluid molecules. For such a surface lattice having a connectivity z_0 ($z_0 = 4$ for a simple square lattice as each site is connected to 4 nearest neighbors), the total number of pairs is $z_0 M/2$ since each of the M sites is paired with z_0 sites but each site pair is double counted $[(i, j) = (j, i)]$. Each neighboring site pair can be occupied as follows: (1) both sites are empty, (2) one site is empty while the other one is occupied, (3) both sites are occupied. Let us denote N_{00} , N_{01} , and N_{11} the number of pairs corresponding to these three configurations (the subscripts '0' and '1' therefore refer to an unoccupied site and an occupied site in the considered pair). N_{00} , N_{01} , and N_{11} necessarily obey the following normalization rules: (1) $z_0 N = 2N_{11} + N_{01}$ and (2) $z_0(M - N) = 2N_{00} + N_{01}$. These two rules can be understood as follows. Each isolated molecule corresponds to one of the N adsorbed molecules and generates $z_0 N_{01}$ pairs but each neighboring molecule pair removes two pairs of type N_{01} . The same reasoning applies for the second rule but with the unoccupied sites.

In what follows, the canonical partition functions of an individual adsorbed molecule and of the whole system made of M sites occupied by N molecules at the temperature T are denoted q and $Q(N, M, T)$, respectively. By noting w the energy of a given pair of neighboring adsorbed molecules, the lateral interaction energy between adsorbed molecules writes $N_{11}w = z_0 N w/2 - N_{01}w/2$. This allows writing the total partition function as:

$$Q(N, M, T) = q^N \sum_{N_{01}} g(N, M, N_{01}) e^{-N_{11}w/k_B T} = q^N e^{-z_0 N w/2k_B T} \sum_{N_{01}} g(N, M, N_{01}) e^{N_{01}w/2k_B T} \quad (1)$$

where $g(N, M, N_{01})$ corresponds to the number of ways the N adsorbed molecules can be distributed among the M solid sites while leading to N_{01} occupied/unoccupied site pairs. To determine $g(N, M, N_{01})$, we first consider the number of ways $\omega(N, M, N_{01})$ each site pair can be assigned to N_{00} , N_{01} , and N_{11} without considering whether these configurations are actually possible or not [$\omega(N, M, N_{01}) \geq g(N, M, N_{01})$]:

$$\omega(N, M, N_{01}) = \frac{[z_0 M/2]!}{[z_0 N/2 - N_{01}/2]! [z_0(M - N)/2 - N_{01}/2]! [N_{01}/2]!^2} \quad (2)$$

Following the approach by Hill,¹ to correct $\omega(N, M, N_{01})$ for impossible configurations and estimate $g(N, M, N_{01})$, we write that $g(N, M, N_{01}) = C(N, M)\omega(N, M, N_{01})$ where $C(N, M)$ is the correction factor that needs to be determined. After noting that $\sum_{N_{01}} g(N, M, N_{01}) = M!/[N!(M - N)!]$, $C(N, M)$ can be determined by writing:

$$\sum_{N_{01}} g(N, M, N_{01}) = C(N, M) \sum_{N_{01}} \omega(N, M, N_{01}) = \frac{M!}{N!(M - N)!} \quad (3)$$

Then, we use the maximum term method which consists of approximating the sum over N_{01} by its maximum contribution obtained for N_{01}^* . In practice, N_{01}^* is determined by maximizing ω , i.e. $\partial \ln \omega / \partial N_{01} = 0$ for $N_{01} = N_{01}^*$. This leads to $N_{01}^* = z_0 N(M - N)/M$ with¹:

$$\omega(N, M, N_{01}^*) = \left[\frac{M!}{N!(M - N)!} \right]^{z_0} \quad (4)$$

and, therefore, the following expression:

$$C(N, M) = \left[\frac{M!}{N!(M - N)!} \right]^{1 - z_0} \quad (5)$$

By introducing $t(N, M, N_{01}) = g(N, M, N_{01})e^{N_{01}w/2k_B T} = C(N, M)\omega(N, M, N_{01})e^{N_{01}w/2k_B T}$, the partition function in Eq. (1) can be expressed as:

$$Q(N, M, T) = q^N e^{-z_0 N w / 2k_B T} \sum_{N_{01}} t(N, M, N_{01}) \sim q^N e^{-z_0 N w / 2k_B T} t(N, M, N_{01}^*) \quad (6)$$

where the last expression is obtained by replacing the sum over N_{01} by its maximum contribution (maximum term method); i.e. $\partial \ln t(N, M, N_{01}) / \partial N_{01} = 0$ for $N_{01} = N_{01}^*$. From the expression of $t(N, M, N_{01})$, this last optimization condition leads to $\partial \ln t(N, M, N_{01}) / \partial N_{01} = \partial \ln \omega(N, M, N_{01}) / \partial N_{01} + w / 2k_B T = 0$. After a little algebra², it is possible to show that $\partial \ln \omega / \partial N_{01} = 1/2 \ln[(\theta - \alpha)(1 - \theta - \alpha) / \alpha^2]$ where $\theta = N/M$ is the occupancy rate and $\alpha = N_{01} / z_0 M$. Using this expression in the condition $\partial \ln t(N, M, N_{01}) / \partial N_{01} = 0$ leads to:

$$\frac{(\theta - \alpha)(1 - \theta - \alpha)}{\alpha^2} = e^{-w/k_B T} \quad (7)$$

The last expression is a second degree equation in α which admits as solutions:

$$\alpha = \frac{N_{01}^*}{z_0 M} = \frac{2\theta(1 - \theta)}{\gamma + 1} \quad (8)$$

with $\gamma = [1 - 4\theta(1 - \theta)(1 - \exp(-w/k_B T))]^{1/2}$ (among the two solutions admitted by this quadratic equation, only the one leading to the correct solution $\alpha = \theta(1 - \theta)$ for $w = 0$ i.e. $\gamma = 1$ is kept).

¹Using Stirling formula, $\ln N! \sim N \ln N - N$, we obtain $\partial \ln N! / \partial N = \ln N$. Applying this formula to $\partial \ln \omega / \partial N_{01} = 0$ for $N_{01} = N_{01}^*$, we obtain $\partial \ln \omega / \partial N_{01} = 1/2 \ln[z_0 N / 2 - N_{01}^* / 2] + 1/2 \ln[z_0(M - N) / 2 - N_{01}^* / 2] - \ln[N_{01}^* / 2] = 0$ which can be recast as $[z_0 N - N_{01}^*][z_0(M - N) - N_{01}^*] = N_{01}^{*2}$ and, hence, $N_{01}^* = z_0 N(M - N) / M$.

²Let us start from the expression derived in footnote 1: $\partial \ln \omega / \partial N_{01} = 1/2 \ln[z_0 N / 2 - N_{01} / 2] + 1/2 \ln[z_0(M - N) / 2 - N_{01} / 2] - \ln[N_{01} / 2]$ which can be recast as $\partial \ln \omega / \partial N_{01} = 1/2 \ln[(z_0 N / 2 - N_{01} / 2)(z_0(M - N) / 2 - N_{01} / 2) / (N_{01} / 2)^2]$. We then factorize the numerator and denominator by $z_0^2 M^2$ and introduce the variables θ and α .

Going back to the approximate partition function given in Eq. (6), it can be recast as:

$$\ln Q(N, M, T) = N \ln[qe^{-z_0 w/2k_B T}] + \ln t(N, M, N_{01}^*) \quad (9)$$

which leads to the following chemical potential expression:

$$\begin{aligned} -\frac{\mu}{k_B T} &= \left(\frac{\partial \ln Q}{\partial N} \right)_{M,T} = \ln[qe^{-z_0 w/2k_B T}] + \left(\frac{\partial \ln t}{\partial N} \right)_{N_{01}^*, M, T} + \left(\frac{\partial \ln t}{\partial N_{01}^*} \right)_{N, M, T} \left(\frac{\partial N_{01}^*}{\partial N} \right)_{M, T} \\ &= \ln[qe^{-z_0 w/2k_B T}] + \left(\frac{\partial \ln t}{\partial N} \right)_{N_{01}^*, M, T} \end{aligned} \quad (10)$$

where the last expression is obtained by noting that $\partial \ln t / \partial N_{01}^* = 0$ since N_{01}^* is the value that maximizes t at given N, M, T conditions. Using the definition $t(N, M, N_{01}^*) = C(N, M)\omega(N, M, N_{01}^*)e^{N_{01}^* w/2k_B T}$, we arrive at $\partial \ln t / \partial N = \partial \ln C(N, M) / \partial N + \partial \ln \omega(N, M, N_{01}^*) / \partial N$ which leads to:

$$\left(\frac{\partial \ln t}{\partial N} \right)_{N_{01}^*, M, T} = -(1-z_0)[\ln N - \ln(M-N)] - \frac{z_0}{2} \left[\ln \left(\frac{z_0 N}{2} - \frac{N_{01}^*}{2} \right) - \ln \left(\frac{z_0(M-N)}{2} - \frac{N_{01}^*}{2} \right) \right] \quad (11)$$

where the first term corresponds to the derivation of $C(N, M)$ given in Eq. (5) while the last two terms corresponds to the derivation of $\omega(N, M, N_{01}^*)$ given in Eq. (2). Using $\theta = N/M$ and $\alpha = N_{01}^*/z_0 M$, Eq. (11) can be recast as:

$$\left(\frac{\partial \ln t}{\partial N} \right)_{N_{01}^*, M, T} = \ln \left[\left(\frac{\theta}{1-\theta} \right)^{z_0-1} \left(\frac{1-\theta-\alpha}{\theta-\alpha} \right)^{z_0/2} \right] \quad (12)$$

Inserting this expression into Eq. (10) yields the following expression:

$$\frac{\mu}{k_B T} = -\ln[qe^{-z_0 w/2k_B T}] + \ln \left[\left(\frac{1-\theta}{\theta} \right)^{z_0-1} \left(\frac{\theta-\alpha}{1-\theta-\alpha} \right)^{z_0/2} \right] \quad (13)$$

Using the relation between α and γ (see above) and introducing the energy of a single adsorbed molecule ϵ_0 so that $q = \exp[-\epsilon_0/k_B T]$, the latter equation can be recast as:

$$\frac{\mu}{k_B T} = \frac{(z_0 w + 2\epsilon_0)}{2k_B T} + \ln \left[\frac{(\gamma-1+2\theta)(1-\theta)}{(\gamma+1-2\theta)\theta} \right]^{z_0/2} + \ln \left[\frac{\theta}{1-\theta} \right] \quad (14)$$

which is equivalent to the formula used in the main text.

2 Additional figures

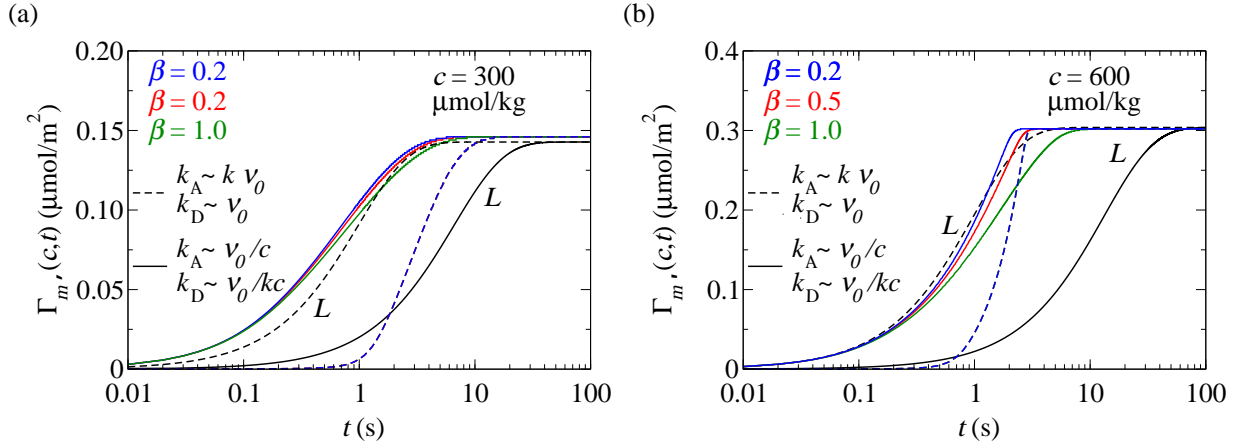


Figure S1: Adsorption kinetics showing $\Gamma_{m'}$ as a function of time t for TX165 surfactant on kaolinite clay for two bulk concentrations: (a) $c = 300 \mu\text{mol/kg}$ and (b) $c = 600 \mu\text{mol/kg}$. The color lines denote the data obtained using the cooperative model with $\beta = 0.2$ (blue), $\beta = 0.5$ (red), and $\beta = 1.0$ (green) while the black lines correspond to kinetics predicted using the Langmuir kinetic model with an adsorption/desorption constant k^L that best matches the experimental adsorption isotherm (see text). In each case, the dashed lines correspond to the case $k_A \sim \nu_0 k$ and $k_D \sim \nu_0$ while the solid lines correspond to $k_A \sim \nu_0/c$ and $k_D \sim \nu_0/kc$. Note that our model predicts that the color dashed lines (i.e. $k_A \sim k$ and k_D constant) are superimposed.

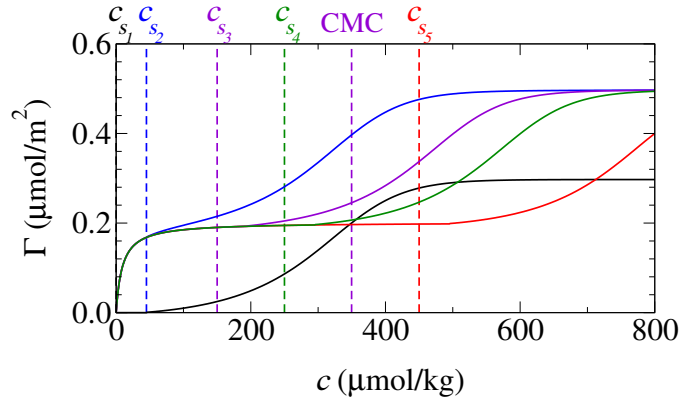


Figure S2: Predicted surfactant adsorption isotherms at $T = 298$ K showing the surface concentration of surfactants Γ onto a silica-based surface as a function of the bulk concentration c . The black, blue, violet, green and red solid lines show the predictions from our model using different values for c_s . The vertical dashed lines indicate the corresponding critical surface concentration c_s as well as the bulk critical micelle concentration CMC.

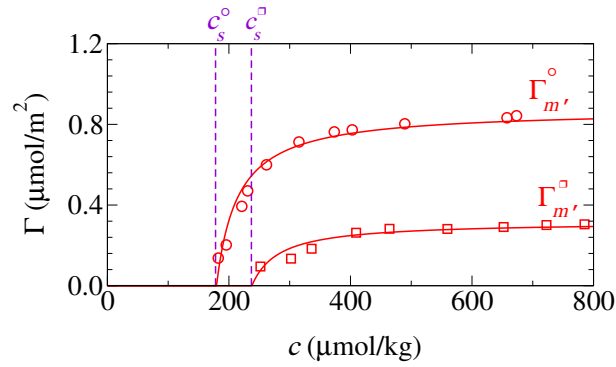


Figure S3: Adsorption isotherm for aggregated monomer at $T = 298$ K showing the surface concentration of aggregated monomers Γ'_m onto a silica-based surface as a function of the bulk concentration c . The circles are for TX100 adsorption on quartz silica while the squares are for TX165 on kaolin. The solid lines denote the fits used to describe the aggregated monomer adsorption. The vertical dashed lines indicate the critical surface concentration c_s for each dataset.

References

- (1) Hill, T. L. *Statistical Mechanics: Principles and Selected Applications*; Dover Publications, New York, 1987.