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Zaineb Zaafouri, Daniela Bauer, Guillaume Batôt, Carlos Nieto-Draghi, Benoit Coasne. Cooperative Effects Dominating the Thermodynamics and Kinetics of Surfactant Adsorption in Porous Media: From Lateral Interactions to Surface Aggregation. *Journal of Physical Chemistry B*, 2020, 124 (47), pp.10841-10849. 10.1021/acs.jpcc.0c08226 . hal-03118492

HAL Id: hal-03118492

<https://ifp.hal.science/hal-03118492>

Submitted on 22 Jan 2021

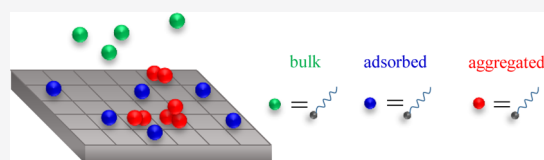
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Cooperative Effects Dominating the Thermodynamics and Kinetics of Surfactant Adsorption in Porous Media: From Lateral Interactions to Surface Aggregation

Zaineb Zaafour, Daniela Bauer,* Guillaume Batôt, Carlos Nieto-Draghi, and Benoit Coasne*

ABSTRACT: Surfactant adsorption in porous media remains poorly understood, as the microscopic collective behavior of these amphiphilic molecules leads to nonconventional phenomena with complex underlying kinetics/structural organization. Here, we develop a simple thermodynamic model, which captures this rich behavior by including cooperative effects to account for lateral interactions between adsorbed molecules and the formation of ordered or disordered self-assemblies. In more detail, this model relies on a kinetic approach, involving adsorption/desorption rates that depend on the surfactant surface concentration to account for facilitated or hindered adsorption at different adsorption stages. Using different surfactants/porous solids, adsorption on both strongly and weakly adsorbing surfaces is found to be accurately described with parameters that are readily estimated from available adsorption experiments. The validity of our physical approach is confirmed by showing that the inferred adsorption/desorption rates obey the quasi-chemical approximation for lateral adsorbate interactions. Such cooperative effects are shown to lead to adsorption kinetics that drastically depart from conventional frameworks (e.g., Henry, Langmuir, and Sips models).



1. INTRODUCTION

Surfactants, which are amphiphilic molecules combining a hydrophilic head with a hydrophobic tail, constitute an important class in Soft Matter. Besides their ability to decrease surface tension by getting adsorbed at interfaces, an important property of surfactants in water is to exhibit a complex phase diagram including a miscibility gap (a temperature/concentration range where demixing occurs from water).¹ Even in the miscibility region, there exists a critical micelle concentration (cmc) above which surfactants form ordered mesoscopic assemblies—typically spherical micelles where the surfactant tails are inside the micelle, while polar or charged heads are at the micelle external surface in contact with water (Figure 1). Owing to their tendency to form micelles and reduce surface tension, surfactants are at the heart of many applications where they are used as detergents, dispersants, emulsifiers, and so forth.^{2–4} In particular, in heterogeneous solutions such as oil/water systems, they are used to trap oil droplets inside the core of surfactant micelles. In many situations, such a phase separation occurs in porous media or in the vicinity of solid surfaces, an important example being the use of surfactants to untrap important oil amounts located in oil reservoirs/rocks.^{5–7}

The rich thermodynamic behavior of surfactants results from competing molecular interactions between the different—hydrophobic and hydrophilic—groups, which combine with large entropy effects for such molecules.⁸ However, despite such an intrinsic complexity, the phase behavior of bulk surfactants is reasonably well understood with available

formalisms to describe phenomena such as self-assembly and phase separation/transition and also nonintuitive temperature effects on liquid immiscibility, solubility, and micellization.^{9–11} In contrast, the physical behavior of surfactants confined in porous materials or close to solid surfaces still challenges existing frameworks.¹² Adding free energy contributions resulting from the head/surface and tail/surface intermolecular interactions leads to intriguing effects such as inverse temperature adsorption and also surface transitions between disordered and/or ordered mesoscopic assemblies (e.g., bilayers, hemi-micelles, vesicles, and elongated micelles).^{9,13–15} The situation is even more puzzling as the observed adsorption type depends specifically on the solid chemistry (e.g., surface affinity/groups with possible amphoteric charges), surfactant molecules (e.g., apolar/polar, cationic/anionic), and thermodynamic/solution conditions (e.g., concentration, temperature, and presence of an electrolyte).^{16–19}

As a result of this complexity, most of the experimental literature on surfactant adsorption focuses on a given family of surfaces or surfactants. In particular, significant research effort has been devoted to unraveling the structural mechanisms followed upon adsorption at increasing concentrations.^{20–24} By

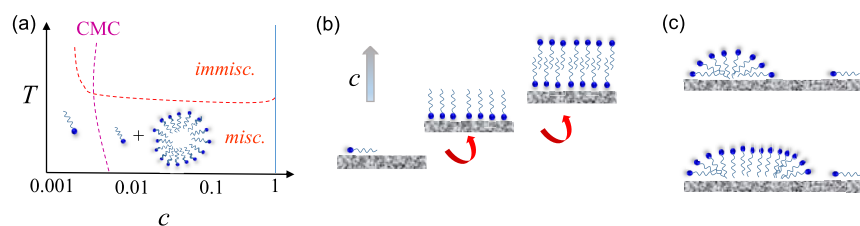


Figure 1. (a) Temperature–concentration (T, c) phase diagram of bulk surfactant solutions. The surfactant monomer is pictured as a hydrophilic head (blue sphere) combined with a hydrophobic chain (grey segment). A miscibility gap separates the high/low T regions with solvent/surfactant miscibility only observed at low T and c . In the miscibility range, for c smaller than the so-called cmc, the monomers are solubilized in the solvent phase. For $c > \text{cmc}$, the monomers coexist with micelles. (b,c) Orientation of surfactant molecules and possible surface aggregates obtained at a solid surface. (b) corresponds to the stepped Langmuir adsorption isotherm with the formation of an adsorbed monomer layer followed by film reorientation and growth. (c) illustrates other ordered or disordered self-assemblies coexisting with isolated adsorbed monomers.

68 combining thermodynamic measurements with structural
 69 analysis, some authors proposed advanced scenarios to
 70 rationalize step adsorption and/or S-shaped adsorption
 71 isotherms observed experimentally.^{25,26} As illustrated in Figure
 72 1b, such mechanisms involve the adsorption of isolated
 73 monomers followed by the formation of a monolayer, which
 74 eventually transforms into more complex structures (e.g.,
 75 bilayer, hemimicelle, and vesicle) upon increasing the
 76 surfactant concentration.²⁷ However, although such combined
 77 structural/thermodynamical studies provide a robust descrip-
 78 tion for a broad class of solid/surfactant situations, there is a
 79 number of systems that lead to more complex data departing
 80 from such a generic picture.^{28,29} In particular, data for
 81 surfactants in various silica-based porous materials display
 82 complex adsorption mechanisms and kinetics involving the
 83 formation of elongated/distorted micelles or vesicles [as
 84 illustrated in Figure 1c] that cannot be captured using
 85 currently available models. Such complex effects arise from
 86 the heterogeneity in the solid surface chemistry and disordered
 87 morphology/topology of the host confining material.
 88 From a theoretical viewpoint, statistical physics is a powerful
 89 framework to predict the complex behavior of surfactants in
 90 bulk solution (including anomalous temperature effects on self-
 91 assembly for instance). In particular, extended lattice gas
 92 theory for monomers including a supralattice for the formation
 93 of micelles was shown to capture most of the physical
 94 phenomena involved in the phase diagram of these complex
 95 objects.³⁰ This method was extended later by Bock and
 96 Gubbins³¹ to account for surface adsorption through the use of
 97 surface interaction terms in the lattice gas Hamiltonian.³⁰
 98 From a thermodynamic viewpoint, several models such as
 99 those described hereafter have been proposed to describe
 100 surfactant adsorption on solid surfaces. Empirical models have
 101 been proposed to describe in an effective fashion the S-shaped
 102 adsorption isotherms. This is the essence of the Sips model,³²
 103 which corresponds to the Langmuir model with the pressure
 104 raised to an empirical power α . The Toth model falls in the
 105 same category, as it consists of accounting empirically for
 106 surface heterogeneity through a stretched Langmuir adsorption
 107 isotherm.³³ Other empirical approaches in this field consist of
 108 combining different physical models such as Henry, Langmuir,
 109 and BET adsorption isotherms to account for nonconventional
 110 surfactant adsorption isotherms.³⁴ More physical pictures have
 111 been proposed such as the model by Zhu and Gu, in which
 112 adsorption is described as a two-step process with two
 113 underlying equilibrium conditions (single-monomer adsorp-
 114 tion and monomer recombination to form self-assemblies).^{35,36}
 115 Other physical models such as those proposed by Temkin³⁷

and Reed–Ehrlich³⁸ rely on the quasi-chemical approximation
 to account for lateral interactions within the adsorbed layer.
 This approximation is an extension of the Bragg–Williams
 approximation, in which the Langmuir model is augmented by
 including a mean-field description of the lateral interactions
 between adsorbed molecules.³⁹

In spite of their physical basis, the models described above
 do not provide a general formalism for surfactant adsorption,
 as they address different aspects (lateral interaction or self-
 assembly). In other words, a reliable thermodynamic
 description of the behavior of surfactants at surfactant/surface
 interfaces should include both lateral interactions and
 transitions from adsorbed monomers to self-assembled objects.
 This task is complex but also crucially needed, as the specific
 adsorption type observed experimentally depends on many
 parameters (surfactant type, surface chemistry, presence of
 electrolytes/other fluid components, etc.). Here, we intend to
 fill this gap by providing a generic theoretical picture of
 surfactant adsorption through a phenomenological model
 based on simple thermodynamic ingredients. In more detail,
 this physical model is obtained by including physical
 cooperative effects that account for both lateral interactions
 between adsorbed molecules and self-assembly at the solid
 surface through a site occupancy parameter that can be larger
 than unity. It is important to recognize here that simply
 accounting for lateral interactions in adsorption models is not
 sufficient to describe the adsorption of mesoscopic objects at
 the solid surface (even if such lateral interactions are physically
 needed to account for self-assembly, a site occupancy > 1 must
 be considered to describe the adsorption of supramolecular
 structures).

In practice, this model is derived by writing a constitutive
 kinetic equation involving adsorption/desorption rates that are
 dependent on the surfactant surface concentration to account
 for facilitated or hindered adsorption. Using experimental data
 for two surfactants on two mineral surfaces, this simple yet
 realistic model is shown to capture different surfactant
 adsorption types as observed upon varying the surfactant
 affinity toward the surface. We note that the present model can
 be extended to almost any surfactant adsorption/porous
 surface type, as it has its roots in generic thermodynamic
 concepts (fluid/surface affinity, occupancy/packing, fluid/fluid
 interactions, etc.). The cooperative effects invoked in our
 model to capture the complex adsorption phenomena
 occurring at the surfactant/surface interface are believed to
 be physically relevant as they can be rationalized using a simple
 quasi-chemical adsorption model (which can be seen as a
 Langmuir model in which interactions between adjacent

164 adsorbed molecules are treated in a mean-field approximation).
 165 It is also shown that the adsorption kinetics is drastically
 166 affected by such cooperative effects, therefore offering an
 167 additional mean to understand the physics of surfactant
 168 adsorption (driving forces corresponding to lateral interactions
 169 and surface self-assembly).

2. THERMODYNAMIC MODEL

170 To derive our model, let us consider the situation depicted in
 171 Figure 2 with a solid surface made up of adsorption sites

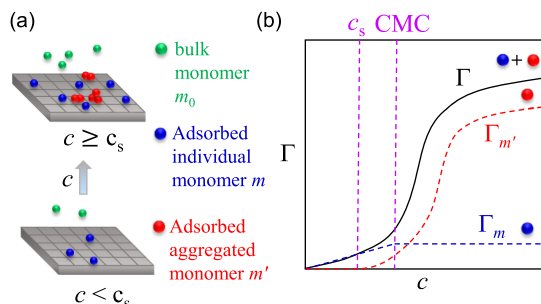


Figure 2. (a) Thermodynamic model of surfactant adsorption onto a solid surface in which the surface concentration Γ as a function of the bulk concentration c is the sum of a contribution Γ_m corresponding to adsorbed individual monomers m and a contribution $\Gamma_{m'}$ corresponding to aggregated monomers m' . (b) Adsorption isotherm corresponding to the model shown in (a). The black line is the total surface concentration Γ , while the blue and red lines correspond to Γ_m and $\Gamma_{m'}$, respectively. For bulk concentration c smaller than the critical surface concentration c_s , only isolated monomers m get adsorbed at the surface—here following a Henry adsorption isotherm $\Gamma_m \sim c$ but any other adsorption regime can be considered. For $c > c_{cmc}$, Γ_m plateaus as the bulk concentration of isolated monomers remains constant. For $c_s < c < c_{cmc}$, both isolated monomers m and monomers in aggregated objects m' adsorb at the surface.

172 denoted as s . Each site s can adsorb a single monomer m (blue
 173 sphere) or $n = 1/\beta$ aggregated monomers m' (red sphere),
 174 where n can be seen as the packing efficiency of aggregated
 175 monomers. $\beta \in [0, 1]$ is a key ingredient which renders our
 176 model versatile, as it allows describing very different physical
 177 situations. $\beta = 1/n$ describes the physical situation previously
 178 considered by Zhu and Gu,³⁵ where a single monomer is used
 179 to aggregate with $n - 1$ other monomers to form a column on
 180 a single solid site s . In contrast, $\beta \rightarrow 1$ corresponds to very
 181 weakly aggregated object, where each monomer m' lies at a
 182 solid site s . Therefore, as will be illustrated in the present
 183 paper, defining β as a variable allows reproducing—at least in
 184 an effective fashion—almost any aggregation type without
 185 having to assume a given shape (micelle, hemi-micelle, vesicle,
 186 disordered aggregate, etc.). In particular, the combined use of a
 187 packing efficiency and surface concentration adsorption
 188 constants allows describing both the adsorption of aggregated
 189 monomers forming at the pore surface (below and above cmc)
 190 and the direct adsorption of micelles formed in the bulk
 191 solution (above cmc).

192 Having introduced the fundamental ingredients of our
 193 model, its constitutive equations for adsorption equilibrium
 194 and kinetics can be derived by writing simple mass-balance
 195 equations between the free monomers m_0 (green spheres) in
 196 solution $c = c[m_0]$, the solid surface sites s , the adsorbed
 197 individual monomers m , and the adsorbed aggregated
 198 monomers m' . Although such conditions can be written

formally, rendering our model tractable requires an additional
 assumption as follows. We introduce a surface critical
 concentration c_s below which only individual monomers m
 adsorb—this critical concentration can be seen as a minimum
 concentration to observe the formation of aggregated (self-
 assembled) structures at the solid surface. In this range, $c < c_s$,
 surface phase equilibrium can be expressed as $s + m_0 \rightleftharpoons m$ with
 the underlying first-order kinetic equilibrium given by

$$\frac{\partial \Gamma_m(c, t)}{\partial t} = k_A c [\Gamma^\infty - \Gamma_m(c, t)] - k_D \Gamma_m(c, t) \quad (1)$$

where $\Gamma_m(c, t)$ is the surface concentration of individual
 adsorbed monomers m and Γ^∞ is the surface site concentration
 in which individual monomers m can adsorb. The first and
 second terms in the right hand side of eq 1 account for the
 adsorption/desorption contributions over a time ∂t (k_A and k_D
 are the adsorption and desorption rates, respectively). The
 solution to this well-known mass-balance condition corre-
 sponds to the Langmuir kinetics (with $k = k_A/k_D$)

$$\Gamma_m(c, t) = \frac{\Gamma^\infty c k}{1 + c k} [1 - e^{-(1+k)k_D t}] \quad (2)$$

which converges in the stationary regime ($t \rightarrow \infty$) toward the
 Langmuir model $\Gamma_m(c, \infty) = \Gamma^\infty c k / (1 + c k)$. In passing, we
 note that taking the limit $\Gamma^\infty \gg \Gamma_m(c, \infty)$ allows recovering
 the Henry regime as usually observed at very low
 concentrations c : $\Gamma_m(c, t) = \Gamma^\infty c k [1 - e^{-k_D t}]$ with the long-
 time limit $\Gamma_m(c, \infty) = \Gamma^\infty c k$.

For $c \geq c_s$, both the individual monomers m and aggregated
 monomers m' adsorb in the surface sites s . As already
 mentioned, using the concept of aggregated monomers, we
 encompass into the same contribution, both the adsorption
 and recombination of adsorbed surfactants into mesoscopic
 assemblies (for $c > c_s$) and the direct adsorption of micelles
 formed in the bulk onto the solid surface (for $c > c_{cmc} > c_s$).
 This is a specificity of our model in which the use of surface
 concentration-dependent adsorption/desorption rates allows
 treating in an effective yet physical fashion these complex
 adsorption phenomena. Here, as a simplification that allows
 straightforward comparison with experimental data without
 changing fundamentally the physical basis of our model, we
 assume that the adsorption of individual monomers m occurs
 on a much shorter timescale than the adsorption of aggregated
 monomers m' . This implies that in the following kinetic
 equation, $\Gamma_m(c, t) \sim \Gamma_m(c, \infty) \forall t$. Moreover, each surface site
 is assumed to adsorb $n = 1/\beta$ aggregated monomers where the
 packing efficiency n allows accounting for nearly any self-
 assembled object. With these approximations, surface phase
 equilibrium for $c \geq c_s$ can be expressed as $s^* + m_0 \rightleftharpoons m'$ where
 * in s^* indicates that only the surface sites that remain available
 for aggregated monomers m' are considered. The correspond-
 ing first-order kinetic equation for the adsorption/desorption
 of the aggregated monomers m' in such a process can be
 expressed as

$$\frac{\partial \Gamma_{m'}(c, t)}{\partial t} = k'_A (\Gamma_{m'}) c \times [\Gamma^\infty - \Gamma_m(c, \infty) - \beta \Gamma_{m'}(c, t)] - k'_D (\Gamma_{m'}) \Gamma_{m'}(c, t) \quad (3)$$

where $\Gamma_{m'}(c, t)$ is the surface concentration in aggregated
 monomers m' , while β accounts for the fact that the adsorption
 of a single monomer in aggregated objects only occupies a
 fraction β of the surface site (therefore, with these definitions,

254 $\beta\Gamma_m'(c, t)$ is the number of such mesoscopic, i.e., aggregated,
 255 objects). Moreover, to account for lateral interactions between
 256 monomers in aggregated objects, we make the adsorption and
 257 desorption rates k_A' and k_D' in the abovementioned equation
 258 explicitly dependent on the surface concentration Γ_m' . At
 259 equilibrium (i.e., in the stationary regime $\partial\Gamma_m'/\partial t = 0$), for a
 260 bulk concentration c , this kinetic equation leads to the
 261 following solution

$$\Gamma_m(c, \infty) = [\Gamma^\infty - \Gamma_m(c, \infty)] \times k'(\Gamma_m')c/[1 + \beta ck'(\Gamma_m')] \quad (4)$$

262 where $k'(\Gamma_m') = k_A'(\Gamma_m')/k_D'(\Gamma_m')$.

263 In summary, this model allows introducing a required degree
 264 of complexity through collective effects in surfactant
 265 adsorption that manifest themselves into two factors. First,
 266 although isolated monomers are assumed to adsorb
 267 independently of each other, lateral interactions between
 268 monomers adsorbing into self-assemblies must be included.
 269 Second, the formation of either ordered (e.g., hemimicelle and
 270 vesicle) or distorted (e.g., elongated micelle) mesoscopic
 271 assemblies is included in an effective fashion through the use of
 272 a packing efficiency n . This generic model relies on a limited
 273 yet important set of assumptions, namely, superimposition of
 274 isolated and aggregated monomer adsorption, fast-isolated
 275 monomer adsorption, and description of self-assemblies
 276 through an effective parameter n . However, despite these
 277 assumptions, as illustrated in the remaining of this paper, this
 278 model allows deriving fundamental insights into the
 279 thermodynamics and kinetics of surfactant adsorption from
 280 simple experimental data. In particular, as shown below, a
 281 merit of this model is that the adsorption-dependent dynamical
 282 coefficients governing the adsorption kinetics of isolated and
 283 aggregated monomers can be estimated from static adsorption
 284 data (because the adsorption/desorption rates k_A' and k_D'
 285 depend explicitly only on Γ_m'). Moreover, this versatile
 286 model can be applied with almost no restriction regarding
 287 the type of surfactants, surfaces, self-assemblies, thermody-
 288 namic conditions, and so forth.

3. RESULTS AND DISCUSSION

290 To test our model, we consider two sets of experimental data,
 291 which are representatives of different surfactant adsorption
 292 behaviors. In more detail, we use the data by Denoyel and
 293 Rouquerol who considered the adsorption at room temper-
 294 ature of two polar (nonionic) surfactants onto silica-based
 295 surfaces (TX100 onto silica and TX165 onto kaolinite clay).²¹
 296 As shown in Figure 3, for both systems, the adsorption
 297 isotherms exhibit two regimes, which correspond to monomer
 298 adsorption at low concentrations c followed by a rapid increase
 299 in the surface concentration, corresponding to surface self-
 300 assembly at concentrations around the cmc. However, a major
 301 difference between the two datasets lies in the monomer
 302 adsorption regime in the low concentration range with a
 303 slow—Henry-like—regime for Figure 3a and a rapid—
 304 Langmuir-like—regime for Figure 3b (we note that in general,
 305 a Langmuir model can be assumed by default, as the Henry law
 306 is simply its asymptotic limit). Because the two surfactants
 307 considered here are similar nonpolar molecules with an OH
 308 group at their end, the origin of this difference has to be found
 309 in the surface chemistry of the different surfaces. Typically, for
 310 the kaolin sample, as discussed by Denoyel and Rouquerol,²¹
 311 the observed strong adsorption phenomenon is thought to
 312 occur on a basal plane—more exactly, the basal plane made up

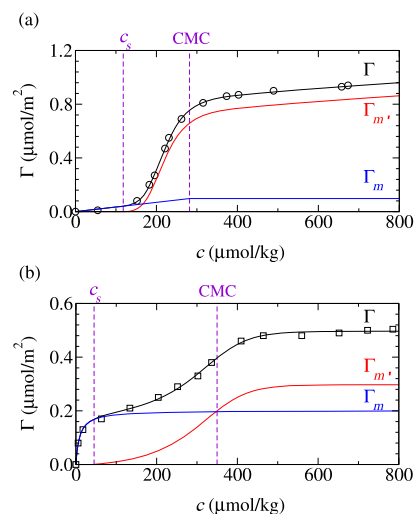


Figure 3. Surfactant adsorption isotherms at $T = 298$ K showing the surface concentration of surfactants Γ onto a silica-based surface as a function of the bulk concentration c : (a) TX100 surfactant on quartz silica and (b) TX165 surfactant on kaolin. The black symbols are the experimental data taken from Denoyel and Rouquerol²¹ with the black line corresponding to smoothed interpolation data. For both systems, the blue and red lines show the predictions of our model for the adsorption of isolated and aggregated monomers, respectively (by construction, the sum of these two contributions is equal to the experimental data). A Henry law and a Langmuir law were used to describe the isolated monomer adsorption in (a,b), respectively. The vertical dashed lines indicate the critical surface concentration c_s and cmc.

of aluminol sites, as the surface concentrations were found to be pH-independent (adsorption sites on this basal plane do not form amphoteric charges with pH).²¹ In contrast, because the weak adsorption phenomenon displayed in Figure 3 for silica is found to be pH-sensitive, it is assumed to occur on neutral adsorption sites that become charged upon increasing the pH.

We use the following procedure to apply our model to the experimental data $\Gamma^{\text{exp}}(c)$ shown in Figure 3. First, to define the surface critical concentration c_s , the interpolated experimental data are fitted against a Langmuir adsorption isotherm over a concentration range $[0, c_{\text{max}}]$. Although the fit is accurate for small c_{max} , the fit does not provide satisfactory results for large c_{max} (because a simple Langmuir or Henry adsorption isotherm cannot describe the raw experimental adsorption data over a large-concentration range). At this stage, it is decided to define c_s as the maximum value for which a correlation coefficient of $R^2 = 0.99$ is obtained. Although the specific cutoff value used is arbitrary, it should be emphasized here that slightly different values would lead to very similar predictions (in practice, with variations in the degree of agreement with experimental data that falls within the experimental error bar). This allows us to have a good approximation to describe the monomer surface concentration $\Gamma_m(c, \infty)$ for $c < c_s$. Here, it is worth mentioning that fitting the Henry or Langmuir model to low-concentration data requires that enough experimental data points are available to ensure rigorous fitting and, hence, robust physical parameterization. As an illustration, Figure S2 shows the different adsorption isotherms obtained as c_s is varied from $c_s \sim 0$ to $c_s > \text{cmc}$. Second, having a fitted model for $\Gamma_m(c, \infty)$, one can estimate the contribution corresponding to the adsorbed aggregated monomers $\Gamma_m'(c, \infty)$ by subtracting $\Gamma_m(c, \infty)$ from $\Gamma^{\text{exp}}(c)$,

345 that is, $\Gamma_{m'}(c, \infty) = \Gamma^{\text{exp}}(c) - \Gamma_m(c, \infty)$. Third, $k'(\Gamma_{m'})$ can be
 346 readily estimated from $\Gamma_{m'}(c, \infty)$ by inverting eq 4

$$k'(\Gamma_{m'}) = \frac{\Gamma_{m'}(c, \infty)}{c[\Gamma_m(c, \infty) - \beta\Gamma_{m'}(c, \infty)]} \quad (5)$$

347 As shown in Figure 3, for both systems, the model including
 348 cooperative effects applies accurately to the experimental data.
 349 From a practical viewpoint, as described above, applying our
 350 model to available experiments requires to determine the
 351 following parameters. Although the Langmuir (Henry)
 352 constant k_H (k_L) must be fitted together with c_s from the
 353 low-concentration range, the maximum adsorbed amount Γ^∞
 354 is determined from the high-concentration range.

355 Figure 4 shows $k'(\Gamma_{m'})$ as a function of $\Gamma_{m'}$ for the two
 356 systems considered here (TX100 on quartz silica and TX165
 357 on kaolin).

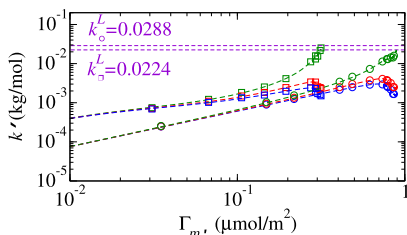


Figure 4. Adsorption constant $k'(\Gamma_{m'})$ for the aggregated monomers m' as a function of their surface concentration $\Gamma_{m'}$, as extracted from the experimental adsorption data shown in Figure 3. The circles are for TX100 adsorption on quartz silica, while the squares are for TX165 on kaolin (experimental data taken from ref 21). For each system, the blue, red, and green data denote data obtained for $\beta = 0.2$, $\beta = 0.5$, and $\beta = 1.0$, respectively. The two horizontal dashed lines in purple indicate the Langmuir adsorption constants that best match the experimental adsorption isotherms in the high-concentration range $c > c_s$.

358 on kaolin). It should be noted that the model applied to the
 359 isothermal adsorption data does not allow estimating β . This is
 360 a drawback of our model, but β can be estimated
 361 independently of $k'(\Gamma_{m'})$ from adsorption kinetic data, as
 362 shown in the last part of this paper. Figure 4 shows that
 363 $k'(\Gamma_{m'})$ increases with increasing $\Gamma_{m'}$ for a given β , therefore
 364 pointing to the existence of collective, that is, cooperative,
 365 effects in surfactant adsorption (otherwise $k'(\Gamma_{m'})$ would
 366 remain constant). Physically, this behavior indicates that
 367 cooperative effects lead to enhanced adsorption with already-
 368 adsorbed molecules, facilitating adsorption of additional
 369 monomers either in the same adsorption sites (when $\beta \neq 1$)
 370 and/or in neighboring adsorption sites ($\beta = 1$). As expected
 371 from eq 5, upon decreasing β , the fraction of available sites to
 372 adsorb aggregated monomers increases, so that $k'(\Gamma_{m'})$
 373 decreases. This is due to the fact that $k'(\Gamma_{m'})$ is an effective
 374 adsorption constant, so that low β corresponds to systems that
 375 tend to self-assemble easily (therefore not requiring large
 376 adsorption constants to pack efficiently at the solid surface).
 377 Figure 4 also shows for the two systems considered here the
 378 Langmuir adsorption constant $k^L = k_A/k_D$, which was estimated
 379 by fitting the concentration range beyond the critical surface
 380 concentration $c > c_s$. In more detail, by restricting the fitting
 381 procedure to the region where the surface concentration
 382 increases rapidly with concentration, it is possible to describe
 383 semiquantitatively the data using a simple Langmuir model
 384 with shifted concentrations $\tilde{c} \sim c - c_s$. As shown in Figure 4,
 385 except for large surface concentrations $\Gamma_{m'}$, regardless of the

system considered, the Langmuir constant k^L overestimates the
 adsorption constant $k'(\Gamma_{m'})$ predicted using our model (Figure
 S3 in the Supporting Information shows the fits of the high-
 concentration experimental data to the Langmuir model). This
 result is due to the fact that the Langmuir model does not
 describe cooperative adsorption, so a larger effective constant
 is needed to capture the increasing adsorption rate upon
 increasing the surface concentration.

For a given surfactant/surface couple, the parameters
 involved in the present model are derived from available
 experimental data. To assess the physical validity and
 robustness of our model, it is important to connect its
 underlying parameters to existing theoretical frameworks. In
 this context, as stated in the Introduction, statistical physics
 offers an efficient and accurate formalism to describe
 cooperative adsorption effects. In particular, the quasi-chemical
 approximation³⁹ allows deriving a simple expression for the
 surface concentration that accounts for lateral interactions
 between adsorbed monomers. Here, for the sake of brevity, we
 provide the main thermodynamic ingredients of this important
 model, which goes well beyond the Langmuir model (an exact
 derivation can be found in the Supporting Information). Let us
 consider free monomers in a bulk solution that can adsorb
 onto surface sites. Assuming additive lateral interactions
 between an adsorbed molecule and its neighbors, the
 adsorption energy E of a monomer cluster made of x
 monomers is $E \sim xw$, where w is the interaction with a single
 neighbor. Phase equilibrium between the adsorbed monomers
 and the free monomers in solution at a temperature T implies
 that the chemical potential is equal in the two phases, that is,
 $\mu = \mu_b$ (the subscript b refers to the bulk solution). In the quasi-
 chemical approximation, as shown in the Supporting
 Information, the chemical potential of the adsorbed phase
 writes $\mu = \mu_0 + k_B T \ln[\theta/(1 - \theta)] + z_0 k_B T/2 \ln[(\gamma - 1 +$
 $2\theta)(1 - \theta)/\theta(\gamma + 1 - 2\theta)]$, where $\theta \in [0, 1]$ is the site
 average occupancy, z_0 is the number of neighboring sites ($z_0 =$
 4 for a surface), and $\gamma = [1 - 4\theta(1 - \theta)(1 - \eta)]^{1/2}$ (with $\eta =$
 $\exp[-w/k_B T]$). In this expression, the reference chemical
 potential $\mu_0 = [z_0 w/2 + \epsilon_0]/k_B T$ corresponds to the energy of
 an adsorbed monomer at full saturation (which includes an
 energy contribution with the surface $\sim \epsilon_0$ and an energy
 contribution with all neighboring adsorbed monomers $\sim z_0 w/$
 2). By noting that $\theta = \beta\Gamma_{m'}/(\Gamma^\infty - \Gamma_{m'})$ and $1 - \theta = (\Gamma^\infty - \Gamma_{m'}$
 $- \beta\Gamma_{m'})/(\Gamma^\infty - \Gamma_{m'})$, the previous expression leads to the
 following expression for $\Delta\mu = \mu - \mu_0$

$$\frac{\Delta\mu}{k_B T} = \ln \left[\frac{\beta\Gamma_{m'}}{\Gamma^\infty - \Gamma_{m'} - \beta\Gamma_{m'}} \right] + \frac{z_0}{2} \ln \left[\frac{\Gamma^\infty - \Gamma_{m'} - \beta\Gamma_{m'}}{\beta\Gamma_{m'}} \right] + \frac{z_0}{2} \ln \left[\frac{(\gamma - 1)(\Gamma^\infty - \Gamma_{m'}) + 2\beta\Gamma_{m'}}{(\gamma + 1)(\Gamma^\infty - \Gamma_{m'}) - 2\beta\Gamma_{m'}} \right] \quad (6)$$

Taking the bulk concentration $c = c_0$ as the concentration at
 the reference point μ_0 and assuming that the concentration
 remains low enough, we can write $\Delta\mu$ for the bulk phase as
 $\Delta\mu_b = k_B T \ln c/c_0$. By inverting eq 6, we obtain $c = 1/k'(\Gamma_{m'}) \times$
 $\Gamma_{m'}/[\Gamma^\infty - \Gamma_{m'} - \beta\Gamma_{m'}]$, which leads to the following
 expression upon insertion in $\Delta\mu_b$

$$\frac{\Delta\mu_b}{k_B T} = \ln \left[\frac{\beta\Gamma_{m'}}{\Gamma^\infty - \Gamma_{m'} - \beta\Gamma_{m'}} \right] - \ln \left[\frac{c_0 \times k'(\Gamma_{m'})}{\beta} \right] \quad (7)$$

To verify that our model of cooperative adsorption is
 consistent with a description of interacting adsorbed species, 440

441 we can check that the chemical potential equality as defined in
 442 the quasi-chemical approximation is obeyed. To do so, by
 443 noting that the first term on the right-hand side, that is, $\mu^* =$
 444 $k_B T \ln[\beta \Gamma_m / (\Gamma^\infty - \Gamma_m - \beta \Gamma_m)]$, is identical in eqs 6 and 7,
 445 we can compare $\Delta\mu - \mu^*$ and $\Delta\mu_b - \mu^*$. As shown in Figure
 446 5, when using the values for k' in Figure 4, a good agreement is

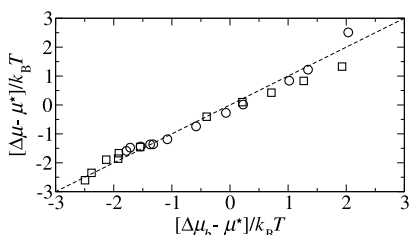


Figure 5. Comparison between the chemical potential shift for bulk and adsorbed surfactants, as predicted within the quasi-chemical approximation using the data derived from our model. The circles and squares refer to the data for TX100 on quartz silica and TX165 on kaolin, respectively (experimental data taken from ref 21). The dashed line is a guide to the eye, which indicates chemical potential equality between the bulk and adsorbed phases.

447 obtained between the two chemical potentials for both TX100
 448 on quartz silica and TX165 on kaolin. When establishing such
 449 a comparison, $\eta = \exp[-w/k_B T]$ and c_0 were used as adjustable
 450 parameters, but we note that they are the only fitting
 451 variables—we found that $\eta \sim 3.3$ for TX100 on silica and η
 452 ~ 4.0 for TX165 on kaolinite. More importantly, it was verified
 453 a posteriori that these values for η , which lead to $w \sim -1.2k_B T$
 454 for TX100 on silica and $w \sim -1.4k_B T$ for TX165 on kaolinite,
 455 are physically relevant, as discussed in what follows. First, as
 456 expected for cooperative effects leading to facilitated
 457 adsorption, w is negative, so that it corresponds to attractive
 458 lateral interactions between adsorbed neighbors. Second, w is
 459 of the order of $k_B T$, as required to observe cooperative
 460 adsorption (indeed, for lower, i.e., less, negative lateral
 461 interactions, thermal motion and therefore desorption would
 462 prevail). Third, the stronger attractive interaction w for TX165
 463 is consistent with the fact that this molecule is similar to
 464 TX100 but with a longer alkyl chain—16 versus 9–10 carbon
 465 groups. In practice, the two datasets used are for different
 466 surfaces—which could affect the comparison made here—but
 467 we recall that η is related to the interaction between two
 468 adsorbed molecules and can, therefore, be considered to be
 469 mostly dependent on their molecular nature/chemistry. A few
 470 remarks are in order here. First, although our thermodynamic
 471 model is found to be consistent with the quasi-chemical
 472 approximation, the latter is insufficient to fully describe
 473 surfactant adsorption over the whole concentration range.
 474 Indeed, the quasi-chemical approximation is only relevant in
 475 the concentration range $c > c_s$, where the surfactant aggregates
 476 at the solid surface to form mesoscopic structures (which stem
 477 from lateral interactions/collective effects). In contrast, in the
 478 low-concentration range, such collective effects are assumed to
 479 be absent, so the quasi-chemical approximation is not relevant.
 480 Second, even if w should formally depend on the surfactant
 481 type only, it is expected to be a function of the solid surface
 482 nature in practice. Indeed, considering that the quasi-chemical
 483 approximation is a mean-field treatment, effective parameters
 484 such as w are expected to depend—even if weakly—on the
 485 strength/nature of the surfactant/solid interactions (in other
 486 words, the lateral interactions in adsorbed surfactants are

necessarily mediated to some extent by the solid/surfactant
 interactions).

As will be shown here, the present model has strong
 implications in terms of surfactant adsorption/desorption
 kinetics on surfaces. In particular, changes in the adsorption/
 desorption rates induce drastic variations in the characteristic
 time corresponding to the transient regime leading to
 thermodynamic equilibrium. Although this feature is not
 specific to our model (because underlying kinetics in the
 Langmuir and Henry models also depend on the adsorption/
 desorption constant rates), the introduced concept of Γ_m
 dependence of k_A and k_D leads to rich and complex kinetics.
 In this respect, it should be emphasized that only such a level of
 complexity allows capturing the intriguing adsorption kinetics
 observed experimentally for surfactant adsorption. In partic-
 ular, all typical non-Langmuirian adsorption dynamics
 observed in transient adsorption experiments but also in
 breakthrough curves, which resist available modeling frame-
 works, point to the existence of cooperative adsorption effects
 and, more generally, complex collective phenomena.¹⁶ To
 illustrate the influence of cooperative effects on adsorption
 kinetics, the dynamical equation given in eq 3 was solved
 numerically for different bulk concentrations c . For TX100
 adsorption on silica, this leads to the time evolution shown in
 Figure 6 (the same data for TX165 on kaolin are not shown
 here for the sake of clarity but can be found in Figure S1 in the
 Supporting Information). Many choices can be made for
 $k'_A(\Gamma_m)$ and $k'_D(\Gamma_m)$ because static adsorption data only
 provide information on $k'(\Gamma_m) = k'_A(\Gamma_m)/k'_D(\Gamma_m)$. Two

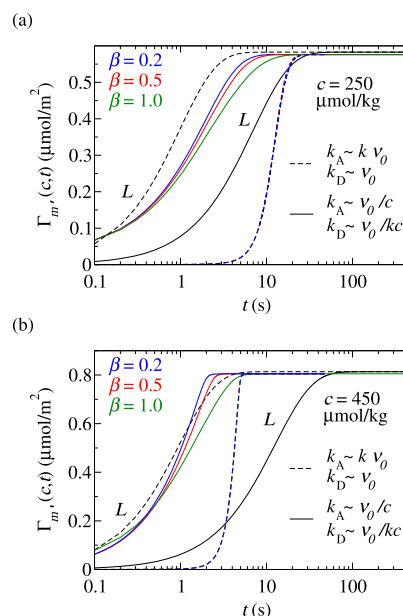


Figure 6. Adsorption kinetics as determined by solving numerically eq 3, showing Γ_m as a function of time t for TX100 on silica for two bulk concentrations: (a) $c = 250 \mu\text{mol/kg}$ and (b) $c = 450 \mu\text{mol/kg}$. The color lines denote the data obtained using the cooperative model with $\beta = 0.2$ (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 $k_A \sim k v_0$ and $k_D \sim v_0$, while the solid lines correspond to $k_A \sim v_0/c$ and $k_D \sim v_0/kc$. Note that our model predicts that the color dashed lines (i.e., $k_A \sim k$ and $k_D \sim$ constant) are superimposed.

516 illustrative situations were considered as shown in Figure 6:
517 (1) $k'_A \sim \nu_0 k'(\Gamma_m)$ and $k'_D \sim \nu_0$ and (2) $k'_A \sim \nu_0/c$ and $k'_D \sim \nu_0/$
518 $k'(\Gamma_m)c$, where ν_0 is a characteristic constant in s^{-1} that sets
519 the typical timescale (because it is used as a constant
520 throughout this study, it does not affect the discussion
521 provided below). We emphasize that the two cases considered
522 here are asymptotic limits as both k'_A and k'_D should depend on
523 k' and hence Γ_m in general. For each situation, we also
524 consider the effect of the aggregation parameter β , which is
525 varied between $\beta = 0.2$ and 1 ($n = 1/\beta$ is the number of
526 aggregated monomers that can be packed into a single
527 adsorption site). Figure 6 also shows for each situation the
528 kinetics obtained using the Langmuir kinetic model with (1) k_A^L
529 $\sim \nu_0 k^L$ and $k_D^L \sim \nu_0$ and (2) $k_A^L \sim \nu_0/c$ and $k_D^L \sim \nu_0/k^L c$, where
530 k^L is the Langmuir adsorption constant that best matches the
531 experimental adsorption isotherm in the high-concentration
532 range $c > c_s$ (see Figure 4 and its caption).

533 Examining in detail the two situations considered here
534 allows gaining insights into the role of cooperative effects on
535 surfactant adsorption/desorption kinetics in porous media. In
536 particular, this illustrates how application of the present model
537 to experimental adsorption kinetic data could be used to probe
538 adsorption and desorption properties including the aggregation
539 constant β .

- 540 • Case [$k'_A \sim k'$, while $k'_D \sim \text{constant}$]. With these
541 assumptions, inserting the expression for k' given in eq 5
542 into the kinetics described by eq 3 shows that the
543 adsorption rate k'_A is constant (i.e., independent of β).
544 Therefore, in this case, both k'_A and k'_D are constant, so
545 that the adsorption kinetics is independent of the
546 aggregation parameter β for all concentrations c (see
547 color dashed lines in Figure 6). Moreover, comparison
548 with the ideal Langmuir model for this case indicates
549 that our cooperative model predicts a much slower
550 kinetics as $k' \lesssim k^L$ for all c (as shown in Figure 4).
551 Indeed, at a constant desorption rate, the kinetics
552 becomes faster with increasing adsorption rate.
- 553 • Case [$k'_A \sim \text{constant}$, while $k'_D \sim 1/k'$]. With these
554 assumptions, β significantly affects the observed
555 adsorption kinetics. As can be inferred from eq 5, k'
556 increases with β , so that $k'_D \sim 1/k'$ decreases. As can be
557 directly illustrated using a simple Langmuir kinetic
558 equation, the adsorption kinetics becomes slower with
559 decreasing desorption constant k'_D while maintaining k_A
560 constant. This interpretation is consistent with the data
561 shown in Figure 6 for $k'_D \sim 1/k'$ and k_A constant, where
562 it is observed that the adsorption kinetics becomes
563 slower with increasing β . Finally, for a given concen-
564 tration with $k'_D \sim 1/k'$ and k_A constant, we observe that
565 the simple Langmuir kinetics is significantly slower than
566 that observed with cooperative effects. This result is
567 consistent with our previous explanation on the role of
568 the desorption rate at constant k_A because $k^L > k'$ for all
569 c leads to $k_D^L < k'_D$ and therefore a slower kinetics for the
570 Langmuir model. Further study is in progress to fully
571 explore the impact of such cooperative effects on
572 adsorption kinetics using available experimental kinetic
573 data.

4. CONCLUSIONS

574 In conclusion, we developed a simple physical model of the
575 thermodynamics and kinetics of surfactant adsorption onto

surfaces that accounts for cooperative effects inherent to such
complex objects. By cooperative effects, we refer here to strong
lateral interactions between adsorbed surfactants but also
intramolecular and intermolecular interactions responsible for
their propensity to form mesoscopic (supramolecular)
structures. With this model, important collective driving forces
that cannot be ignored for such self-assembling molecules are
taken into account to describe the nonconventional static and
dynamic adsorption behavior observed experimentally when
surfactant solutions are set in contact with solid surfaces. Such
collective effects are also at the root of surface aggregation at
solution/air interfaces, which stems from mutual interactions
between adsorbed molecules.⁴⁰ This cooperative behavior was
also recently discussed in the context of surfactant adsorption
at the water/oil interface, where adsorbed oil molecules were
found to enhance surfactant adsorption.⁴¹ In practice, the
simple thermodynamic model derived in this paper involves a
simple kinetic formalism involving adsorption/desorption rates
that vary with the surfactant surface concentration. Such a
formalism can be extended to any class of objects that is
expected to involve adsorption cooperative effects such as ionic
liquids,⁴² long-chain molecules (e.g., normal alkanes),⁴³ and so
forth. Moreover, although all cases treated here involved a
surface concentration c_s lower than the cmc, our model also
deals without any further development to nonwetting
situations where surface aggregation occurs beyond its bulk
counterpart. The fact that, in all cases, the adsorption isotherm
reaches a plateau at a concentration close to the cmc can be
rationalized as follows. The cmc corresponds to the chemical
potential at which the surfactants in bulk solution condense to
form dense surfactant objects (micelles). Within perturbation
theory, near a solid surface, the chemical potential where such
condensation occurs can be written as the bulk value shifted by
a surface interaction contribution.

Once applied to available experimental data, this framework
provides a valuable tool to infer key quantities that govern the
microscopic behavior of any adsorbed surfactant onto various
solid surfaces including surface self-assembly into ordered or
disordered structures. More generally, this robust and versatile
model, which is found to be consistent with rigorous
microscopic treatments such as the quasi-chemical approx-
imation in statistical physics of surface adsorption, can be
extended in principle to surfactant adsorption but also
transport in porous materials. Beyond immediate practical
implications, the results reported here about the nonstandard
surfactant adsorption thermodynamics and kinetics in porous
materials also raise new challenging questions. In particular,
owing to cooperative effects in surfactant adsorption, strong
departure from the adsorption/dynamics interplay observed
for more classical fluids is to be expected in agreement with
experimental observations in breakthrough or injection experi-
ments. This issue is particularly important, as diffusion is
usually considered as the main transport mechanism leading to
adsorption on surfaces. The present work offers a well-
grounded thermodynamic basis to address such questions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08226>.

635 Description of the quasi-chemical approximation and
636 additional data on the influence of cooperative effects on
637 adsorption kinetics for TX165 on kaolinite (PDF)

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655 Notes

656 The authors declare no competing financial interest.

657 ■ ACKNOWLEDGMENTS

658 The authors are grateful to Elise Lorenceau and Julie Wolanin
659 from Laboratoire Interdisciplinaire de Physique for helpful
660 comments. Z.Z. acknowledges Ph.D. funding at Univ.
661 Grenoble Alpes from IFP Energies Nouvelles.

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