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Kinetics and Thermodynamics of Surfactant Adsorption at Model Interfaces: Evidence of Structural Transitions in the Adsorbed Films

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An in situ method, based on two liquid phase contact angle measurements, is developed to investigate the mechanisms of simultaneous adsorption of surfactant at solid–liquid and liquid–liquid interfaces. Well-characterized model systems (methyl-terminated monolayer–hydrocarbon drop–aqueous surfactant solution) and (methyl-terminated monolayer–air bubble–aqueous surfactant solution) have been used to allow reliable connection between surface characteristics and observed phenomena. The adsorption kinetics at such complex interfaces was analyzed through the balance of interfacial forces. For both nonionic surfactants (C_8E_{10} and $C_{12}E_7$) and air bubble used in these studies, we have found that the adsorption kinetics exhibit intermediate transition plateaus at some critical bulk concentrations (around the cmc). These transitions were related to structural rearrangements in the adsorbed surface phase.

Introduction

The relevance of interfacial phenomena to biological and industrial processes, and especially those involving adsorption of surface active molecules, is of fundamental importance. For biological and biomedical systems, the solid–liquid interface is the most relevant, since these adsorption mechanisms involve the interface between a living cell and a liquid which may contain natural or synthetic proteins.

When surfactant adsorbs at an interface, molecules undergo a structural rearrangement by either a monotonic or a discontinuous process, resulting in an equilibrated assembled film. Most of existing works in this field^{1–3} have been so far concerned with equilibrium aspects of this problem where transitions are related to the Gibbs plot of equilibrium quantities of adsorption. In addition, most of these investigations^{2,3} are based on ex situ and indirect methods (weighing of adsorbent, optical density of bulk solution, ...), as they commonly use heterogeneous substrates, in both their nature (SiO_2 , $SiOH$, mica) and morphology (particles, powder, or gel). Correspondingly, these studies may suffer from a lack of information, regarding the dynamic behavior of interfacial parameters which definitely govern the overall adsorption process. Besides existing spectroscopic⁴ and optical⁵ techniques, in situ methods based on the JKR (Johnson–Kendall and Roberts) analysis of the contact area between two solids (an hemisphere and a plate), and the two liquid phase-contact angle measurements have been introduced recently.^{6,7}

In the present paper, a direct and in situ method, based on the two liquid phase contact angle method, is developed to directly determine the actual thermodynamic quantities governing the adsorption process. The specific interest of this method relies on the opportunity it offers to study

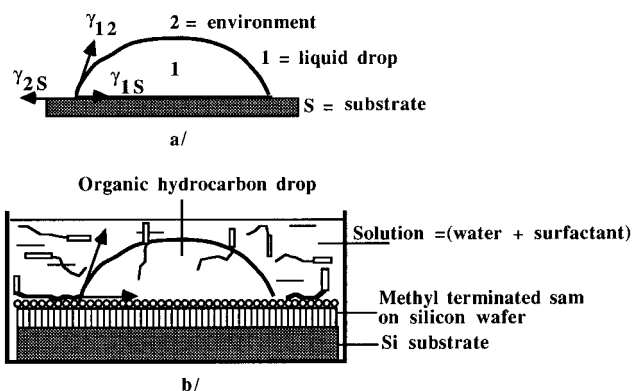


Figure 1. Principle of the two liquid phase method: (a) general case, 1 = liquid drop, 2 = liquid environment, S = solid surface; (b) squalane drop (respectively air bubble) on silicon-based methyl monolayer in aqueous surfactant solution.

both kinetics and structural aspects of competitive adsorptions at thermodynamically related interfaces (liquid 1–solid–liquid 2). Methyl-terminated self-assembled monolayers have been used as model surfaces, affording thus the chemical and structural homogeneity necessary for both reproducibility and reliable interpretation of interfacial thermodynamic quantities. In the following, we report results concerning two different systems: the (methyl-terminated surface–squalane drop) and the (methyl-terminated surface–air bubble), both in aqueous solution of nonionic alkyl poly(oxyethylene) surfactant. Then, we shall discuss the adsorption mechanism in such systems, before we conclude with some remarks and future prospects.

Method

The principle of the two liquid phase contact angle method^{8,9} is schematically represented in Figure 1a, where the surrounding atmosphere of the usual sessile drop method is replaced by a second liquid phase. The two fluids (liquid 1–liquid 2) are nonmiscible in experimental conditions (temperature and duration of experiment). The interfacial equilibrium of the system is described by

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Young's equation:

$$\gamma_{12} \cos \Theta = (\gamma_{2S} - \gamma_{1S}) \quad (1)$$

where the interfacial free energies γ_{ij} between phases i and j are related to the reversible work of adhesion $W_{1S/2}$, through the equation of Dupré

$$W_{1S/2} = \gamma_{12} + \gamma_{2S} - \gamma_{1S} \quad (2)$$

$W_{1S/2}$ is the work of adhesion between fluid 1 and solid S, in equilibrium with the environmental phase 2.

For simplicity, we will adopt the following specifications for indices (see eqs 1 and 2) corresponding to the different phases of the system: 1 = O for organic phase (squalane) or air bubble; 2 = W for aqueous surfactant solution; S = the methyl-terminated monolayer on silicon substrate.

In addition to the assumption of nonmiscibility, the two liquid phase method relies on the thermodynamic assumption that the water phase is "completely" displaced by the squalane over the methyl end groups.⁹

Upon addition of surfactant, the interfacial parameters are modified at both squalane-solution and methyl end groups-solution interfaces, and the actual behavior of the system is simply described by Young's equation where each term depends on the bulk concentration of the surfactant (C_S). This equation (eq 1) contains three unknown interfacial tensions which are reduced by the following considerations:

First, the Gibbs isotherms corresponding to the flat oil-aqueous surfactant solution or air-aqueous interface (γ_{O-W} vs C_S) are determined independently, using the direct and usual Wilhelmy plate method.¹⁰

From this experimental isotherm ($\partial\gamma_{O-W}/\partial C_S$) and concentration dependence of the contact angle $\Theta(C_S, t)$, the first derivative of eq 1 is used for the adsorption at the solid-solution interface (γ_{S-W}), according to

$$\partial[\gamma_{S-W}(C_S) - \gamma_{S-O}]/\partial C_S = \partial[\gamma_{O-W}(C_S) \cos \Theta(C_S, t)]/\partial C_S \quad (3)$$

The unknown γ_{S-O} appearing in relation 3 is independent of the adsorption process, since physisorbed surfactant molecules around the triple line cannot diffuse along the (S-O) interface, essentially for energetic reasons due to their polar heads. If they had to do so, the only favorable ways will either consist of extending their alkyl parts or forming inverted micelles along that oil-methyl-terminated interface. It is noteworthy that while the second case is just unrealistic, the first one will not modify the interfacial tension γ_{S-O} , the surfactant alkyl tails being quite identical to those in the oil phase. Assuming separated contributions of alkyls and polar heads (p.h) to the surface free energy variation of a surfactant chain, a barrier of the order of $\Delta f \sim (f_{\text{alkyl}/w} + f_{\text{p.h}/w})_{\text{rupture}} - (f_{\text{p.h}/\text{alkyl}})_{\text{formation}}$ has to be overcome upon transfer of surfactants from the aqueous to the oil phase. This gives a surface free energy variation $\Delta f(\text{mJ/m}^2) \sim 2(\gamma_{\text{alkyl}} + \gamma_w + \gamma_{\text{p.h}}) - \gamma_{\text{alkyl}/w} - \gamma_{\text{p.h}/\text{alkyl}} - \gamma_{\text{p.h}/w}$. Since $\gamma_{\text{p.h}/\text{alkyl}} < \gamma_{\text{alkyl}/w}$ (~ 50) and $\gamma_{\text{p.h}/w} < \gamma_{\text{p.h}}$, the barrier Δf is at least $\geq 2(\gamma_{\text{alkyl}} + \gamma_w + \gamma_{\text{p.h}}) - 2\gamma_{\text{alkyl}/w} - \gamma_{\text{p.h}}$, which is a quite positive quantity. In addition to these theoretical considerations, this particular assumption has been ascertained through complementary experiments, using infrared and surface tension measurements.

It then results that both concentration and time dependent derivatives at the oil-methyl-terminated interface are identically zero: $(\partial\gamma_{S-O}/\partial C_S) = (\partial\gamma_{S-O}/\partial t) =$

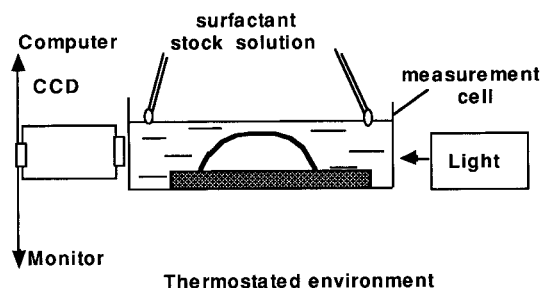


Figure 2. Simplified schematic view of the experimental setup. Relevant dimensions of the working cell are 6 cm (length) and 3.5 cm (width).

0. The Gibbs adsorption isotherm being defined through the first derivatives of interfacial free energies, one finally ends with the following expression for eq 3

$$\partial\{\gamma_{S-W}(C_S)\}/\partial C_S = \partial\{\gamma_{O-W}(C_S) \cos \Theta(C_S)\}/\partial C_S \quad (4)$$

Equation 4 is sufficient to draw both kinetics—through $\Theta(C_S, t)$ —and equilibrium isotherms of adsorption at related (S-W) and (O-W) interfaces.

We may emphasize that the transposition of independently measured $\gamma_{O-W}(C_S)$ isotherm from the Wilhelmy plate method, to the two liquid phase experiment should not create any significant problem for the following reason. As in the two liquid phase experiment, the surfactant is introduced in an identical volume of water, below the equilibrated squalane-water (respectively air-water) interface. Then, the system is allowed to reach equilibrium. If we consider the drop curvature to have a negligible effect on interfacial tension and excess (especially for the squalane drop where Θ ranges from 16 to 45° (see Results)), the equilibrium quantities are identical in both cases.

The interfacial tension and excess Γ upon adsorption are then related according to the Gibbs equation

$$d\gamma = -RT\Gamma_S d \ln(x_S/(1 - x_S)) \quad (5)$$

where x_S is the molar fraction of surfactant in the bulk solution.

In the limit of dilute solutions ($C_S < \text{cmc}$), $x_S \ll 1$ and $(1 - x_S) = x_W \approx 1$. The substitution of C_S to the molar fraction x_S in these conditions leads to the usual simplified Gibbs relation

$$d\gamma/d \ln(C_S) = -RT\Gamma_S \quad (6)$$

In this work, relation 6 has been used to determine interfacial excess Γ_S and molecular area σ_S , while the time-concentration dependence of the measured contact angles $\Theta(C_S, t)$ were used for kinetics.

Experimental Section

The simplified experimental setup is shown in Figure 2. After equilibration of the water-squalane drop interface (about 1.5 μL of squalane was used), a measured amount of surfactant stock solution is added to a constant volume of water (10 mL) to meet the required final concentration. The surfactant is introduced simultaneously at both sides of the vessel to achieve a symmetric and homogeneous diffusion toward the triple line. The initial contact angle and its time-concentration dependence $\Theta(C_S, t)$ are recorded using an automatic goniometer (Krüss G402), giving both kinetics and equilibrium values of the adsorption process. Typical intervals of data acquisition were 5, 30, or 60 s, depending on the kinetics. The independent measurement of the Gibbs isotherm at the squalane-aqueous solution interface is performed on a Cahn tensiometer (DCA 322), using microscope glass slides

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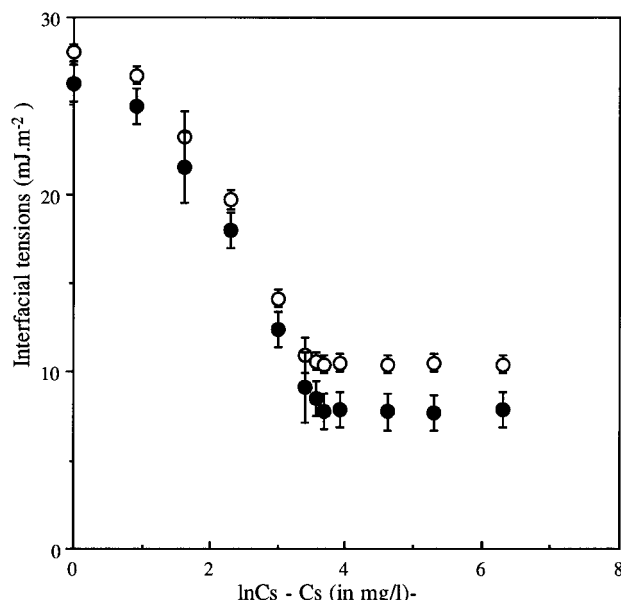


Figure 3. Gibbs plots at squalane-solution interface (○) and methyl-terminated surface-solution interface (●).

as probe solid surfaces. The glass slides are cleaned with absolute ethanol and then flamed to give high surface energy solid probes.

Nonionic surfactants, the octaethylene glycol mono-*n*-decyl ether $C_{10}E_8$ and heptaethylene glycol mono-*n*-dodecyl ether $C_{12}E_7$ are respectively from Aldrich and Fluka; the squalane was chromatographic grade from Prolabo. The water is deionized and double distilled. The measured surface tensions for squalane and water are respectively 28.5 and 72.8 mJ/m². The alkylsilane used to elaborate methyl-terminated monolayers is a hexadecyltrichlorosilane $Cl_3Si(CH_2)_{15}CH_3$ from ABCR (Karlsruhe, Germany). Both products—surfactant, squalane, and chlorosilane—have been used without further purification.

The methyl monolayer is self-assembled onto silicon wafers by immersion in 10^{-3} M solutions of chlorosilane in cyclohexane at about 22 °C. Silicone wafers are polished single crystals, (111) oriented and p doped, from Philips Electronic, Caen, France. Slices are cut from these wafers in squares of about 2.5×2.5 cm. These plates are cleaned with absolute ethanol and immersed for 30 min in warm (60 °C) piranha solution (3:7 H_2O_2/H_2SO_4 in volume) to hydroxylate the surface. After piranha treatment, further hydroxylation is achieved by a thorough cleaning and storage of the plates for about 24 h in deionized and double distilled water.¹¹ The substrates are then dried under N_2 and immediately immersed in the silane solution for an overnight (about 14 h) adsorption. After that adsorption step, the samples are sonicated for about 20 s in cyclohexane, rinsed with cyclohexane and then dried under N_2 before immediate use for experiments. The advancing and receding contact angles for water on these silicon-based methyl-terminated monolayers are respectively $\theta_a = 115^\circ$ and $\theta_r = 105^\circ$. The surface free energy as usually obtained from the equilibrium contact angle of hexadecane ($\theta_e = 42^\circ$) using the geometric mean equation of Fowkes is $\gamma_s = 21.0$ mJ/m², in agreement with reference data reported for such surfaces.^{11,12}

Results and Discussion

The independently determined Gibbs plots $\gamma_{O-W}(C_S)$ at squalane-water and air-water interfaces are used with the measured two liquid phase contact angle $\Theta(C_S)$, to draw the corresponding isotherm $\gamma_{S-W}(C_S)$ at the solid-solution interface according to eq 4. The equilibrium adsorption isotherms at (O-W) and (S-W) interfaces are given in Figure 3 for $C_{12}E_7$. The similarity of these isotherms is likely to result from the similar hydrophobic nature of the adsorbents (methyl-terminated surface and

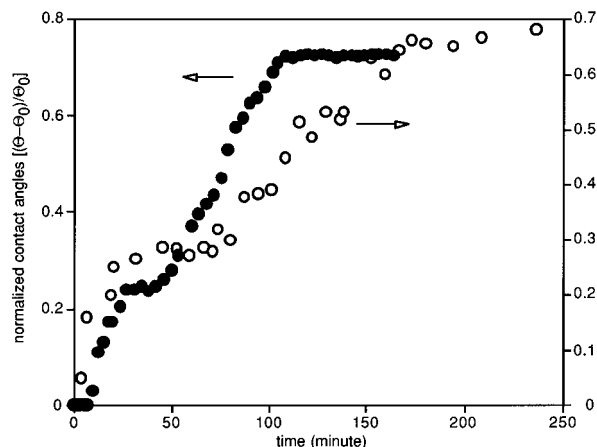


Figure 4. Adsorption kinetics: squalane drop methyl-terminated surface (○) and air bubble methyl-terminated surface (●) in $C_{10}E_8$ solutions at the cmc.

squalane) as well as the thermodynamic interdependence of the two interfaces through the contact angle $\Theta(C_S)$. However, a slight shift of the cmc (35 mg/L for the squalane-solution interface) toward a higher value is observed at the methyl monolayer-solution interface (cmc ~ 40 mg/L). An explanation to the fact that a higher C_S is needed to reach the cmc at S-W interface could be the existence of nanoscale defects in the monolayer (pinholes, crystallites, borders),¹³ where surfactant molecules can penetrate. The maximum excess Γ of adsorbed surfactant at O-W interface and corresponding molecular area $\sigma = (N_{\text{Avogadro}}\Gamma)^{-1}$ obtained from the slope of the isotherms before cmc are respectively $10^6\Gamma_O = 3.3 \pm 0.2$ mol·m⁻² and $\sigma_O = 51 \pm 3$ Å². At the S-W interface, these equilibrium adsorption quantities are quite similar, with $10^6\Gamma_S = 3.4 \pm 0.3$ mol·m⁻² and $\sigma_S = 49 \pm 4$ Å². These values are compatible with the slight shift observed in the cmc at the S-W interface, since only accessible adsorbed surfactant molecules will contribute to $\gamma_{S-W}(C_S)$. It is interesting to mention here that the isotherm obtained at the S-W interface in this study is in very good agreement with that found for a quite identical system with the JKR method already introduced in ref 6 ($10^6\Gamma_S = 3.4$ mol·m⁻² and $\sigma_S = 53$ Å²).

The adsorption kinetic studies are based on the time-concentration dependence of the measured contact angles. Figures 4 and 5 represent these concentration dependent kinetics for both oil and air bubble drops, with contact angles normalized to their initial equilibrium value in pure water $[\Delta\Theta(C_S, t)/\Theta_0]$. The most striking feature of these results is the onset of an intermediate plateau near the cmc region, for both $C_{10}E_8$ and $C_{12}E_7$. It is noteworthy that these transitions occur during the adsorption kinetical process and are thus basically different from concentration dependent transitions, sometimes observed within Gibbs plots versus $\ln(\text{of equilibrium concentrations } C_S)$.¹⁴ Based on the numerous available investigations on adsorption at water-oil and water-air interfaces where such transitions were never reported for adsorption kinetics of homogeneous surfactants, these intermediate plateaus have been related to the solid-liquid interface which appears to govern the adsorption process. This point just results from the experimental fact that the contact angle Θ increases monotonically upon adsorption (except on plateaus). This can be seen from eq 4, where the time

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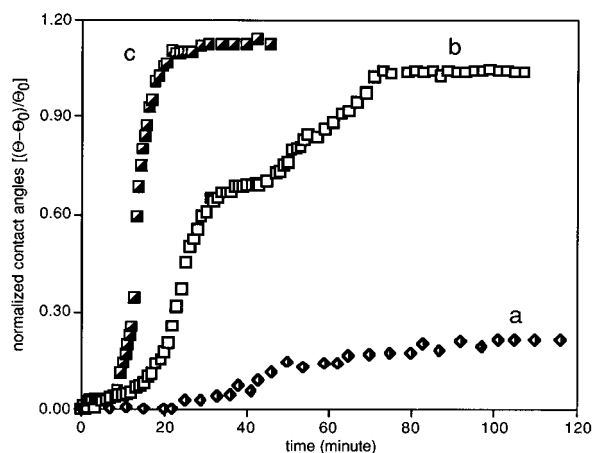


Figure 5. Adsorption kinetics: squalane drop methyl-terminated surface in $C_{12}E_7$ solutions at 0.25 cmc (a), cmc (b), and ~ 100 cmc (c).

dependent variation of $\cos \Theta$ may be expressed in a similar way as

$$(d\gamma_{O-W}/dt) \cos \Theta + \gamma_{O-W}[d(\cos \Theta)/dt] = d\gamma_{S-W}/dt \quad (7)$$

As we know from experiment, both $[d(\cos \Theta)/dt]$ and $(d\gamma_{O-W}/dt)$ are < 0 , while γ_{O-W} and $\cos \Theta$ ($16^\circ < \Theta < 45^\circ$ for squalane) are > 0 . Therefore, giving an arbitrary value $\Theta(t)$, a finite adsorption along the two interfaces over a finite time dt , will result in a quantity $(d\gamma_{S-W}/dt)$ which decreases more rapidly than the opposing "in plane" component $(d\gamma_{O-W}/dt) \cos \Theta$, due to the (O-W) interface. Correspondingly, the system will move toward a higher S-W interfacial area. It then seems that the competitive adsorption and related phenomena are driven by that interface as further discussed hereafter.

One can find according to eq 7, the condition which results in a plateau. Taking into account that $\Theta(t)$ is constant at the transition, the term with the derivative of the cosine is $= 0$. The corresponding integral expression for eq 7 then reads $\gamma_{S-W}(t) = \gamma_{O-W}(t) \cos \Theta(t) + \alpha$, which represents Young's equilibrium equation with the constant $\alpha = \gamma_{SO}$, i.e. the methyl monolayer-oil (respectively air bubble) interfacial tension. Since $\alpha = \gamma_{SO}$ is an upper limit to the variation of $[\gamma_{S-W}(t) - \gamma_{O-W}(t) \cos \Theta(t)]$ upon adsorption, the unique solution which physically satisfies the situation is the equilibrium (final) plateau at saturation. The intermediate plateaus should then be related to some transient process involving a mismatch over a finite time between the local concentration $C_S(\text{interface}, t)$ and the adsorption $\Gamma_S(C_S, t)$. The reasons for such a mismatch which will result in a structural rearrangement of adsorbed films are not obvious. In the following, a critical review of a few mechanisms which are likely to explain the observed transitions are proposed, before we conclude with the surface phase restructure process which constitutes the basic mechanism developed in this study.

First, intermediate transitions during adsorption kinetics can arise because of the presence of discrete species having significant differences in their diffusion coefficients D . In this case, the duration of the transition plateau should scale with the difference among diffusion coefficients. A complementary experiment simulating the worst possible heterogeneity for a "pure" surfactant has been done to verify this hypothesis, using a mixture of $C_{12}E_7$ (reference surfactant) with a 0.1 molar fraction of $C_{16}E_8$ (heterogeneity). A unique transition plateau was still observed before saturation. This transition being already present with the homogeneous phase $C_{12}E_7$, it

can be concluded that the $C_{16}E_8$ heterogeneity does not introduce any equivalent transition plateau.

The micellar dissociation process can also be evoked for these transitions, since stock solutions used in these studies were well above the cmc (100 cmc). At such a concentration, the free monomer fraction is quite constant and comparable to that at the cmc, whereas aggregation number and aggregates shape are modified. This usually results (for steric reasons) in an increase of the micellar dissociation constant in the solution as the aggregate shape shifts from spheroids to ellipsoids and cylinders for $C_S \gg \text{cmc}$.¹⁵ Therefore, using different stock solutions (100, 300, and 700 cmc) to prepare the same final working solution (concentration) should lead to some meaningful difference in the adsorption kinetics. More precisely, the dissociation would be increasingly faster from working solutions prepared with 100 cmc to 700 cmc. This will result in a shorter delay to have available free monomers and correspondingly to a shorter intermediate plateau length. We performed these complementary experiments and did not find any modification of the plateau length toward the expected direction. Instead, a more complex behavior which will deserve further attention is observed at higher stock solution concentrations (around 700 cmc). Moreover, in the hypothesis of micellar dissociation, one could expect for working solutions above the cmc a plateau length Δt such that $\Delta t(\text{for } C_S \gg \text{cmc}) \leq \Delta t(\text{at cmc})$. What we observe over the many experiments performed in this study is just that no intermediate plateau is seen, even at $C_S = 10$ cmc (see Figure 5 for the case of $C_{12}E_7$).

Bulk micelles diffusion (without dissociation) can also be proposed as a possible mechanism since the high aggregation number may induce a significant shift in the diffusion coefficients compared to free monomers. In this case, the lately diffused micelles can adsorb onto the first adsorbed surfactant monolayer, with their external polar heads in contact with both water and polar groups of the sublayer. In addition, this adsorption should be done against repulsive interactions between hydrated polar heads. It will therefore not reduce the S-W interfacial tension necessary to explain the last rising branch, the interface retaining the same intermolecular feature (polar heads/water interactions). Furthermore, if this mechanism is relevant, the transitions would be observed even at higher concentrations of working solutions ($C_S > \text{cmc}$). This is not the case.

It then seems so far, that the only reliable hypothesis left to explain the intermediate plateau is the existence of a surface phase transition related to a structural rearrangement of the adsorbed surfactant layer at the S-W interface. At the O-W interface, alkyl tails of surfactant can penetrate oil and air phases without creating structural rearrangement, because of the high thermodynamic compatibility and the absence of a significant conformational barrier. At the methyl monolayer-solution interface instead, the restructure is somehow imposed by the adsorption mode. In Figure 6 are represented the consecutive steps of the adsorption at the S-W interface, which possibly lead to the observed structural transitions. Adsorption to an interface is dependent upon both diffusion to the interface which determines the boundary concentration $C_S(\text{interface}, t)$ and interactions with previously adsorbed surfactant $\Gamma(C_S, t)$ at that interface. Therefore, the intermediate transitions could be explained by a mismatch among the time dependent variations of these two quantities over a short, but finite time interval. During

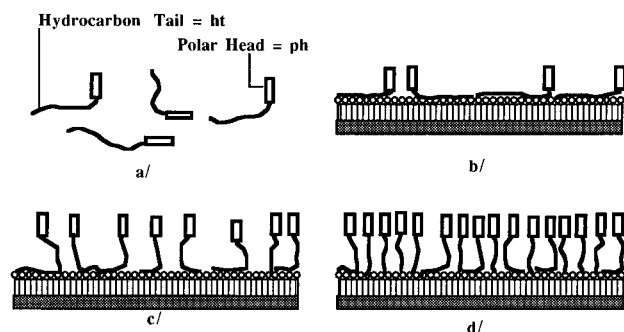


Figure 6. Adsorption process of surfactant molecules at methyl-terminated surface-solution interface; (a) surfactant in bulk solution; (b) first step of adsorption, or adsorption at low concentration; (c) restructuration step; (d) further adsorption and packing toward monolayer.

this time, initially adsorbed molecules, which have already occupied almost all the available area by their spatial extension, should undergo some restructuring before any further adsorption can occur. Because of the time delay due to this process, a shift in the boundary concentration $C_s(\text{interface}, t)$ toward higher values can appear, since bulk diffusion still continues to bring surfactant at the interface. This kinetical nonequilibrium situation between the adsorbate and the adjacent boundary concentrations will result in a local chemical potential gradient ($\Delta\mu$), normal to the interface. It may be possible that the system tries to reduce this gradient through a cooperative rearrangement (straightening) of the adsorbed molecules, to make more room for further adsorption. This process will result in the equilibration of the local chemical potentials, as

$$\Delta\mu = (\mu^{\text{boundary}} - \mu^{\text{adsorbed layer}})_{\text{surfactant}} \rightarrow 0 \quad (8)$$

As described in Figure 6, from low concentrations (or initial step of adsorption for a given C_s), the adsorbed molecules

will progressively straighten at the transition plateau, making more space for further adsorption. The fact these transitions are observed mainly in the near cmc region is somewhat expected, since at low C_s , the maximum adsorption plateau is reached, while free adsorption areas are still available. For higher C_s , the phenomena may exist or not, but the corresponding time scale would be too short for any accurate observation.

Though we have proven that the two liquid phase method constitutes a reliable method to investigate adsorption at complex interfaces, the driving mechanisms of the observed surface phase transition would deserve further investigations. Work in that direction is planned with systems involving monolayers of different chemical end groups or packing densities, as well as ionic surfactants.

Conclusion

The two liquid phase contact angle method has been used for in situ and direct study of adsorption mechanisms at related solid-liquid and liquid-liquid interfaces.

It is shown from these results that the use of self-assembled monolayers as model surfaces, presenting both chemical and structural homogeneity could allow some tentative modeling of adsorption phenomena. In addition to thermodynamic equilibrium quantities, the method appears to be a quite sensitive and accurate tool for studying kinetics of surfactant (polymer) adsorption.

Clear experimental evidence of a surface phase transition and its concentration dependence was established.

Further understanding of these adsorption mechanisms at thermodynamically related interfaces is expected from investigations, on both methyl-terminated and polar group terminated monolayer surfaces, as well as ionic surfactants.

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