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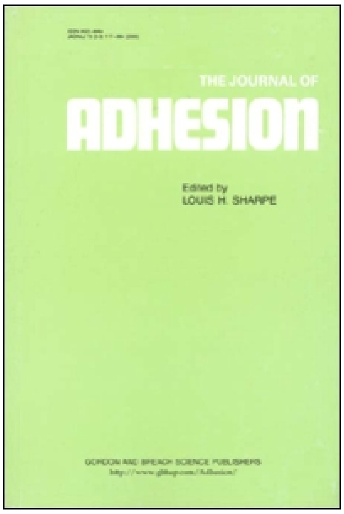

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In Situ Study of Simultaneous Adsorption of Surfactant at Model Solid-Liquid and Liquid-Liquid Interfaces Using the Two-Liquid Contact Angle Method*

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A direct method of *in situ* investigation of adsorption mechanisms at related solid/liquid and liquid/liquid interfaces is presented, based on the two-liquid-phase contact angle measurement. Using a model system represented by a self-assembled monolayer (SAM) surface/hydrocarbon drop/aqueous surfactant solution, it is shown that the method constitutes a simple way to characterize both the dynamic behavior and equilibrium quantities of adsorption. In addition to the consistency of these results with the usual diffusion controlled models, some interesting phenomena such as structural transitions in the adsorbed layer are clearly evidenced from adsorption kinetics.

KEY WORDS: two liquid contact angle; model surface; surfactant adsorption; kinetics; structuring of adsorbed layer

INTRODUCTION

The relevance of interfacial phenomena to biological and industrial processes, 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 all these adsorption mechanisms involve the interface between a living cell and a liquid which may contain natural or synthetic proteins.

Although many studies have been concerned with surfactant systems, some obscure points still remain. The most important of these to be clarified concerns the hypotheses on adsorption mechanisms and structural rearrangement of adsorbate at solid-liquid interfaces.[1] These structural arrangements of the adsorbate being highly dependent on the morphology and chemical homogeneity of the solid surface, any fundamental

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understanding of this problem should involve some model systems fullfiling these requirements. Most previous investigations are characterized by the diversity and heterogeneity of the substrates, in both their nature (SiO_2-SiOH, mica, Al_2O_3, etc.) and morphology (plate, particles, powder or gel). In addition, many of these investigations are based on indirect or *ex situ* methods,[2,3] including adsorption density measurement of bulk surfactant by light diffusion and adsorbent weighing. These techniques may perturb the system and they do not give any information on the structure of the adsorbed layer. This justifies the effort to develop *in situ* methods, directly related to relevant interfacial properties of the adsorption process. In addition to existing spectroscopic[4] and optical[5] techniques, an *in situ* method based on the JKR[6] analysis of the contacting area in aqueous surfactant solution was introduced recently by Haidara, Chaudhury and Owens.[7]

In the present work, the technique of contact angle measurement in a two-liquid-phase system is proposed to investigate adsorption at a solid-liquid interface, using a model surface. The specific interest of this method is that it offers the opportunity to study adsorption mechanisms at thermodynamically related solid-liquid and liquid-liquid interfaces, especially their kinetic and structural aspects. It can, therefore, constitute a step towards a further understanding of the adsorption process of proteins and other molecules in technological or biological systems, where aggregates can attach to a wall in liquid media. We shall present in this paper the results obtained with the system represented by a silicon-based dodecyltrichlorosilane, a squalane drop, and an aqueous phase containing a non-ionic alkyl polyoxyethylene surfactant. Then we shall discuss the adsorption mechanism in such systems, before we conclude with some remarks and future prospects.

METHOD

The contact angle measurement is a highly surface-sensitive technique in monitoring surface induced modifications, when a controlled environment, including both materials and surrounding media, is used. The principle of the two-liquid contact angle method[8] is schematically represented in Figure 1a, where the atmosphere is replaced by a liquid phase 2. The liquid phases are non-miscible in the experimental conditions (temperature and duration of experiment). At equilibrium, the drop parameters–usually the contact angle–are only a function of the surface tensions and given by the equation of Young:

$$\gamma_{12} \cos \Theta_{1S/2} = (\gamma_{2S} - \gamma_{1S}) \tag{1}$$

where the γ_{ij} represent the interfacial free energies between i and j.

These equilibrium interfacial free energies are also related to the reversible work of adhesion $W_{1S/2}$, through the equation of Dupré, according to

$$W_{1S/2} = \gamma_{12} + \gamma_{2S} - \gamma_{1S} \tag{2}$$

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

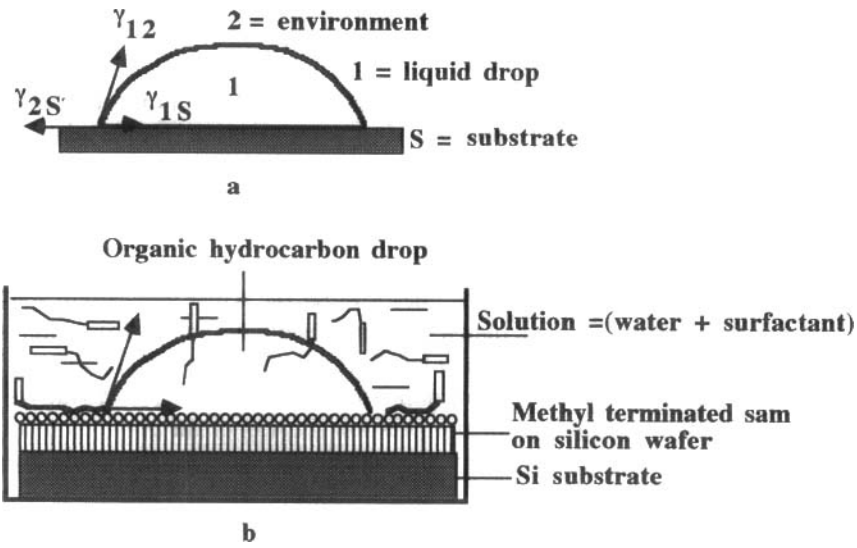

FIGURE 1 Principle of the two-liquid-phase method. 1a general case, 1 = liquid drop, 2 = liquid environment, S = solid surface. 1b squalane drop on Si-based, methyl-terminated, self-assembled monolayer (SAM), in aqueous surfactant solution.

When considering our experimental system shown in Figure 1b, the previous equations and indices are specified as follows:

$1 = O$ (*for organic hydrocarbon phase* = squalane)
$2 = W$ (for aqueous surfactant solution)
S = for methyl-terminated monolayer on silicon substrate

In the absence of any surfactant molecules (Fig. 1a), equation (3) is derived[8] for the two-liquid method, using the Young-Dupré equation (Eq. (1)–(2)), in combination with the Fowkes geometric mean relation:[9]

$$\gamma_{OW}\cdot\cos\Theta_0 = \gamma_W - \gamma_O + 2\{(\gamma_S\cdot\gamma_O)^{1/2} - (\gamma_S\cdot\gamma_w^d)^{1/2}\} \tag{3}$$

where the contact angle Θ_0 is only a function of the surface characteristics of the pure phases.

In addition to the assumption of non-miscibility, the derivation of equation (3) relies on the thermodynamic assumption that the water phase is "completely" displaced by the squalane over the methyl end groups.[10] Since all thermodynamic parameters in equation (3)., except γ_S, are known (or measurable) quantities, this relation has been used to determine the surface free energy of the freshly elaborated self-assembled monolayers (see experimental section).

On introduction of the surfactant, the interfacial parameters are modified at both the squalane-solution and metyl end groups-solution interfaces and the actual behavior of the system is simply described by the Young equation, where each term is dependent on the bulk concentration of the surfactant (C_S). This equation (1) contains three unknowns–the interfacial tensions–which are reduced by the following considerations.

First, the Gibbs isotherm corresponding to the flat squalane-aqueous surfactant solution interface ($\gamma_{O\text{-}W}$ *versus* C_S) is determined independently, using the direct and usual Wilhelmy plate method.[11]

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

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

The unknown $\gamma_{S\text{-}O}$ appearing in relation (4) is independent of the adsorption process. Indeed, the physisorbed surfactant molecules around the triple line cannot diffuse along the (*S-O*) interface over more than a fractional length of their hydrocarbon tail, both for steric and energetic reasons (polar head). Under these conditions, $(\partial\gamma_{S\text{-}O}/\partial C_S) = (\partial\gamma_{S\text{-}O}/\partial t) = 0$. Since the Gibbs adsorption isotherm is defined by derivatives of surface (interface) free energies, the final expression (Eq. (5)) of the previous relation (Eq. (4)) is sufficient to draw both kinetics, through $\Theta(C_S, t)$, and isotherms of adsorption at the solid-solution interface

$$\partial\{\gamma_{S\text{-}W}(C_S)\}/\partial C_S = \partial\{\gamma_{O\text{-}W}(C_S)\cos\Theta(C_S)\}/\partial C_S \tag{5}$$

We emphasize that the transposition of the independently measured $\gamma_{O\text{-}W}(C_S)$ 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 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, the equilibrium quantities are identical in both cases.

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

$$d\gamma = -RT\Gamma_S \cdot d\ln(x_S/(1 - x_S)) \tag{6}$$

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 for the molar fraction x_S in these conditions leads to the usual simplified Gibbs relation,

$$d\gamma/d\ln(C_S) = -RT\Gamma_S \tag{7}$$

In this work, relation (7) is used for adsorption, to determine interfacial excess Γ_S and molecular area σ_S, while the time-concentration dependence of the measured contact angles, $\Theta(C_S, t)$, is used for kinetics.

EXPERIMENTAL

The simplified experimental device 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 was added at the surface of a constant volume of water (10 ml), to meet the required final concentration. The initial contact angle and its

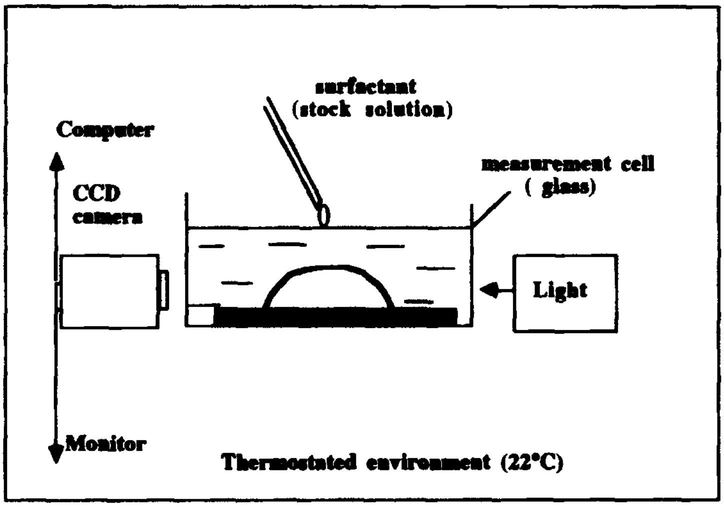

FIGURE 2 Simplified schematic view of the experimental set-up.

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 aquisition were 5, 30 or 60 seconds, 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 as probe solid surfaces. The glass slides were cleaned in warm Piranha solution (see below), rinsed with deionized and doubly-distilled water, and then flamed to give high surface energy solid probes.

The non-ionic surfactant, heptaethylene glycol mono *n*-dodecyl ether, $C_{12}H_{25}(OCH_2CH_2)_7OH$, was from Fluka, the squalane of chromatographic grade from Prolabo and the water was deionized and doubly distilled. The measured surface tensions for squalane and water were, respectively, 28.5 and 72.8 mJ/m^2. The alkylsilane used to elaborate the SAM was a dodecyltrichlorosilane, $Cl_3Si(CH_2)_{11}CH_3$, from Aldrich. All three products–surfactant, squalane and chlorosilane–were used without further purification.

The self-assembled monolayer was evaporated onto polished single crystal silicon wafers, (111) oriented and *p*-doped, from Philips Electronics, Caen, France. Slices were cut from these wafers in squares of about 2.5 × 2.5 cm. These plates were cleaned with absolute ethanol and immersed for 30 minutes in warm (60°C) Piranha solution (3 parts H_2O_2/7 parts H_2SO_4 by volume) to hydroxylate the surface. After Piranha treatment, further hydroxylation was achieved by a thorough cleaning and storage of the plates for about 24 hours in deionized and doubly distilled water.[12] The method of vapor phase silane deposition[13,14] was applied, according to the procedure used by Chaudhury *et al.*[14] 100 µl of silane in 3 g of purified mineral oil is first evacuated for trapped air under vacuum. The plates are then introduced and the desiccator brought to about 6×10^{-3} Torr for 1 hour. The vapor phase silane then adsorbs onto the surface *via* a hydrolysis reaction between surface silanols and chlorine atoms of the silane.

TABLE I
Wetting properties and surface characteristics of the Si-based, self-assembled monolayer of dodecyltrichlorosilane

Test liquids	Contact angles (°)		Surface energy (mJ/m^2)	
	one liquid in air	two liquid method	Fowkes relation (geometric mean)	Relation (3) of two liquid method
water	$\theta_a = 111 \pm 1$ $\theta_r = 100 \pm 1.5$			
hexadecane	$\theta_a = 42 + 1.5$ $\theta_r = 40 \pm 1$	$\theta_{\text{equil.}} < 15$		
squalane	$\theta_a = 42 \pm 1$ $\theta_r = 41 \pm 1.5$	$\theta_{\text{equil.}} = 20 \pm 1.5$	21.6	21.7

The advancing and receeding contact angles for water, hexadecane and squalane on these Si-based, methyl-terminated monolayers are given in Table I. For water and hexadecane, which are the usual reference liquids for these SAM, the contact angles are in very good agreement with reported data.[12] The surface free energy of the methyl monolayers was characterized by the two-liquid method using water and squalane, according to equation (3). A value of $\gamma_S = 21.5\,\text{mJ/m}^2$ was obtained, in agreement with reference data reported for fully methyl-terminated surface layers, which range[14] from 20 to 22 mJ/m^2.

RESULTS AND DISCUSSION

The independently-determined Gibbs plot $\gamma_{O\text{-}W}(C_S)$ at the squalane-solution interface was used, with the measured two-liquid contact angle $\Theta(C_S)$, to draw the corresponding $\gamma_{S\text{-}W}(C_S)$ at the solid-solution interface according to equation (5). The clear similarity of the two isotherms plotted in Figure 3 is likely to be the result of the similar hydrophobic nature of the adsorbents (methyl-terminated monolayer and squalane), and also the thermodynamic interdependence of the two interfaces through $\Theta(C_S)$. However, a slight shift of the CMC (35 mg/l for the squalane-solution interface) towards a higher concentration is observed at the methyl monolayer-solution interface (CMC ~ 40 mg/l). An explanation for the fact that a higher C_S is needed to reach the CMC at the *S-W* interface could be the existence of nanoscale defects in the SAM layer (pinholes, crystallite borders),[15] where surfactant molecules can penetrate. The maximum excess of adsorbed surfactant at the *O-W* interface determined from the slope before the CMC is $10^6 \cdot \Gamma_O = 3.3 \pm 0.2\,\text{M} \cdot \text{m}^{-2}$ and the corresponding molecular area is given by $\sigma = (N_{\text{Avogadro}} \cdot \Gamma)^{-1}$ is $\sigma_O = 51 \pm 3\,\text{Å}^2$. At the self-assembled monolayer-solution interface, these equilibrium adsorption quantities are quite similar, with $10^6 \cdot \Gamma_S = 3.4 \pm 0.3\,\text{M} \cdot \text{m}^{-2}$ and $\sigma_S = 49 \pm 4\,\text{Å}^2$. 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 $\gamma_{S\text{-}W}(C_S)$. It is interesting to mention here that the Gibbs isotherm at the *S-W* interface obtained in this work is quite similar in both slope and equilibrium values to that found, for the same system, by the JKR method,

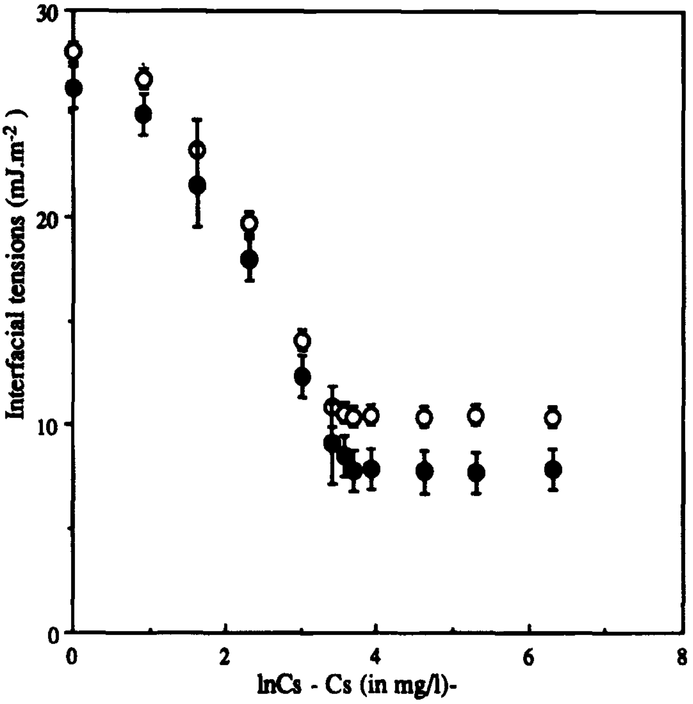

FIGURE 3 Gibbs plots at squalane-solution interface (○) and methyl SAM surface-solution interface (●).

see Reference 7. The related adsorption at these interfaces can be roughly described through simple surface energetic considerations. We consider that Figure 4 represents the adsorption configuration at the *O-W* interface, while Figure 5 gives the successive states of adsorption at the *S-W* interface (see below for kinetics proof). The interfacial free energy variation per mole of surfactant upon adsorption (Fig. 5) is given as a first approximation by:

$$\Delta F_S \sim N a_{ht}\{(\gamma_{S\text{-}ht}+\gamma_{ht\text{-}W})/2-(\gamma_{S\text{-}W}+\gamma_{W\text{-}ht})\} \tag{8}$$

In this relation, $-\gamma_{S\text{-}W}$ stands for removed water-methyl group interactions, to establish half of the water-hydrocarbon tail (*W-ht*) and methyl-hydrocaron tail (*S-ht*) interactions per adsorbed surfactant molecule $(\gamma_{S\text{-}ht}+\gamma_{ht\text{-}W})/2$ and, $-\gamma_{W\text{-}ht}$ is for removed water-hydrocarbon tail interactions in bulk solution. N and a_{ht} are, respectively, the Avogadro's number and the area of the hydrocarbon tail. The unchanged contribution in the two states is the $\gamma_{W\text{-}ht}$ term representing the polar head-water interactions. This free energy component, ΔF_S, will progressively contain a growing hydrophobic term (*ht-ht* interaction), in place of the (*S-ht*) and (*W-ht*) interactions as adsorption and lateral interactions increase, rendering ΔF_S more negative and the adsorbed layer more structured. Yet, using measured and estimated values based on the assumption that the (*ht*) in the heptaethylene glycol dodecyl ether, $CH_3\text{-}(CH_2)_{11}$ $(EO)_7OH$, has a surface energy contribution equivalent to that of a dodecane, a quite

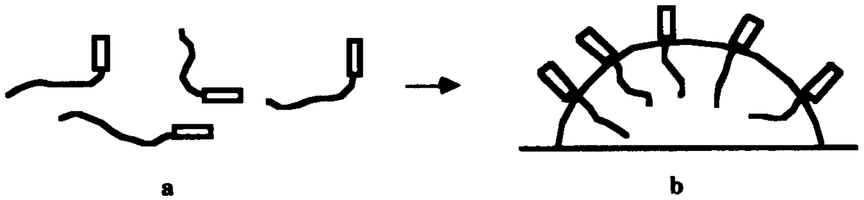

FIGURE 4 Adsorption scheme of surfactant molecules at squalane-solution interface. a. molecules in the bulk solution; b. adsorbed molecules at the interface.

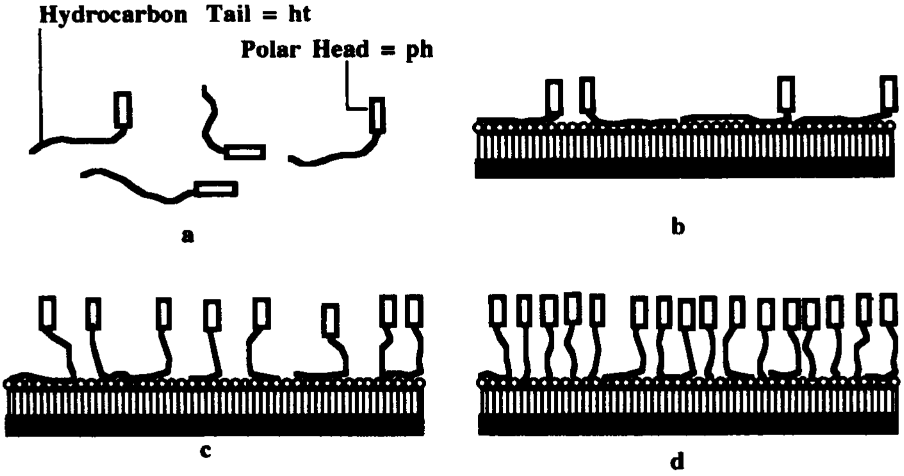

FIGURE 5 Adsorption process of surfactant molecules at methyl SAM surface-solution interface. a. surfactant in bulk solution; b. first step of adsorption, or adsorption at low concentration; c. restructuration step; d. further adsorption and structuration.

negative free energy variation, $\Delta F_S \sim -80\, Na_{ht}$ (mJ/m^2), is obtained. In the same way, the interfacial free energy variation upon surfactant adsorption at the squalane drop interface is given, according to Figure 4, by

$$\Delta F_O \sim Na_{ht}\{\gamma_{O\text{-}ht} - (\gamma_{O\text{-}W} + \gamma_{W\text{-}ht})\} \tag{9}$$

Since $\gamma_{O\text{-}ht} \sim 0$ and $\gamma_{O\text{-}W} \sim \gamma_{W\text{-}ht}$, relation (9) reduces to $\Delta F_O \sim 2Na_{ht}\gamma_{O\text{-}W} \sim -100Na_{ht}$ (mJ/m^2).

Based on these variations of interfacial free energies, adsorption at both methyl-solution and, of course, at squalane-solution interfaces can take place simultaneously. Furthermore, it can be seen from the Young equation (Eq. (1) and related figure (Fig. 1) that adsorption at the methyl-solution interface constitutes the driving force for the contact angle variation. In fact, since $\partial(\cos\Theta)/\partial C_S < 0(\Delta\Theta > 0)$, it follows from the Young equation (Eq. (1) that $(\partial\gamma_{SW}/\partial C_S) < (\partial\gamma_{OW}/\partial C_S)\cos\Theta$ (recall that $\partial\gamma_{S\text{-}O}/\partial C_S = 0$, because no surfactant molecules can diffuse along that interface). This condition means that the increase in Θ arises because the S-W interfacial energy is reduced more upon adsorption than the horizontal component from the O-W interface

(Fig. 1). Therefore, the overall increases of Θ constitutes an experimental proof that the adsorption at the (*S-W*) interface has a greater influence on the observed modification of interfacial parameters. Another striking proof is brought to this statement by considering the virtual situation where adsorption takes place at the squalane-water interface, leaving the solid-water one free from adsorption. Such a situation would lead, as it is mandatory for the wetting process, to an expansion of both squalane-water and squalane-solid interfaces. The overall effect would result in a decreasing contact angle, which is the opposite of experience. However, we can expect adsorption equilibrium to be first completed at the *O-W* interface, owing to the unbalanced molar free energy term, $\delta\Delta F_{S\text{-}O} \sim -20\,Na_{ht}$, between the two interfaces. These results are interesting in that they show how model surfaces, because of their chemical and structural homogeneity, can be used for further modelling and understanding of adsorption phenommena.

The adsorption kinetics was based on the time-concentration dependence of the measured contact angles as shown in Figure 6. Figure 7 represents these kinetics, with the contact angles normalized to their initial equilibrium value in pure water, $\Theta(C_S, t)/\Theta_0$.

The time dependence of $\Theta(C_S, t)$ has been plotted *versus* $t^{1/2}$ to assess whether the adsorption process is diffusion controlled, as is usually observed for such unperturbed systems.[2,3] In that respect, the linear dependence on the square root of time, as observed in Figure 7 on a large time scale, confirms the diffusional character of this adsorption process. The low bulk concentration part of the kinetics is mainly charac-

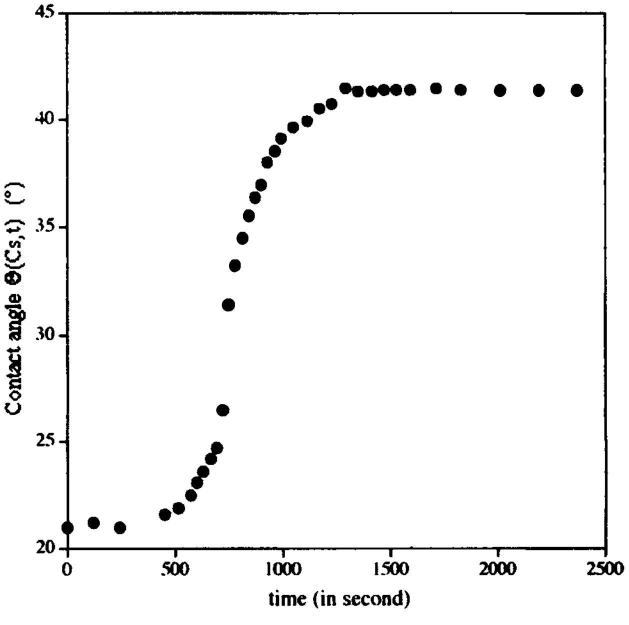

FIGURE 6 Time dependence of contact angle (●) between squalane drop and methyl SAM surface. Bulk concentration is 100 mg/l.

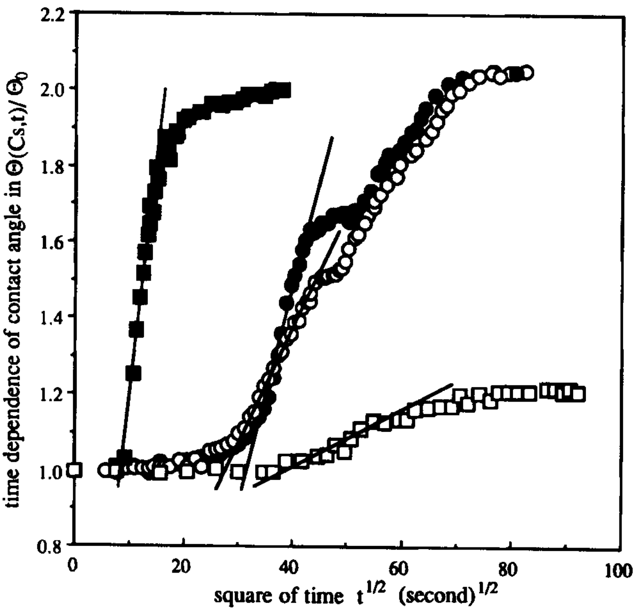

FIGURE 7 Adsorption kinetics for different concentrations: (□) 10 mg/l; (○) 35 mg/l; (●) 40 mg/l and (■) 500 mg/l. Transitions are around the CMC (35–40 mg/l). Each curve is an average of 3 (reproducible) experiments.

terized by an induction period, corresponding to the larger diffusion time required by the molecules to reach the interface in that case. The most striking feature of these results is the onset of a pseudo-plateau near the CMC region, between 30 and 50 mg/l. These intermediate plateaus, where the diffusional process is locally perturbed, have been related to the structural arrangement of the adsorbed surfactant molecules. Based on the numerous studies of adsorption at water-oil and water-air interfaces where no such transition was reported for adsorption kinetics, these intermediate plateaus have been related to the structural transition in the adsorbed layer, as already observed for the adsorption isotherms of some non-ionic surfactants.[16] As shown in Figure 4, surfactant hydrocarbon tails penetrate the squalane phase where no particular structure is formed, avoiding any significant rearrangement process during this adsorption. At the methyl monolayer-solution interface, however, the restructuration is somewhat imposed by the adsorption mode, as illustrated in Figure 5. Adsorption at the interface is dependent upon both diffusion to the interface which determines the local concentration C_S (interface, t) and interaction with previously adsorbed surfactant at the interface, related to the amount of adsorption, $\Gamma(C_S, t)$. Therefore, the intermediate transitions could be explained by a mismatch between these two quantities over a short, but finite, time interval. During that time, the adsorbed molecules, which have occupied almost all the available area by their spatial extension, should undergo some restructuring before further adsorption can occur. Due to this process, a slight shift in the local concentrations, $C_S(\text{local}, t)$ and $\Gamma(C_S, t)$, towards a higher value can exist, leading to an osmotic pressure (ΔP) between this boundary surfactant concentration and that in the adsorbed layer. It may be possible that the system tries to reduce this concentration difference through a cooperative rearrangement (straightening) of the adsorbed molecules, to make more place for further adsorption. This process will result in the equilibration of the local chemical potentials, according to

$$(\Delta p)^{\text{near interface}}_{\text{adsorbed layer}} = (\mu^{\text{near interface}} - \mu^{\text{adsorbed}})_{\text{surfactant}} = 0$$

As described in Figure 5, from low concentrations (or the initial step of adsorption or a given C_S), the adsorbed molecules will progressively straighten at the transition plateau, making more space for further adsorption. The fact that 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 might exist or not, but the corresponding time scale would be too short for any accurate observation.

An alternative explanation to these structural transitions can be proposed, based on the surface energetic balance which has been discussed above. We have indicated (Eq. (9)) that the free energy of adsorption at the O-W interface is more favorable than at the S-W interface. Therefore, coverage of the O-W interface could be completed before sorption at the S-W interface is complete at these intermediate concentrations.

Though we have proved that the two-liquid method constitutes a reliable way to study both the equilibrium and kinetics of adsorption at related interfaces, some mechanisms (adsorbate restructing) need to be clearly verified through further investigations on systems presenting different sizes of the hydrocarbon tail, monolayer nature and packing densities.

CONCLUSION

The wo-liquid contact angle method has been used for *in situ* and direct study of the 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, even grossly, some tentative modelling 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 restructuring mechanism of the adsorbed layer and its concentration dependence was established.

A further understanding of these adsorption mechanisms at thermodynamically-related interfaces are expected from investigations on both methyl and polar group terminated monolayer surfaces.

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