Adsorption of different amphiphilic molecules onto polystyrene latices

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Received 23 September 2003; accepted 26 August 2004

Abstract

In order to know the influence of the surface characteristics and the chain properties on the adsorption of amphiphilic molecules onto polystyrene latex, a set of experiments to study the adsorption of ionic surfactants, nonionic surfactants and an amphiphilic synthetic peptide on different latex dispersions was performed. The adsorbed amount versus the equilibrium surfactant concentration was determined. The main adsorption mechanism was the hydrophobic attraction between the nonpolar tail of the molecule and the hydrophobic regions of the latex surface. This attraction overcame the electrostatic repulsion between chains and latex surface with identical charge sign. However, the electrostatic interactions chain–surface and chain–chain also played a role. General patterns for the adsorption of ionic chains on charged latex surfaces could be established. Regarding the shape, the isotherms presented different plateaus corresponding to electrostatic effects and conformational changes. The surfactant size also affects the adsorption results: the higher the hydrophilic moiety in the surfactant molecule the lower the adsorbed amount.

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Keywords: Interfaces and colloids; Amphiphilic molecules; Surfactant and peptide adsorption; Latex particles

1. Introduction

The adsorption of molecular chains such as surfactants onto solid/liquid interfaces is of a great interest because of its role in nature and industrial applications. Each improvement in the knowledge of this phenomenon has important consequences for different fields including industry, medicine, and biology [1].

Many industrial processes require the utilization of colloidal dispersions that are typically unable to maintain their dispersed state on their own. Attaching molecular chains onto the surface may alter the properties of these dispersions. By controlling the main mechanisms of this adsorption phenomenon, dispersions can be stabilized/destabilized, so that they perform in the process properly.

Our general aim in this work was to contribute to knowledge of the behavior of molecular chains at the solid/liquid interface. Due to the large number of chains with different characteristics currently used, we chose five representative amphiphilic molecules. This amphiphilic character guaranteed their adsorption onto surfaces and their stabilizing properties. The latter will be studied in a future article.

The chains studied in this work were an anionic surfactant, a cationic surfactant, two nonionic surfactants, and a peptide. Several examples of the application of these surfactants in industry, cosmetics, pharmacology, and biology can be found in Refs. [2–4]. We designed the peptide by combining 25 different amino acids to form an amphiphilic structure. Essential characteristics of the peptide included its detection by means of spectrophotometry, solubility in aqueous solution, adsorption on hydrophobic surfaces, and charge dependency on pH. Peptides of this size have been found to be of biological interest [5].

A thorough characterization of these molecules was essential for proper interpretation of the adsorption results and of the changes of the surface properties upon adsorption. In this work, the techniques available in our laboratory
Four different latices synthesized in our laboratory were used as the adsorbent surfaces. There are three anionic latices, namely, Lx(SO$_3$H), Lx(HEMA), and Lx(COOH), and an amphoteric one, namely, Lx(anfo). All of them were prepared by emulsifier-free polymerization in a discontinuous reaction using a thermostatic batch reactor (spherical vessel). The solution was stirred with a Teflon palette located 1 cm over the bottom of the vessel. Lx(SO$_3$H) is a styrene (Merck)/sodium styrenesulfonate (NaSS, Fluka) copolymer. The co-initiator NaSS makes particles present a negative charge on the surface independent of the pH. The synthesis conditions were based on recipes given in Refs. [6,7]. Lx(COOH) and Lx(anfo) were synthesized using styrene as the monomer. The surface-charged groups of the former come from the initiator 4,4′-azobis(4-cyanopentanoic acid) (ACPA, Aldrich); therefore, the surface charge depends on the pH. Azo-N$\cdot$N$\cdot$N$^\prime$-dimethyl-enesorbutramidine hydrochloride (AMDBA) donated by Dr. J.W.S. Goosen from Bayer, A.G., was used as the initiator in the synthesis of the Lx(anfo). The temperature conditions of that synthesis led to an amphoteric surface, with positive charge at acid pH and negative one at basic pH. It has been demonstrated [8,9] that polystyrene particles synthesized with the AMDBA initiator present a more hydrophobic surface than those synthesized with other initiators. Justification lies in the fact that their charged groups (amidine) are placed in an organic heterocycle, and then they are embedded in a more apolar environment than sulfonate or carboxyl groups.

Lx(HEMA) is a styrene/NaSS and a hydrophilic polymer (2-hydroxethylmethacrilatum, HEMA) in the synthesis of the Lx(anfo). The temperature conditions of that synthesis were based on recipes given in Refs. [6,7]. Lx(COOH) and Lx(anfo) were synthesized using styrene as the monomer. The surface-charged groups of the former come from the initiator 4,4′-azobis(4-cyanopentanoic acid) (ACPA, Aldrich); therefore, the surface charge depends on the pH. Azo-N$\cdot$N$\cdot$N$^\prime$-dimethyl-enesorbutramidine hydrochloride (AMDBA) donated by Dr. J.W.S. Goosen from Bayer, A.G., was used as the initiator in the synthesis of the Lx(anfo). The temperature conditions of that synthesis led to an amphoteric surface, with positive charge at acid pH and negative one at basic pH. It has been demonstrated [8,9] that polystyrene particles synthesized with the AMDBA initiator present a more hydrophobic surface than those synthesized with other initiators. Justification lies in the fact that their charged groups (amidine) are placed in an organic heterocycle, and then they are embedded in a more apolar environment than sulfonate or carboxyl groups.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade. The water was purified by a Milli-Q Academic Millipore system. When necessary, sample pH was controlled using a buffer solution (borate for pH 9, phosphate for pH 7, and acetate for pH 5), keeping the ionic strength at a constant value of 2 mM.

2.2. Latex particles

Four different latices synthesized in our laboratory were used as the adsorbent surfaces. There are three anionic latices, namely, Lx(SO$_3$H), Lx(HEMA), and Lx(COOH), and an amphoteric one, namely, Lx(anfo). All of them were prepared by emulsifier-free polymerization in a discontinuous reaction using a thermostatic batch reactor (spherical vessel). The solution was stirred with a Teflon palette located 1 cm over the bottom of the vessel. Lx(SO$_3$H) is a styrene (Merck)/sodium styrenesulfonate (NaSS, Fluka) copolymer. The co-initiator NaSS makes particles present a negative charge on the surface independent of the pH. The synthesis conditions were based on recipes given in Refs. [6,7]. Lx(COOH) and Lx(anfo) were synthesized using styrene as the monomer. The surface-charged groups of the former come from the initiator 4,4′-azobis(4-cyanopentanoic acid) (ACPA, Aldrich); therefore, the surface charge depends on the pH. Azo-N$\cdot$N$\cdot$N$^\prime$-dimethyl-enesorbutramidine hydrochloride (AMDBA) donated by Dr. J.W.S. Goosen from Bayer, A.G., was used as the initiator in the synthesis of the Lx(anfo). The temperature conditions of that synthesis led to an amphoteric surface, with positive charge at acid pH and negative one at basic pH. It has been demonstrated [8,9] that polystyrene particles synthesized with the AMDBA initiator present a more hydrophobic surface than those synthesized with other initiators. Justification lies in the fact that their charged groups (amidine) are placed in an organic heterocycle, and then they are embedded in a more apolar environment than sulfonate or carboxyl groups.

Lx(HEMA) is a styrene/NaSS and a hydrophilic polymer (2-hydroxethylmethacrilatum) copolymer and it was synthesized following previous work [8,10]. The surface charge comes from the NaSS, but for several reasons [11,12], some weak acid groups are present on the surface. Subsequently, the surface charge is weakly dependent on the pH. Cleaning was carried out following Wilkinson et al.’s recommendations [13]. Particle size was obtained by transmission electron microscopy using an H-7000 FA Hitachi microscope. The mean diameter and the polydispersity index of these latices (Table 1) were obtained by averaging over 500 individual particles (automatically analyzed with Bolero software, AQ Systems). In all cases, the particle size distribution is considered extremely narrow. Surface charge densities of the latices were determined by conductometric and potentiometric automatic titrations employing a pH meter (Crisson Instruments, Model 2002), a conductometer (Crisson Instruments, Model 525), and a Dosimat 665 (Metrohm) to add the titrant agent. These measurements were made in the presence of low concentrations of NaCl (2–3.5 mM). The maximum surface charge density ($\sigma_{\text{max}}^0$) of Lx(COOH), Lx(anfo), and Lx(HEMA) was obtained by conductometric back titration as explained in Ref. [14]. However, strong acid groups are difficult to determine directly by means of conductometric titration. Therefore an alternative method was used for Lx(SO$_3$H): adsorbing a cationic lipid (distearoyl dimethylammonium bromide, DSDMA) (Fluka) in a 50% (v/v) ethanol/water mixture as explained elsewhere [15,16].

### Table 1

<table>
<thead>
<tr>
<th>Latex</th>
<th>Mean diameter (nm)</th>
<th>PDI</th>
<th>$\sigma_{\text{max}}^0$ (mC/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lx(SO$_3$H)</td>
<td>138 ± 7</td>
<td>1.007</td>
<td>−96 ± 4</td>
</tr>
<tr>
<td>Lx(COOH)</td>
<td>364 ± 13</td>
<td>1.004</td>
<td>−205 ± 3 (pH 9)</td>
</tr>
<tr>
<td>Lx(anfo)</td>
<td>320 ± 15</td>
<td>1.007</td>
<td>175 ± 3 (pH 4)</td>
</tr>
<tr>
<td>Lx(HEMA)</td>
<td>261 ± 12</td>
<td>1.007</td>
<td>−62 ± 2 (pH 9)</td>
</tr>
</tbody>
</table>

Note. PDI: polydispersity index. $\sigma_{\text{max}}^0$: maximum surface charge density.
employed in this work, Triton X-100 and Triton X-405. Both of
these are polyoxyethylene p-t-octylphenol and differ with
respect to the number of PEO groups. The structural for-
mula of Triton X surfactants is shown in Fig. 2c, where
X = 9–10 for Triton X-100 and X = 40 for Triton X-405.
They were supplied by Sigma with a high grade of purity. In
addition, the mass spectroscopy spectrum was obtained. The
results exhibited a Gauss distribution in molar mass. How-
ever, the polydispersity indexes of our samples (2) were
measured in our lab using (a) spectrophotometry, (b) surface
tension, and (c) conductivity. Other authors’ data: (1) spectrophotometry [19],
(2) pyrene 1:3 ratio [20], surface tension [21], and spectrophotometry [22];
(3) Sigma, FDS [23]; (4) [27].

Due to the aromatic ring in the molecules shown in Fig. 2,
their detection in aqueous media is possible by means of a
direct spectrophotometry method. Triton X-100 and Triton
X-405 have already been well characterized by other au-
thors [19–23]. However, less information was found for the
ionic surfactants mentioned above. This is why we used ad-
ditional techniques (surface tension measurements and con-
ductivity) to obtain more information about NaDBS and DB.

The main characteristics of all these surfactants are sum-
martized in Table 2. $M_w$ is the molar mass, $\lambda_{\text{max}}$ is the
wavelength at which the maximum absorbance is found and
$\varepsilon_a$ is the molar extinction coefficient. These values corre-
spond to surfactant in water at 25°C. The effect of the
buffers mentioned previously on the absorbance results for
the ionic surfactants was found to be negligible. The area
per molecule at the air/solution interface, $a_m$, was obtained
by means of surface tension measurements (ADSA-P tech-
nique, pendant drop method [24–26]) in pH 7 buffer (phos-
phate, 2 mM) at 23°C. The critical micelle concentration
(CMC) is the surfactant concentration at which micelles start
forming. Determining the CMC is based on observing the
change of specific properties of the solution by increasing
the surfactant concentration. For instance, the spectropho-
tometric technique consists of measuring the absorbance at
the $\lambda_{\text{max}}$ for different surfactant concentrations [19]. The

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**Table 2**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$M_w$ (g/mol)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>CMC (mM)</th>
<th>$\varepsilon_a$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$a_m$ (nm$^2$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaDBS</td>
<td>348.48</td>
<td>262</td>
<td>1.5 ± 0.4</td>
<td>532 ± 9</td>
<td>0.430 ± 0.008</td>
</tr>
<tr>
<td>DB</td>
<td>414.48</td>
<td>269</td>
<td>0.49 ± 0.10</td>
<td>1430 ± 40</td>
<td>0.54 ± 0.04</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>625</td>
<td>275</td>
<td>0.51 ± 0.01</td>
<td>1910 ± 30</td>
<td>(0.48–0.54)$^4$</td>
</tr>
<tr>
<td>Triton X-405</td>
<td>1966</td>
<td>275</td>
<td>0.58 ± 0.01</td>
<td>1005 ± 9</td>
<td>0.88$t^4$</td>
</tr>
</tbody>
</table>

Note: Data measured in our lab using (a) spectrophotometry, (b) surface tension, and (c) conductivity.

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### 2.3. Amphiphilic molecules

#### 2.3.1. Surfactants

The anionic surfactant is sodium dodecylbenzenesul-
fonate (NaDBS, Aldrich). The structure of the pure sur-
factant is shown in Fig. 2a. The mass spectroscopy spec-
trum (Centre of Scientific Instrumentation, University of
Granada) showed that it was a mixture of homologues
with different alkyl chain lengths: 12.5% (10 C), 32.8% (11 C), 29.5% (12 C), 25.2% (13 C). The cationic surfactant
is Domiphen bromide or dodecyl(dimethyl-2-phenoxymethyl
ammonium bromide (DB, Aldrich). Its structure is shown
in Fig. 2b. The mass spectroscopy spectrum reveals that it
is a pure sample. Two nonionic surfactants were also em-
ployed in this work, Triton X-100 and Triton X-405. Both of

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![Fig. 1. Surface charge density of Lx(SO$_3$H) (●), Lx(COOH) (▲), Lx(anfo) (■), and Lx(HEMA) (▼) vs pH.](image)

![Fig. 2. Surfactant structures: (a) NaDBS, (b) DB, (c) Triton X-100 (X = 9–10) and Triton X-405 (X = 40).](image)
value at which the slope of the absorbance versus concentration curve changes corresponds to the CMC. However, it is well known that different methods lead to differences of up to 50% in the CMC. In Table 2, we show the CMC data obtained in our lab using several techniques: (a) spectrophotometry (Beckman DÅ 7400 spectrophotometer) in water at 25°C, (b) surface tension (ADSA-P technique, pendant drop method) in pH 7 buffer (2 mM) at 23°C, (c) conductivity in pH 7 buffer (2 mM) at 25°C. We also include other authors’ data (in water at 25°C): (1) spectrophotometry [19]; (2) pyrene 1:3 ratio [20], surface tension [21], and spectrophotometry [22]; (3) Sigma, FDS [23]; (4) [27].

2.3.2. Peptide

The amino acid sequence of the peptide is as follows: NH2-LWAPIMF GSCGTY DKDKDKDKDK G. It was synthesized by SIGMA GENOSYS with a high purity. The amphiphilic character of the chain is guaranteed, as it has a clear apolar moiety made of 14 noncharged amino acids and a polar tail composed of 10 polar ones. Its molar mass is 2817.23 g/mol and λmax = 277 nm. This peptide presents a positive charge at pH 3 and a negative one at pH 11. The molar extinction coefficients for these solutions are εa(pH 3) = (4.58 ± 0.13) (mg/ml)−1 cm−1 and εa(pH 11) = (1.38 ± 0.03) (mg/ml)−1 cm−1.

2.4. Methods

The adsorbed amount was determined by means of the depletion method, that is, as the difference between the surfactant concentration in solution before and after adsorption. To measure the surfactant concentration, the spectrophotometric method was chosen. This method is accurate and able to detect very low concentrations, as proven by other authors [19,28]. There exists a linear relation between absorbance and surfactant concentration for the values we are interested in. The molar extinction coefficient (see Table 2) was used to determine the surfactant concentration in solution by directly measuring the absorbance of the sample. Known values of polystyrene latex, surfactant, and buffer were mixed to get a final volume of 8 ml. Buffer solutions were used for ionic surfactant adsorption, and as mentioned previously, the ionic strength was maintained at 2 mM. The nonionic surfactant adsorption was carried out in water. For the peptide, the pH was adjusted without using buffer and the ionic strength was set at 1 mM NaCl. The amount of latex was chosen in such a way that the overall area presented by the spherical particles was equal to 0.3 m². The kinetics of adsorption was previously monitored to determine the best conditions for the equilibrium adsorption experiments. The samples were kept in a thermostatic bath at 25°C and subjected to shaking. After 4 h the supernatant was separated by centrifugation and filtered using a filter (Millipore, pore diameter 0.1 µm) with an extremely low affinity for protein adsorption.

3. Results and discussion

3.1. Ionic surfactants

To understand the influence of the surface characteristics on the adsorption of ionic surfactants we chose different adsorbent surfaces. Three negative surfaces were used, namely, Lx(COOH) at pH 9, Lx(COOH) at pH 7, and Lx(anfo) at pH 9. One positive surface, Lx(anfo) at pH 5, was also employed.

For the sake of clarity, we will present separately the adsorption isotherm of each ionic surfactant. The equilibrium concentration is normalized with respect to the CMC obtained from surface tension (Table 2 in italics). This technique provided the most accurate results. We will distinguish between the case in which surface and surfactant have opposite charge signs and the case in which they have the same sign.

3.1.1. Anionic surfactant (NaDBS)

Considering the data shown in Fig. 3, the influence of the surface characteristics was analyzed as follows:

(a) Surface and surfactant with opposite signs: the adsorption of NaDBS on the positive surface (Lx(anfo) at pH 5) was very different from the other cases. An intermediate plateau was found around Γ = 1.25 µmol/m². This quantity was slightly lower than the theoretical number of charged groups necessary to cancel the surface charge (1.44 µmol/m²). In fact, the aggregation of the system took place at Γ = 1.07 µmol/m². This indicates that the adsorption at this plateau was not 1:1. One possible explanation is that other components of the solution (ions) could adsorb onto the surface, leading to a previous neutralization [29]. Several adsorption regimes could be
Fig. 4. Adsorption pattern for ionic surfactants on an oppositely charged latex surface: (A) adsorption of tails and heads, (B) surface neutralization, (C) hindered adsorption (D₁ and D₂) different ways of surfactant association on the surface.

distinguished by increasing the surfactant concentration (see Fig. 4):
• Strong adsorption at low concentrations due to the combination of the electrostatic and hydrophobic attractions (Fig. 4A).
• After surface neutralization (Fig. 4B), the adsorption got weaker due to the fact that only tail adsorption was possible (Fig. 4C). In addition, the interface became negative. This is supported by electrophoretic mobility measurements (data not shown). The adsorption was hindered because of the electrostatic repulsion between the adsorbed surfactants and those approaching from the solution. This gave rise to a plateau in the adsorption isotherm.
• Then, a new increase in the adsorption took place due to the rearrangement of the chains that tend to be perpendicular to the surface (Fig. 4D₁). Other authors [30,31] explain this increase by means of the association of surfactants on the surface (Fig. 4D₂).
• A new plateau was found when the maximum package was reached. It continued up to the CMC.

(b) Surface and surfactant with the same sign: as expected, even though electrostatic repulsion exists between surface and surfactant, the adsorption took place due to the fact that the hydrophobic attraction between the polystyrene latex and the apolar surfactant tail overcame that repulsion [30,32]. Surface characteristics influenced this adsorption. By increasing the surfactant concentration we observed
• Adsorption at low concentrations due to the hydrophobic attraction between the apolar surface regions and the surfactant tails (Fig. 5A). As can be seen in Fig. 3, both the surface hydrophobicity and the surface charge influenced this stage. On one hand, the affinity was higher for the most hydrophobic latex (Lx(anfo)). On the other hand, above a certain adsorbed amount, differences in affinity for Lx(COOH) appeared at pH 9 and 7. Higher surface charge led to higher repulsion between the interface at a certain coverage and the surfactant coming from solution in the regime represented in Fig. 5B.
• A plateau up to the CMC. In agreement with Paxton’s results [32], the more apolar surface (Lx(anfo) at pH 9) led to the highest $\Gamma_{\text{max}}$. The fact that this amount was similar to that found for the same latex at pH 5 could point to some type of surfactant association on the surface (Fig. 5C₁). In the case of Lx(COOH) the conformation is most likely that shown in Fig. 5C₂. Differences at pH 7 and 9 were inside the error range ($\pm 0.18 \mu\text{mol}/\text{m}^2$). Therefore, the maximum adsorbed amount depended on the hydrophobic character of the latex, but not on the surface charge value.

Even though adsorption at the air–water interface can be higher than on the solid surfaces, because in the first case the hydrophobic tail protrudes in the air and on the solid it may lead to crowding of segments, the former quantity is used by many authors as an approximation for the latter one. In all the cases discussed above, $\Gamma_{\text{max}}$ was lower than the amount adsorbed in a monolayer at the air/water interface obtained through surface tension measurements and using the following equation: $\Gamma_m = 1/N_A\Gamma_m = 3.86 \mu\text{mol}/\text{m}^2$. This is usually interpreted as a more spread-out conformation of the surfactant at the latex/solution interface. Paxton [32] and Zwetsloot and Leyte [33] also found a lower value for the adsorption of NaDBS on polystyrene latex with sulfonate surface groups, with an isotherm shape similar to Lx(COOH).

3.1.2. Cationic surfactant (DB)
The adsorption isotherms of this surfactant are presented in Fig. 6.
Surface and surfactant with opposite signs: the adsorption steps represented in Fig. 4 were also found when surface and surfactant sign were changed. Surface hydrophobicity and charge played a role in this process. Less charged surface provoked the “hindered adsorption step” (Fig. 4C) to take place at lower adsorbed amount. That is why the adsorption at surfactant concentrations in the range (0.1–0.3) CMC was higher for Lx(COOH) at pH 9 (the surfactant–latex complexes still present negative surfaces) than at pH 7 (the surfactant–latex complexes already show a positive charge). The fact that Lx(COOH) at pH 7 aggregated at $\Gamma = 0.78$ and $0.91 \mu\text{mol/m}^2$ and the electrophoretic mobility results support these conclusions. However, the hydrophobic character of the surface had an important influence on the adsorption, as shown by the higher maximum adsorbed amount observed on Lx(anfo) at pH 9. On the other hand, the step found in the case of this surface and Lx(COOH) at pH 7 at high surfactant concentrations pointed once more to some type of surface association (Fig. 4D$_2$). However, for Lx(COOH) at pH 9, electrostatic repulsion at the “hindered adsorption step” was strong enough to avoid a new increase in the adsorbed amount and a plateau was reached. This plateau continued up to the CMC. The maximum adsorbed amount reached corresponded to that obtained in a monolayer at the air/liquid interface (3.1 $\mu\text{mol/m}^2$).

Surface and surfactant with the same sign: the adsorption of the DB on the positive surface, Lx(anfo) at pH 5, can be represented as in Fig. 5 by changing surfactant and surface sign to positive. However, due to the high surface charge, the hydrophobic attraction was not able to overcome the electrostatic repulsion above certain coverage and a plateau is reached. It was maintained up to the CMC.

3.2. Nonionic surfactants

There exist recent works about the adsorption of Triton X-100 and Triton X-405 on polystyrene latex particles [19,34,35]. In this work, we compare the effect of the surface hydrophobic/hydrophilic character, working with two latices, Lx(SO$_3$H) and Lx(HEMA), as adsorbent surfaces. But also, we study the effect of the surfactant size on that adsorption. For this reason we have chosen the mentioned surfactants Triton X-100 and Triton X-405 as adsorbates. As can be seen in Fig. 2c, these chains have the same hydrophobic moiety and different length of the hydrophilic one.

3.2.1. Effect of the surface hydrophobicity

The adsorption isotherms of Triton X-100 on Lx(SO$_3$H) and Lx(HEMA) are shown in Fig. 7 (black and white circles, respectively). The data correspond to concentrations below the CMC (0.25 mM).

The hydrophobic character of the surface influenced the adsorption isotherm both qualitatively and quantitatively. The shape and the maximum adsorbed amount were different for the two surfaces studied. The adsorption was driven by surfactant tail–surface apolar region attraction. Therefore, the affinity was higher when the surface was more hydrophobic (Lx(SO$_3$H)). A heterogeneous distribution of the hydrophilic polymer (HEMA) on the polystyrene core allowed the presence of hydrophobic patches on the latex surface, and thus the adsorption through hydrophobic attraction between chain and surface could occur.

By increasing the surface coverage, the adsorption of new chains should be gradually hindered until the maximum coverage possible is reached. However, a step appeared in the case of the Lx(SO$_3$H) that pointed out, once more, that the surfactants can associate on the surface before reaching a final plateau, as has been shown theoretically for this kind of surfactant [36]. The fact that the highest adsorbed amount of Triton X-100 corresponded to the most hydrophobic sur-
face was also found by comparing the adsorption of this surfactant on a latex with carboxylic groups and on another one with amide groups (more hydrophobic) [35]. By using the molecular area of the surfactant at the air/solution interface, we could calculate an approximated adsorbed amount in monolayer of (3.1–3.5) µmol/m$^2$. This value was reached for Lx(SO$_3$H) but it was higher than the maximum adsorbed amount on Lx(HEMA).

The adsorption isotherms for Triton X-405 on Lx(SO$_3$H) and Lx(HEMA) are also presented in Fig. 7 (black and white triangles, respectively). The equilibrium concentrations are below the CMC (0.81 mM). An effect of the surface hydrophobicity was seen only at low concentrations.

As expected, the adsorption isotherm corresponding to the Lx(HEMA) presented lower affinity. It is worth highlighting the sudden increase in the isotherm on Lx(SO$_3$H) at low concentrations. The formation of surface aggregates of this surfactant on hydrophobic surfaces has been theoretically predicted elsewhere [36] and could be one explanation for that behavior. The maximum adsorbed amount was similar for both latices and was lower than the amount corresponding to a monolayer at the air/solution interface (1.9 µmol/m$^2$).

3.2.2. Effect of the surfactant size

With the aim of analyzing the influence of the hydrophilic moiety size of the surfactant on the adsorption on the surfaces under study, we compared the adsorption data of Triton X-100 and Triton X-405 on the same surface (Fig. 7).

For the most hydrophobic surface (Lx(SO$_3$H), black symbols), we could not discern any affinity difference at low concentrations. This means that when there was a hydrophobic region wide enough on the surface, the effect of the interaction among chains was negligible. This further supported the idea that the main adsorption mechanism was the attraction tail–hydrophobic surface region, which was similar for both surfactants. The maximum adsorbed amount diminished when the number of PEO units increased. As mentioned briefly before, if some chains are previously adsorbed on the surface, the steric repulsion among the hydrophilic heads hinders the approaching and subsequent adsorption of new molecules. A higher hydrophilic head (Triton X-405) leads to a higher repulsion. The shape of the adsorption isotherm was also different for both surfactants. These shapes are predicted to correspond to surfactant aggregates on the surface [36].

For the most hydrophilic latex (Lx(HEMA), white symbols) differences appeared at both low and high concentrations. The higher polar character of the Triton X-405 leads to a higher repulsion. The shape of the adsorption isotherm was also different for both surfactants. These shapes are predicted to correspond to surfactant aggregates on the surface [36].

3.3. Peptide

To understand the mechanisms that govern the adsorption of the peptide that we designed, we chose the smallest latex, Lx(SO$_3$H). This latex presents a higher area/volume ratio. Studying the adsorption at acid pH (pH 3) and at basic pH (pH 11) allows the analysis of the formation of complexes Lx$^-$/peptide$^+$ and Lx$^-$/peptide$^-$, respectively. Lx(anfo) at pH 3 was also used to analyze the complex Lx$^+$/peptide$^+$, the surface charge is assumed to be constant at pH lower than 4. The three adsorption isotherms are presented in Fig. 8. A logarithmic concentration axis is used in this case to make easier the discussion at low concentration. The sign inside the symbol represents the surface sign. The results are compared with those obtained with ionic surfactants on charged latices.

An important result was that this peptide was able to form stable complexes by adsorbing to polystyrene latex at both basic and acid pH. The adsorption occurred even though there did exist electrostatic repulsion between the chain and the surface. This pointed to the hydrophobic attraction as the main adsorption mechanism.

(a) Surface and peptide with opposite signs: in the case of Lx(SO$_3$H)/peptide at pH 3, even though the existence of more than one charge per molecule head, the adsorption process could be represented in first approximation as in Fig. 4:

- At low concentrations, apolar tail–apolar surface region attraction, together with cationic head–anionic surface groups electrostatic attraction, led to high affinity. However, since the number of charges per peptide was higher than 1, the charge neutralization occurred at lower coverage than that expected at 1:1 adsorption (Fig. 4B). The aggregation of the system took place at $\Gamma = 0.154$ mg/m$^2$, corresponding to...
0.055 \, \mu \text{mol/m}^2. \text{ As the number density of surface charge is 0.996 \, \mu \text{mol/m}^2, the number of charges presented by the peptide has to be around 18. However, the peptide has five charged lysines at pH 3. This difference can be only explained if the adsorption of other ions is also considered.}

- Above this adsorbed amount, the complexes no longer aggregated. The interface became positive and the adsorption of new peptides would be hindered. The slope in the adsorption isotherm changed slightly, however, a sharp increase in the adsorption was still observed. This could indicate that some type of surface aggregation occurred before a plateau was reached.

**Surface and peptide with the same sign**: in general, the adsorption was similar to the surfactant pattern shown in Fig. 5. Tail adsorption was only possible. Differences were found when comparing surfaces with different characteristics:

- Even at low concentrations, due to the high charge per peptide, the electrostatic repulsion interface–peptide became important when the surface charge was high enough (Lx(anfo) at pH 3).
- After a gradually hindered adsorption, a plateau was reached for Lx(SO_3H) at pH 11. Despite the fact that the adsorbed amount on Lx(anfo) at pH 3 was expected to be lower than on the former surface at any concentration, above certain value the adsorbed amount became higher. It is possible that the peptide association on the surface is favored at this pH.

4. Conclusions

Examining the adsorption isotherms of all the amphiphilic molecules studied on the different latices, we can conclude that the hydrophobic attraction between the nonpolar part of the molecule (tail) and the apolar regions of the surface is the main mechanism involved in the adsorption. In fact, higher adsorption is achieved by increasing the hydrophobic character of the surface (Lx(anfo)) and is hindered when a hydrophilic polymer is used as a copolymer in the synthesis.

Nevertheless, although the hydrophobic interaction is the most important contribution, the electrostatic effects also play a significant role. Different patterns are proposed depending on the sign of the surface and the surfactant charge. Plateaus at surfactant concentrations below the CMC are found when surfactant and surface have opposite sign. They are related to the sign inversion of the interface charge by increasing the adsorbed amount. The value of the surface charge plays a role in this behavior. The surfactant characteristics clearly influence the adsorption behavior at high surfactant concentrations. The ability to self-assemble for DB chains is higher than that for NaDBS chains, as seen by comparing the CMC. This can explain why the maximum adsorbed amount is always lower than that corresponding to a monolayer for the anionic surfactant, whereas for the cationic one higher coverage is found under certain conditions. On the other hand, unlike NaDBS, in the case of DB the electrostatic interaction plays an important role at high surfactant concentrations.

When the surface and the surfactant are oppositely charged, it is possible to determine the amount of surfactant that provokes the destabilization of the system. Above this quantity, stable complexes are formed again. This is an important point to take into account in the application of these surfactants as stabilizer agents.

As can be seen in the adsorption isotherms corresponding to nonionic surfactants, steps exist at concentrations below the CMC. This would point out that the surfactants prefer forming surface aggregates instead of adsorbing separately. This behavior has also been found theoretically in the case of Triton X-100 and Triton X-405 on hydrophobic surfaces [36]. The length of the hydrophilic moiety of the surfactant has an important effect on the isotherm shape and the maximum adsorbed amount. This shows the role of the chain–chain interaction in the adsorption.

The peptide adsorbs onto latex particles at both acid pH (at which it has a positive charge) and basic pH (at which it has a negative charge). Generally speaking, the adsorption behavior is similar to that observed for ionic surfactants on latices.

Acknowledgments

Financial support from ‘Comisión Interministerial de Ciencia y Tecnología’ Project MAT2003-01257, AGL2001-3483-C02-02 and AGL2004-01531/ALI are gratefully acknowledged. Ana Belén Jódar Reyes would like to thank the Spanish Ministry of Education, Culture and Sport and to the University of Granada to support her research in this University.

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