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ORIGINAL CONTRIBUTION

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Electrokinetic behaviour of polymer colloids with adsorbed Triton X-100

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Abstract An experimental study on the electrophoretic mobility (μ_e) of polystyrene particles after adsorption of Triton X-100 (TX100) is described. Three polystyrene particles with different functionality (sulphate, carboxyl and amidine) were used as solid substrate for the adsorption of the surfactant. The electrophoretic mobility of the polystyrene-TX100 complexes at different electrolyte concentrations has been studied versus the amount of adsorbed surfactant. The presence of TX100 onto the colloidal particles seems to produce a slight shifting of the slipping plane. This is observed for electrolyte concentrations above $\sim 10^{-3}$ M. On the other hand, the electrophoretic mobilities of the latex–surfactant complexes with maximum surface coverage were measured versus pH and salt concentration. Specific ion interactions between H^+/carboxyl groups and OH^-/amidine groups appeared at extreme pH which explain the anomalous electrophoretic behaviour encountered in the region where surface charge change.

Keywords Polymer colloids · Surfactant–latex complexes · Electrophoretic mobility

Introduction

Polymer colloids are usually considered as "model" particles, as they can posses a high monodispersity, spherical shape, smooth and homogeneous surfaces, and well-defined surface functional groups. In addition, colloidal systems show a large ratio surface/volume, which makes them extremely suitable in adsorption studies. Due to these reasons, latex particles have often been used as ideal carriers for studying the adsorption of surfactants, polymers and other macromolecules like proteins. The interest of studying such systems lies on the fact that there are numerous natural, technical and industrial phenomena in which polymer adsorption processes take place onto different substrates [1, 2, 3]. Most applications involving the adsorption of surfactants onto latex particles have been developed without profoundly characterizing the solid–liquid interface of the latex–surfactant systems.

In most cases these adsorption processes contribute to the creation of new materials and systems. Consequently, a through characterization of the adsorbed layer becomes necessary, albeit it may become a difficult task due to the microscopic dimensions of this kind of structured interfaces. However, valuable information can be obtained using electrophoretic mobility measurements, a technique based on a non-equilibrium process.

This paper is an effort to determine the electro-superficial properties of non-ionic surfactant–latex complexes under different experimental conditions. Triton-X100 was chosen as the non-ionic surfactant since it is one of the most frequently used. The electrokinetic behaviour of these systems depend, at least, on (a) the amount of adsorbed surfactant, (b) the nature of both, the surfactant and the adsorbent surface, (c) the pH, and (d) the medium ionic strength.

In the present work, experiments have been performed with different amounts of adsorbed surfactant and various pH and ionic strength values for maximum coverage complexes and polymer colloids with different surface groups: carboxyl, sulphate (anionic surface) and amidine (cationic surface). It appears that no other study has systematically investigated all these parameters simultaneously, even this area of colloid science has been widely studied since Ottewill et al. [4, 5, 6] described the effect of the low-molecular-weight non-ionic surfactants on the colloid stability of latexes.

When the mobilities of the surfactant–latex complexes are determined as function of the medium pH for carboxyl and amidine latexes, an anomalous behaviour was encountered in the region where surface charge changes. The results are interpreted in terms of adsorption or specific interaction between the surfactant–latex complexes and the counterions H^+ and OH^-, respectively. In a previous paper [7], the colloidal stability of surfactant–latex complexes was explained in terms of this specific interaction. When a sulphate latex acts as adsorbent, the resultant colloidal stability of the surfactant–latex complex was explained only by the use of an additional steric repulsive interaction potential. For these systems, the diffuse potential that originates in an electrostatic repulsion between particles remained constant after adsorption of TX100. However, when the latex used as adsorbent had a carboxyl or amidine functionality it was necessary to modify the diffuse potential to explain the colloidal stability results. The introduction of a steric repulsive interaction potential was not enough to explain the colloidal stability within that pH region, where specific interactions seemed to appear. In order to explain the colloidal stability of those systems, the diffuse potential of the particles was then modified. In this work, electrophoretic mobility measurements seem to indicate that these specific interactions are indeed present when the substrates consist of latexes with carboxyl and amidine functionalities. As a result, the fact that the diffuse potentials that needed to be modified in the stability studies with such systems is further elucidated in this study.

Materials and methods

All Chemicals in this study were of analytical grade and were used without further purification. Ultrapure water with an electrical conductivity less than 1 μS/cm was used in all experiments.

The latexes used in this work were synthesized in our laboratories. Styrene (Merk) was previously distilled under low pressure (10 mm Hg and 40 °C). All colloidal systems were synthesized using the emulsifier-free method. The first latex, a negatively charged polystyrene latex (PS-S) was prepared, with potassium persulphate as initiator, in a discontinuous reaction, according to Kotera et al. [8]. The other two colloidal systems were synthesized using 4,4′-azo-bis(4-cyanopentanoic acid) (PS-C) and *N*,*N*′-azo-bis(dimethyl-isobutylamide hydrochloride) (PS-CAT) as initiators [9, 10, 11]. The latexes were cleaned by serum replacement until the conductivity of the supernatant was similar to that of the water. The particle diameters and the surface charge densities were determined by transmission electron microscopy and conductimetric/potentiometric titration, respectively. Table 1 shows the main characteristics of the particles.

Triton X-100 (*p*-(1,1,3,3-tetramethylbutyl)phenylpolyethyleneglycol), a gas chromatography grade material from Merk was used without further purification. Surfactant concentrations during adsorption experiments were determined by UV spectrophotometry at 275 nm [12, 13, 14] using a Spectronic Genesys 5 spectrophotometer (Milton Roy, USA). The extinction coefficient obtained was equal to 1.33×10^3 $M^{-1}cm^{-1}$. The critical micelle concentrations (CMC) were determined by the change in slope of the absorbance versus concentration, which indicated the onset of a micellization process. The value of this characteristic magnitude was of $(5.1 \pm 0.1) \times 10^{-4}$ M, which is found to be in the range given by other authors [15, 16, 17]. In order to gain more information of the surfactant purity, a mass spectroscopy spectrum was obtained (Centre of Scientific Instrumentation, University of Granada). The results showed that the surfactant is of good purity, with a polydispersity index ($\langle M_w \rangle / \langle M_n \rangle$) of 1.031 [18], where $\langle M_w \rangle$ and $\langle M_n \rangle$ are the number average molecular weight and the weight average molecular weight, respectively.

Surfactant adsorption was performed in batteries for 24 h at (25.0 ± 0.1) °C by adding different amounts of surfactant on 0.25 m^2 of latex surface. The surfactant–latex mixtures were gently shaken during and after the addition of the latex suspension. More details of adsorption phenomena and complexes preparation have been previously published [19].

The electrophoretic mobility measurements were carried out with a Malvern Zetamaster S device. A first set of measurements, where the solid concentration was varied to find the best conditions, led us to use 5.0×10^{-3} g/l ($\sim 10^8$ particules/cm^3) for μ_e determination. A series of μ_e against pH and electrolyte concentration measurement were carried out for bare and covered particles. pH was adjusted with anionic or cationic buffer solution for anionic and cationic particles, respectively. The anionic buffers used were acetate at pH 4–5, phosphate at pH 6–7 and borate at pH 10. The cationic buffers used were Bis-Tris (bis[2-hydroxyethyl]imino-tris[hydroxymethyl]methane) at pH 6, Tris (tris [hydroxymethyl]aminomethane) at pH 8–9 and AMP (2-amino-2-methyl-1-propanol) at pH 10. The final ionic strength was of 2 mM. The mobilities were taken as the average of at least ten measurements and the standard deviation of these measurements was considered to be the experimental error.

Table 1 Characteristics of colloidal systems

Latex	Functionality	Diameter (nm)	P.D.I.	Surface charge ($\mu C/cm^2$)	
PS-S	Sulphate	413 ± 14	1.0035	–3.2 ± 0.5	
PS-C	Carboxyl	303 ± 9	1.0029	–21 ± 3 at pH 10	0 ± 2 at pH 4
PS-CAT	Amidine	192 ± 10	1.0066	9.2 ± 2.4 at pH 4	4 ± 2 at pH 10

Results

Effect of the coverage degree

In an attempt to relate the electric double layer structure of the latex–surfactant complexes to the bare latex, we have performed electrokinetic experiments to determine the change in the electrical properties as a consequence of the adsorption process. The electrophoretic mobility (μ_e) of the latex particles was determined as a function of the amount of Triton X-100 adsorbed onto them at different electrolyte concentrations ([NaCl] = 10^{-4}, 5×10^{-3} and 0.1 M). The results for the three latexes are shown in Fig. 1.

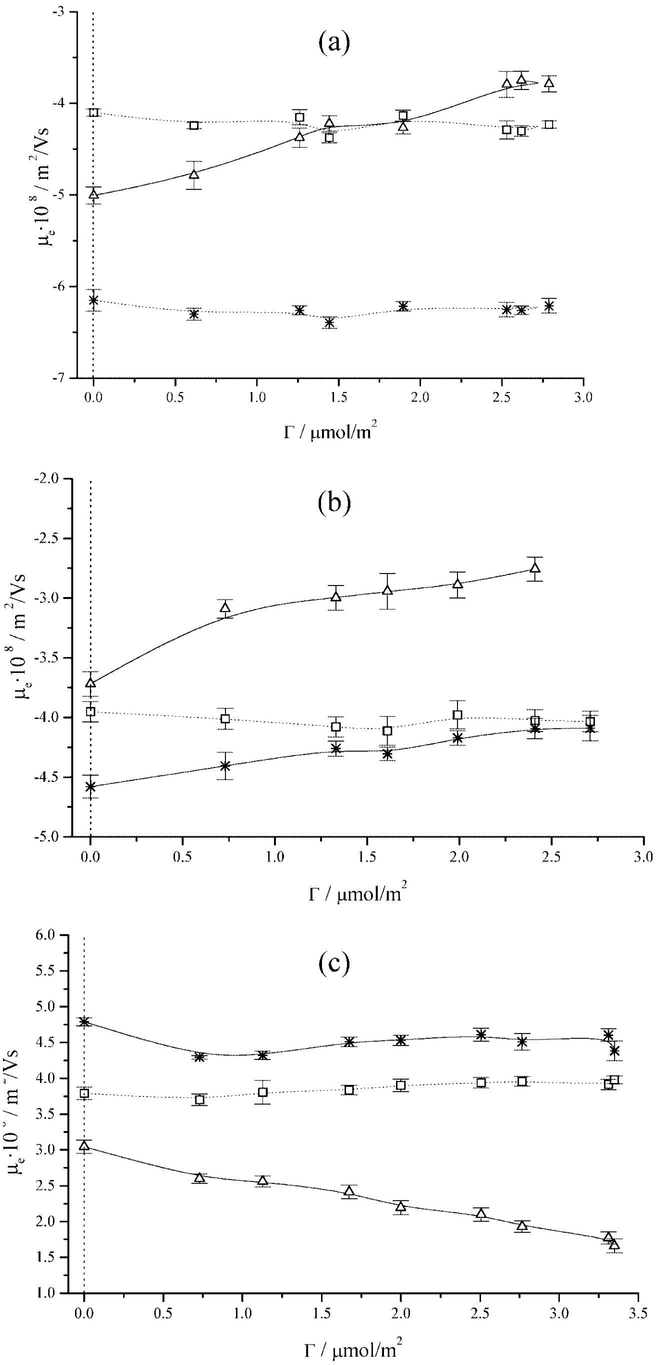

Fig. 1 Electrophoretic mobility versus amount of Triton X-100 adsorbed on **a** PS-S, **b** PS-C, and **c** PS-CAT latexes: (open squares) 10^{-4} M, (asterisks) 5×10^{-3} and (triangles) 0.1 M of NaCl

On the basis of the diffuse double layer theory, the μ_e of the latex–surfactant complexes should decrease as a results of the adsorption of surfactant, and should also decrease as the amount of surfactant onto the latex surface increases. The decrease in μ_e as a results of the adsorption of non-ionic polymers indicates that a relative thick adsorption layer has been formed on the surface (with liquid immobilized in these layers) which shifts the slipping boundary towards the bulk solution [20, 21]. This behaviour depends on the electrolyte concentration and can be understood within the classical electric double layer (e.d.l.) theory (see Fig. 2). At low

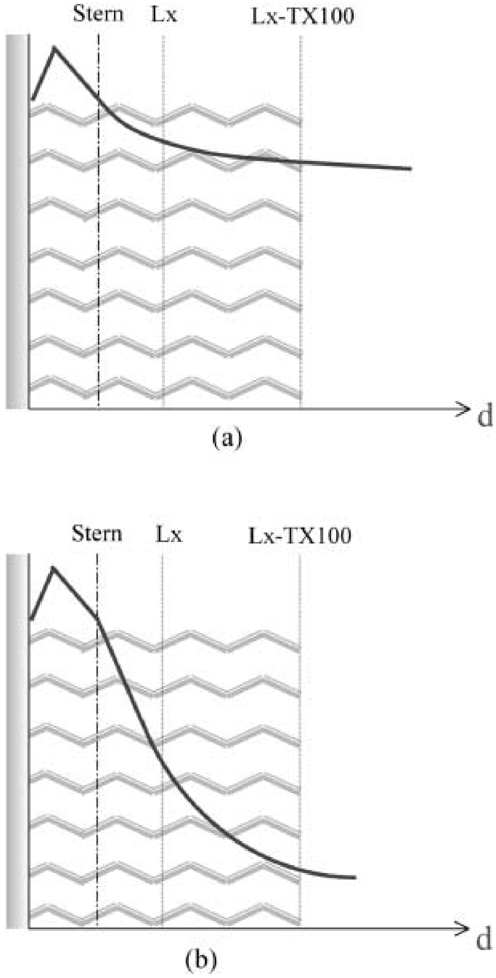

Fig. 2 A diagram of the surface potential versus surface distance trends at **a** low and **b** high electrolyte concentration

electrolyte concentration the potential decreases towards the bulk solution slowly due to the extended state of the electric double layer (Fig. 2a). Under this condition it is not possible to observe any effect in μ_e related with the surfactant coverage degree. In fact, for a salt concentration of 10^{-4} M, the mobility remains almost unaltered with the different coverage degrees. However, when the electrolyte concentration is increased, the e.d.l. is compressed and the electric potential decays much faster as we depart from the particle surface (see Fig. 2b). Under these circumstances the effect of surfactant coverage becomes noticeable as is clearly observed for a salt concentration equal to 0.1 M.

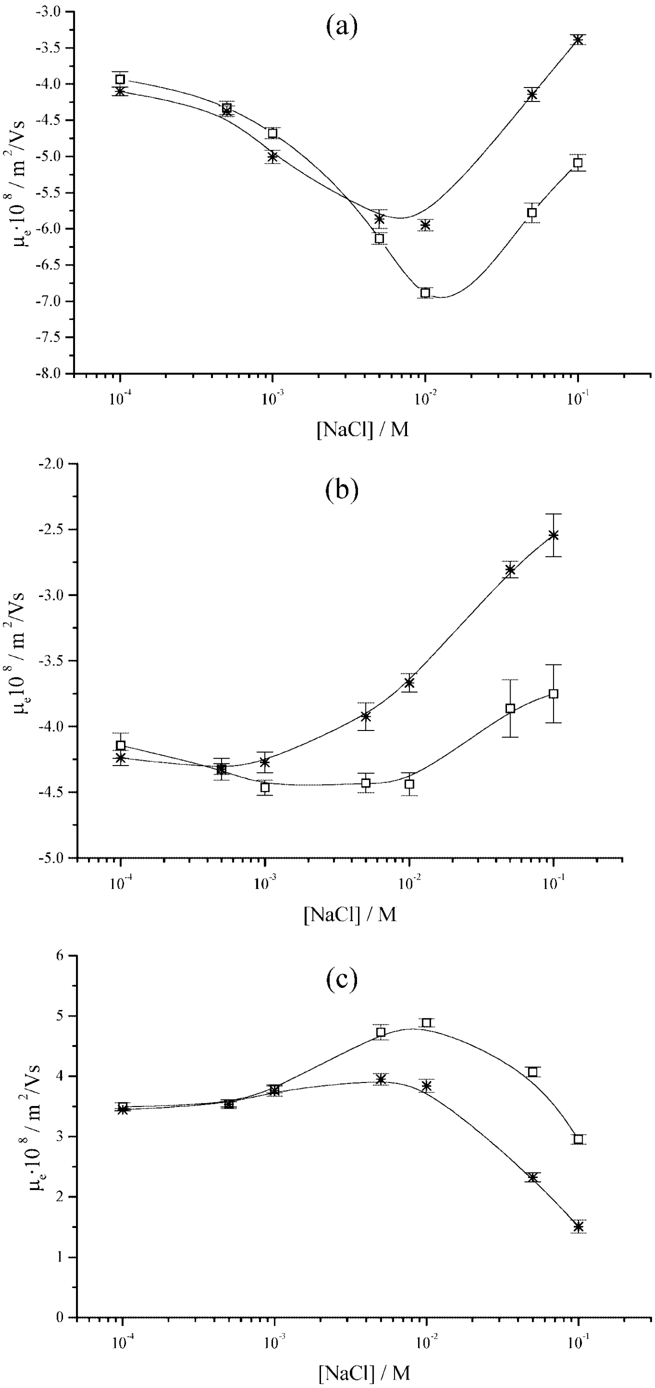

Fig. 3 Electrophoretic mobility versus NaCl concentration for bare latex (open squares) and maximum coverage PS/TX100 complex (asterisks): **a** PS-S, **b** PS-C, and **c** PS-CAT

It is worth stressing that the electrophoretic mobilities presented in Fig. 1 for every latex do not show the classically predicted decrease with salt concentration. However, this fact is in some way expected, since the electrophoresis of polymer latexes has some inherent complexities due to non-equilibrium effects. These give rise to the well-known maximum in the μ_e-salt curves that has been reported in most of the mobility studies and has also been widely discussed [22, 23]. In order to see if this is the case for the colloidal systems under consideration in this work, these measurements were overtaken for bare and totally covered particles (Fig. 3). The maximum is seen in all situations, explaining the trends observed in Fig. 1.

It can also be seen in Fig. 3 that at low NaCl concentration, no differences between bare and covered particles electrophoretic mobilities are found. However, for an electrolyte concentration above $\sim 10^{-3}$ M the mobility of covered particles begins to decrease due to the shifting of the slipping boundary position towards the solution. These results allow us to estimate the thickness of the adsorption layer by using the Eversole and Boardman equation [24], which relates the variation in the electrokinetic or zeta potential (ζ) with the thickness (Δ) of a layer of water (in other cases oligomers) that surrounds the particles:

$$\tanh\left(\frac{ze\zeta}{4kT}\right) = \tanh\left(\frac{ze\psi_\mathrm{d}}{4kT}\right)\exp(-\kappa\Delta) \qquad (1)$$

where z is the valence of the counterion, c is the elementary charge, κ^{-1} is the Debye length and ψ_d is the diffuse potential. Electrophoretic mobilities data were transformed into ζ potential values using the Dukhin and Semenikhin theory [25]. Table 2 shows the calculated thickness for bare particles (Δ_b) and complexes (Δ_c) with maximum coverage for an electrolyte concentration of 0.1 M.

Bare particles have a significant thickness that is in accordance with other authors [26, 27]. The surface

Table 2 Calculated thickness for bare particles (Δ_b) and complexes (Δ_c) with maximum coverage

Latex	Δ_b (nm)	Δ_c (nm)
PS-S	0.43 ± 0.03	0.81 ± 0.02
PS-C	0.75 ± 0.10	1.12 ± 0.12
PS-CAT	0.85 ± 0.06	1.53 ± 0.07

roughness [28] or the electroviscous effect [29] could be a plausible explanation for this fact. On the other hand, the presence of hydrophilic chains onto the particles surface causes an increase of this thickness. However, the value of this parameter (Δ_c) is not in agreement with the real thickness of the surfactant layer for the maximum coverage complexes. On the basis of previous adsorption and colloidal stability studies [19, 30] the thickness of the surfactant layer for maximum coverage complexes, does not depend on the latex characteristics and should be higher than 2 nm. On the basis of molecular structure studies [31, 32] the length of a EO moiety with 10 EO units is around 2.68 nm. In our calculation Δ is around 1 nm or lower. We must then question the possible use of the Eversole-Boardman equation as an alternative technique to determine the thickness of a surfactant layer in latex–surfactant complexes.

Effect of the pH in complexes with maximum coverage

Figures 4 and 5 show the mobilities of the surfactant–latex complexes completely covered with surfactant as function of the medium pH and an ionic strength of 2 mM. As expected, in the case of a sulphate latex no differences between bare latexes and surfactant–latex complexes were found. However, for carboxyl and amidine latexes an anomalous behaviour appears in the region where surface charge is changing. We would expect for these systems no differences in μ_e–pH curves between bare and surfactant latex complexes for all pH values (case of sulphate latex). A possible explanation of these anomalous results could be the change in the ionisation constant for carboxyl and amidine groups due to the non-ionic surfactant adsorption. In fact, the discrepancies in pK_a found between free chemical groups and those that are onto surface particles are usually explained due to the hydrophobic atmosphere of the particle surface [33, 34]. However, this explanation does not justify the negative value of the electrophoretic mobility for the cationic latex at pH 12. A new explanation is proposed based on the facts that bare and covered latexes curves are parallel in this anomalous region and that there is a relative independence of this phenomenon with coverage degree. This last fact is shown in Fig. 6, where the electrophoretic mobility (μ_e) of PS-C and PS-CAT latex particles is plotted as a function of the Triton X-100 coverage degree at pH 4 and pH 10, respectively, and 2 mM of NaCl. In these conditions, the decrease in μ_e can not be explained due to a slide in the slipping boundary. This anomalous behaviour could be completely explained due to the adsorption or specific interaction between the complexes surface and the counterions H^+ and OH^-. This phenomenon will cause a charge screening and consequently a decrease in the electrophoretic mobility. In relation to the cationic latex, the adsorption of OH^- ions onto its

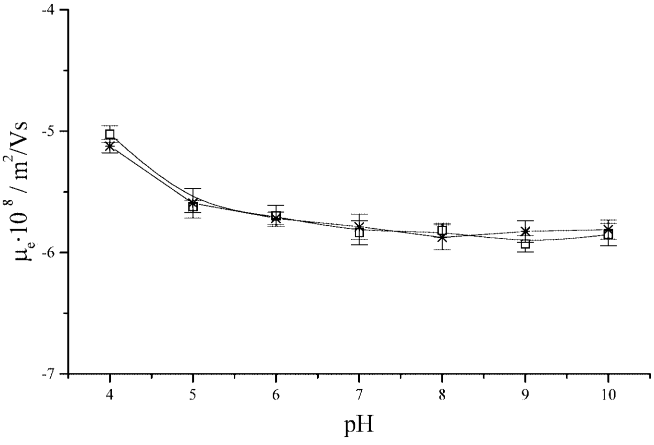

Fig. 4 Electrophoretic mobility versus pH for PS-S latex (open squares) and maximum coverage PS-S/TX100 complex (asterisks)

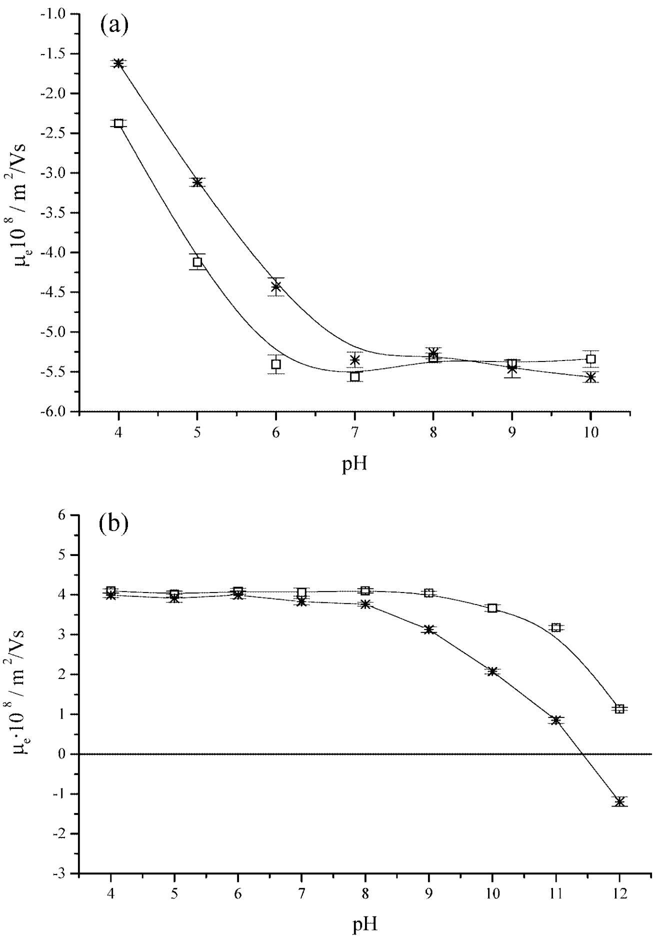

Fig. 5 Electrophoretic mobility versus pH for bare latex (open squares) and maximum coverage PS/TX100 complex (asterisks): **a** PS-C and **b** PS-CAT

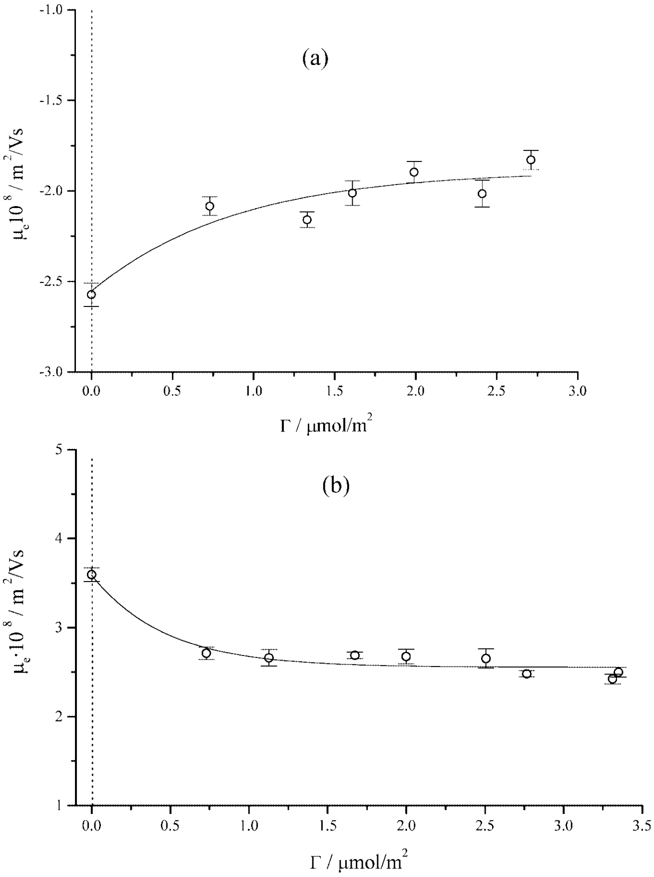

Fig. 6 Effect of the coverage degree for **a** PS-C latex at pH 4 and **b** PS-CAT latex at pH 10

surface is well known [35, 36]. Additionally, the presence of hydrophilic EO chains seems to improve this adsorption even causing a reverse in charge (see Fig. 5b). On the other hand, the specific interaction between EO chains and COO^- groups through H^+ ions present in the medium [37] explains with the same reasoning the carboxyl latex results. The occurrence of strong hydrogen bonding between carboxylic acid groups, which act as H-bond donors, and ether oxygens, which act as H-bond acceptors, is well recognized in classical chemistry [38]. Our electrokinetic results and another previous colloidal stability study [39] seem to indicate the possible excess of positive charge (H^+) in the mentioned interaction. In this way, the appearance of hydrogen bonding can explain the phenomena called "enhanced steric stabilization" [18, 39] due to the change in the surfactant layer configuration, passing from flat to extended.

Conclusions

The electrokinetic behaviour of latex particles after adsorption of non-ionic surfactant depends on the surface charge and functionality of solid surface: there is practically no effect on sulphate latex, while the amidine and carboxyl latexes show specific interaction between the functional group (amidine or carboxyl) and ions in solution (H^+ or OH^-). This specific interaction with a steric barrier can explain the colloidal stability behaviour of these complexes at extreme pH values.

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