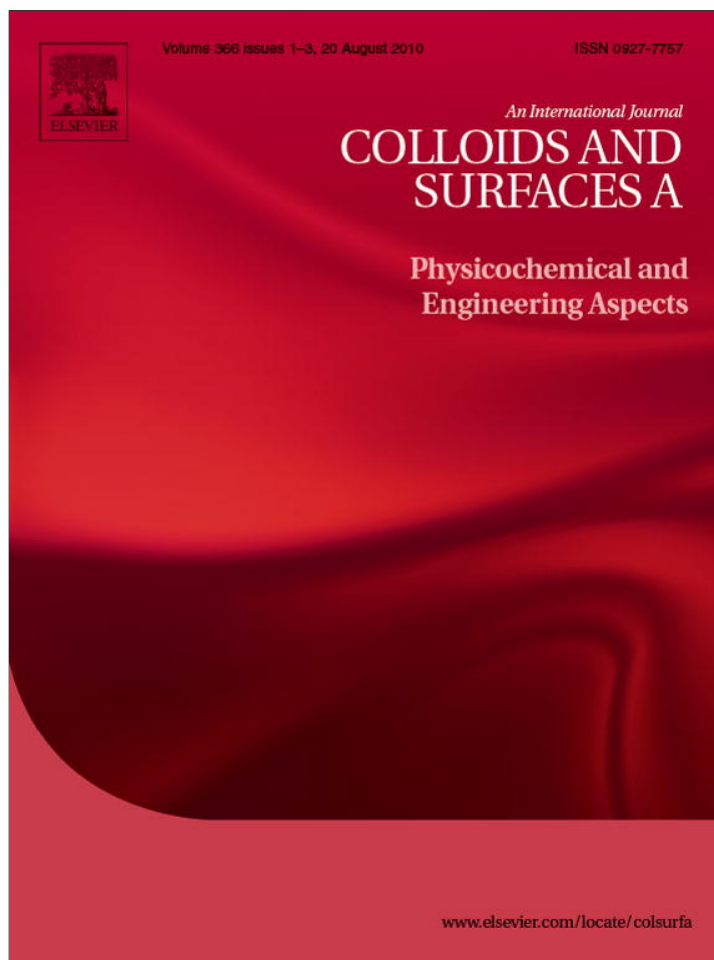




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Properties of CHAPS micelles modulated by different polyelectrolytes

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ABSTRACT

Fluorescence probing, and ζ -potential measurements have been used to study the interactions between the zwitterionic surfactant 3-[(3-cholamidopropyl)-dimethyl-ammonium]-1-propanesulphonate, CHAPS and two polyelectrolytes with different electric charge. The polyelectrolytes chosen are poly (diallyl-dimethyl-ammonium chloride), PDADMAC, and poly (sodium styrene sulphonate), PSS. Results show that the zwitterionic surfactant CHAPS interacts with both, polyanion and polycation molecules, resulting in polymer–surfactant micelles. The dominating factor in this interaction is the electrostatic attraction. We found that the ζ -potential of polymer–surfactant micelles can be modulated by the addition of different type of polyelectrolytes or modifying the polymer concentration. Using dynamic surface tension measurements we estimate the micelle dissociation rate constants. Results show that the addition of polymers increases the micelle lifetime.

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1. Introduction

Surfactant–polymer mixtures [1,2] are commonly used in many practical applications such as cosmetic, industrial and technological applications, because mixtures often provide more desirable properties than pure surfactants. Surfactant–polymer mixtures are extensively used in a wide range of domestic, industrial, and technological applications, which include foodstuffs, paints, drug delivery systems, coating fluids, laundry products, and cosmetics [1].

In the last years, a great number of works about polymer–surfactant interactions in solution have been carried out [1,2]. In a great number of mixtures, micelle formation is facilitated and a lowering of the cmc is observed. A drastic lowering occurs for oppositely charged polymer and surfactant molecules that it is reduced by the presence of electrolytes. All these facts suggest that synergism is due to attractive polymer–surfactant interactions. Synergism has been also observed in mixtures of non-ionic polymers and ionic surfactants; however, the synergic effect is always more important in oppositely charged systems [3]. The polymer interactions at the air–water interface have also been studied; detailed information relative to the structure and composition of layers formed by the adsorption of polymer–surfactant mixtures at the interface have been obtained by several groups [4–10]. In all these works the surfactant molecules chosen are mainly ionic surfactants while the zwitterionic ones have received less attention. However, zwitterionic surfactants, molecules with hydrophilic

moieties with negatively and positively charged groups, are widely employed in a huge variety of uses, as detergency, emulsification and foaming, since they are less toxic for humans and for environment than the ionic ones [11]. Thus, because modern surfactant systems have to be ecofriendly, one of the scientific research goals must be to identify mixtures containing zwitterionic surfactants to improve their applications. In this context, we have studied the equilibrium and dynamic properties of monolayers of different zwitterionic surfactants such as carboxybetaines [12] or tryptophan–glycerol–ether derivatives [13,14]. Results obtained in these works indicated that the thermodynamic parameters such as cmc or surface excess at saturation, are practically independent of the ionic strength of the medium and of the chemical surfactant form, while the kinetic parameters such as monomer surfactant diffusion coefficient or micelle dissociation rate constant are very sensitive to both the ionic strength and the surfactant structure [12,14,15]. We have also studied the effect of the ionic surfactants on both mixed micelles [16] and mixed monolayers of different sulfobetaine surfactants [17]. In these works we demonstrated that anionic–zwitterionic mixed micelles exhibit weak synergic effect when the surfactant chain lengths are identical while no synergism was detected in cationic–zwitterionic micelles. The addition of electrolytes induced synergism in both cationic and anionic–zwitterionic micelles [16]. In contrast, mixed monolayers of cationic or anionic surfactant with zwitterionic sulfobetaines shown synergism. As in the case of mixed micelles the synergic effect is more pronounced in anionic–zwitterionic monolayers; the effect also increases with the surfactant counterions concentration [17]. From ours results we concluded that several contributions must be considered to interpret synergism in mixtures of zwitterionic–ionic surfactants [15–18]. We have also studied mix-

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tures of betaines with poly(sodium styrene sulphonate). Results showed strong interactions between betaines and PSS resulting in the formation of complexes in bulk [19,20]. The complex (1:1), from electrostatic origin, determines the properties of the monolayers adsorbed at the interface air–water [20].

All the experimental results evidence that the synergism is more pronounced in the zwitterionic-anionic than in the zwitterionic-cationic surfactant mixtures. However, to the best of our knowledge, there is no information about the effect of electric charge of polymers on the zwitterionic surfactant–polyelectrolyte interactions. Therefore, we study the interaction between the zwitterionic surfactant 3-[(3-cholamidopropyl)-dimethyl-ammonium]-1-propane sulphonate, CHAPS and two polyelectrolytes with different electric charges, poly(sodium styrene sulphonate), PSS, and poly(diallyl-dimethyl-ammonium chloride), PDADMAC. We have chosen this surfactant because it is widely used in biochemical applications such as protein solubilization [21] or disaggregation [22], and as eluting agent in separation processes to provide selectivity [23,24]. Despite the wide amount of works found in literature about micellization or adsorption of CHAPS [25–32] only a few works are related to mixtures with other surfactants [31] or with polymers [33]. However, we think that it is possible to improve the CHAPS properties by adding polymers.

The remaining sections of this paper are organized as follows: the next section contains experimental details and description of methodologies and techniques. In the results and discussion section we present the cac values of surfactant–polymer micelles determined by fluorescence measurements. The ζ -potential values for aggregates with different polymer composition and the micelle dissociation rate constant obtained by dynamic surface tension measurements are also presented in this section. Finally, the main conclusions are presented.

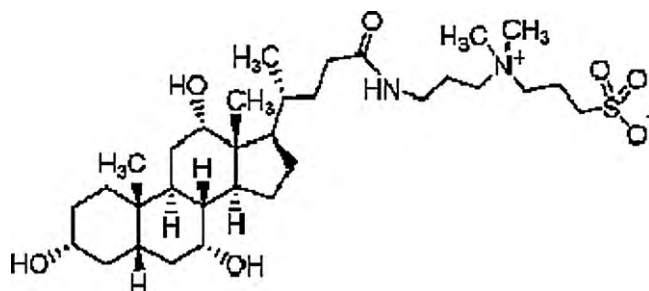
2. Materials and methods

2.1. Materials

The surfactant CHAPS (Sigma Ultra TLC), Scheme 1, and the polyelectrolytes poly(sodium styrene sulphonate) ($M_r = 70$ kDa), PSS, and poly(diallyl-dimethyl-ammonium chloride) (20 wt% aqueous solution) PDADMAC ($M_r = 150$ kDa) were from Sigma–Aldrich and were used as received. The polymer molecular weights were provided by manufacturer. The fluorescent probe Nile red (HPLC grade) was from Sigma BioChemika for fluorescence ($M_r = 318.37$). All the materials are stored at vacuum.

Water was purified with a combination of RIOs and Milli-Q systems from Millipore. The polymer solutions were prepared by direct weight. The surfactant is then dissolved in a given polymer concentration.

Incorporation of Nile red into micelles was as follows: an appropriate volume solution of Nile red dissolved in methanol was poured into a volumetric flask and the solvent was evaporated.



Scheme 1. Molecular structure of CHAPS surfactant.

The solutions of surfactant or polymer–surfactant mixtures were added to the evaporated residue, and the solution was stirred until the fluorescence probe was solubilized. The Nile red concentration was kept constant at $2.0 \mu\text{M}$.

2.2. Methods

2.2.1. Steady state fluorescence measurements

The emission spectra of Nile red incorporated to surfactant or polymer–surfactant mixtures were recorded with the LS-50B spectrofluorometer from Perkin-Elmer. The excitation wavelength was 549 nm and the excitation and emission slits were kept constant at values of 5/5 or 7/7 nm as a function of the fluorescence intensity. All spectra were recorded at 25°C .

2.2.2. ζ -Potential analyzer

The electrophoretic mobility measurements were carried out by means of the laser Doppler electrophoresis technique using the Zetasizer 3000 device (Malvern, UK). The equipment uses a He-Ne-laser 5 mW, 632.8 nm. All experiments were made in a $5 \text{ mm} \times 2 \text{ mm}$ rectangular quartz capillary. The electrophoretic mobility, μ_e , was measured at 25°C and converted into ζ -potential, ζ , using the Smoluchowski's relation, $\zeta = (\mu_e \eta / \epsilon)$ where η and ϵ are the viscosity and the permittivity of the solvent, respectively. Each reported value is an average over 30 measurements and the standard deviation of these measurements was considered the experimental error.

2.2.3. Surface tension measurements

The measurements of the dynamic surface tension were carried out with two different tensiometers as a function of time. A drop tensiometer model TVT-1 from Lauda [34] employing the dynamic method was used for dynamic surface tension in the range of time above 10 s, while a maximum bubble pressure tensiometer model MPT-2 from Lauda [35] was used for times below 10 s. The best conditions to ensure the correct determination of the equilibrium surface tension values have been chosen using criteria published elsewhere [12,17]. At the drop tensiometer the inner radius of the steel capillary was 1.345 mm and the employed syringe was of 5 ml.

All measurements were performed at 25°C . Temperature in tensiometers was controlled by means of thermostat/cryostat RM 6 and thermostat/cryostat Ecoline RE 104 from Lauda, respectively.

3. Results and discussion

3.1. Determination of the critical micelle concentration by steady state fluorescence measurements

The study of surfactant–polymer interactions is carried out by determining the cmc of micelles in absence and presence of polymers. The cmc of a surfactant can be determined by the appearance of a discontinuity in the variation of some solutions properties as a function of surfactant concentration. One of the most widely used techniques is fluorescence probing [36]. We choose Nile red as fluorescent probe because is a hydrophobic molecule with photophysical properties sensitive to changes on the polarity of the solvent [37,38]. In particular the fluorescence maximum is blue shifted when the dielectric constant decreases. This probe has been used to determine the cmc of micelles and vesicles [39–42].

The maximum of the fluorescence spectrum of Nile red is represented against CHAPS concentration in Fig. 1. In dilute surfactant concentrations the maximum of the fluorescence emission of Nile red is the same value as in aqueous solutions, this fact indicates that the fluorescence probe is dissolved in water. When surfactant concentration increases the maximum of the fluorescence spectrum is

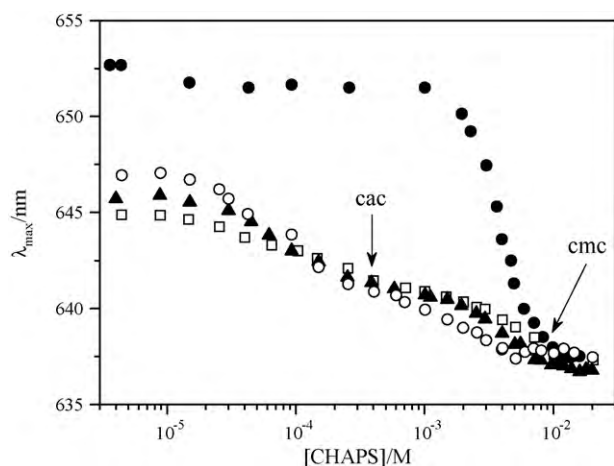


Fig. 1. Effect of CHAPS concentration on the position of the maximum of the Nile red fluorescence spectrum: solid circles, aqueous solutions; open circles, 0.05 wt% PSS; triangles, 0.1 wt% PSS; and open squares, 0.2 wt% PSS. All measurements were performed at 25 °C.

blue shifted indicating that the fluorescence probe is transferred to a more hydrophobic microenvironment, finally the maximum of fluorescence reaches a constant value at the critical micelle concentration, cmc. The cmc is obtained from the intercept of the two different behaviors [36]. The cmc value obtained by fluorescence measurements is 6.8 mM in agreement with the value obtained in the literature [29].

We study the effect of polyelectrolyte addition on the aggregation of CHAPS by fluorescence measurements. Fig. 1 presents the results for mixtures with different PSS concentrations. In dilute surfactant solutions the position of the maximum of the fluorescence spectrum of Nile red solubilized in surfactant–polymer mixtures is the same value as the one in pure polymer solutions of a given polymer concentration (not shown). The maximum of fluorescence emission of Nile red in pure polymer solutions is blue shifted respect to the maximum in water. This means that in polymer solutions the microenvironment of Nile red is more hydrophobic than in water. Fig. 1 also shows that the curves present two break points, corresponding to the classical behavior of strongly interacting polymer–surfactant mixtures initially described by Jones [43] with two break points at surfactant concentrations corresponding to the onset of micellar aggregation on the polymer, critical aggregation concentration (cac), and to the concentration at which free micelles form, critical micelle concentration (cmc). The cac values found for different PSS concentrations are practically independent of polymer concentration and the average value found is $4 \times 10^{-4} \text{ mol dm}^{-3}$. In contrast, the cmc linearly increases with the polymer concentration. Taking into account that the cmc corresponds to the polymer saturation and to the formation of pure surfactant micelles in bulk, from the cmc dependence on polymer concentration it is possible to obtain the surfactant molecules/polymer repeat unit ratio [44], being the value found for these mixtures close to 1.

We also study the interaction between CHAPS and the polycation PDADMAC. Fig. 2 shows the variation of the maximum of the fluorescence spectrum of Nile red with surfactant concentration for mixtures with a given polymer concentration. The polymer concentrations used were 0.2 and 0.5 wt%.

Comparison of results in Figs. 1 and 2 shows that curves obtained for mixtures of CHAPS with PSS or with PDADMAC present similar shapes. Thus two break points are observed and are ascribed to the cac and cmc, respectively. The cac is independent of the polymer concentration and the average value found is $1.3 \times 10^{-3} \text{ mol dm}^{-3}$. This value is lower than the cmc of the sur-

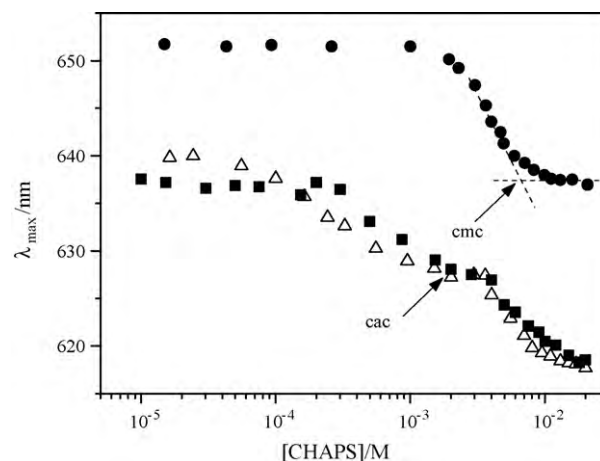


Fig. 2. Effect of CHAPS concentration on the position of the maximum of the Nile red fluorescence spectrum: solid circles, aqueous solutions; squares, 0.2 wt% PDADMAC; and triangles, 0.5 wt% PDADMAC. All results were obtained at 25 °C.

factant alone (6.8 mM) while is higher than the cac for CHAPS–PSS mixtures. As in the case of CHAPS–PSS mixtures, the second break point, cmc, linearly depends on polymer concentration and from the cmc dependence on polymer concentration we obtain a surfactant molecules/PDADMAC repeat unit ratio of 1.

From these results it is possible to conclude that the surfactant CHAPS interacts with both polyanion and polycation molecules resulting in polymer–surfactant micelles. The onset of surfactant–polymer micelles, cac, is lower than the cmc of the surfactant alone. This means that the surfactant molecules prefer to micellize with polymer molecules than themselves. Because zwitterionic surfactant has both cationic and anionic groups, it is possible to attribute this behavior to attractive interactions of electrostatic origin between polymers and CHAPS. This behavior differs from that observed for zwitterionic–ionic surfactants mixtures, where no interactions were observed in mixtures of cationic surfactant with zwitterionic betaines surfactants [16,45]. It is possible to interpret differences considering that the chemical structure of CHAPS is quite different than the linear hydrocarbon chain of betaines, therefore one can expect specific interactions between CHAPS and the cationic polymer PDADMAC. The specific interactions are an additional contribution to the free energy of mixed micelles aggregation [46,47], and in these mixtures, they favor the formation of mixed polymer–surfactant micelles.

3.2. Determination of micelle dissociation rate constant by dynamic surface tension measurements

It is well known that the dynamic surface tension of micellar solutions allows estimating the rate constant for demicellization. Some reviews dedicated to the effect of micelles on the dynamic of surfactant adsorption have been published [48,49]. Therefore we use these measurements to obtain information about the properties of surfactant–polymer mixed micelles. All measurements were carried out with solutions with surfactant concentrations between the cac and cmc values. Within this surfactant concentration range mixed micelles of surfactant and polymer predominate. For comparative purposes the rate constant for demicellization of pure micelles of CHAPS has been also determined.

The main model to analyze the dynamic surface tension curves considers dynamic adsorption at the interface as a diffusion-controlled process [48]. This model is known as Ward and Tordai equation. This equation cannot be solved analytically and therefore, asymptotic solutions have to be employed at short and long times

[49]. The short times approximation is given by:

$$\gamma(t)_{t \rightarrow 0} = \gamma_0 - 2CRT \sqrt{\frac{Dt}{\pi}} \quad (1)$$

and the long times asymptotic solution reads:

$$\gamma(t)_{t \rightarrow \infty} = \gamma_{eq} - RT \frac{\Gamma_{\infty}^2}{C} \sqrt{\frac{\pi}{4Dt}} \quad (2)$$

In these equations D denotes the diffusion coefficient of the monomer surfactant and γ_0 and γ_{eq} are the equilibrium surface tension of solvent and solution, respectively. C is the bulk surfactant concentration and Γ_{∞} represents the maximum excess surface concentration.

When surfactant concentration exceeds the cmc, the micelles are formed and if they have a breakup lifetime, τ_2 , within the time needed to reach the equilibrium surface tension the micellized surfactant are not available for adsorption and the dynamic surface tension decays more slowly. This fact is employed to calculate the micelle dissociation rate constant [15,50,51], $k_2 = 1/\tau_2$. Assuming a diffusion mechanism for the surfactant adsorption and neglecting the micelle diffusion because is much slower than the monomer surfactant diffusion, the following equation for dynamic surface tension can be derived [50]:

$$\gamma(t)_{t \rightarrow \infty} = \gamma_{eq} + \frac{RT\Gamma_{\infty}^2}{2Ct} \sqrt{\frac{\pi}{Dk_2}} \quad (3)$$

The first-order rate constant for micelle breakdown is dependent on the surfactant concentration, C , thus for a monodisperse system of aggregation number n , the dependence of the inverse of the relaxation time τ_2 with surfactant concentration is given by [15,52]:

$$k_2 = \frac{1}{\tau_2} = nk_n^- \left(\frac{C - \text{cmc}}{\text{cmc}} \right) \quad (4)$$

where k_n^- is the reverse rate constant for micelle aggregation equilibrium.

The dynamic surface tension curves of aqueous solutions of CHAPS and CHAPS polyelectrolyte mixtures have been analyzed according to Eqs. (1) and (3). At the beginning of adsorption all systems were consistent with surfactant monomer diffusion-controlled mechanism, Eq. (1). Using this equation and the dynamic surface tension values the diffusion coefficients can be calculated. The values found are collected in Table 1. Results in Table 1 show that in all cases the diffusion coefficients agree within the experimental uncertainty with the diffusion coefficient of the monomer surfactant. However, at long times the dynamic surface tension shows a linear dependence with t^{-1} , Eq. (3), and shown a poor dependence of $t^{-1/2}$, Eq. (2). According to it, the micelle dissociation rate constant k_2 can be estimated from the slope of the linear fit at long times, Eq. (3), using the diffusion coefficient presented in Table 1 and the maximum surface excess concentration calculated from the equilibrium surface tension values (not shown) and the Gibbs law, see Table 1.

The k_2 values are represented against the relative micellar concentration in Fig. 3. As can be seen in the figure, the experimental k_2

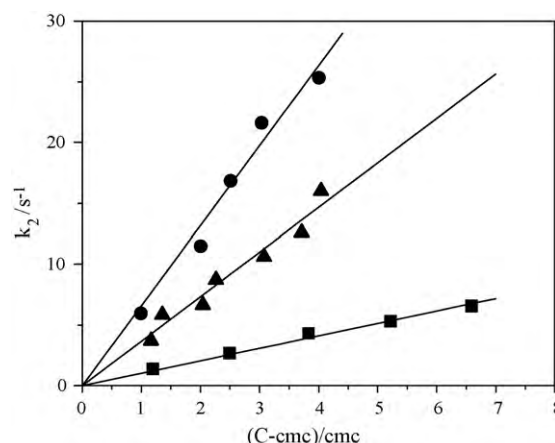


Fig. 3. Variation of k_2 with the relative micellar concentration of CHAPS dissolved in: circles, water; triangles, 0.5 wt% PDADMAC; and squares, 0.1 wt% PSS.

values present a linear dependence with the relative micellar concentration according to Eq. (4); from the slope we calculate nk_n^- . The values found are also collected in Table 1. Using the aggregation number taken from the literature for CHAPS, $n=10$ [53], we estimated a k_n^- value of 0.7 s^{-1} and from k_n^- we obtain a micelle lifetime value of 1.4 s. This value is longer than the micelle lifetime of ionic micelles, while it is in the same order of magnitude of the lifetimes for non-ionic surfactants [15,51].

On the other hand, results in Table 1 also show that the nk_n^- values decrease with polyelectrolyte addition. We do not know the aggregation number of the polymer-surfactant micelles, however it is generally accepted that the aggregation number of polymer-surfactant micelles is quite similar [54] or even higher than the surfactant aggregation number [6,55]. Consequently, from a qualitative point of view we can conclude that the micelle dissociation rate constants decrease in micelles bound to polymer molecules. According to SANS measurements [56,57] the structure of surfactant-polymer micelles involves the polymer chain wrapped around the bound micellar surface for linear polymers, this is consistent with the results found in this work, because the polymer molecules seem to protect micelles and the dissociation process becomes slower than in pure surfactant micelles.

3.3. Electrophoretic mobility results

The effect of the addition of polyelectrolytes on the surface electric charge of micelles was investigated using electrophoretic mobility measurements. For the sake of comparison the ζ -potential of CHAPS micelles was determined. The values obtained for CHAPS micelles with different surfactant concentrations above the cmc are independent of the surfactant concentration and the average value found was -5 mV . This value indicates that the pure zwitterionic surfactant micelles are practically neutral with a very small negative ζ -potential. This small ζ -potential is consistent with theoretical calculations carried out with semiempirical methods [58], which show that the headgroup of amphoteric surfactants has a small negative electric charge. We have also measured the ζ -potential of PSS solutions with different polymer concentration, the values are represented against polymer concentration in Fig. 4. Results in Fig. 4 show that the ζ -potential values of polymer solutions are practically independent of polymer concentration and the average value found is -70 mV . Fig. 4 also represents the ζ -potential values of CHAPS-PSS micelles. These micelles are prepared with a surfactant concentration constant and above the cac (1.5 mM) and with polymer concentrations ranging from 0.05 to 0.5 wt%. The ζ -potential of PSS-surfactant micelles is always negative and higher in absolute

Table 1

Thermodynamic and kinetics properties calculated for CHAPS dissolved in polyelectrolyte aqueous solutions.

System	$D (\times 10^{10} \text{ m}^2 \text{ s}^{-1})$	$\Gamma_{\infty} (\times 10^6 \text{ mol m}^{-2})$	$nk_n^- (\text{s}^{-1})$
Water	2.6 ± 0.3	1.68 ± 0.05	7.0 ± 0.6
PSS (0.1%)	1.6 ± 0.4	1.43 ± 0.05	1.0 ± 0.1
PDADMAC (0.5%)	2.8 ± 0.3	1.64 ± 0.04	3.7 ± 0.3

Results were obtained at 25°C .

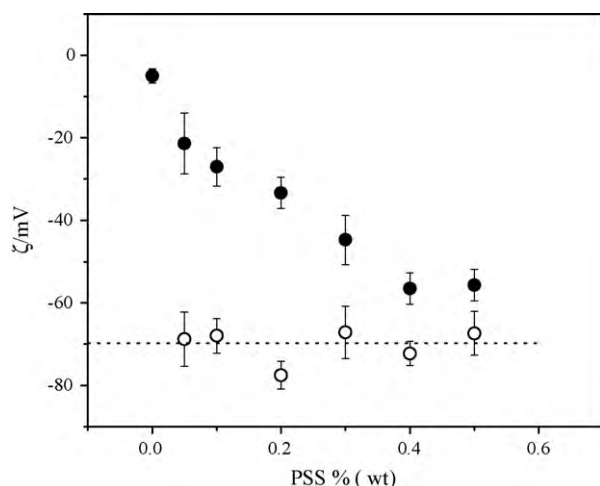


Fig. 4. ζ -Potential values of polymer-surfactant micelles prepared with different polymer concentration and 1.5 mM of CHAPS (solid circles). Open circles represent the ζ -potential values of aqueous polymer solutions. The line is guide to the eyes. All results were obtained at 25 °C.

value than the CHAPS micelles value. In addition the surface electric charge of polymer-surfactant micelles increases with polymer concentration. A similar trend is observed in PDADMAC-CHAPS micelles (not shown), however the surface of these micelles is positively charged while the CHAPS-PSS micelles bear negative charge.

From the ζ -potential measurements it is possible to conclude that the polyelectrolyte-CHAPS micelles are charged in contrast with the pure CHAPS micelles. The sign of the electric charge depends on the polyelectrolyte nature. Thus, the polyanion PSS screens the positive charge of the cationic group of CHAPS and the surface of polymer-surfactant micelles becomes negatively charged. A similar behavior is observed when the polycation (PDADMAC) is added to the surfactant solutions and in this system the micelles are positively charged.

4. Conclusions

We have analyzed the effect of the electric charge of polyelectrolytes on the interactions between polymers and the zwitterionic surfactant CHAPS, because the interactions between zwitterionic surfactant and polyelectrolytes have received lesser attention than the interaction between ionic surfactants and polyelectrolytes with opposite electric charge. However, zwitterionic surfactants are widely used because they are less toxic for us and for environment than ionic ones. We have demonstrated that the zwitterionic surfactant CHAPS forms complexes in solution with both the polyanion and polycation molecules resulting in polymer-surfactant micelles. Results also demonstrate that the formation of micelles bound to polymers is favored relative to the formation of pure CHAPS micelles. We also showed that it is possible to modulate the electric charge of CHAPS micelles by adding polyelectrolytes with different electric charge or varying the polyelectrolyte concentration. Finally, the rate constant of polymer-surfactant micelle dissociation is smaller than the one of pure CHAPS micelles. This fact seems to indicate that the polymer molecules wrapped around micelles inhibit the micelles breakup.

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