ASSOCIATION OF BRANCHED POLYETHYLENE IMINE WITH SURFACTANTS IN AQUEOUS SOLUTION

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Three polymer-surfactant systems comprised of branched polyethylene imine (PEI) with an anionic surfactant (sodium dodecylsulfate; SDS), a cationic surfactant (tetradecyltrimethylammonium bromide; TTAB), and a zwitterionic surfactant (*N*-tetradecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate; SB3-14) were studied based on the properties of surface tension, pyrene fluorescence emission, dynamic light scattering, pH, and zeta potential measurements. The critical aggregation concentration (*cac*) and polymer saturation point (*psp*) were determined for all three systems. The effect of these surfactants on the physico-chemical characteristics (diameter and surface charge) of the complexes formed was determined. Polymer-surfactant interactions occurred in all of the systems studied, with the strongest interactions, electrostatic in nature, occurring in the SDS-PEI system. After the neutralization of the polymer charges with the addition of the surfactant, the hydrophobic effect started to control the interlacing of the polymer chains. For the PEI-TTAB system, a very dense film was formed at surfactant concentrations above 2.0 mmol L^{-1}. In this case, the bromide counter-ion interacted with both the positively-charged PEI and the head of the surfactant, which is responsible for the formation of double layer coordination complexes. For the system composed of PEI and the zwitterionic surfactant, less cooperative associations occurred in comparison with the other systems.

Keywords: polymer-surfactant interactions; pyrene fluorescence; polyelectrolytes.

INTRODUCTION

Branched polyethylene imine (PEI; Scheme 1) is a polyelectrolyte with variable molar weight, being of great importance due to its large number of applications.[1,2] This polymer is of particular interest due to its use for the nanoparticle stabilization in the development of catalytic systems[3] and because of its ability to bind nucleic acids, acting in the transfection of genes.[4] In addition, PEI has in its structure many amino groups, which allow the design of different modified polymers with the potential to be applied in different fields of knowledge. Recent examples of the applications of PEI include its use in gene therapy,[5,6] in the design of nanoparticles in aqueous dispersions,[7,8] and in the encapsulation of drugs.[9]
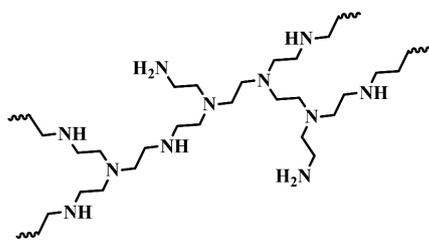
Scheme 1. *Structure of branched polyethylene imine (PEI)*

In aqueous solution, polymer–surfactant mixtures form associated thermodynamically stable complexes with physicochemical properties which differ from those observed in micellar media.[10-12] The association of a polyelectrolyte with an oppositely charged surfactant is generally accepted to involve an anion exchange process, where the electrostatic attraction is enhanced by the cooperative aggregation of surfactant molecules. Once all charges in the polymer chain are

neutralized, the hydrophobic effect begins to control the association, which induces restructuring of the polymer chain due to the formation of complexes with the surfactant.[13]

Studies on polymer–surfactant complexes show that surfactants can cooperatively interact with the polymer from the critical aggregation concentration (*cac*), forming micellar aggregates along the polymer. This is the basis for almost all systems that consist of polymers and ionic surfactants.[10,14] The values of the *cac* are lower than those for the critical micelle concentration (*cmc*) of the surfactant. In these various polymer–surfactant systems,[10,15-18] the *cac* is dependent on the electrostatic forces, the structural characteristics of the charged groups and other factors, such as the flexibility of the polymer chain and of the counter–ions.[16,19] At a certain concentration of surfactant, the so–called polymer saturation point (*psp*), the surfactant no longer forms complexes with the polymer, this concentration being directly proportional to the polymer concentration. Above the *psp*, regular micelles of surfactant are formed in equilibrium with the polymer–surfactant complexes.[20]

In this paper, the properties of aqueous systems comprised of PEI and a surfactant were investigated by way of surface tension, pyrene fluorescence, dynamic light scattering (DLS), pH, and zeta (ζ) potential measurements. Three surfactants were used (Scheme 2): an anionic surfactant (sodium dodecylsulfate; SDS), a cationic surfactant (tetradecyltrimethylammonium bromide; TTAB), and a zwitterionic surfactant (*N*–tetradecyl–*N*,*N*–dimethyl–3–ammonio–1–propane-sulfonate; SB3–14). Experimental data were used to determine the aggregation parameters for each polymer–surfactant system.

EXPERIMENTAL

Materials and methods

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The surfactants (99% pure) and the PEI (Mw 25,000 g mol^{-1})
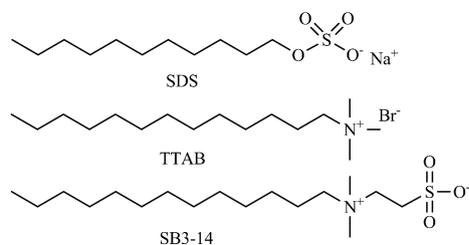
Scheme 2. *Molecular structures of the surfactants*

were purchased from Sigma–Aldrich. The primary/secondary/tertiary amine ratios for these polymers were 1:2:1, which corresponds to a branch every 3-3.5 nitrogens. Pyrene (99%, Sigma-Aldrich) was purified through recrystallization from methanol. Aqueous stock solutions of PEI were prepared under magnetic stirring for at least 12 h, deionized water, obtained through previous distillation followed by purification employing a Millipore Milli–Q system, was used in all measurements. These stock solutions were used to prepare those containing SDS, SB3–14, and TTAB, in order to maintain a constant PEI concentration (c(PEI) = 2.0 mg mL^{-1}). This concentration was used because it is below the overlap concentration.[18]

Surface tension experiments

The surface tension experimental data were collected at 25.0 ± 0.1 °C on a Kruss K8 GMBH interfacial tensiometer, equipped with a Pt–Ir–20 ring. All polymer–surfactant solutions were prepared at least two hours before use, to each concentration surfactant.

Fluorescence measurements

Fluorescence emission spectra were made on a Hitachi F4500 spectrofluorimeter equipped with a thermostated cell holder set at 25.0 ± 0.1°C. An aqueous pyrene solution (1.0×10^{-6} mol L^{-1}) was used to prepare the surfactant, PEI, and surfactant–PEI solutions. The slits of the excitation and emission were set at 2.5 nm and all the solutions were measured using a quartz cell with excitation wavelength at 336 nm. The intensities of the first emission band at 372.8 nm and of the third emission band at 384.0 nm were used to calculate the I_1/I_3 ratio.[17,21-26]

pH measurements

The pH measurements were performed at 25.0 ± 0.1 °C using a Beckman pH meter model ϕ 71, with a combined glass electrode. The pH meter was previously calibrated with standard solutions with pH = 7.0 and pH = 10.0.

Zeta potential measurements

The ζ values were obtained for the solutions containing SDS–PEI, TTAB–PEI, and SB3–14–PEI. The solutions were prepared from an aqueous solution containing 2.0 mg mL^{-1} of PEI, in order to keep the PEI concentration constant, and to allow the addition of surfactant to increase its concentration. The ζ measurements were performed with a Malvern Zetasizer Nano ZS system equipped with a 4.0 mW He–Ne laser (632.8 nm) using folded capillary cells with electrodes.

DLS studies

DLS measurements were taken at a fixed angle of 90° on a light scattering spectrometer (Brokhaven Instruments Corporation,

BI–200 goniometer, digital correlator BI–9000 AT, with He–Ne laser, wavelength 632.8 nm) at 25.0 ± 0.1°C. The solutions containing SDS–PEI, TTAB–PEI, and SB3–14–PEI were prepared from an aqueous solution containing 2.0 mg mL^{-1} of PEI in order to keep the PEI concentration constant and to allow the addition of surfactant to increase concentration. The samples were filtered through cellulose acetate membranes (0.45 μm) and placed in cylindrical cuvettes.

RESULTS AND DISCUSSION

Surface tension measurements

Figure 1 shows the variation in the surface tension as a function of the SDS concentration (c(SDS)) in deionized water, for solutions of pure SDS and SDS–PEI. The plotting of data obtained for pure SDS shows a discontinuity at 38.2 mN m^{-1} with a *cmc* value of 7.0 mmol L^{-1}, which is consistent with reports in the literature.[14,27] However, a high surface–activity was observed for the SDS–PEI system, because the surface tension decreased sharply at lower surfactant concentrations in comparison with the system without PEI. A plateau occurred at 35.9 mN m^{-1}, this being attributed to the *cac* at 0.17 mmol L^{-1}, and this behavior is consistent with a densely packed interface.[27] Further addition of surfactant leads to lower surface tension values compared with those observed for pure SDS. In addition, when the *cmc* value is reached the surface tension of the SDS–PEI system increases, reaching values that are similar to the micellar SDS. This occurs because of the possible migration of some surfactant ions, initially connected to the PEI chain at the air–liquid interface, into the solution during the micellization process.[27] When the surface tension reaches values similar to those obtained for pure SDS solutions, above the *cmc*, the polymer is saturated and the *psp* occurs at 37.9 mN m^{-1} for c(SDS) = 24.9 mmol L^{-1}.
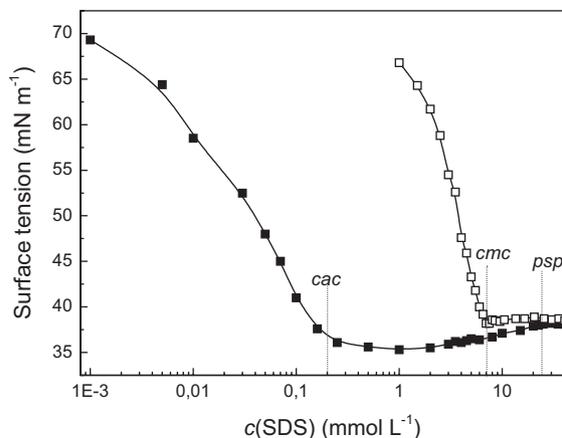
Figure 1. *Surface tension with increasing concentrations of SDS; (□) pure SDS and (■) SDS–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C*

Figure 2 shows the plots for the surface tension data in water as a function of the TTAB concentration (c(TTAB)) for solutions of TTAB and TTAB–PEI. For the solutions of TTAB, the plot exhibits a classical profile[28] with a decrease in the air–liquid interface associated with increasing surfactant concentration, until the *cmc* is reached (this being at 3.30 mmol L^{-1} of TTAB for a surface tension stabilized at 38.5 mN m^{-1}). For solutions with PEI, the profile changed and with only 0.03 mmol L^{-1} of TTAB a plateau occurred, which is related to the *cac* for the polymer–surfactant system. On increasing the surfactant concentration the surface tension decreases again, stabilizing at 44.2 mN m^{-1} with 0.85 mmol L^{-1} of TTAB. The formation of a very dense film on the solution surface hindered the taking of

measurements at c(TTAB) > 2.0 mmol L^{-1}. Similar behavior has been observed by other authors in studies carried out using mixtures of PEI and cationic surfactants,[29-31] this being attributed to the formation of mesostructured thin films at the air–liquid interface. In some cases this formation can be detected by the naked–eye at concentrations close near to the *cmc* of the surfactant.[29,30] At the interface, highly ordered rod–like aggregates have been observed while in the bulk solution elliptic aggregates have been detected.[32] Comas–Rojas *et al.*[29,30] reported similar behavior for the interaction between cetyltrimethylammonium bromide (CTAB) and two PEIs with different molar weights (2,000 and 750,000 g mol^{-1}). They studied the formation of CTAB–PEI films using different techniques and determined 0.77 mmol L^{-1} as the CTAB concentration in solution above which the film formation reached equilibrium. This concentration is very close to that observed in this study for the saturation of the aqueous system.
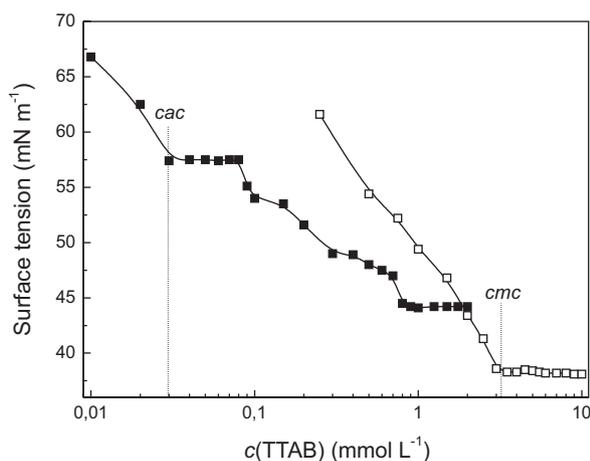
Figure 2. Surface tension with increasing concentrations of TTAB; (□) pure TTAB and (■) TTAB–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C

Figure 3 shows the data obtained for the changes in surface tension in water as a function of the SB3–14 concentration (c(SB3–14)) for solutions of SB3–14 and SB3–14–PEI system. The addition of PEI led to almost no alteration in the curve, indicating that the polymer-surfactant system does not exhibit surface properties. The plotting of the data obtained for SB3–14 indicated a *cmc* for the surfactant of 0.27 mmol L^{-1} at 37.7 mN m^{-1}, which is in agreement with surface tension measurements reported in the literature (0.27 mmol L^{-1}).[33] The profile obtained for the SB3–14–PEI system indicates polymer-surfactant interaction,[11,14,34] with a break in the profile and a small plateau being observed at 47.6 mN m^{-1} for 0.07 mmol L^{-1} of surfactant, which characterizes the *cac* for the system. With an increase in the SB3–14 concentration, the surface tension values start to decrease again and stabilize at 38.2 mN m^{-1} and c(surfactant) = 0.39 mmol L^{-1}. Above this value, which corresponds to the *psp*, only regular SB3–14 micelles are formed in equilibrium with SB3–14–PEI complexes.

Fluorescence measurements

The steady–state fluorescence technique was used, with pyrene as a fluorescent emission probe, to confirm the formation of polymer–surfactant complexes. The fluorescence emission spectrum for pyrene has five vibronic bands and the ratio between the intensities of the first (I_1) band at 372.8 nm and the third (I_3) band at 384.0 nm is highly sensitive to small changes in the microenvironment of the medium.[35,36] For instance, the I_1/I_3 value for hexane is equal to 0.6 while a value of 1.8 is reported for water.[37] This type of probe is widely used in the study of micelles[26,38] and lipophilic environments,[39,40] as
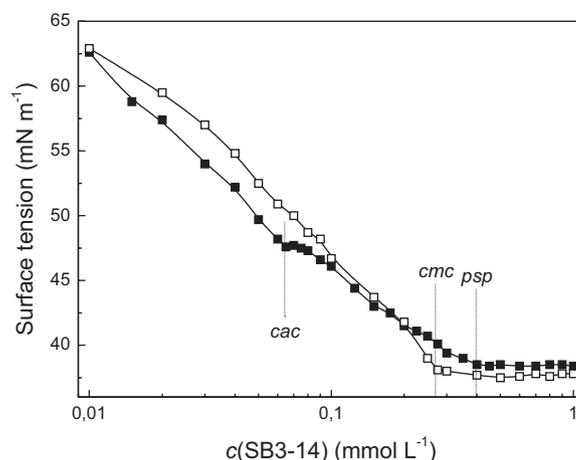
Figure 3. Surface tension with increasing concentrations of SB3–14; (□) pure SB3–14 and (■) SB3–14–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C

well as in the investigation of aqueous mixtures of polyelectrolytes and surfactants.[17,18] A micellization process can be followed by the decrease in the I_1/I_3 ratio due to the migration of pyrene from aqueous solution to the micellar core microenvironment.[24,25]

Figure 4 shows plots of the I_1/I_3 ratio for pyrene in aqueous solution as a function of c(SDS) for solutions of SDS and SDS–PEI. The *cmc* value was determined to the surfactant concentration at which the upper plateau ends, this being 7.0 mmol L^{-1}.[17] The addition of PEI to the system causes a significant change due to the SDS–PEI association. The results indicated that the onset of association (*cac*) occurred at 0.09 mmol L^{-1}. At low surfactant concentration the I_1/I_3 ratio is similar the water polarity (~1.80),[36] while for high concentrations of SDS, above the *cmc* and *cac*, the I_1/I_3 ratio decreased to around 1.15, which is consistent with values reported for SDS micelles.[41]
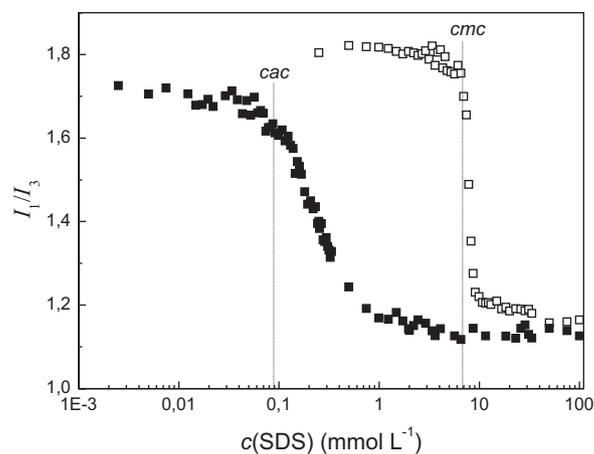
Figure 4. I_1/I_3 ratio for pyrene fluorescence emission with increasing concentration of SDS; (□) pure SDS and (■) SDS–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C

Figure 5 shows the influence of TTAB on the I_1/I_3 values for pyrene in water for solutions of TTAB and TTAB–PEI. For solutions of pure surfactant a classical behavior was observed, with a well–defined *cmc* of 1.75 mmol L^{-1}, lower than the value obtained through surface tension measurements (3.30 mmol L^{-1}). In general, the *cmc* values obtained using the fluorescence technique are slightly lower than the values determined by other methods. This difference is attributable to the fact that pyrene, because of its low solubility in water, induces the formation of pre–micellar aggregates.[14] Above the *cmc*, the I_1/I_3 ratio decreased reaching 1.31, which is attributed to the presence of

surfactant micelles.[36,42] In the presence of PEI the profile changes and shows the *cac* at *c*(TTAB) of 0.03 mmol L^{-1}.
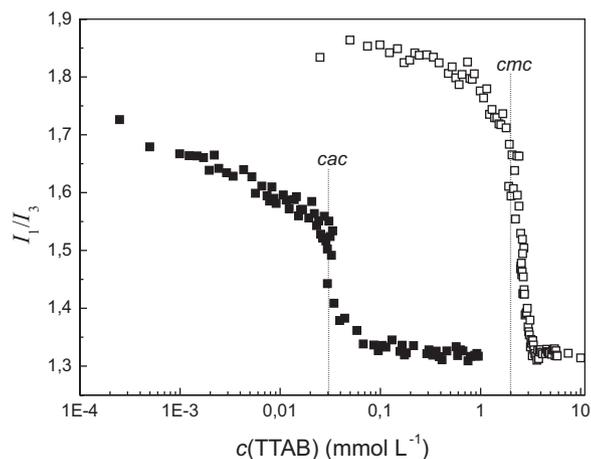
Figure 5. *I_1/I_3 ratio for pyrene fluorescence emission with increasing concentration of TTAB; (□) pure TTAB and (■) TTAB–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C*

The influence of the addition of SB3–14 on the I_1/I_3 values of the aqueous solutions of pyrene for solutions of SB3–14 and SB3–14–PEI is shown in Figure 6. The *cmc* value of 0.25 mmol L^{-1} was obtained for SB3–14. For SB3–14–PEI solutions the I_1/I_3 ratio begins to decrease at ca. 0.02 mmol L^{-1}, determining the *cac*, but the value for the ratio gradually decreases, stabilizing at I_1/I_3 = 1.32 with the addition of SB3–14 at a concentration above 0.40 mmol L^{-1}. This behavior is attributed to a less cooperative association,[42,43] compared with other systems.[14]
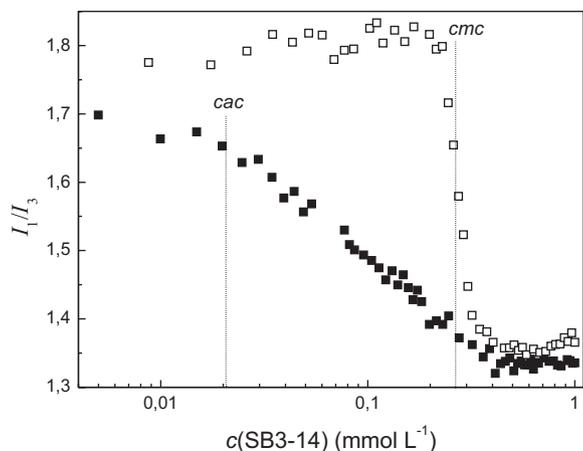
Figure 6. *I_1/I_3 ratio for pyrene fluorescence emission in water with increasing concentration of SB3–14; (□) pure SB3–14 and (■) SB3–14–PEI (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C*

pH of the surfactant–PEI aqueous solutions

The pH values of the aqueous solutions of PEI at a concentration of 2.0 mg mL^{-1} were measured alone and with increasing amounts of SDS (Figure7A). The pH value was close to 9.5 for PEI alone and increased to 11.2 for *c*(SDS) = 20 mmol L^{-1}. The amino groups present in PEI act as a weak base, abstracting protons of the water molecules, with formation of hydroxide,[18] which becomes alkaline its aqueous solutions. If SDS is added, the acid–base equilibrium is displaced because of the specific binding of the negative charge from anionic surfactant with the positive charge from PEI, increasing *c*(OH$^-$) and consequently increasing also the pH.[18]
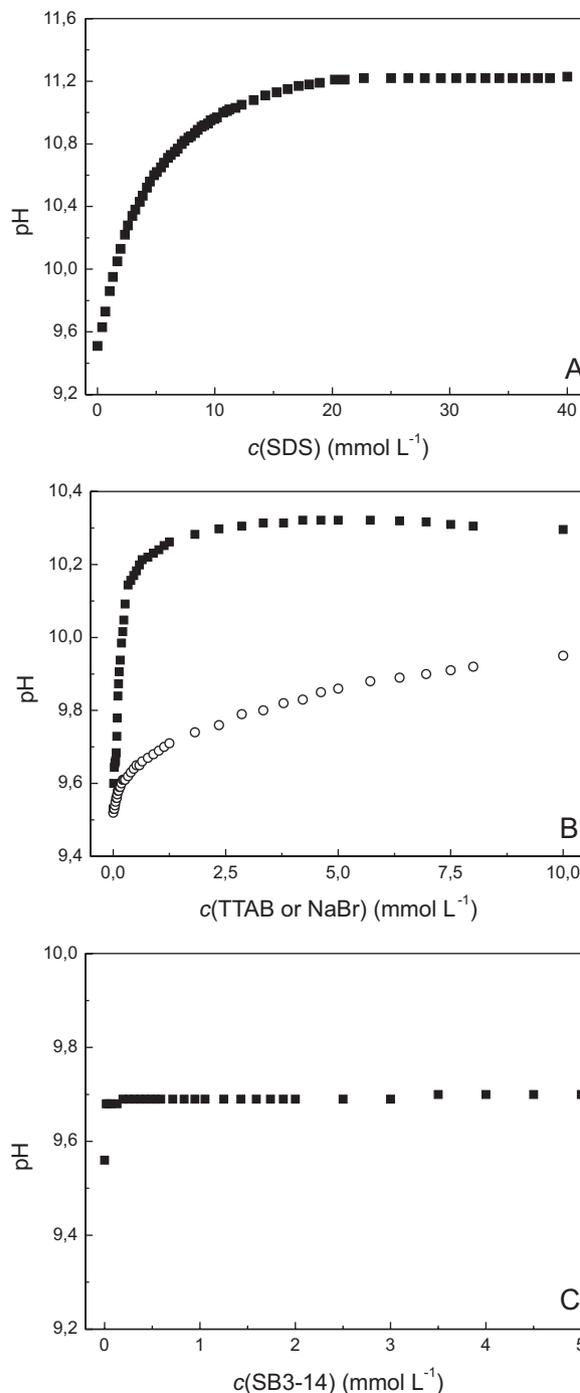
Figure 7. *Change on the pH of aqueous solutions of (**A**) SDS–PEI, (**B**) TTAB–PEI (■), NaBr–PEI (○), and (**C**) SB3–14–PEI. (c(polymer) = 2.0 mg mL^{-1}) at 25.0 ± 0.1 °C*

Figure 7B shows the influence of the addition of TTAB on the pH of the aqueous solutions of PEI, a large increase in the pH values being observed with an increase in the surfactant concentration: with the addition of TTAB at a concentration as low as 1.25 mmol L^{-1} the pH increases from 9.5 to 10.30 and above this concentration the pH remains practically constant. The data suggest that the Br$^-$ counter–ion influences the pH of the solution and therefore a similar study was carried out adding NaBr to an aqueous solution of PEI. For comparison, experimental data are also shown in Figure 7B, where it can be observed that there was an increase in the pH value with increasing *c*(NaBr), but the pH value reaches 9.95 at *c*(NaBr) = 10.0 mmol L^{-1}, while for the same TTAB concentration the pH value reaches 10.30.

These differences suggest that Br⁻ is able to interact with both the positively charged polymer and the head of the surfactant, forming double layer coordination complexes,[44,45] which leads to a more accentuated increase in the pH value than that observed for the system with only NaBr. The formation of these complexes can explain the films observed when this system was studied by way of surface tension measurements (see above).

For the system comprised of PEI and SB3–14, no significant changes in the pH values occurred (Figure 7C). In this case, the zwitterionic surfactant was not able to bind specifically with the positively charged sites on the polymeric chains, and thus did not displace the acid–base equilibrium. The interaction of SB3–14 with PEI occurs through hydrophobic effect.

Zeta potential of the surfactant–PEI aqueous solutions

The ζ data are related to the surface charge density of the complexes. The PEI solution (c(PEI) = 2.0 mg mL⁻¹) had a positive ζ value (+15.1 ± 2.0 mV) due to the positive charges of the protonated amino groups. On the other hand, a negative ζ value from –49.8 ± 5.1 mV was obtained for pure SDS aqueous solutions, in a concentration above the cmc. As expected, the addition of SDS to the PEI solutions led to a change in the ζ value from positive to negative (Figure 8A). This behavior should be explained considering the SDS–PEI interactions. Below *cac* concentration, the specific interaction between SDS and PEI leads to very small changes in ζ values and it remains positive. Above the *cac*, due to the SDS–PEI complex formation, the ζ value gradually decreases until concentrations near to *psp*, because of the global charge changes in the SDS–PEI complex. In the TTAB case (Figure 8B), there is no ζ charge inversion and the changes in ζ values are very small compared to SDS–PEI system. These observations are in agreement with surface tension data (Figure 2). Near to *cac*, the ζ value starts to increase due the TTAB–PEI complex formation, but it stops to increase at ~0.9 mmol L⁻¹, which is the concentration observed for the formation of mesostructured thin films at the air-liquid interface in surface tension measurements. At this point, the ζ values of TTAB–PEI solutions (+20.1 ± 2.2 mV) are very small if compared to the pure TTAB solutions (+51.1 ± 4.3 mV), because in this technique the ζ potential is measured only from the species in solution. The increase in the zwitterionic concentration in presence of PEI had practically no change on the ζ values (Figure 8C), which is in agreement with the results obtained through the other experimental techniques used.

DLS data for PEI and surfactants in aqueous solution

The PEI–surfactant systems were studied by way of DLS measurements, in order to understand the influence of the surfactant on the conformation of the polymeric chains in solution through analysis of the hydrodynamic diameter (D_H) of the aggregates. Figure 9 shows the D_H values for SDS–PEI (A), TTAB–PEI (B), and SB3–14–PEI (C), along with the corresponding surface tension profiles for comparison. Figure 9A indicates that when the c(SDS) was close to the *cac* (determined by way of the surface tension) a considerable increase in the D_H occurred, indicating an association between SDS and PEI, which promotes a conformational change in the polymer chain. The specific binding of SDS molecules to the PEI chain increases the exclusion volume of the polymer in solution and, consequently, its D_H value. Since the polymer charges are neutralized, the hydrophobic effect starts to control the interlacing, leading to the relaxation of the polymer chains and more folding conformations, as described by Wang *et al.*.[13] The D_H value decreased with the further addition of SDS to the solution, probably due to the minimization of the inter chain repulsion
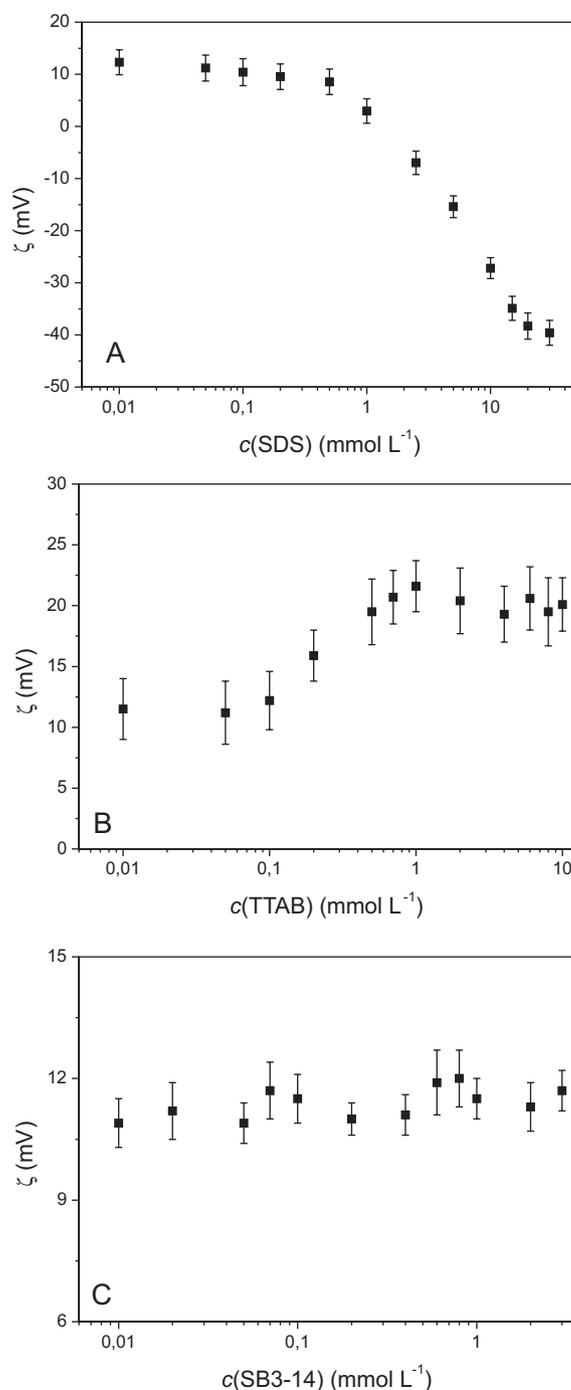
Figure 8. Change on the ζ values of aqueous solutions of (A) SDS–PEI, (B) TTAB–PEI, and (C) SB3–14–PEI; c(polymer) = 2.0 mg mL⁻¹ at 25.0 ± 0.1 °C

(double electric layer contraction) promoted by an increase in the ionic strength (*self–salt effect*). The TTAB–PEI system (Figure 9B) shows that at low surfactant concentrations (<0.02 mmol L⁻¹) the behavior was very similar to that observed for the SDS system: at the *cac*, the D_H value increased due to the beginning of the TTAB–PEI interaction. Above the *cac*, the D_H value decreased with the further addition of surfactant, due to the folding of the polymeric chains. Figure 9C shows the data for the SB3–14–PEI system. Its behavior at close to the *cac* value determined by way of the surface tension was very similar to that of the SDS–PEI system, the observed increase in D_H providing evidence for the beginning of the formation of SB3–14–PEI aggregates. In the same way, the addition of more surfactant leads to a folding of the polymeric chains.
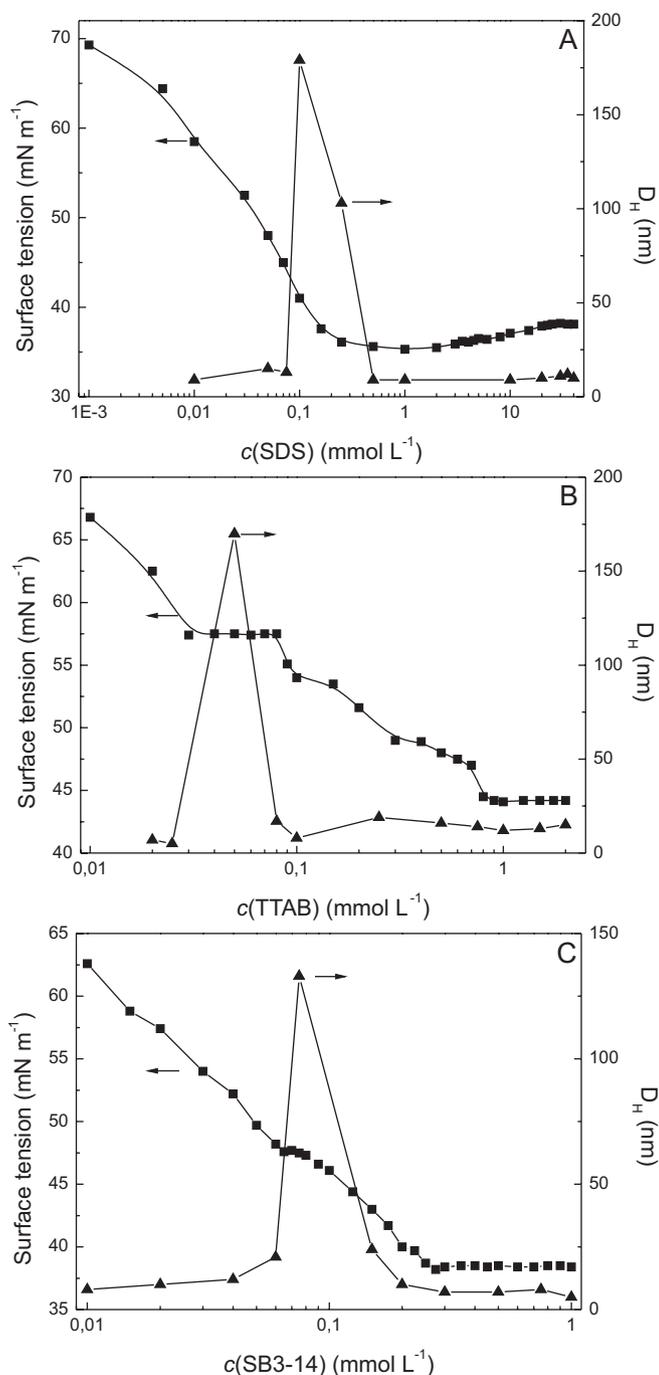
Figure 9. *D_H values obtained through DLS experiments with (A) SDS–PEI, (B) TTAB–PEI, and (C) SB3–14–PEI, (c(polymer) = 2.0 mg mL⁻¹). The respective surface tension plots are included for comparison*

CONCLUSIONS

The association of PEI with three surfactants, SDS, TTAB, and SB3–14, was investigated by means of surface tension, fluorescence, pH, ζ potential and DLS measurements. The combined results from all of these techniques clearly showed that the strongest interactions occurred in the SDS–PEI system, presumably due to the opposing charges of its components. The TTAB–PEI system showed different behavior, with the formation of a film on the surface of the solution. A similar PEI–cationic surfactant film has been previously reported by Comas-Rojas *et al.*.[29,30] In our case, the formation of the film is due to layer-by-layer complexation of TTAB and PEI, via the bromide anion.

Although the anionic SDS was the only surfactant to exhibit a strong electrostatic interaction towards PEI, all of the other surfactants were able to produce complexes with the polymer, mostly due to the minimization of the hydrophobic effect arising from their non-polar chains in water. The D_H of the complexes increased with the addition of surfactant up to a maximum value close to the *cac*; further addition of surfactant produced more compact complexes, due to the folding and entanglement of the PEI chains.

ACKNOWLEDGEMENTS

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