Journal of chemical & engineering data

Article

pubs.acs.org/jced

Interaction between Cetyltrimetylammonium Tosylate and Two Poly(oxyethylene)−Poly(oxypropylene)−Poly(oxyethylene) Block Copolymers Studied by Cyclic Voltammetry

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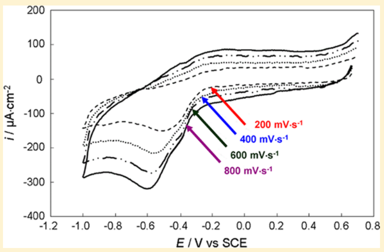
S *Supporting Information*

ABSTRACT: Mixtures of hexadecyltrimethylammonium tosylate (hexadecyltrimethylammonium *p*-toluene sulfonate or cetyltrimethylammonium tosylate, CTAT) with two Pluronic block copolymers, F127 and F68, were studied using cyclic voltammetry. The hydrodynamic radii of aggregates were analyzed in light of the aggregate composition. It was confirmed that the mixtures CTAT-F127 and CTAT-F68 have different behaviors. This corroborates that the interaction between different Pluronics and the same conventional surfactant depends on the kind of copolymer surfactant and also that differences in the size of the hydrophobic and the hydrophilic parts of the molecule may cause different behaviors. The penetration of CTAT into the micelle core may be more or less hindered by the size and structure of the hydrophilic shell. However, once the conventional surfactant has penetrated the corona and reached the polyoxypropylene core in a cooperative manner, the aggregates tend to disappear, thus being replaced by smaller structures, which are probably complexes having a finite number of CTAT molecules per copolymer molecule.



1. INTRODUCTION

Since surfactant mixtures are commonly used in numerous technical applications because their properties show an enhanced performance when compared with single surfactant systems,[1] it is of paramount importance to understand the interactions involved in surfactant mixing, especially the factors influencing the structure and properties of the mixed aggregates. This knowledge may be used to improve the theories dealing with the influence of the structure of the polar layer and the electrostatic effects in micellization[2] and mixed micellization.[3,4]

In a previous work[5] we studied the critical aggregation concentration of mixtures consisting of two poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymers, known as poloxamers or Pluronics, with hexadecyltrimethylammonium *p*-toluene sulfonate (cetyltrimetylammonium tosylate, CTAT). The Pluronics used for these studies were F127 ($PEO_{97}PPO_{69}PEO_{97}$) and F68 (PEO_{76} PPO_{30} PEO_{76}).

There is in literature contradictory information about the nature of mixed aggregates produced when Pluronics and conventional surfactants interact. Low molecular weight amphiphiles seem to interact with Pluronics in a manner which depends on both the copolymer and the short-chain surfactant nature. As examples, both sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) seem to destabilize the block copolymer (F127) aggregates.[6] However, cyclic voltammetry measurements have shown that mixtures of F127 with tetradecyltrimethylammonium bromide (TTAB), CTAB, or Brij 35 form mixed micelles in all of the proportions studied.[7] The same conclusion was informed for the Pluronic F68 mixtures with CTAB, TTAB, or Triton X-100.[8] The formation of mixed micelles with mixtures of Pluronic L64 and SDS at low SDS content was informed, while at higher SDS proportions a bicontinuous structure was found.[9] Ionic surfactants such as SDS and CTAB interact stronger than nonionic surfactants with Pluronic block copolymers.[10]

It is generally supposed that the conventional surfactant tail binds to the hydrophobic PPO region of the Pluronics.[11,12] The resulting complex becomes more hydrophilic when the conventional surfactant proportion increases, and when the copolymer molecules are saturated with the low-molecular weight amphiphile, the Pluronic assembly disappears.[10−12] Then, the system is composed by conventional surfactant micelles and complexes formed by one Pluronic chain bonded to a number of low-molecular weight molecules.

The addition of SDS to L64 micelles reduces the size of the polymer micelles, eventually leading to aggregates similar to SDS having an average of less than one Pluronic molecule per mixed micelle.[10] The F127 micelles are completely suppressed

Received: April 12, 2012
Accepted: October 18, 2012
Published: October 26, 2012

by addition of SDS. It was found that SDS binds cooperatively with the Pluronic molecules, which become hydrophilic. Between four and five SDS molecules saturate one F127 molecule. This saturation amount of SDS increases somewhat when the polymer concentration is augmented.[12] The complex is not coiled, but it is in an extended conformation.[10] Since the addition of electrolytes does not alter this conformation, the disappearing of F127 micelles is not uniquely due to electrostatic repulsion between aggregates. It was suggested by other authors that the F58 and L64 copolymers exist as solubilizates in the SDS micelles.[12]

In our previous work, we found that the interaction between CTAT and F68 is different from that observed between CTAT and F127.[5] To obtain more information about the nature of these interactions, in this work we have determined the aggregates' diffusion coefficient, which is related with the aggregates' size and shape. The physicochemical and electrochemical aspects of such interactions are of significant importance due to the use of such polymers in several applications,[13] along with a variety of other surfactants. Since in literature the reported nature of aggregates obtained when dissimilar Pluronics are mixed with different conventional surfactants is very diverse, we used the concept of the "critical aggregation concentration" (CAC) instead of that of the critical micelle concentration (CMC).

The determination of the aggregation number (N_{agg}) of aggregates by using electrochemical procedures via the measurement of the self-diffusion coefficient (D_M) was used in many works. Polarography[14−21] and cyclic voltammetry (CV)[22] techniques were used to determine the diffusion current density of aggregates doped with an electroactive probe. It is assumed that the inclusion of a small number of these probes in the aggregates does not affect their size and shape.[18] Since both polarographic and voltammetric techniques give the self-diffusion coefficient of the kinetic units, both aggregates' size and shape can be obtained.

Understanding the copolymer−surfactant interactions is not only of theoretical but also of technological interest due to the numerous applications of these systems. Thus, the obtained results will not only be helpful in understanding the electrochemical and physicochemical properties of the mixed ionic surfactant−Pluronic block copolymer system, but also in the developing of many other applications.

2. MATERIALS AND METHODS

Hexadecyltrimethylammonium *p*-toluene sulfonate or tosylate (CTAT), Pluronics F68 ($PEO_{76}PPO_{30}PEO_{76}$ MW = 8400 $g\cdot mol^{-1}$) and F127 ($PEO_{97}PPO_{69}PEO_{97}$ MW = 12600 $g\cdot mol^{-1}$), and 9-anthracenecarbonitrile 97 % (electroactive probe) were obtained from Sigma-Aldrich. Surfactants were of analytical grade and used as received.

Concentrated samples were prepared by weighing the appropriate amount of each surfactant and then adding water to obtain the desired concentration. Mixtures having $\alpha_{CTAT} = 0$ (pure Pluronic), 0.15, 0.25, 0.35, 0.50, 0.75, 0.85, and 1 (pure CTAT) were prepared; α_{CTAT} being the mole fraction of CTAT in the surfactant mixture without considering the solvent. Solutions at twice the critical aggregation concentration (CAC), obtained from a previous work,[5] were prepared by dilution of a concentrated one. 9-Anthracenecarbonitrile from a solution with a concentration of $5\cdot10^{-4}$ $mol\cdot kg^{-1}$ was used as an electroactive probe, by adding to each solution an amount equal to 1/4 of the micelles concentration, to ensure that each micelle has no more than one electroactive probe. This was computed by using the [micelles concentration] = (C − CAC)/200 (assuming an aggregation number of about 200). To verify the effect of the added supporting electrolyte, measurements were made with the same concentration of each surfactant and concentrations ranging from (0.001 to 0.050) $mol\cdot kg^{-1}$ of KCl. We have not found significant differences in the diffusion coefficient of Pluronic micelles (D_M) with the increase of the supporting electrolyte's concentration. Then, a concentration of 0.050 $mol\cdot kg^{-1}$ of KCl was used in all the experiments, since with this concentration it was found that the signal-to-noise ratio obtained was the best possible. At this concentration of supporting electrolyte it was unnecessary to make corrections for resistance loss.

Before use the glassy carbon (GC) electrodes were washed carefully with 4-fold quartz-distilled water, polished using an alumina powder (0.3 μm), and washed again as described above. All aqueous solutions were prepared with 4-fold quartz-distilled water and purged with N_2 prior to every experience. The measurements were run twice.

To perform the CV measurements, a conventional three-electrode electrochemical cell was employed. A GC disk having a 0.07 cm^2 area was used as working electrode, while a Pt wire was the counter electrode, and the reference one was a saturated calomel electrode (SCE) inside a Luggin capillary. Unless stated otherwise, all reported potentials are referred to the SCE. A computer-controlled EG&G Princeton Applied Research Model 273A potentiostat-galvanostat was used to carry out the electrochemical measurements. Scan rates were varied between 200 $mV\cdot s^{-1}$ and 1000 $mV\cdot s^{-1}$.

All measurements were made at 25.0 °C, thermostatted with water circulation and at atmospheric pressure.

3. THEORY

In CV, the peak current i_p (μA) for a redox-active reversible system at 25 °C is given by:

$$i_p = (2.687\cdot10^5)n^{3/2}AD_M^{1/2}C\nu^{1/2} \tag{1}$$

where n is the number of electrons involved in oxidation or reduction ($n = 2$), A is the area of the electrode (cm^2), D_M is the diffusion coefficient of the kinetic unit carrying the electroactive probe, that is, the micelles ($cm^2\cdot s^{-1}$), C is the concentration of the electroactive probe in the solution ($mol\cdot cm^{-3}$), and ν is the sweep rate ($V\cdot s^{-1}$). From the slope of i_p vs $\nu^{1/2}$ plot, the D_M values for various micelle concentrations were obtained at various probe concentrations.

Using the aggregates' self-diffusion coefficients obtained from CV measurements, the aggregation number (N_{agg}) was obtained. The hydrodynamic radius R_h of a sphere with equivalent behavior (i.e., the radius of a spherical micelle having the same D_M value) was obtained from the Einstein−Stokes equation:

$$D_M = k_BT/6\pi\eta R_h \tag{2}$$

where k_B and T are the Boltzmann constant and the absolute temperature, and η is the viscosity of the medium, in this case water.

To compute the interaggregates interaction, the method of Corti and Degiorgio[21] was used, which considers a hard-core repulsion, a screened Coulomb repulsion, and a London−van der Waals attraction. This gives:

$$D_{\mathrm{M}} = D_{\mathrm{M},0}[1 + k_{\mathrm{D}}(C - \mathrm{CAC})] \tag{3}$$

and

$$k_{\mathrm{D}} = [0.5 + 2(1 + x)^2(1 + 4x) - (15/8)(1 + x)^{-1}]V_{\mathrm{M}} \tag{4}$$

where $D_{\mathrm{M},0}$ is the diffusion coefficient corrected to eliminate the interaction between aggregates, $x \approx \kappa^{-1}/R_{\mathrm{h}}$, κ^{-1} is the Debye length, and V_{M} is the partial specific volume of the micelles. To compute κ^{-1} we used the KCl concentration as the ionic strength, because the CAC values are an order of magnitude smaller, and only the CTAT component is ionic. To compute the value of V_{M} the volume of the equivalent surfactant molecule (V_{s}) was calculated as:

$$V_{\mathrm{s}} = V_{\mathrm{CTAT}}x_{\mathrm{CTAT}} + V_{\mathrm{Pluronic}}x_{\mathrm{Pluronic}} \tag{5}$$

where x_{CTAT} and x_{Pluronic} are the mole fraction of the components in micelles (taken from a previous work[5]); the volumes of the components (V_{CTAT} and V_{Pluronic}) were computed from the partial molar volumes (PMV) of CTAT and Pluronics F127 and F68 in the micellar state. The partial molar volume of CTAB is $\mathrm{PMV}_{\mathrm{CTAB}} = 365.4$ cm^3·mol^{-1},[23] which by subtraction of the PMV of Br$^-$ (29.2 cm^3·mol^{-1} [24]) gives a value for $\mathrm{PMV}_{\mathrm{CTA^+}}$ of 336.2 cm^3·mol^{-1}. For the tosylate ion, the partial molar volume is 127.54 cm^3·mol^{-1}.[24,25] The partial molar volumes of both Pluronics were computed from that of Pluronic P64 ($\mathrm{PEO_{13}PPO_{30}PEO_{13}}$), with a value of 2577.0 cm^3·mol^{-1} at 28 °C[26] and taking into account the group contributions to the partial molar volume $\mathrm{PMV_{PEO}} = 37.2 \pm 0.9$ cm^3·mol^{-1} as an average of several values found in the literature[27−30] and a value of $\mathrm{PMV_{PPO}} = 56.5 \pm 3.1$ cm^3·mol^{-1}.[27] This gave the following values: $\mathrm{PMV_{F127}} = 11044$ cm^3·mol^{-1} and $\mathrm{PMV_{F68}} = 7241$ cm^3·mol^{-1}.

The partial specific volume of micelles was computed as $V_{\mathrm{M}} = V_{\mathrm{s}}/M_{\mathrm{s}}$, with M_{s} being the equivalent surfactant molecular weight:

$$M_{\mathrm{s}} = M_{\mathrm{CTAT}}x_{\mathrm{CTAT}} + M_{\mathrm{Pluronic}}x_{\mathrm{Pluronic}} \tag{6}$$

Using eq 2 with the values of the D_{M} obtained from the i_{p}, the uncorrected equivalent hydrodynamic radius was obtained (R_{h}). Then R_{h} was used to determine k_{D}, and the value of $D_{\mathrm{M},0}$ was computed. Then using eq 2, the corrected equivalent for the hydrodynamic radius of micelles ($R_{\mathrm{h},0}$) was computed.

The values of $R_{\mathrm{h},0}$ were then compared with the length of a fully extended surfactant molecule l_{s}. If $l_{\mathrm{s}} \geq R_{\mathrm{h},0,}$ then micelles were supposed to be spherical, otherwise they were considered as rod-like. Subsequently, the volume of spherical micelles (V_{sp}) was computed using the $R_{\mathrm{h},0}$ value. To obtain the dimensions in the case of the rod-like micelles, the following equation was used:[28]

$$R_{\mathrm{h},0} = L/(2\sigma - 0.19 - 8.42/\sigma + 12/\sigma^2) \tag{7}$$

where L is the length, r the radius of the cylinder, and $\sigma = \ln(L/r)$. This equation was solved numerically by taking $r = l_{\mathrm{s}}$. Then, the volume of the rod-like micelle was calculated as:[31]

$$V_{\mathrm{rod}} = 4/3\pi l_{\mathrm{s}}^3 + 2\pi l_{\mathrm{s}}^2(L - 2l_{\mathrm{s}}) \tag{8}$$

where

$$l_{\mathrm{s}} = l_{\mathrm{CTA^+}} \tag{9}$$

Here the length of each surfactant molecule was computed in nanometers by:[32]

$$l_{\mathrm{i}} = 0.13n_{\mathrm{C}} + 0.1704 + 2r_{\mathrm{ph}} \tag{10}$$

where n_{C} is the number of carbon atoms in the chain and r_{ph} is the radius of the hydrated polar headgroup, obtained from its contribution to the PMV. For the micellized headgroups, $\mathrm{PMV}_{\mathrm{N(CH_3)_3^+}} = 70.6 \pm 3.4$ cm^3·mol^{-1}.[33]

To obtain the aggregation number, the volume of the micelles was divided by that of the equivalent surfactant molecule, V_{s}.

4. RESULTS

Figure 1 shows an example of the obtained voltammograms. Figure 2 depicts the dependence of the peak current i_{p} on the square root of the scan rate for the same system. Figure 3 shows the uncorrected diffusion coefficients of mixed micelles at 25 °C, as a function of the mole fraction of CTAT in the overall mixed system, α_{CTAT}.

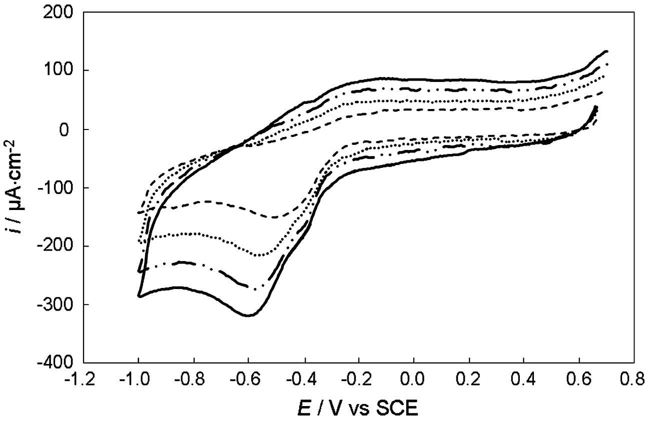


Figure 1. Voltagrams of the CTAT-F68 mixture with $\alpha_{\mathrm{CTAT}} = 0.15$; $C = 2.8 \cdot 10^{-3}$ mol·kg^{-1}, at different speeds: —, 200 mV·s^{-1}; —··—, 400 mV·s^{-1}; ···, 600 mV·s^{-1}; and ---, 800 mV·s^{-1}.

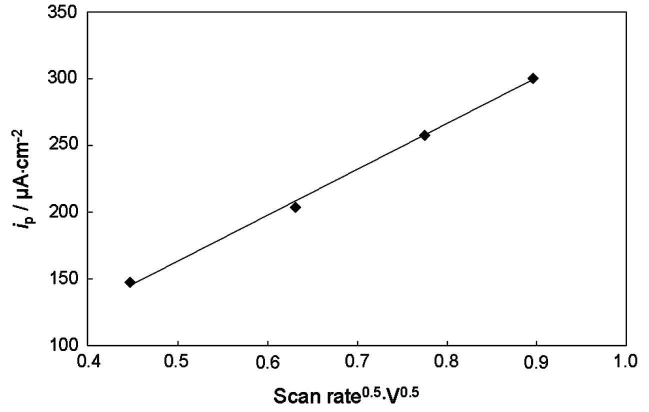


Figure 2. Dependence of the peak current i_{p} on the square root of the scan rate for the system with $\alpha_{\mathrm{CTAT}} = 0.15$; $C = 2.8 \cdot 10^{-3}$ mol·kg^{-1}.

The composition of the mixed micelles of both systems was determined in a previous work,[5] and it is shown in Table 1 of the Supporting Information. Using these data, the corrected mixed micelle's diffusion coefficient $D_{0,\mathrm{M}}$ is represented in Figure 4 as a function of the CTAT mole fraction in the mixed micelles, x_{CTAT}.

Figure 5 shows the corrected hydrodynamic radius of the mixed micelles as a function of x_{CTAT}.

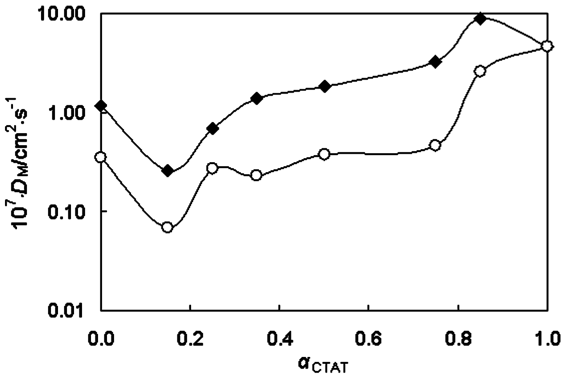


Figure 3. Uncorrected micelle diffusion coefficient of mixed micelles as a function of the mole fraction of CTAT in the overall mixed surfactant at 30 °C: ◆, CTAT-F68; ○, CTAT-F127. Curves are guides for the eye.

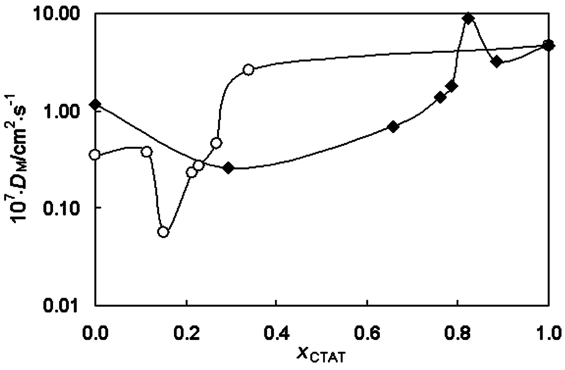


Figure 4. Corrected diffusion coefficient of mixed micelles as a function of the mole fraction of CTAT in the micelles at 30 °C: ◆, CTAT-F68; ○, CTAT-F127. Curves are guides for the eye.

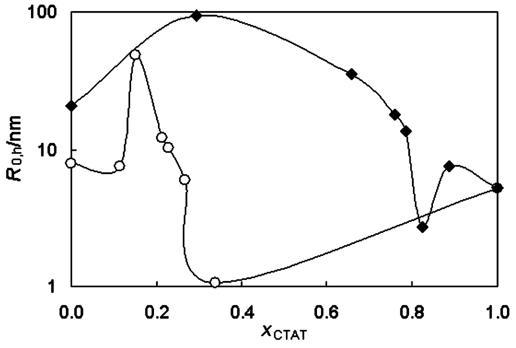


Figure 5. Hydrodynamic radius of mixed micelles as a function of the micellar mole fraction of CTAT: ◆, CTAT-F68; ○, CTAT-F127. Curves are guides for the eye.

Figure 6 shows the interaction parameter β (in k_BT units) as a function of the mole fraction of CTAT in mixed micelles, obtained from a previous work of this laboratory.[5] The interaction parameter was obtained from the CAC dependence on the composition of the surfactant mixtures, following the regular solution theory (RST),[34] by being interpreted as the excess energy of micellization. Positive values indicate an antagonism between the components in the mixed micelles, while negative values indicate the interactions are of attractive nature and a value of $\beta = 0$ indicates an ideal mixing behavior.

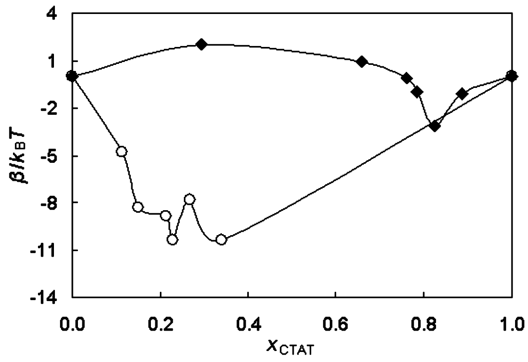


Figure 6. Interaction parameter β as a function of the mole fraction of CTAT in mixed micelles: ◆, CTAT-F68; ○, CTAT-F127. Curves are guides for the eye.

5. DISCUSSION

5.1. Pure Surfactant Results. Narayanan et al.[35] measured the diffusion coefficients of the CTAT micelles with and without the addition of KCl. An extrapolation of their results to the concentration of the surfactant here used, with the addition of 0.1 mol·dm^{-3} of KCl (the lowest concentration used by these authors), gave a value of $D_M \approx 3.50 \cdot 10^{-7}$ cm^2·s^{-1}, which is similar to our results ($4.68 \cdot 10^{-7}$ cm^2·s^{-1}). They did not compute the correction to obtain $D_{0,M}$. Kaler et al.,[36] using freeze-fracture transmission electron microscopy, found in a 0.1 wt % (0.0022 mol·kg^{-1}) solution the presence of very long micelles of 5 nm in diameter and a persistence length of about 10^4 nm. Narayanan et al.[35] found evidence of cylindrical micelles with a 5 nm diameter and 40 nm length in a 0.2 wt % (0.0044 mol·kg^{-1}) solution. They also concluded that a concentration of 0.7 wt % (0.0150 mol·kg^{-1}) is the overlap concentration, beyond which the micelles get entangled. They verified that this concentration is reduced by the addition of KCl, but the supporting electrolyte concentration used in this work was lower than the lowest used by these authors, and the micelle's diffusion coefficient we measured for CTAT micelles at twice the CMC was higher than that found by these authors for the semidilute regime in which the solution exhibits viscoelastic properties.[35] As a consequence of the above discussion, we concluded that the D_M value we measured corresponds to the nonentangled micelles, and the dimensions computed for the CTAT micelles from the corrected hydrodynamic radius ($R_{0,h}$ = 5.195 nm), that is, a micelle's radius of 2.51 nm (diameter 5.02 nm) and a length L = 13.1 nm are reasonable values. Using the CTAT partial molar volume, the aggregation number was estimated as N_{agg} = 291. At the same temperature, Mata et al.[37] determined a value for N_{agg} = 103 at the CMC and without the use of any supporting electrolyte.

It is known that the hydrodynamic radius of the micelle is an upper limit for the real micelle's radius,[38] and then the value of N_{agg} here found is also the upper limit.

On the other hand, micellar solutions of block copolymers were investigated with many different techniques, including NMR,[39−41] static and dynamic light and neutron scattering,[42,43] fluorescence spectroscopy, and small-angle X-ray spectroscopy (SAXS).[44,45] It was concluded from these measurements that the micelles are built from a core consisting of a PPO block and a corona which contains the PEO blocks. The hydrophobic core is formed by poly(propylene oxide) chains, surrounded by a shell or corona of hydrated poly(ethylene oxide) chains.[46,47]

Goldmints et al.[48] stated that the micelle's core cannot consist only of PPO units, but it must also contain significant quantities of water. The existence of some water in the PPO region, which may also include some more hydrated EO units, was also proposed by other authors.[48−50] Some techniques give the radius of the hydrophobic core (R_{HC}) and the radius of the corona (R_{corona}). Moreover, in some cases the maximum radius R_{mx} and the hydrodynamic radius R_h are given.

At 40 °C, Almgren et al.[12] determined for F68 micelles values of R_h = 4.7 nm and N_{agg} = 145. We have obtained a value of $D_{0,M} = 1.17 \cdot 10^{-7}$ cm$^2 \cdot$s^{-1}, which in turn gives a value of $R_{0,h}$ = 20.8 nm. The length of a fully extend F68 molecule is 70.2 nm; thus the $R_{0,h}$ value is compatible with an spherical micelle. Bahadur and Li[51] found that the Pluronic F68 micelles are less compact and more solvated than those formed by the more hydrophobic members of the Pluronics family. They proposed the relationship $R_h = 2.5(N_{agg})^{0.37}$, which applied to our measured value of $R_{0,h}$ gives a value of N_{agg} = 22.5. On the other hand, using the PMV$_{F68}$ value, we obtain a value of N_{agg} = 3137. As mentioned above, this value of N_{agg} is an upper limit. There may be an additional cause for this high N_{agg} value: the inclusion of a supporting electrolyte in the polyethylene palisade may charge the chains causing a stretching of them, thus increasing the hydrodynamic radius without changing the aggregation number. This kind of interaction depends on the nature of the nonionic surfactant. This was observed in Tween 20, but not in Triton X-100.[52] In this case, part of the volume of the micelles is supplied by the trapped water molecules, and then, the aggregation number computed by using the PMV$_{F68}$ value is excessively high.

Some literature data for pure F127 micelles are listed in Table 2 of the Supporting Information. For a 5 wt % (0.00397 mol·kg^{-1}) F127 solution, from small-angle neutron scattering (SANS) measurements, it is known from the literature that the micelles are spherical at moderate temperatures, and the transition to rod-like micelles occurs at $T > 90$ °C.[53]

From the data found on literature, the volume of one F127 molecule in the micelles was computed as the average of:

$$V_{M,F127} = 4\pi R_{max}^3 / 3N_{agg} \tag{11}$$

where R_{max} and N_{agg} are the maximum micelle's radius and the corresponding aggregation number, giving a average value for $V_{M,F127}$ = 50.7 nm^3. With the value of $D_{0,M} = 3.73 \cdot 10^{-8}$ cm$^2 \cdot$s^{-1}, the value of $R_{0,h}$ = 7.89 nm and from the volume of a sphere with this radius, a value of N_{agg} = 40.7 is obtained. Using the computed value for PMV$_{F127}$, we obtained a value for N_{agg} = 112. In this case, it seems that the effect of the supporting electrolyte is much less important that in the case of the F68 micelles, which may be caused by an initially more compact structure of the F127 micelles when compared with those of F68.

5.2. Mixed Surfactant Results. As discussed in the Introduction section, there are discrepancies in the literature about the structure of mixed aggregates of Pluronics and the more conventional surfactants. In some cases, the conventional mixed micelles are proposed, while in other cases it is claimed that the micelles are broken and the surfactant−Pluronic complexes appear. The interaction with the common surfactants seems to depend on the nature of both the Pluronic and the more conventional surfactant molecules. As a consequence, we have not postulated any general structure for the aggregates, and the analysis of results in mixed systems is limited to the evolution of the diffusion coefficient and the hydrodynamic radius, without the computing of any aggregation number. To obtain a better understanding of these results, these values were represented as a function of the mixed micelle's composition (x_{CTAT}, the mole fraction of CTAT in the micelles, obtained from ref 5 and given in Table 1 of the Supporting Information).

The results show that the interaction in the F68-CTAT and F127-CTAT systems is different, a conclusion which was also found by studying the critical aggregation concentration.[5] A comparison between Figures 3 and 4 with Figure 5 shows that there is a good correspondence between the evolution of $D_{0,M}$, $R_{0,H}$, and β as a function of the x_{CTAT}.

From ref 5, pure F68 micelles' structure differ only slightly of F68-CTAT mixed ones. However, the neighbors of CTAT molecules in the mixed micelles are very different from those in micelles of pure CTAT. In F68-CTAT aggregates below $\alpha_{CTAT} \approx 0.25$ ($x_{CTAT} < 0.76$) the interaction is repulsive, while it is attractive at higher CTAT contents. At $x_{CTAT} \approx 0.82$ there is a minimum in β, indicating that the maximum attraction between components occurs. When $x_{CTAT} > 0.75$, a structural transformation of aggregates occurs which differs strongly from both the pure CTAT and the pure F68 micelles.

Below $x_{CTAT} \approx 0.76$, the F68 acts as a solvent for the CTAT in the aggregates. Since in this region the activity coefficient of the F68 in the mixed aggregates, f_{F68}, is close to unity,[5] the neighbors of the F68 molecules in the mixed aggregates are only slightly different from those of the pure copolymer micelles. The values of both activity coefficients indicate that there is a low mutual solubility, which is more pronounced for CTAT. In conclusion, in this composition range F68 aggregates act as solvent with only a slight change in structure with respect to the pure F68 micelles, while CTAT molecules act as a solute whose neighbors are very different from those in pure cationic surfactant micelles. For $x_{CTAT} > 0.76$, both the neighbors of the F68 and the CTAT molecules are very different from those existing in the respective pure surfactant micelles, and there is a mutual solubility, which is higher for the CTAT than for the F68.

In the light of the comparison between β (Figure 5) and $R_{0,h}$ (Figure 4), this difference in behavior is evident, and it may be interpreted as follows: below $x_{CTAT} \approx 0.76$ the F68 micelles are slightly modified by the inclusion of the CTAT molecules, causing the increase of the $R_{0,h}$. This may be caused by a micelle swell up or a change from a spherical to a nonspherical shape. Above this composition, the micelles are probably disrupted forming complexes more or less extended, which reduces strongly the value of $R_{0,h}$. In ref 5, the complex in the minimum of β is F68:7.8CTAT. If this complex is composed by one Pluronic molecule, it might explain the strong difference between the neighbors of the F68 and the CTAT in the mixed aggregates and the pure surfactant micelles.

On the contrary, in the F127-CTAT mixtures, the interaction factor is monotonically negative indicating attraction between the components. Then, it may be concluded that the interactions in the F68-CTAT mixed aggregates and in the F127-CTAT ones are somewhat different. At all F127-CTAT proportions the aggregates' structure differs from both the pure F127 and the pure CTAT micelles. The inclusion of the CTAT molecules in the F127 aggregates alters its structure more deeply than that of the F68. The complex composition is F127:8.1CTAT.

From the analysis of the activity coefficients of components in the CTAT-F127 aggregates, it can be concluded that the neighbors of both the CTAT and the F127 in mixed aggregates are different from those in the pure component ones, that is, one cannot suppose that mixed aggregates are similar to those of one of the components having the other as a solute. From Figure 4, it seems that, for $x_{\mathrm{CTAT}} = 0.114$, the structure of the F127 micelles is not significantly affected by the inclusion of the CTAT, giving almost the same hydrodynamic radius of the pure Pluronic micelles. Mixed aggregates then strongly increase the $R_{0,\mathrm{h}}$ value when $x_{\mathrm{CTAT}} = 0.15$, which may indicate an aggregate swell up or a change from a spherical to a nonspherical shape. But above this composition there is a rapid decrease of the hydrodynamic radius, which probably reflects the destruction of the micelles and the formation of low-weight complexes.

6. CONCLUDING REMARKS

The interpretation of the evolution of the $R_{0,\mathrm{h}}$ values in both mixed systems is the same: a stronger interaction between the Pluronic and the CTAT molecules probably causes the replacement of the mixed aggregates by smaller complexes. The difference in the behavior between the two studied systems is caused by the different interaction caused by differences in hydrophobicity and sterical hindrances between the two Pluronics, as discussed in ref 5.

In spite that the measurements made in this work do not indicate the exact nature of the aggregates (i.e., mixed micelles or Pluronics-CTAT complexes), they have shown that the inclusion of the conventional surfactant causes a profound change in the structure of these aggregates. The obtained results confirm that the interaction between different Pluronics and the CTAT depends on the nature of the copolymer amphiphile and that the differences in the length of the hydrophobic and hydrophilic chains may cause different behaviors. The penetration of the cationic surfactant into the micelle core may be more or less hindered by the size and structure of the hydrophilic shell. However, once it has penetrated the corona and reached the poly(oxypropylene) core in a cooperative manner, the aggregates tend to disappear being replaced by smaller structures, probably complexes having a finite number of CTAT molecules per copolymer molecule.

This research has not concluded the study of this system. Light scattering and freeze-fracture transmission electronic microscopy experiments will probably give an exact picture of the nature of mixed aggregates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Composition of the block copolymer−CTAT mixed aggregates and literature aggregation data of pure F127 aqueous solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

E.N.S., R.E.A., and M.B. would like to thank Consejo Nacional de Investigaciones Cientificas y Técnicas de la República Argentina (CONICET) for a fellowship granted. E.N.S. and R.E.A. would like to thank the Instituto de Ingenieria Electroquímica y Corrosión (INIEC) for the laboratory and equipment used to carry out this work. This work was supported by a grant of the Universidad Nacional del Sur.

Notes

The authors declare no competing financial interest.

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