THE BEHAVIOR OF CARBOPOL 980 IN AQUEOUS SOLUTIONS OF NONIONIC SURFACTANTS. II. EVIDENCE OF COMPLEX FORMATION BY ELECTRICAL CONDUCTIVITY, STEADY-STATE FLUORESCENCE, DYE SOLUBILIZATION AND TURBIDITY MEASUREMENTS

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The effect of cross-linked PAA (Carbopol 980) on the micellization of two nonionic surfactants [polydisperse decaoxiethylene mono nonylphenyl ether ($NPEO_{10}$) and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock-copolymer ($EO_{76}PO_{29}EO_{76}$, Pluronic F68, F68)] is investigated by electrical conductivity, static fluorescence, dye solubilization and turbidity. In the Carbopol-surfactant systems the conductivity decreases at a surfactant concentration below the critical micelle concentration (CMC), passes through a minimum and then increases. Static fluorescence indicates that the polymer-bound aggregates have similar micropolarity as the surfactant micelles, and the F68 aggregates bound to polymer are more hydrophobic than those of $NPEO_{10}$. The Carbopol-F68 solubilizes higher amounts of oleophilic dye than the Carbopol-$NPEO_{10}$ mixtures. Unlike the surfactant solutions, those containing Carbopol become turbid above a threshold surfactant concentration. These peculiarities demonstrate that Carbopol interacts with the investigated nonionic surfactants and the formed complexes are explained by the interplay between the hydrogen and the hydrophobic bondings.

INTRODUCTION

Aqueous systems of ethoxylated nonionic surfactants (C_iEO_j) and linear poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMA) have been thoroughly investigated by a score of methods including viscosity, surface tension, calorimetry, potentiometry, spectrophotometry, dye solubilization, static and dynamic fluorescence, ellipsometry, NMR, SAXS, rheometry, photon correlation spectroscopy, etc.[1-17] In the case of PAA, the main findings of these studies are: The onset of binding occurs at lower C_iEO_j concentrations with increasing i.[7,8,10,11-13,15] The binding is slightly dependent on j,[8,13] and independent of temperature.[3] The polymer-bound surfactant clusters have smaller aggregation numbers than the surfactant micelles,[10] and the polymer wraps the surfactant aggregates.[10]

Comparatively, the information available on systems containing cross-linked PAA (Carbopol) and ethoxylated nonionic surfactants is less numerous.[1,18,19] Our previous data of surface tension, viscosity and pH on aqueous mixtures of Carbopol 980 and polyethoxylated nonylphenol ($NPEO_{10}$) or polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) triblock-copolymer (Pluronic F68; F68) proved the existence of polymer-surfactant (PS) complexes and allowed to identify the critical points of the interaction.[1] Here, we present the results obtained on the same systems by electrical conductivity, static fluorescence, dye solubilization and turbidity. The objective of this study is to obtain information at the molecular level, about the role of hydrophilic and hydrophobic forces in the interactions between the cross-linked PAA and nonionic surfactants. There is also important to

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identify the peculiarities generated by the hydrophobic part of the surfactants, which is the nonylphenyl radical for $NPEO_{10}$ and the poly(propylene oxide) for Pluronic F68. The gathered information is a useful means to selecting the appropriate polymer-surfactant mixture for pharmaceutical formulations.

EXPERIMENTAL

Carbopol 980 and the nonionic surfactants were the same as previously used.[1] Pyrene with purity greater than 99 % was purchased from E. Merck, Germany and used as received. Yellow OB (Wako Pure Chemicals Co, Japan) was purified by three re-crystallizations from methanol. Solutions were prepared with Millipore water obtained from a Simplicity UV Millipore apparatus. In the polymer-surfactant systems, the polymer concentration was kept constant at 0.1 % (wt.) and the surfactant concentration was changed from 10^{-5} to 20 % (wt.). All the measurements were done at $25 \pm 0.1°C$.

The electrical conductivity measurements were carried out on a Hanna HI 9033 conductometer. The static fluorescence measurements were made with a Fluoromax 4P spectro-fluorimeter, Horiba-Jobin-Yvon. Pyrene was excited at 340 nm and the slits were set at 5.8 nm (excitation) and 2.0 nm (emission). The emission spectra were recorded in the 350 - 550 nm range. The turbidities of the polymer-surfactant mixtures were measured at 716 nm with a Varian - Cary 100 Bio spectrophotometer. The solubilization experiments were done by adding excess dye into screw-capped vials containing surfactant or polymer-surfactant mixture. The mixtures were kept three weeks in dark with occasional stirring to attain equilibrium. The excess dye was removed by centrifugation and the supernatant absorbance was measured at 440 nm.

RESULTS

Figure 1 presents the variation of electrical conductivity against the surfactant concentration in the absence and presence of Carbopol. In polymer-free systems, the conductivity is very small and does not change until the surfactant concentration reaches a threshold value, when it starts increasing. The point indicates the onset of surfactant aggregation and the measured critical micellar concentration (CMC) is 6×10^{-3} % (wt.) for $NPEO_{10}$ and 1×10^{-2} % (wt.) for F68. The values are comparable with those previously obtained by us by surface tension measurements.[1]

In the presence of Carbopol, the electrical conductivity increases being of 39 μS/cm for $NPEO_{10}$ and of 48 μS/cm for F68. Minute additions of surfactants do not change the above mentioned values of conductivities that remain in both cases constant. The plateau ends at 8×10^{-3} % (wt.) for $NPEO_{10}$ and at of about 6×10^{-3} % (wt.) for F68 when the conductivity decreases. These values are shown in Table 1 and represent the critical aggregation concentrations (CAC or T_1). They match the previously determined values by surface tension, viscosity and pH measurements.[1] Because our PS systems have several critical points of interaction, we adopted the T_n denomination.[20] The conductivity decline ends at 8×10^{-2} % (wt.) for $NPEO_{10}$ and at 8×10^{-1} % (wt.) for F68. These concentrations denoted by T_2 represent the polymer saturation with surfactant, beyond which further addition of surfactant gives only regular micelles.
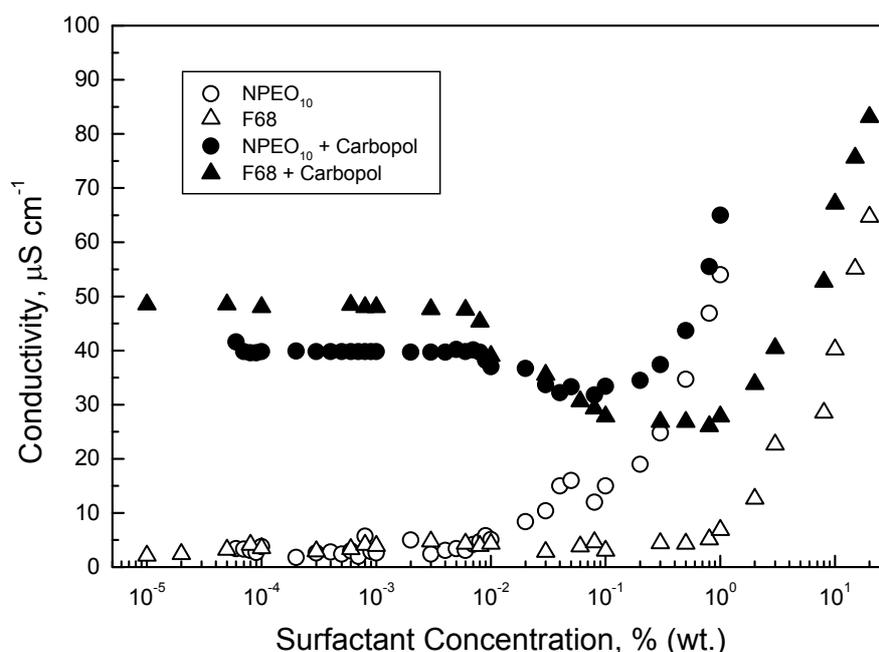

Fig. 1 – Conductivity of aqueous solutions of surfactants in the presence and absence of Carbopol, at 25 °C.

In systems that self-assembly like those of surfactants, polymer-surfactant aggregates, etc. the hydrophobic microdomains are evidenced with the aid of molecular probe. The probes are dyes or fluorophores whose properties depend on the polarity of the surrounding medium.[21] We used pyrene as probe because in its monomeric emission spectrum, the intensity of the first peak (I_1, $0 \rightarrow 0$ band) enhances significantly with the solvent polarity whereas the third peak (I_3, band $0 \rightarrow 2$) is not affected.[22-24] Therefore, the I_1/I_3 ratio measures the solvent polarity and is called polarity index (PI). PI equals 1.9 – 2.0 in polar solvents and 0.5 – 0.6 in hydrocarbons.[24] In surfactant micelles, I_1/I_3 takes values of 1.2 – 1.4.[25]
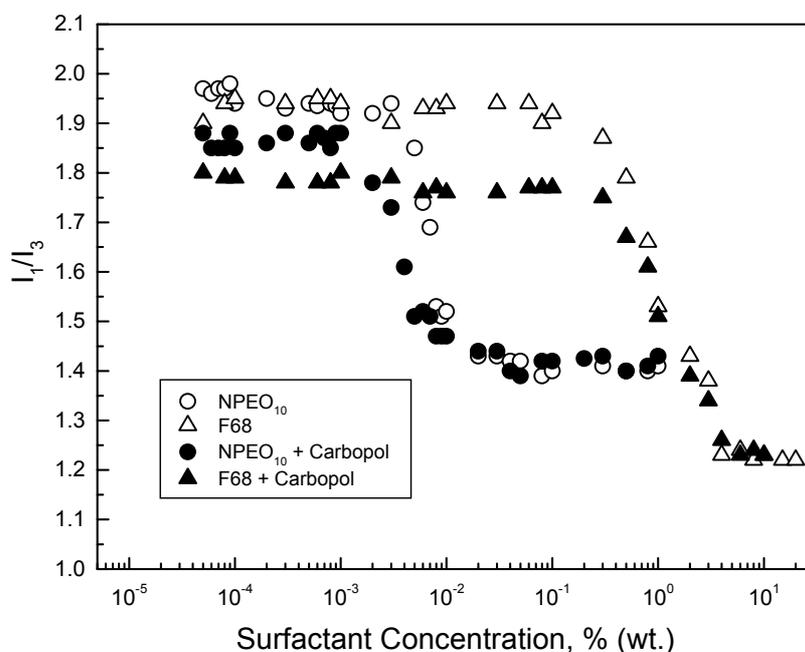

Fig. 2 – Changes in the ratio I_1/I_3 of Py emission as a function of surfactant concentration in the presence and absence of Carbopol, at 25 °C.

Figure 2 shows the variation of I_1/I_3 as a function of surfactant concentration in our systems. In surfactant solutions, at minute surfactant levels, the ratio is constant and describes a plateau. The high I_1/I_3 values show that pyrene is located in water. At a certain surfactant concentration, the polarity index decreases abruptly to reach a lower plateau at higher surfactant concentrations. The concentrations where I_1/I_3 begins decreasing are 3×10^{-3} % (wt.) for NPEO$_{10}$ and 1×10^{-1} % (wt.) for Pluronic F68. They stand for the CMC values and are also included in Table 1. In the post-micellar region, I_1/I_3 decreases more precipitously for NPEO$_{10}$ than for Pluronic F68. However, the plateau at high surfactant concentrations is at lower I_1/I_3 values for F68, and infers more hydrophobic aggregates than those of NPEO$_{10}$.

For the PS mixtures the curves depicting the evolution of fluorescence curves have similar shape, but the polarity indexes are smaller in the region of low surfactant concentrations and attest that pyrene is hosted in a less hydrophilic medium

(see Figure 2). We took the surfactant concentration that marks the decrease of I_1/I_3 as the T_1 critical point determined by fluorescence and the values obtained are given in Table 1. The surfactant concentration where the I_1/I_3 curve of PS merges the curve of surfactant alone marks the polymer saturation with the surfactant, and the resulting T_2 data are summarized in Table 1. An interesting feature of Figure 2 is the lower I_1/I_3 values recorded in the micellar area for the systems containing F68 in comparison with NPEO$_{10}$. The result points out that F68 makes more hydrophobic micelles than NPEO$_{10}$, which is difficult to admit and will be subsequently discussed.

Figure 3 presents the variation of Yellow OB absorbance at 440 nm as a function of surfactant concentration in the absence and presence of Carbopol 980. For the polymer-free systems, the absorbance is constant until a certain surfactant concentration is reached. Then, the absorbance begins to increase, which proves that the surfactants solubilize the dye only when they are

associated in micelles. In the polymer-surfactant systems, the absorbance has a similar trend. We took the point at which the absorbance starts increasing as the beginning of surfactant aggregation onto the polymer (T_1). It corresponds to the formation of surfactant aggregates onto the polymer, which have the capability to solubilize the hydrophobic dye. The data in Figure 3 also indicate that $NPEO_{10}$ has a higher capacity to solubilize dye than the PS mixture. Such a

behavior was also found in the case of Yellow OB solubilized in the systems of $NPEO_{10}$ or $C_{12}EO_5$, and PAA.[6] At the same time, the Carbopol-F68 solubilizes higher amounts of dye than F68 alone, but smaller than the Carbopol-$NPEO_{10}$ does. Such a situation aroused previously in systems of PAA and $OPEO_{20}$ or $NPEO_{20}$, and was attributed to the enhanced capacity of dye solubilization conferred to the PS complexes by the surfactants with longer PEO chains.[6]

Table 1

The values of CMC, T_1 and T_2 at 25 °C

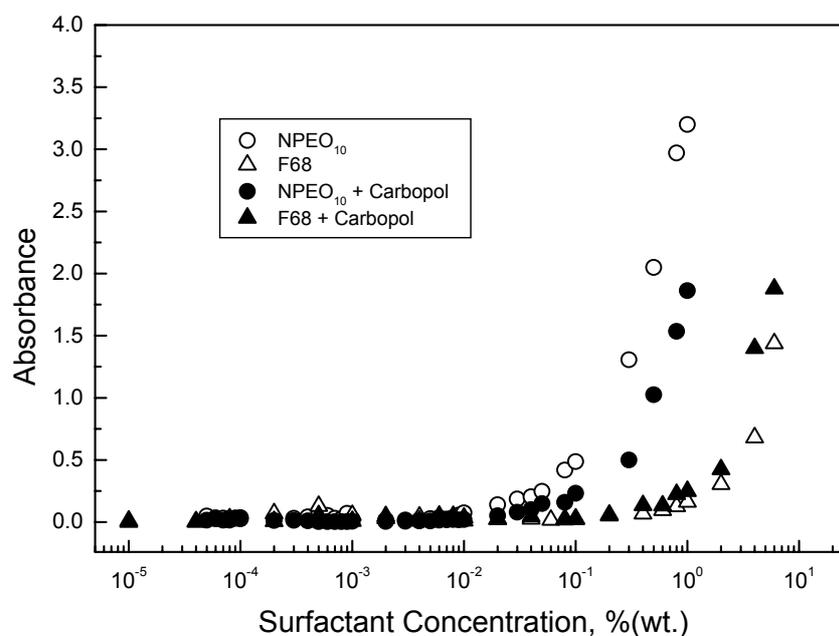| Method	CMC, % (wt.)		T_1, % (wt.)		T_2, % (wt.)	
	$NPEO_{10}$	F68	$NPEO_{10}$	F68	$NPEO_{10}$	F68
Electrical Conductivity	1×10^{-2}	1	8×10^{-3}	6×10^{-3}	8×10^{-2}	8×10^{-1}
Fluorescence	3×10^{-3}	1×10^{-1}	1×10^{-3}	2×10^{-2}	5×10^{-2}	4
Dye solubilization	1×10^{-2}	6×10^{-1}	1×10^{-1}	8×10^{-1}	-	-
Transmittance	-	-	1×10^{-2}	4×10^{-3}	1×10^{-1}	1×10^{-1}

Fig. 3 – Yellow OB absorbance as a function
of surfactant concentration in presence and absence of Carbopol, at 25 °C.

For surfactants with small ethoxylation degrees, which solubilize the dye in the nonpolar micellar core, the Yellow OB solubilization is higher in the absence of polymer. This is in accord with the results attesting that the PAA-bound micelles of nonionic surfactants are smaller than the free micelles,[10] and solubilize smaller amounts of hydrophobic dye.[26]

Figure 4 presents the data of optical transmittance as a function of surfactant concentration for the Carbopol-$NPEO_{10}$ and Carbopol-F68 mixtures. In the

diluted regime, the mixtures are clear, having a very high and almost constant transmittance. Above 1×10^{-2} % (wt.) of $NPEO_{10}$ and 4×10^{-3} % (wt.) of F68 the solutions become turbid. This means that the surfactants interact cooperatively with the PAA and the process is so strong that produces phase separation. The respective surfactant concentrations were assigned to T_1 and the values are included in Table 1. Figure 4 shows the utmost turbidity for both PS systems at a surfactant concentration of about 1×10^{-1} % (wt.). Thereafter, the turbidity decreases. The

surfactant concentration at which the transmittance no longer decreases is consistent with the minimum recorded in the viscosity measurements (T_v) and corresponds to the saturation of polymer with the surfactant.[1] For the investigated polymer-surfactant mixtures, the transmittance curve as a function of surfactant concentration correlates well with the physical aspect of the systems after leaving them to attain equilibrium by setting. We observed that the

sediment was very dense at a surfactant concentration around 1 x 10^{-1} % (wt.), and became fluffy in excess of surfactant. These results confirms that the phase separation associated with the PS complex formation, initially observed in linear PAA-ethoxylate mixtures,[2-6] is present in systems containing the same surfactants but grafted PAA.
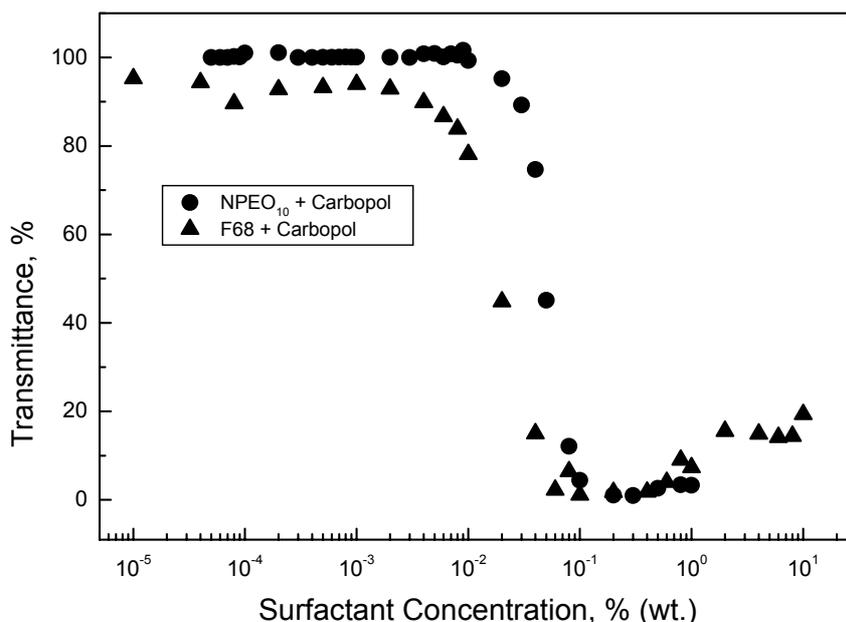

Fig. 4 – Plots of the optical transmittance as a function
of surfactant concentration in presence of Carbopol, at 25 °C.

DISCUSSION

As shown in Results, addition of Carbopol to surfactant solutions brings about behaviors specific to every surfactant, reflected in the data presented in Figures 1 – 4. In this respect, it is useful to discuss first the peculiarities of NPEO$_{10}$ and F68. Both are nonionic and water-soluble surfactants, having similar hydrophile, and different hydrophobe groups. The hydrophobe of NPEO$_{10}$ is the nonylphenyl radical, whereas the one of Pluronic F68 is the poly(propylene oxide) (PPO) chain, a nonhydrocarbon hydrophobe. Nonylphenol is obtained by phenol alkylation with iso-nonene, being a complicated mixture of isomers both in the alkyl chain and in the position of substitution. Another problem arises from the large number of oligomers in the PEO hydrophilic part. For example, it has been unveiled that NPEO$_{10}$ has 20 oligomers in the PEO chain with ethoxylation degrees from 2 to 21.[27] These peculiarities are reflected by the hydrophobicity parameters,[28,29] the

thermodynamic properties,[30] and the partition coefficients of NPEO$_{10}$ between two non-miscible phases.[31] As for the Pluronics, being synthetic polymeric molecules, they are polydisperse both in the overall size and in the ratio of the block sizes. In addition, they contain PEO-PPO diblock impurities of high hydrophobicity. For example, it has been proved by size exclusion chromatography that the impurities may amount to as high as 26 % (wt.).[32] To make matters worse, the polydispersity of a given Pluronic is most likely batch dependent, a fact which may explain the often cited observation that CMC, the critical micellization temperature (CMT), and other properties are hardly reproducible. Therefore, we have to take into account these facts when discussing the obtained results.

The conductivity and turbidity data presented in Figures 2 and 4 for the PS mixtures show a plateau at low surfactant concentrations. Increasing the surfactant concentration, the plateau is followed by a zone of decrease and another of increase and a

minimum appears in-between. The decline is coincident with the viscosity drop, the increase of pH and the starting point of the surface tension plateau previously observed in these systems.[1] It is related to the CAC or T_1 and corresponds to the beginning of surfactant binding to the Carbopol. The minimum of conductivity appears in the zones of maximum turbidity, and corresponds to T_2 in the surface tension and pH curves and to the T_v of viscosity.[1,19] At T_1, the Carbopol starts shrinking as a result of surfactant binding in a micellar-like state induced by the hydrogen bondings between the PEO moiety and the carboxyl groups of the polymer.[33] This process is accompanied by a concomitant increasing of turbidity, which reaches the apex at T_2, and the viscosity is at the bottom.[1,8,11,13,15,17,19] It is considered that at T_2, almost all the binding sites of the polymer are saturated with micelle-like aggregates, and the extra surfactant added into system forms only free micelles.[8,11,13-15] In this situation, the residual binding sites of the polymer interact with the free micelles and form large network complexes. This produces the increase of viscosity, the release of hydrogen ions and the growth of conductivity. However, the coexistence of complexes and free micelles is not precluded at this stage because both are energetically similar.

The data in Figure 2 show that the polarity index decreases more precipitously for $NPEO_{10}$ than for F68. The phenomenon is connected with the cooperative aggregation of the surfactant, which is stronger for $NPEO_{10}$. In polymer-surfactant systems, the Carbopol promotes surfactant aggregation onto its binding sites, and T_1 is lower than CMC. The slope of I_1/I_3 vs. surfactant concentration is smaller in presence of Carbopol, and suggests that the polymer decreases the cooperativity of binding. Another aspect that needs explication is the lower polarity index values recorded in F68 micellar systems relative to those of $NPEO_{10}$ (See Figure 2). They are difficult to accept because the hydrophobic part of F68 contains oxygen and should be more hydrophilic than the nonylphenyl radical of $NPEO_{10}$. To explain this, we measured the emission of pyrene fluorescence in pure poly(propylene glycol) 2000 (PPG 2000). PPG 2000 has 34 monomer units, which is close to 30, the average number of PO units in the molecule of F68. The obtained I_1/I_3 value was of 1.19, being practically equal to 1.20 obtained in F68 micelles. This result attests that the core of F68 micelle has the same polarity as the

pure PPG 2000. Because PPG 2000 is not miscible with water, one may conclude that the micellar core of F68 does not contain water. At the same time, there are NMR,[34,35] FT-Raman,[36] ATR-FTIR,[37] and high sensitive DSC[38] data proving that micellization of Pluronics entails dehydration of the PPO blocks. Therefore, the micelles of F68 have a less polar core than the micelles of ethoxylated fatty alcohols or alkylphenols. On the other hand, it has been shown that medium chain-length aliphatic alcohols,[39] and hydrophobic drugs,[40] promote micellization in aqueous Pluronic solutions at temperatures well below the CMT. Taking into account these data and the high hydrophobia of pyrene, one may assume that pyrene also induces the aggregation of Pluronic F68 unimers and assists the formation of polymeric micelles. This assumption may explain the data in Figure 2, but needs further work to confirm it.

The surfactants used in this study have the PEO chain as hydrophile and it is expected to interact similarly with Carbopol. However, the obtained results show differences, and we will try to explain them. Complex formation between PEO and poly(carboxylic acid), *i.e.*, PAA, PMA, etc., has been observed long time ago,[41] and rationalized in terms of hydrogen bondings between the oxygens of the PEO chains and the hydrogens of the carboxylic groups. To form stable complexes with PAA and PMA, the PEO chain has to have at least 200, and respectively 40 units. This points out the important role played by the hydrophobic interactions in the process of complexation. In PAA-ethoxylated nonionic surfactant systems, the key role of hydrophobic interaction is more evident since a very short chain of 6 PEO units is needed to produce complexes.[8] This scenario holds true for the present situation of Carbopol-$NPEO_{10}$. The case of Carbopol-Pluronic is different because this surfactant has two kinds of oxygen atoms.[9] The oxygen atoms of the PEO chains are hydrophilic, but those of the PPO groups are hydrophobic. The hydrophilic oxygens interact with the carboxylic groups by hydrogen bondings, like $NPEO_{10}$ does. The hydrophobic oxygens interact with the hydrogen atoms of the CH_2 groups. Although the hydrophobic part of Pluronics is different of the alkyl or alkylaryl group of the classical nonionic surfactants, they interact strongly with Carbopol as witnessed by our data. It is also important to notice that in a series of Pluronics with different PEO/PPO ratios, the stability and the bio-adhesive properties of the PAA-Pluronic complexes are the

highest for the Pluronics with high PEO and PPO content.[9] This result emphasizes the importance of hydrophobic and hydrophilic forces in designing PS systems for pharmaceutical applications.

CONCLUSIONS

The present study shows that Carbopol 980 and Pluronic F68 or NPEO$_{10}$ form complexes at a certain surfactant concentration. Measurements of electrical conductivity, static fluorescence, dye solubilization and turbidity put into evidence several break points. These discontinuities, assigned to the critical points of interaction, agree well to each other, and with previous results obtained by surface tension, viscosity and potentiometry. The static fluorescence results prove that the Carbopol-Pluronic complexes have a more hydrophobic inner core than the Carbopol-NPEO$_{10}$ counterparts. The amount of dye solubilized by the surfactants alone is higher for NPEO$_{10}$ than for Pluronic F68, a situation that reverses in the presence of Carbopol. The PS systems undergo phase separation, a phenomenon initiated by hydrogen bondings and reinforced by hydrophobic interactions. These findings are helpful to advancing the knowledge on phenomena governing the interaction between polymers and surfactants, as well as to produce custom-tailored nanomaterials for development of new drugs.

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