Poly(acrylic acid) microgels (carbopol® 934)/ surfactant interactions in aqueous media Part II: Ionic surfactants

R. Barreiro-Iglesias, C. Alvarez-Lorenzo, A. Concheiro*

Departamento de Farmacia y Tecnología Farmacéutica, Facultad de Farmacia, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Abstract

The interaction of sodium dodecylsulfate (SDS) or benzalkonium chloride (BkCl) with carbopol microgels (0.25% (w/w)) in water was studied through pH, trasmittance, viscosity, surface tension, conductivity, fluorescence, oil solubilization, and microcalorimetry measurements. In the case of the anionic surfactant, enthalpy-driven hydrophobic absorption of SDS into carbopol microgels began when SDS concentration reached 0.05–0.08% and ended around 0.6%. These concentrations were estimated as the critical aggregation (cac) and saturation binding concentration, respectively. The hydrophobic absorption of the surfactant accompanied by its counter-ion caused carbopol microgels to swell and promoted the occurrence of bridges among several carbopol microgels. As a consequence, the consistency of the dispersions increased significantly. Above binding saturation, further addition of SDS produced a shielding effect among the anionic charges of carbopol and its dehydration, which was shown as a decrease in the viscosity of the dispersions. At low shear rates, the dispersions behaved as pseudoplastic owing to orientation of carbopol/SDS aggregates in the flow direction. Increasing shear rates caused the inter-microgel bridges to break, the water layer surrounding them to diminish, and the system to show a shear-thickening behavior. In contrast, carbopol/BkCl aggregates showed shear-thickening flow in the whole range of shear rates analyzed. Electrostatic interactions between BkCl and carbopol carboxylic groups release protons to the medium and decrease the internal osmotic pressure of the microgels. This may favor the establishment of hydrophobic interactions among surfactant tails, and induces carbopol microgels to collapse. The cac was approximately 0.01% BkCl. Saturation binding occurred at 0.3–0.5%, indicating that only 25–40 mol% carboxylic groups were neutralized with BkCl. The shrinking of carbopol microgels as BkCl is absorbed prevents additional surfactant molecules from interacting with the remaining carboxylic groups. Microcalorimetry assays revealed that the aggregation process occurred with a strong gain in enthalpy.
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1. Introduction

Volume-phase transitions in slightly cross-linked polymer networks can be induced by the presence of surfactants in the medium, which may interact with the polymer through hydrophobic or electrostatic forces (Philippova et al., 1996; Sokolov et al., 1996; Philippova et al., 1998; Mironov et al., 1999; Hansson et al., 2000; Sjöström and Piculell, 2001). When a nonionic gel is added to a solution of ionic surfactant, polymer/surfactant hydrophobic interaction

* Corresponding author. Fax: +34-981-547148.
E-mail address: ffancon@usc.es (A. Concheiro).

favors polymeric associations, which induce the gel to shrink, and simultaneously adds ionic groups to the networks, which induces the gel to swell. Additionally, an excess of free ionic surfactant acts as a salt increasing the ionic strength of the medium. The balance of these three factors determines the final degree of swelling or shrinking of the gel (Sjöström and Piculell, 2001). In the case of polyelectrolyte gels, the absorption of a similarly charged surfactant is favorable when hydrophobic interactions overcome the electrostatic repulsion between charged groups (Philippova et al., 1996). Low proportions of surfactant may swell the gel by an increase in its internal osmotic pressure, while for high surfactant concentrations, the salt effect may be predominant. In contrast, in the case of opposite charged gel/surfactant systems, both hydrophobic and electrostatic forces contribute to the interaction. The critical aggregation concentration (cac) is usually lower than in the other cases, and much lower than the critical micellar concentration (cmc). An ion-exchange reaction of surfactant with polymer counter-ions results in gel shrinkage. Despite these general tendencies, the conformation, flexibility and hydrophobicity of the chains, and the local environment of the ionic groups in the gel and surfactant, exert a strong influence on the structure and stoichiometry of the complex (Sokolov et al., 1996; Mironov et al., 1999; Sjöström and Piculell, 2001). In consequence, gel response is difficult to predict.

Surfactant-induced gel phase transitions may also be explained considering the binding mechanisms of surfactants with linear polymers. Association of poly(acrylic acid) or other anionic acrylic polymers with cationic surfactants, such as alkyltrimethylammonium bromide surfactants (C_nTAB with $n = 10$–16) or alkylpyridinium ions, has been extensively studied, using surfactant-selective electrodes, surface tension, fluorescence probes, and viscometry (Kiefer et al., 1993; Oliveira et al., 1996; Kogej and Skerjanc, 1999; Olea et al., 2000; Schillén et al., 2000). Studies performed in pH buffering systems (Shimizu, 1994; Katsuura et al., 2001) or at constant polymer charge density controlled by salts (Kiefer et al., 1993) have shown that the cac is lower for degrees of ionization below 0.4, which for an expected electrostatic interaction was somehow surprising. This observation was attributed to changes in the conformation of the polymer chains. At low pH, the degree of dissoci-

ation of the carboxylic acid groups is low and the polymer adopts a coiled conformation, while at high pH, the chain expands as a result of intrapolymeric electrostatic repulsions. The polymer appears more hydrophobic when the chain is in a compact conformation, which favors hydrophobic interactions with the surfactant. In the coiled conformation, two- or three-dimensional interactions among the hydrocarbon tails of bound surfactants become possible, which seem to be able to compensate for the weaker electrostatic stabilization of the aggregates (Kiefer et al., 1993; Katsuura et al., 2001). As a consequence, the beginning of the association is favored for copolymers of hydrophobic co-monomers (Oliveira et al., 1996) and surfactants with longer alkyl tails (Schillén et al., 2000) that also lead to coiling of the polymer (Wang et al., 2001). On the other hand, the total amount of binding, defined as the fraction of charges on the polymer chain that is occupied by surfactant ions (Kogej and Skerjanc, 1999), increases as the degree of ionization increases. Degree of ionization is also raised by the binding of the surfactant, owing to a counter-ion exchange mechanism (Fundin et al., 1997). At pH 6.8 or above, the interactions are mainly electrostatic and all cationic surfactants bind similarly irrespectively of their hydrophobicity (Schillén et al., 2000). When neutralization is complete, the complex adopts a tightly packed conformation, which is usually insoluble in water. Finally, if there is an excess of surfactant, the aggregates may be swollen because of ionic repulsions among the charged groups of the surfactant or micelle solubilization of hydrophobic aggregates (Moriyama et al., 2000; Schillén et al., 2000; Mylonas and Satikos, 2001; Wang et al., 2001).

Association of poly(acrylic acid)s with anionic surfactants is weaker than for cationic surfactants, and its effect less pronounced (Maltesh and Somasundaran, 1992; Bromberg et al., 2000). A sensitive technique such as titration microcalorimetry has shown that the electrostatic repulsions can in fact be easily overcome by hydrophobic interactions, especially in the presence of salts in the medium and if the surfactant is double-tailed. Even in the case of single-tailed surfactants, polymer interaction is slightly exothermic suggesting that the polymer stabilizes the surfactant micelles (Kevelam et al., 1996).

The practical interest of surfactant-induced phase transition is especially important in the case of

microgels constituting colloidal systems, in which the swelling/collapse of the microgels is responsible for the behavior of the whole system, especially its rheological properties (Lin and Sung, 2000; Barreiro-Iglesias et al., 2001; Gilányi et al., 2001). In two previous papers, we reported the strong effect that the addition of 0.01–0.50% ionic and nonionic surfactants exerts on the macro- and micro-viscosity of concentrated carbopol dispersions (Barreiro-Iglesias et al., 2001), and analyzed the binding process for two nonionic surfactants in dilute dispersions (Barreiro-Iglesias et al., 2002). In this paper, a systematic study of carbopol interactions with sodium dodecylsulfate (SDS) and benzalkonium chloride (BkCl) is presented.

2. Experimental

2.1. Materials

Carbopol® 934NF (62.6% carboxylic groups, molecular weight 3×10^6 Da) was provided by BF-Goodrich Europe, UK. Benzalkonium chloride (BkCl) and sodium dodecylsulfate (SDS) were from Sigma. Orange OT and pyrene were from Aldrich Chemical Co. Ultrapure water obtained by reverse osmosis (resistivity > 18.2 MΩ cm; MilliQ®, Millipore Spain) was used. The other chemicals were of analytical grade.

2.2. Preparation of carbopol/surfactant dispersions

Carbopol/surfactant samples were prepared by mixing, under stirring, concentrated carbopol and surfactant aqueous solutions at the appropriate ratio, and dilution with ultrapure water to obtain a constant carbopol concentration (0.25% (w/w)) and a wide range of surfactant concentrations (0.001–2.0% (w/w)). The samples were left to stand at room temperature at least 24 h before measurements. All subsequent experiments were carried out in triplicate at 298.0 K.

2.3. Characterization of carbopol/surfactant dispersions

Cloudiness, pH, viscosity, conductivity, dye solubilization, and steady-state fluorescence measure-

ments were carried out as described elsewhere (Barreiro-Iglesias et al., 2003).

2.3.1. Surface tension

Surface tension measurements were taken following the platinum ring method using a Lauda Tensiometer TD1 (Lauda-Königshofen, Germany) applying the needed density corrections. The concentration of surfactant at the interface (Γ) in the presence and absence of polymer was estimated applying the modified Gibbs adsorption equation (Rosen, 1989):

$$d_\gamma = -RT\Gamma d \ln C \tag{1}$$

in which γ is the surface tension (mJ/m²) of a surfactant solution of molar concentration C, R is the gas constant (8.31 J/mol K), T is the absolute temperature, and Γ is the surface excess of surfactant molecules or the concentration of surfactant at the interface (mol/1000 m²). From the surface excess concentration, the area per molecule at the interface, in square angstroms, was calculated as follows:

$$A_s = \frac{10^{23}}{N\Gamma} \tag{2}$$

where N is Avogadro's number. Adopting the phase separation model for the aggregate formation, the strength of the interaction with carbopol was estimated as the free energy per mole of surfactant for the reaction: free micelle $\leftrightarrow$ polymer-bound micelle, as follows (Wang et al., 1997; Singh and Nilsson, 1999):

$$\Delta G_i = \Delta G_{agg} - \Delta G_{mic} = (1 + K_c)RT \ln(cac/cmc) \tag{3}$$

where K_c is the effective micellar charge fraction, which is about 0.85 for both surfactants (Wang et al., 1997), cac is the critical aggregation concentration, and cmc is the critical micellar concentration of the surfactant estimated by the techniques described above.

2.3.2. Rheology

Rheological behavior of 0.25% carbopol dispersions in the absence and presence of different ionic surfactant concentrations (0.001–2.0%) was evaluated in triplicate at 298.0 K in a Rheolyst AR-1000N rheometer (TA Instruments, Newcastle, UK) equipped with an AR2500 data analyzer, a thermostatted

concentric-cylinder adapter and a medium coaxial cylinder-recessed end. Ostwald's equation was fitted to the flow curves:

$$\eta = m\dot{\gamma}^{n-1} \tag{4}$$

where η represents viscosity, $\dot{\gamma}$ is the shear rate, m is the consistency index, and n is the fluidity index. When different patterns of rheological behavior were observed in the same rheogram, the cycle was subdivided into different ranges that were analyzed separately, disregarding the former and the following regions, using AR2500 software.

2.3.3. Titration microcalorimetry

Calorimetric experiments were performed in duplicate using a Tronac-450 isoperibol microcalorimeter and Tronac FS101 calorimetry software (Tronac Inc., Orem, Utah), as described previously (Barreiro-Iglesias et al., 2003). Briefly, in each experiment, a 47.5-ml carbopol solution with a concentration of 0.25% (w/w) was placed in a dewar reaction vessel, and a relatively concentrated surfactant solution (15%) was loaded into a 2 ml calibrated buret. The entire assembly was then immersed in a constant temperature water bath (298.0 K). After thermal equilibration, the surfactant solution was delivered at a constant rate of 0.3332 ml/min into the reaction vessel, in which a stirrer mixed the two solutions rapidly. The rise or decrease in the temperature of the system was monitored using a thermistor, and later reproduced using a heating coil in the reaction vessel. The apparent enthalpy was calculated from the applied current and voltage and the heating time. As a blank, a diluted HCl aqueous solution (pH 3) was used instead of carbopol dispersion. The enthalpy of carbopol dilution (final concentration was 3% lower) was negligible. The integral binding heat for the polymer/surfactant aggregation (Q_{agg}) process was estimated by subtracting from the measured heat produced by addition of surfactant to the carbopol dispersion (Q_p), the heat effects due to the dilution/demicellization of the surfactant in the HCl aqueous solution used as a blank (Q_d) and due to the change in the ionization degree of carbopol carboxylic groups (Q_{ion}) (Eatough et al., 1974).

$$Q_{agg} = Q_p - Q_d - Q_{ion} \tag{5}$$

From the integral heats of the reaction at different times, in the surfactant concentration range where the interaction with the polymer begins (at least 10 points were used), K_{agg} (the apparent binding equilibrium constant), ΔH_{agg} and ΔG_{agg} were estimated using FS101 software, by iterative convergence applying the least squares technique (Eatough et al., 1974).

3. Results and discussion

3.1. Carbopol/anionic surfactant systems

Carbopol/SDS aqueous dispersions were in general homogeneous and only at around 0.4–1.0% SDS a slight cloudiness was observed (Fig. 1A), which can be related to the appearance of aggregates or surfactant micelles in the medium, as indicated by the surface tension pattern (Fig. 1C). SDS cmc in pure water was around 0.2–0.3% (Figs. 1C and D), which is in accordance with previously reported values (Mujerkee and Mysels, 1971; Blokhus and Klokk, 2000). The minimum in the surface tension plot may be caused by the presence of traces of impurities. In the presence of 0.25% carbopol, which presents some surface activity (60 mN/m), surface tension plot versus surfactant concentration (Fig. 1C) showed an initial lower slope, a shift in the minimum of surface tension towards lower SDS proportions (0.06%), a subsequently significant increase (with a maximum at 0.2% SDS), and, finally, surface tension values overlap the free SDS pattern for concentrations above 0.6%. The initial decrease in surface tension might be attributed to an increase in the ionic strength of the medium caused by carbopol, but this would not explain the rise around 0.2%. The pattern is typical of an interacting surfactant/polymer system, in which SDS molecules are drawn into the bulk solution as they adsorb onto carbopol. Table 1 shows a decrease in the number of SDS molecules per unit area at the air/water interface. The area per molecule obtained for SDS in pure water agreed well with the values reported in the literature (Goddard, 1993).

The cac can be regarded as the SDS concentration at which surface tension begins to rise (0.06%), while saturation binding is reached when surface tension values again decrease to those observed with SDS in water (0.6%) (Fig. 1C). Conductivity plots (Fig. 1D) confirm this tendency, presenting two inflexion points at the cac and saturation binding concentration, respectively. The conductivity of SDS/carbopol dispersions
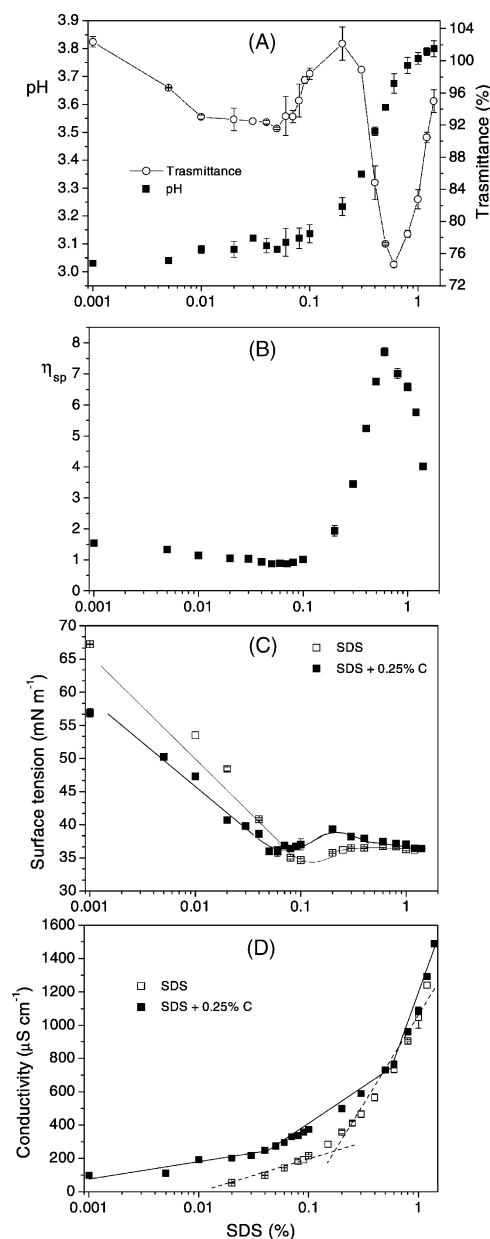
Fig. 1. Effect of SDS concentration on (A) pH and trasmittance, (B) viscosity, (C) surface tension, and (D) conductivity of 0.25% carbopol solutions. The lines are a guide for the eye.

Table 1
Surface excess and area per molecule of sodium dodecylsulfate (SDS) and benzalkonium chloride (BkCl) aqueous dispersions in the presence and absence of 0.25% carbopol; mean value (standard deviation)

System	Surface excess (mol/m^2)	Area per molecule (Å^2)
SDS	3.03×10^{-6} (0.22×10^{-6})	54.7 (3.9)
SDS + carbopol	2.11×10^{-6} (0.13×10^{-6})	78.5 (4.8)
BkCl	3.34×10^{-6} (0.16×10^{-6})	50.1 (2.4)
BkCl + carbopol	1.32×10^{-6} (0.08×10^{-6})	125.9 (7.6)

Gibbs equation (Eq. (1)), correlation coefficients (r) > 0.99.

Bystryak et al. (1999) reported an unusual increase in conductivity upon binding of SDS to weak polyelectrolytes, which was attributed to an enhanced mobility of the sodium counter-ions and to the contribution of OH$^-$ ions as a consequence of hydrogen ion consumption. However, Moriyama et al. (2000) referred to an increase in the mobility of the complexes between sodium dextran sulfate and cationic surfactants due to the shrinkage of the polymer, which increased the mobility of the complexes. These hypotheses can be tested measuring changes in pH or viscosity. In our case, carbopol/SDS dispersions presented an increase in pH, from 3.1 to 3.8, as SDS was added to the medium (Fig. 1A). The pH rise is related to the addition of sodium ions from SDS and to a decrease in the degree of ionization of carbopol microgels as SDS is being absorbed. On the other hand, the relative viscosity, measured using capillary viscometers, decreased slightly between 0.05 and 0.1% SDS, increased strongly from 0.2 to 0.6% SDS, and finally decreased again (Fig. 1B). Therefore, considering that the effect of pH on the conductivity of SDS solutions is negligible (Bystryak et al., 1999), the increase in conductivity in carbopol/SDS systems may be due to the combination of several factors such as an easier movement of Na$^+$ and OH$^-$ in the medium and from one aggregate to another, and differences between the shapes of the aggregates and that of normal SDS micelles.

The effect of this surfactant on the viscosity of carbopol dispersions may be attributed to two opposite mechanisms: hydrophobic absorption and the salt effect (Philippova et al., 1996). Hydrophobic absorption of SDS into carbopol should be less intense than in the case of hydrophobically modified poly(acrylic acids). On the other hand, the small molecular size and

was greater than that observed for SDS solution up to 0.6%. Usually, nonionic polymers/SDS solutions present specific conductivities less than or equal to those in the absence of polymer (Bystryak et al., 1999).

anionic character of SDS cause an increase in the ionic strength of the medium, which produces a shielding effect among the anionic charges of carbopol and its dehydration. Therefore, for SDS concentrations around cac and below 0.1%, an increase in the ionic strength of the medium, screens the repulsive electrostatic interactions among carboxylic groups and induces microgel particles to shrink slightly (Carnali and Naser, 1992; Kjøniksen et al., 1997; Jeon et al., 1998). As SDS concentration increases, to maintain electroneutral conditions, the absorbed surfactant is accompanied by its counter-ion, which increases the osmotic pressure inside the carbopol microgel particles and causes them to swell. In consequence, the viscosity of the system rises. This agrees with the higher intrinsic viscosity of carbopol obtained in 0.3% SDS medium than in pure water (Barreiro-Iglesias et al., 2001). Above binding saturation (0.6%), further addition of SDS, contributes to the presence of more ions and free micelles in the medium that induces the carbopol microgels to shrink and the viscosity to decrease. The difference between the cac and the cmc of the surfactant is an index of the strength of carbopol/SDS interaction. The free energy values obtained are summarized in Table 2. Note that the values obtained for carbopol/SDS interaction are similar or even higher than those reported for carbopol/nonionic surfactants or nonionic polymer/surfactant systems (Wang et al., 1997).

Knowing the important dependence of the rheological behavior of carbopol dispersions on the shear conditions (Barreiro-Iglesias et al., 2001), these effects were also studied applying flow rheometry instead of capillary viscometry, recording shear stress-shear rate pairs in a wide range of shear rates. 0.25% carbopol dispersions present shear-thickening behavior (fluidity index > 1), which is characteristic of a system constituted by individualized *fuzzball* units. In the presence of low proportions of SDS (0.02%, Fig. 2A), carbopol rheological behavior remains almost unal-

Table 2

Critical association concentration (cac), critical micellar concentration (cmc) and free energy of interaction per mole (ΔG_i) of SDS and BkCl in 0.25% carbopol solution

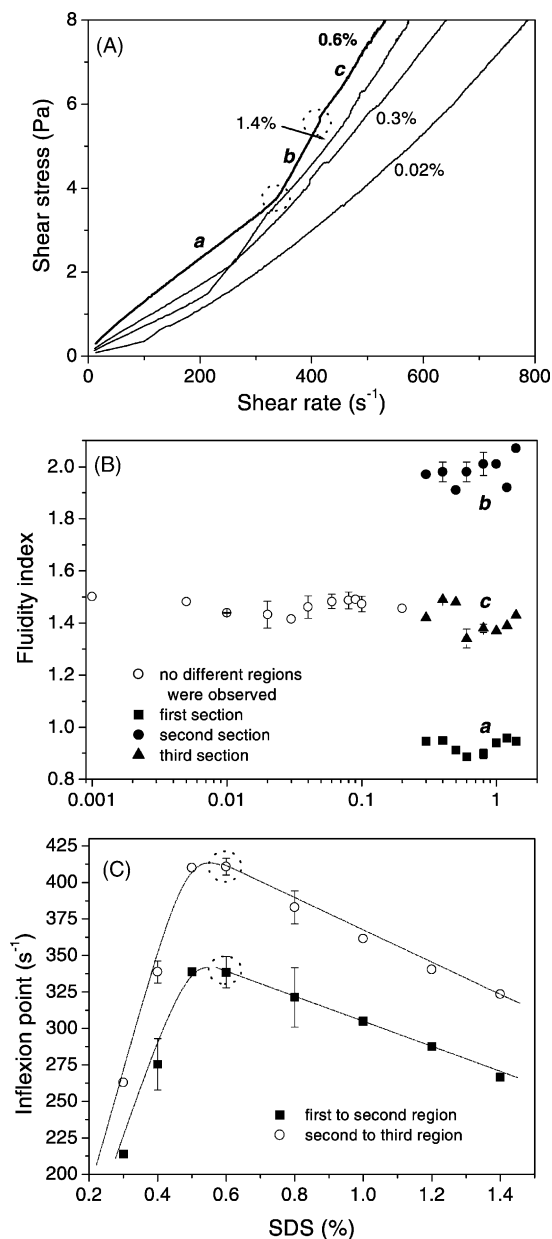| Surfactant	cac (mM)	cmc (mM)	ΔG_i (kJ/mol)
SDS	1.736	8.333	−7.190
BkCl	0.278	4.722	−12.98

Fig. 2. (A) Flow behavior of carbopol/SDS solutions. (B) Below 0.1% SDS, the behavior of the is shear-thickening (fluidity index around 1.5) in the whole range of shear rates considered. Above 0.1% SDS, the rheograms can be subdivided into three different regions: region (a) corresponds to pseudoplastic flow while regions (b) and (c) present shear-thickening flow with different flow indeces. (C) The shear rate at which each region appears depended on SDS concentration.

tered (Fig. 2B). In contrast, the addition of more SDS causes the appearance of three regions of different behavior. The data of each region were fitted by Ostwald equation (Eq. (4)) to estimate the corresponding fluidity index. For increasing shear rates, the system initially responded as pseudoplastic (fluidity index < 1), then as a marked shear-thickening suspension (fluidity index ≈ 2) (Otsubo, 1998), and finally showed a less pronounced shear-thickening behavior similar to that developed in the presence of SDS concentrations lower than 0.1% (fluidity index ≈ 1.5). The shear rates at which the transition between each behavior occurred are shown in Fig. 2C. These observations may be explained as follows. The swelling of carbopol microgels during SDS absorption may be responsible for the establishment of surfactant bridges among several carbopol microgel particles. This connectivity is shown in Fig. 1B as an increase in viscosity and in Fig. 2B(a) as an initial pseudoplastic region owing to a breakage of the interpolymeric bridges and reorientation of the aggregates in the flow direction. Further increase in shear rate, caused the aggregates to lose the water layer that acted as a lubricant among them, increasing their resistance to flow (region b in Fig. 2A and B). Finally, the aggregates may reorient again or some surfactant molecules may be depleted (Choi and Kim, 1994), decreasing the hydrodynamic size of the microgels. For example, in the case of carbopol dispersions containing 0.6% SDS, in which the swelling and interpolymeric connections are responsible for the maximum increase in viscosity using capillary viscometers (Fig. 1B), the highest shear rate ($335 \, \text{s}^{-1}$) had to be applied to break their most structured three-dimensional network (Fig. 2C). Also, as these aggregates had the greatest hydrodynamic size, the strongest resistance to flow in the shear-thickening region was observed (Fig. 2A). In the case of SDS concentrations ranged between 0.7 and 1.4% (above binding saturation), a salt effect caused the microgels to gradually shrink. In consequence, the interpolymeric connections are diminished and the network can be broken at lower shear rates.

Polymer/surfactant association was also studied considering the solubilizing power of the system (Fig. 3). Two hydrophobic probes were selected: pyrene, which fluorescence emission spectra is sensitive to the microenvironmental polarity around the pyrene molecule (Oliveira et al., 1996; Olea et al.,
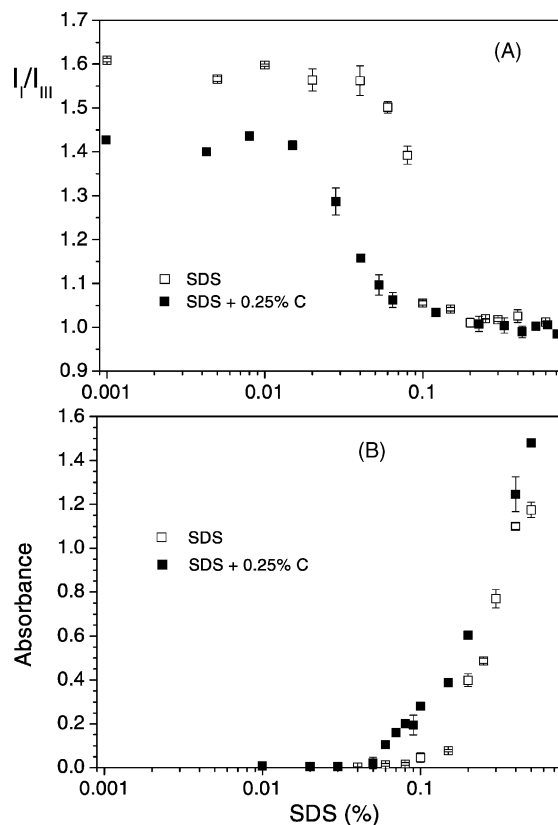

Fig. 3. (A) Ratio of the first to third vibronic peaks of pyrene as a function of SDS concentration in the absence and presence of 0.25% carbopol. (B) Orange OT absorbance recorded in SDS solution alone or another containing 0.25% carbopol.

2000); and Orange OT, a water insoluble dye the solubilized fraction of which inside surfactant micelles or polymer/surfactant aggregates can be quantified by UV absorption. As can be observed in (Fig. 3A and B, above 0.05% surfactant, carbopol/SDS aggregates are formed and provide a polarity low enough to be able to solubilize Orange OT. The solubilizing power of carbopol/SDS systems was much more intense than in the absence of polymer.

3.2. Carbopol/cationic surfactant systems

The addition of BkCl above 0.01% caused a significant decrease in transmittance, pH, and viscosity of 0.25% carbopol dispersions (Fig. 4A and B). The medium became more acidic (pH changed from 3.1 to 2.0) when BkCl concentration increased from 0.01
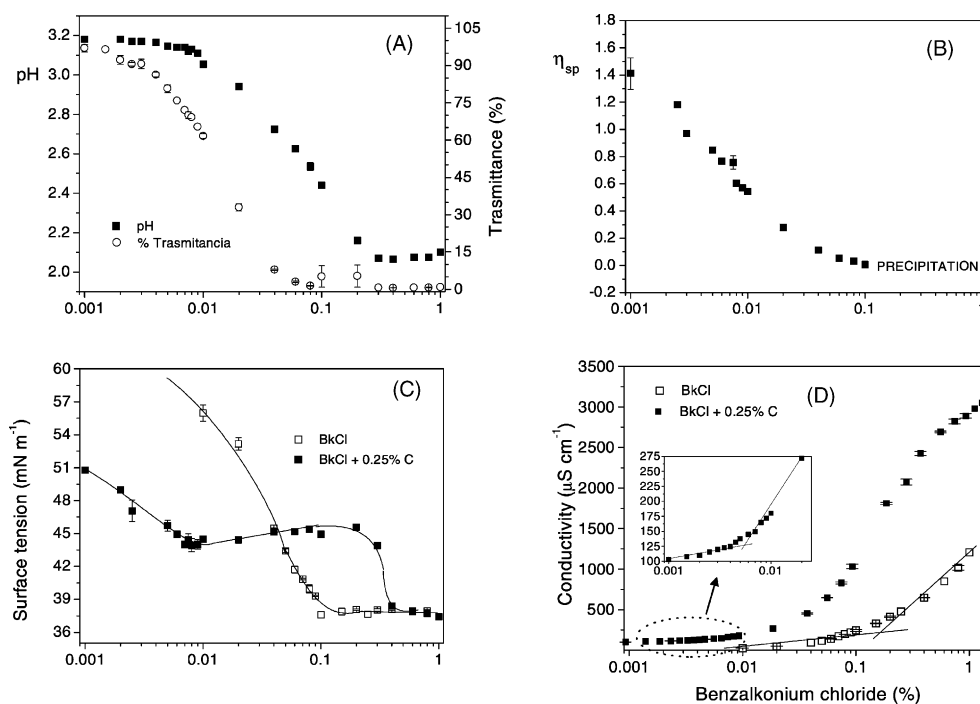
Fig. 4. Effect of BkCl concentration on (A) pH and trasmittance, (B) viscosity, (C) surface tension, and (D) conductivity of 0.25% carbopol solutions. The lines are a guide for the eye.

to 0.30%, which indicates a proton exchange mechanism of absorption. These BkCl concentrations may be considered as the cac and saturation binding concentration, respectively. IR analysis of films made from carbopol/BkCl blends (Barreiro-Iglesias et al., 2002) showed the capability of the ammonium groups of BkCl to interact with carbopol through an ionic exchange with the proton of the carboxylic groups, resulting in the formation of surfactant/polymer pairs. This reduces the internal osmotic pressure of the microgels (Oliveira et al., 1996; Philippova et al., 1998) and favors the establishment of hydrophobic interactions among the tails of bonded surfactant molecules.

The initial absorption of the surfactant into hydrophobic and ionic domains of the polymer chains acts as a cross-linker in linear polymers, favoring interpolymeric aggregates (Shimizu, 1994; Schillén et al., 2000; Katsuura et al., 2001; Wang et al., 2001). In the case of the gels, there is a contraction as the polymer charges are gradually neutralized (Coquelet et al., 1996; Ashbaugh et al., 2000). A 0.10–0.50% BkCl (10–40 mol% of the amount needed to neutralize all

carboxylic groups) produced an insoluble complex in 0.25% carbopol dispersions, which made the rheological evaluation of these systems impossible. Philippova et al. (1998) observed that poly(methacrylic acid) gels collapse at acidic pH upon absorption of only 4 mol% of cetylpyridinium chloride, and Ashbaugh et al. (2000) reported that the swelling of poly(acrylic acid) gels decreases linearly with the fraction of dodecyl trimethylammonium bromide absorbed by the gel, and that for an amount of surfactant bonded equivalent to a 40 mol% of the carboxylic groups of the gel, this almost completely collapsed. In our case, the interaction between carbopol and a cationic surfactant involves, as was mentioned, hydrophobic and electrostatic forces. As a consequence of the electrostatic binding, the surfactant heads interchange with protons of carbopol carboxylic groups, and this reduces the internal osmotic pressure of the gel. It also favors the hydrophobic binding of the tails among themselves and with the polymer backbone (Kjøniksen et al., 1997). The shrinking of the microgel particles due to the shielding of the charges and the dehydration
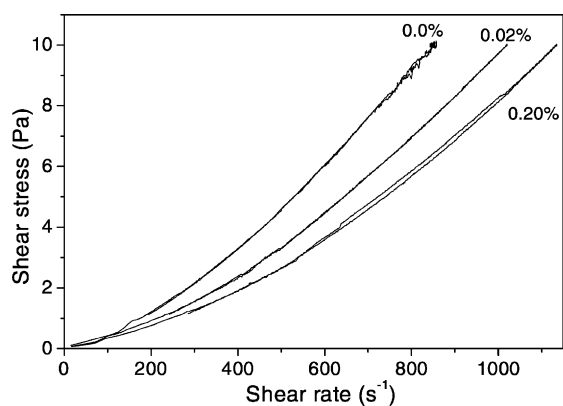
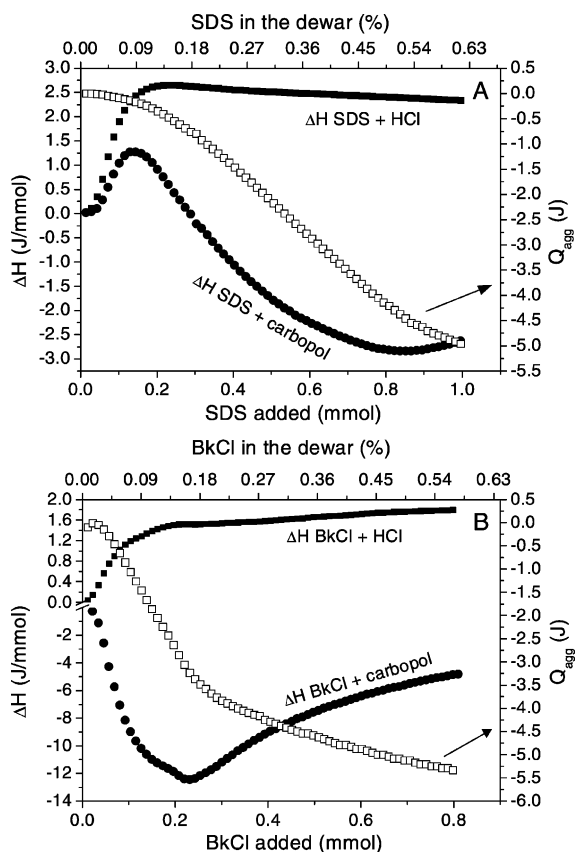Fig. 5. Flow behavior of some carbopol/BkCl solutions.

Fig. 6. Calorimetric titration curves observed during addition of small volumes of 15% SDS (A) or BkCl (B) into a dewar containing 0.25% carbopol solution. The corresponding dilution plots of each surfactant into diluted HCl aqueous solution (blank) are also given. Filled circles represent the difference between the heat evolved in the presence and absence of carbopol, Q_{agg}.

of the polymer caused a decrease in the consistency of the system and favored the appearance of shear-thickening flow behavior in the whole range of shear rates analyzed (Fig. 5). As a consequence of this associative process, the potentially toxic effects of BkCl, when incorporated in ocular drug dosage forms, may be reduced (Coquelet et al., 1996).

Surface tension results (Fig. 4C) indicated that the absorption of BkCl onto carbopol decreases the concentration of BkCl at the air/water interface compared to the values observed for surfactant only solution (Table 1). In the surfactant concentration range in which polymer–surfactant interaction occurs, the concentration of free surfactant remains practically constant and, in consequence, no significant changes in surface tension values were observed. There is a plateau region from 0.01 to 0.30% BkCl, which agreed with the concentrations estimated as cac and saturation binding, respectively. More BkCl causes surface tension values to drop brusquely, indicating the formation of free micelles in the medium. The conductivity of carbopol/BkCl dispersions was particularly high. This may be attributed to proton release to the medium when the surfactant interacts electrostatically with carbopol carboxylic groups, as well as the presence of free Cl^- ions. Above 0.5% BkCl, the increase in conductivity (i.e. the slope of the plot) was similar to that observed in BkCl aqueous solution, which indicates no further binding to carbopol. Solubilization power of the carbopol/BkCl aggregates could not be measured due to the cloudiness of the samples.

3.3. Thermodynamic analysis

Fig. 6 shows the apparent enthalpies and the heat evolved during the demicellization, the interaction with carbopol, and the micellization processes of SDS (Fig. 6A) and BkCl (Fig. 6B) in 0.25% carbopol dispersions compared to pure water. Microcalorimetric techniques have been demonstrated to be reliable and sensitive tools to study the micellization of surfactant molecules in aqueous solutions (Kevelam et al., 1996; Wang et al., 1997; Turco Livieri et al., 1993; Das Burman et al., 2000). Before being added to the dewar containing water or carbopol dispersion, both surfactants were above their cmc in the buret (15%

(w/w)). Therefore, when the surfactant solution was slowly added into water adjusted to pH 3 with HCl (blank of the same pH as carbopol dispersion), the micelles broke up until the concentration in the dewar reached cmc. Then, micelles were only diluted in a solution of micelles. For both surfactants, demicellization process was endothermic, while micelle dilution was slightly exothermic (Fig. 6). For both SDS and BkCl, the transition occurred at around 0.15–0.20%. The apparent enthalpy of micellization ($\Delta H_{mic} = -2.6 \, kJ/mol$) and the transition concentration (5 mM) observed for SDS in pure water agrees well with the values obtained by Wang et al. (1997). No reference data were found in the case of BkCl.

When a SDS solution was added to the carbopol dispersion, an initial endothermic demicellization process was also observed. However, this stopped when SDS concentration in the dewar reached 0.08%, and a new exothermic process began. When SDS concentration was above 0.5%, further addition of SDS did not increase the heat evolved. Carbopol concentration in the dewar changes from 0.25% at the beginning of the experiment to 0.24% after the total addition of the surfactant solution. The enthalpy of carbopol dilution was negligible, and the change in polymer concentration was small enough to avoid modifications in the saturation binding surfactant concentration.

In the case of BkCl, the initial endothermic step almost disappeared, which indicates that as the micelles broke up, the surfactant units were absorbed into carbopol through ionic interactions, which is a strongly exothermic process. The maximum binding enthalpy was reached around 0.2% BkCl, although the process is exothermic up to 0.5% BkCl in the dewar. This finding, together with the surface tension and viscosity results, clearly showed that the collapse of carbopol network as BkCl is absorbed prevents additional BkCl molecules from interacting with the remaining carboxylic groups in the microgel (maximum absorption involved around 25–40 mol% carboxylic groups). Further addition of BkCl may provide free surfactant micelles.

From the slope of the linear portion of the plot Q_{agg} values versus surfactant concentration (surfactant concentration range 0.09–0.27% SDS or 0.05–0.18% BkCl), the binding constant K_{agg} and the thermodynamic parameters of the process were estimated. The

Table 3
Thermodynamic parameters for ionic surfactant-carbopol aggregation, expressed per mole of surfactant and mole of polymer

Surfactant	K_{agg}	ΔG_{agg} (kJ/mol)	ΔH_{agg} (kJ/mol)
SDS	11.48	−6.027	−250433
BkCl	16.98	−6.994	−794611

Standard deviations were in all cases lower than 2%.

different order of magnitude of ΔG_{agg} and ΔH_{agg} impeded a precise estimation of ΔS_{agg}. Nevertheless, the results showed in Fig. 6 and Table 3 suggest that the titration of the anionic surfactant is accompanied by a relatively small gain in enthalpy and loss in entropy. The enthalpic effect can be attributed, especially in the postmicellar region, to the stabilization of the surfactant micelles by the polymer as expected on the basis of Debye-Hückel considerations (Kevelam et al., 1996). In the case of BkCl, the aggregation process is enthalpically driven and may occur with a loss of entropy, which is characteristic of a tight host–guest inclusion (Wang et al., 1997).

4. Conclusions

Both anionic and cationic surfactants significantly altered the properties of carbopol microgels solutions. Fig. 7 is an attempt to explain graphically such changes. Anionic surfactant binds hydrophobically to carbopol. Initially, the degree of ionization of carbopol decreases and the volume of the microgels diminish slightly, resulting in a decrease in the viscosity of the system. As more SDS is absorbed, the microgels swell owing to the sodium counter-ions that accompany the bound surfactant into the microgels. The internal osmotic pressure rises, and the swelling is shown as a dramatic increase in the consistency of the solutions. Above binding saturation, the presence of free anionic surfactant in the medium increases its ionic strength, which causes carbopol microgels to shrink. The relatively high free energy values obtained for the carbopol/SDS binding process indicate that their anionic groups are not an important impediment for the association.

The cationic surfactant, BkCl, binds carbopol mainly through a proton exchange mechanism, although hydrophobic interactions may also occur. The
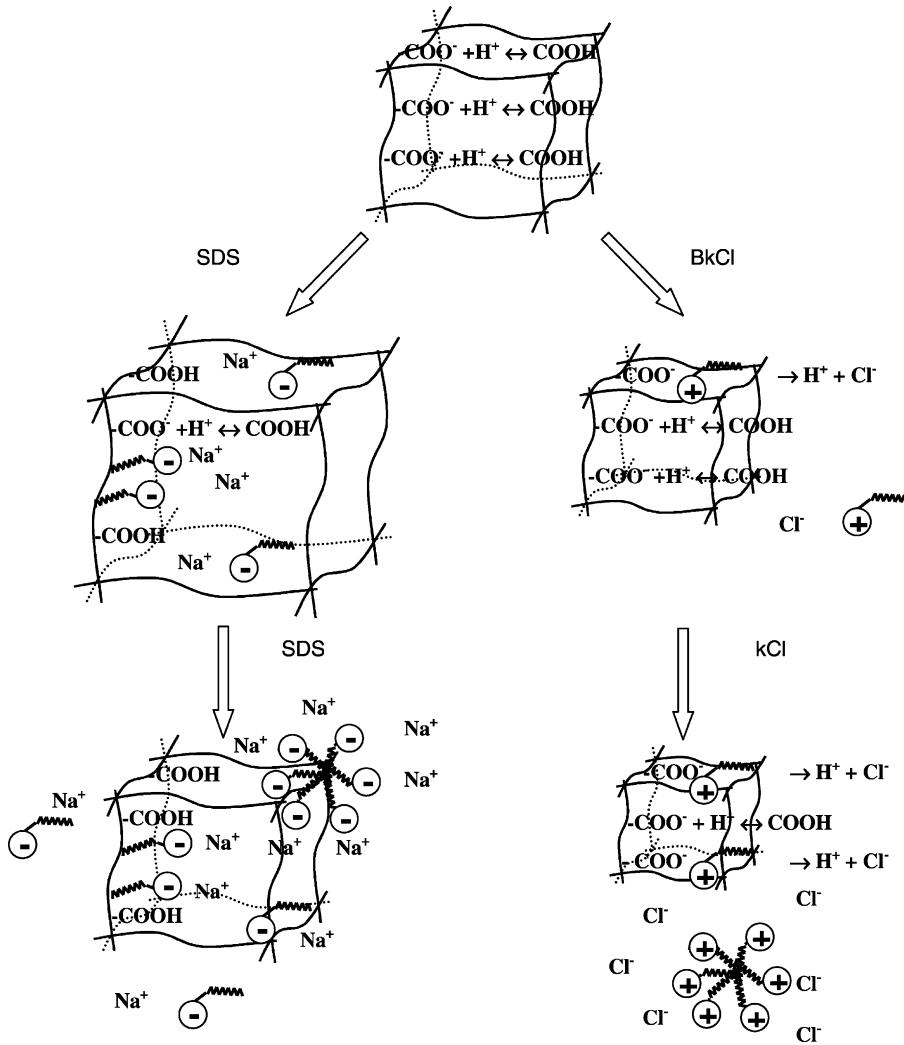
Fig. 7. Schematic representation of the changes in carbopol microgel volume caused by the association process of the ionic surfactants.

complexes of carbopol with oppositely charged surfactants can be nonstoichiometric due to the collapse of the microgels when the degree of neutralization of carboxylic groups reaches 40 mol%. There may be a steric hindrance for BkCl to penetrate the microgel and/or to bind to the carboxylic groups if the distance between the charges along the polymer chain is not big enough. The formation of well-ordered complexes of carbopol/BkCl is an enthalpically driven process that overcomes the unfavorable contribution from the entropy and makes the overall process thermodynamically favorable.

From pharmaceutical and technological points of view, the results obtained evidence the possibility of modulating the rheological and solubilizing properties of carbopol microgels solutions through the addition of the appropriate surfactant at the adequate concentration.

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