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SURFACTANT–CHITOSAN INTERACTIONS AND APPLICATION TO EMULSION STABILIZATION

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Complexes obtained from the electrostatic interactions between chitosan, a cationic polysaccharide, and sodium decylsulfonate, an anionic surfactant, were characterized by their conductimetric and surface-active properties. Such surfactant/polyelectrolyte complexes (SPECs) present very interesting surface-active properties, even at very low surfactant concentrations (much lower than the critical micellar concentration, CMC, of pure surfactant), influencing either surface tension or viscoelastic properties of the adsorbed layers. This allows their use as emulsion stabilizers, while the very low surfactant concentration makes them potential candidates for cosmetic applications.

Keywords: chitosan, anionic surfactant, complex, conductivity, surface-active properties, emulsion stabilization

INTRODUCTION

Chitosan, the main chitin-derivative water-soluble polyelectrolyte, is obtained by partial or full N-deacetylation of chitin[1]. It presents interest since it is a non-toxic, biodegradable polymer, soluble under acidic conditions due to the protonation of amino groups.[2] Owing to their interesting properties, chitosan and chitin derivatives have been widely used in many applications, such as cosmetics, pharmaceuticals, food industries, biotechnology.[3,4] Amphiphilic systems based on chitin and chitosan derivatives may be obtained by two different processes: either by chemical modification of the macromolecular backbone,[5] or by the interaction between the hydrophilic chains and surfactant molecules.[6]

The interactions between polymers and surfactants in aqueous solutions have been a subject of intensive research, as well as of fundamental scientific studies.[7] Many practical systems for industrial applications contain mixtures of polymers and surfactants, widely used in foods, cosmetics, detergents, or as thickeners in water-based formulations, such as paints, drilling muds, etc. In these applications, polyelectrolytes are of particular interest due to the important role of polymer charges. Moreover, of special interest is the association between the oppositely charged polymer-surfactant pairs. The association between a polyelectrolyte and oppositely charged surfactants is generally accepted as an ion-exchange process, in which electrostatic attraction is reinforced by a cooperative aggregation of the bound surfactant molecules.[8,9] It gives rise to soluble or insoluble aggregates, the properties of which may be tuned by many variables, such as hydrophobicity, backbone rigidity and charge density of the polyion, surfactant chain length, nature and quantity of the added salts.[10,11] Changes in these variables may affect stoichiometry and, therefore, the solubility of the complex. These specific interactions and the systems elaborated on their basis are important for many practical applications, such as colloidal stabilization, wettability and adhesion.

Previous studies[12-14] have shown that chitosan, a cationic polyelectrolyte in acidic medium, can interact with anionic surfactants to form soluble or insoluble complexes, called SPECs. These complexes, stabilized by electrostatic and hydrophobic interactions, can be formed even when the surfactant concentration is well below its critical micelle concentration (CMC).[15,16] The mechanisms of formation of complexes between chitin derivatives and oppositely charged surfactants are well-studied in the literature,[13,17,18] particularly, the determination of critical aggregation concentration (CAC).

The utilization of emulsions is recommended for many applications, as in foods, cosmetics, pharmaceutics, etc., as they maintain stability for a long time. Also, to ensure the stability of emulsions, surfactants are often used, as they have the ability to modify surface properties due to their amphiphilic character. For environmental or safety reasons, the use of a large quantity of surfactants is not recommended. Studies on surfactant-polyelectrolyte complexes demonstrate the interest for the surface properties of such systems.[17,19,20]

This paper reports the behaviour of systems based on chitosan, a cationic polysaccharide, and of an oppositely charged surfactant (sodium decylsulfonate), as well as their applications to emulsion stabilization.

EXPERIMENTAL

Chemicals

Chitosan samples obtained from Pronova (Norway) were purified according to the following procedure: they were prepared in a protonated form through dissolution in a dilute hydrochloric acid solution. The solution was then filtered under a sintered glass (porosity 2, pore diameter between 40 and 90 μm) to eliminate the aggregates. A sodium chloride solution was added (to reach a salt concentration around 10 g/L), to decrease solvent quality and to facilitate polymer precipitation. Ethanol (EtOH) was used to precipitate chitosan hydrochloride, the precipitate thus obtained being washed with EtOH/water mixtures, with successive volume ratios of 70/30, 80/20, 90/10 and 100/0. Finally, the precipitate was dried at room temperature.

The degree of acetylation (DA) was determined from ^{1}H NMR spectroscopy.[21] Non-protonated chitosan was dissolved in D_2O/HCl (pH ≈ 4), then freeze-dried. The obtained solid was dissolved in D_2O, to exchange the labile protons; the procedure was repeated twice. DA was calculated from the integrals of signals dedicated to the protons of anomeric carbon atoms from the acetylglucosamine and glucosamine units.

The viscosity-average molar mass was measured using a 0.3M acetic acid (AcOH)/0.2M sodium acetate (AcONa) mixture as solvent, at 25.0 ± 0.1 °C. Taking into account the measured degree of acetylation, the Mark Houwink parameters were:[22]

$[\eta]_{mL/g} = 0.076\ M_v^{0.76}$ (for DA > 0.10)

The characteristics of the chitosan samples are given in Table 1.

Table 1
Physico-chemical parameters for chitosan samples

Parameters	Chitosan 1	Chitosan 2
Viscosity-average molar mass ($g.mol^{-1}$)	89000	295000
Degree of acetylation (DA)	0.15	0.18
Charge parameter (λ)	1.17	1.13
Manning transport coefficient (f)	0.74	0.77
Overlap concentration ($monomol.L^{-1}$)	0.012	0.0045

The surfactant sample preferentially used in this study was sodium decylsulfonate from Sigma, applied without further purification after mass spectroscopy analysis. Its Kraft temperature is equal to 23 °C and its HLB was 41.

Preparation of emulsions

Analogously with the reverse phase process, leading to emulsions with very small droplets, the emulsions were prepared as follows: the aqueous (water and surfactant) and the organic (vaseline oil) phase were mixed together at 13500 rpm with an Ultraturrax, for 30 min (15 min at 70 °C and 15 min at room temperature). The composition was 80 vol% for the aqueous phase and 20% for the organic one.

Techniques

Conductivity was measured on a CD78 conductimeter from Tacussel (France), at a temperature of 25.0 ± 0.1 °C. The experiments were performed in a double-walk thermo-stated cell.

The tension surface properties were studied from dynamic measurements. They were carried out using a Tracker tensiometer from TECLIS (Longessaigne, France), at 25.0 ± 0.2 °C. An air bubble was formed in the aqueous polymer solution. The shape of the bubble was followed on a CDD camera and surface tension was deduced from the mathematical analysis of this axial symmetrical shape (Laplacian profile).[23]

The bubble volume was kept constant by automatic adjustment. Time t = 0 was measured immediately after bubble formation. The tensiometer allows observing the visco-elastic characteristics of the adsorption layer, by applying a controlled dilatational perturbation $\Delta A(t)$ to the bubble area A and by simultaneously recording the variation of surface tension $\gamma(t)$. From the variations of $A(t)$ and $\gamma(t)$, and taking into account a rheological model, the viscoelastic moduli E' and E" (respectively, the real and the imaginary parts of the total dilatational elasticity module E) and the phase angle φ (defined by $\tan \varphi = E''(\omega)/E'(\omega)$, where ω is the applied frequency) may be calculated.[24]

Emulsion stability was studied using the Turbiscan™ MA 2000 from FORMULACTION (L'Union, France).

RESULTS AND DISCUSSION

Properties of surfactant

Conductimetric properties

When hydrochlorated, chitosan becomes a cationic polyelectrolyte, which permits to study the surfactant–polymer complexes (SPECs) by means of an anionic surfactant. It has been already demonstrated[25] that sodium dodecylsulfate (SDS) may be hydrolysed in an acidic solution during long storage to form dodecanol, which is known as a very surface-active substance, so that a sulfonate surfactant was preferred. The application conditions of a surfactant depend upon its critical micelle concentration (CMC) and its Kraft temperature, when ionic. Considering that sodium dodecylsulfonate has a Kraft temperature of about 36 °C (leading to poor solubility at 25 °C), and that sodium hexylsulfonate has a very high CMC, sodium decylsulfonate ($C_{10}H_{21}SO_3Na$) was used. It will be called TA.

A conductimetric study of surfactant solutions will permit to determine CMC, as well as the micelle characteristics. From the variation of conductivity as a function of surfactant concentration (Fig. 1), the critical micelle concentration can be determined from slope breaking.

The first linear part matches the surfactant dissolution without micellisation. After micellisation, the occurrence of new ionic species (the micelles) contributes to the change in slope. A CMC value of 0.041 mol/L, comparable to that of other sodium sulfonate surfactants, was determined.[26] According to the theory of Onsager for low surfactant concentrations, the slope of the linear part before micellisation can be considered as:

$$P_{TA} = \lambda°_{TA^-} + \lambda°_{Na^+} \qquad [1]$$

$\lambda°_i$ being the equivalent conductivity of the i species, extrapolated at infinite dilution. Knowing $\lambda°_{Na^+}$ (equal to 50.10 S cm^2 mol^{-1}), $\lambda°_{TA^-}$ can be deduced and found as 19.45 S.cm^2.mol^{-1}, which is in good agreement with the values recorded for other surfactants.[27]

From the slope of the second part of the curve (at a concentration higher than CMC), it is possible to determine the ionization coefficient of the micelle with Evans' method. Assuming, among others, that the ionic concentration of surfactant remains constant after CMC, and that Stokes' law was applied to free the ionic surfactant and the charged micelles, the Evans equation may be deduced:

$$N^{2/3} \alpha^2 (p_{\alpha v} - \lambda°_{Na}{}^+) + \alpha \lambda°_{Na}{}^+ - \rho_{\alpha\rho} = 0 \qquad [2]$$

where N is the aggregation number of micelles, α the ionization coefficient of micelles, p_{av} and p_{ap} are the slopes of the straight lines, respectively, before and after CMC, while $\lambda°_{Na}{}^+$ is the limit equivalent conductivity of the Na^+ ion. Taking into account[28] that the aggregation number of sodium decylsulfonate is equal to 35, the ionization coefficient of surfactant micelles is 0.37, which is in good agreement with the data for other sulfonate surfactants.

Surface active properties and adsorption layers

The dynamic tensiometer allows determining adsorption kinetics and equilibrium surface tension at different surfactant concentrations, but also the viscoelastic properties of the adsorbed layer.

Different stages of sodium decylsulfonate adsorption

Figure 2 shows how the surface tension, γ, of the TA solutions depends on both concentration, c_s, and time of formation (ageing), t_f, of the adsorption layers.

For relatively high surfactant concentrations, c_s, (*e.g.*, curves 7 and 8, corresponding to $c_s = 3.9 \cdot 10^{-2}$ mol·L^{-1} and $c_s = 4.7 \cdot 10^{-2}$ mol·L^{-1}), surface tension γ reaches instantly the minimal value $\gamma_{\min}$ = 37-38 mN/m), which only slowly decreases down to ~34 mN/m after an ageing time of ~10^3 s. However, for other curves, corresponding to concentrations ranging from $2 \cdot 10^{-6}$ to $2 \cdot 10^{-2}$ $\text{mol} \cdot \text{L}^{-1}$, different stages are observed, as already demonstrated for amphiphilic polymers,[29] while, for concentrations lower than CMC, the equilibration times are extremely long.[30]

The kinetic curves (1-4) corresponding to relatively low surfactant concentrations have some induction (lag time), t_l, during which surface tension $\gamma(t)$ decreases very slowly. For higher concentrations (curves 5 and 6), the lag time cannot be easily recorded because of its low value. This stage corresponds to the diffusion-controlled adsorption of the surfactant molecules from the bulk of solution to the interface, when reverse diffusion from the surface could be neglected.[31] It will be the time required for the absorption of sufficient surfactant molecules, thus giving rise to a significant decrease of surface tension. The duration t_l of this stage for curves 1-4 could be estimated as ~$8 \cdot 10^4$ s (curve 1), ~$5 \cdot 10^3$ s (curve 2), ~80 s (curve 3), and 10-20 s (curve 4), respectively. Assuming that the corresponding surfactant concentration remains unchanged, dependence $t_l(c_s)$ is approximately scaled as $t_l \sim c_s^{-2}$ and corresponds to the Ward-Tordai relationship:[32]

$$\Gamma(t) \cong c_s \sqrt{Dt} \qquad [3]$$

where $\Gamma(t)$ is the surfactant surface concentration and D the bulk diffusion coefficient of surfactant molecules.

The lag stage of the formation of adsorption layers is followed by the so-called post-lag stage, characterised by a maximal rate of surface tension decrease. The practically linear negative slope, $d\gamma / d\log t_f$, of the kinetic curves at this stage testifies for the exponential decrease of γ with the time of ageing t_f, *i.e.* $\gamma \sim \exp(-t_f/\tau_2)$, where τ_2 is the characteristic time of relaxation at this stage.

For low surfactant concentrations, one can markedly distinguish the third (last) stage in the kinetic curves, which follows the post-lag stage. The rate of the $d\gamma/d \log t_f$ decrease in this stage suddenly diminishes, such a sharp inflection of the kinetic curves reminding of a saturation of the adsorption layers when the newly-arrived molecules have to overcome an energy barrier to reach the surface. This barrier can be due to the electrostatic or steric repulsion onto the newly-arrived molecules from molecules belonging to the adsorption layer.

Effective diffusion coefficients of surfactants

The gradual decrease of surface tension $\gamma(t)$ during all stages of the adsorption process testifies for the continuous transformation in the structure of these adsorption layers. When the kinetic curves $\gamma(t)$ are presented as a function of $\sqrt{t}$ (Fig. 3), the portions of these curves, corresponding to different stages of the adsorption process, may be interpolated by linear functions.

If one interprets this feature as the manifestation of the diffusion mechanism for the formation of adsorption layers,[33] according to equation [3] one can estimate some effective diffusion coefficients, D_i, corresponding to different adsorption stages. Remember that the applicability of this relationship is based on the assumption that back diffusion of surfactants to the bulk is insignificant. Table 2 presents the results of the formal calculation of these effective diffusion coefficients according to relation [3].

Table 2
Effective diffusion coefficients, D_{eff}, calculated from equation [3]

C_s [$\text{mol} \cdot \text{L}^{-1}$]	Effective diffusion coefficient, D_{eff} [$\text{m}^2 \cdot \text{s}^{-1}$]		
	Lag stage	Post-lag stage	Last stage
10^{-5}		$9.8 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$
10^{-4}	$3 \cdot 10^{-16}$	$0.27 \cdot 10^{-12}$	$2.6 \cdot 10^{-14}$
10^{-3}	$2 \cdot 10^{-14}$	$0.52 \cdot 10^{-12}$	$2.0 \cdot 10^{-16}$
$1.8 \cdot 10^{-3}$		$0.12 \cdot 10^{-12}$	$2.4 \cdot 10^{-17}$

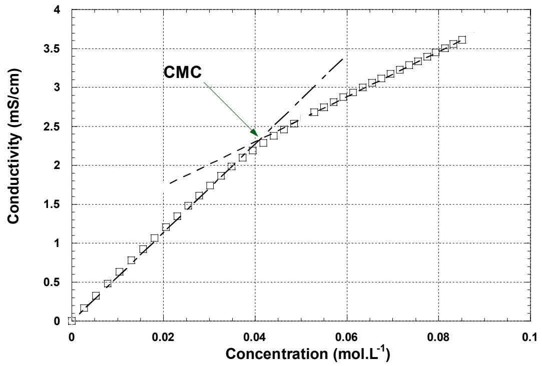


Figure 1: Conductivity curve for a sodium decylsulfonate solution in water (T = 25 °C)

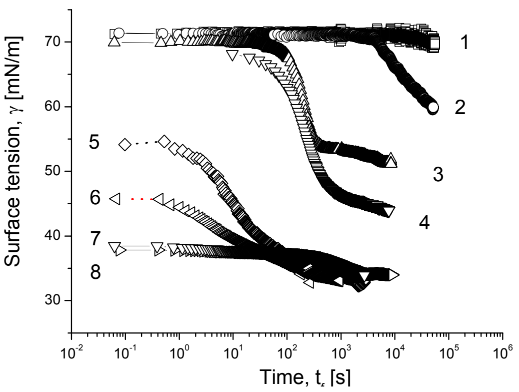


Figure 2: Kinetic curves of surface tension for different concentrations of sodium decylsulfonate c_s [$mol\cdot L^{-1}$] in water: 1) $2.0\cdot10^{-6}$; 2) $1.0\cdot10^{-4}$; 3) $1.0\cdot10^{-3}$; 4) $1.8\cdot10^{-3}$; 5) $2.0\cdot10^{-2}$; 6) $2.1\cdot10^{-2}$; 7) $3.9\cdot10^{-2}$; 8) $4.7\cdot10^{-2}$

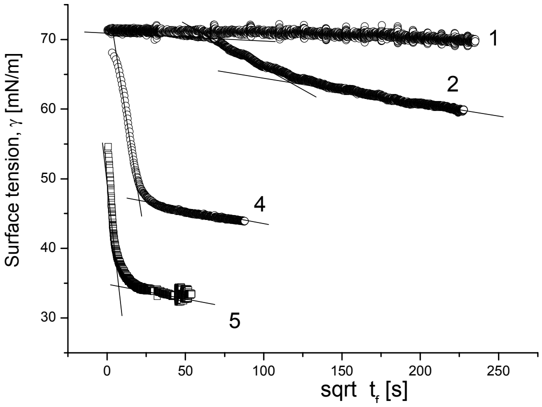


Figure 3: Kinetic curves of surface tension for different concentrations of sodium decylsulfonate c_s [$mol\cdot L^{-1}$] in water: 1) $2.0\cdot10^{-6}$; 2) $1.0\cdot10^{-4}$; 3) $1.0\cdot10^{-3}$; 4) $1.8\cdot10^{-3}$

Although the values of the diffusion coefficients D_{eff} given in Table 2 have been obtained under some simplistic assumptions (applicability of the Ward-Tordai equation, zero back diffusion), some valuable conclusions on the mechanisms of the formation of adsorption layers of surfactants at different stages of adsorption may be nevertheless drawn. Surprisingly, the values of D_{eff} for the lag time of adsorption are too low, comparatively with those obtained from the Einstein-Smolukhovski equation $D = \kappa_B T/6\pi\eta R_h$ (where η is the viscosity of the medium and R_h is the effective hydrodynamic radius of surfactant molecules), which are of the $D \cong 10^{-10}$ m^2/s order. The end of the lag time is identified with the beginning of the steric interaction between the surfactant molecules inside the adsorption monolayer. The low values of D_{eff} may be explained by the electrostatic repulsion between the already adsorbed surfactants and the newly-arrived molecules from the bulk of solution. This electrostatic repulsion prevents the adsorption of the latter molecules, which decreases the rate of adsorption and leads to low D_{eff} values.

It is also surprising that, in the post-lag stage, the values of D_{eff} are the closest to the real diffusion coefficients D, being only 10-100 times lower than the latter. The end of this stage is identified with the formation of dense adsorption monolayers of surfactant molecules whose hydrophobic chains are oriented preferentially perpendicularly to the interface. One may assume that the Debuy-Hückel length, or the thickness of the double electric layer, decreases, because of the high local concentration of the charged sulfonate groups with their counter-ions, so that the repulsion electrostatic force, acting on arrival of the diffusive surfactant molecules, decreases, as well. In terms of the activation adsorption theory, this means that, according to expression $E_a \sim kT \ln (D/D_o)$, the activation energy is of the ~10 kT order. The obtained value for E_a agrees with the energy of the electrostatic repulsion between the ions at the characteristic Debye-Hückel distance δ_{DH} ~10nm.

At the third (last) stage of the adsorption process, the monolayer is almost completely formed and the intercalation of the newly-arrived molecules inside this adsorption layer requires some work. Additionally to the electrostatic work, it may be identified with the activation energy of adsorption and must be spent to form the hole inside the adsorption layer: $E_a \cong \pi . a_1$, where π is surface pressure and a_1 is the area per molecule inside the adsorption layer. With π~20 mN/m and a_1~1 nm^2, one obtains for this additional contribution to the activation energy value E_a ~ 2 kT.

Isotherm of surface tension for sodium decylsulfonate

The surface tension isotherm for TA is presented in Figure 4. Whilst surface tension γ depends on the time of formation, t_f, of the adsorption layers, isotherm $\gamma(c_s)$ has been conventionally constructed with data corresponding to $t_f = 10^3$s.

The CMC value, which is around 10^{-2} mol.L^{-1}, was determined as the surfactant concentration corresponding to the break of curve $\gamma(c_s)$, and agrees with the published data.[34] It must be pointed out that, although the form of the $\gamma(c_s)$ curve depends on the choice of the adsorption layer formation time, t_f, the CMC value remains almost insensitive to this choice. The CMC value is slightly different from the one determined by conductimetry, but it is derived from a dynamic technique.

The surface tension isotherm $\gamma(c_s)$ has been fitted by the Shishkovski formula (Fig. 5):

$$\Pi = \gamma_o - \gamma = A \ln\left(1 + Bc_s\right) \quad [4]$$

where Π is surface pressure, $A = 5.6 \pm 0.5$ [*mN/m*] and $B = (0.5 \pm 0.2)\ 10^5$ [*L/mol*]. The maximum adsorption amount has been found to be equal to: $\Gamma_{max} = A/RT = (2.7 \pm 0.2)\ 10^{-6}$ [*mol/m*^{2}]. Area a_1 per one surfactant molecule in the saturated adsorption layer at $t_f = 10^3$ s being equal to $a_1 = 1/\Gamma_{max} N_A = 0.62 \pm 0.05$ [*nm*^{2}], it corresponds to the estimations valid for ionic surfactants.

Dilational viscoelasticity of the adsorption layers of sodium decylsulfonate

The rheological properties of the interface are related to the properties of the monolayer. The interface may present viscoelastic properties if the monolayer shows resistance against deformation (elastic modulus) and relaxation (surface viscosity). This relaxation is mainly due to the reorientation of molecules into the monolayer, while the adsorption-desorption of molecules is governed by the diffusion of solution at the interface.[36] The elastic moduli are determined at a frequency of 0.42 rd.s^{-1} (corresponding to a period of 15 seconds, Fig. 6), at this frequency the elastic modulus E' being very close to the complex total elasticity modulus (E). The interfacial film has elastic properties, which increase with the adsorption of surfactant molecules and with the formation of a structured monolayer. Such surfactant adsorption is related to the decrease of surface tension as a function of time (Fig. 6).

Self-association of surfactant molecules at the interface *via* hydrophobic interaction should increase the rheological properties of surfactant monolayers. The elastic modulus depends on bulk surfactant concentration, reaching a maximum in the range of the inflection point of the surface tension curve (Fig. 7).

For concentrations much lower than CMC, there is not enough surfactant to reach maximal elasticity, modulus E being predominantly due to the diffusion of the molecules from solution towards the interface. For concentrations higher than CMC, there is so much surfactant that, when the interfacial film is stretched, the interface is immediately saturated, presenting null elasticity. This behaviour was already observed[36] for non-ionic surfactant monolayers. The surfactant exchange rate increases with concentration. However, at high surfactant concentrations, it exchanges very quickly, compared to the oscillation frequency, and the modulus is quite null.

Properties of surfactant-chitosan complex

The polyelectrolyte-surfactant systems often have physico-chemical characteristics that differ from those of the non-ionic polymer/surfactant systems.[37-40] Various types of interactions may occur and interactions other than the electrostatic ones (hydrophobic, hydration, etc.) may play important roles, according to the nature of components. Moreover, the composition of such complexes will influence their structure[41,42] and hence, their properties. Surfactant-chitosan complexes were characterized by their conductimetric and surface-active properties.

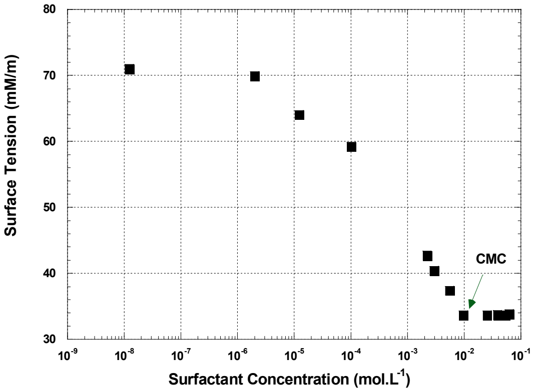


Figure 4: Isotherm of sodium decylsulfonate surface tension in water (T = 25 °C)

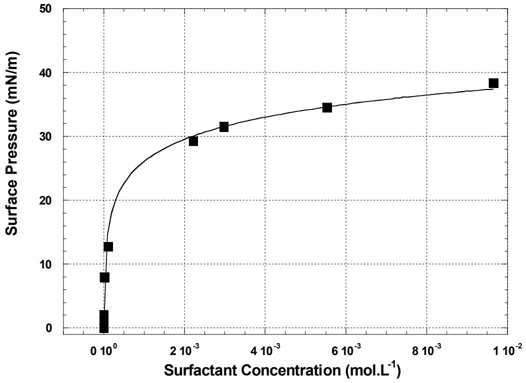


Figure 5: Surface pressure as a function of sodium decylsulfonate concentration below CMC (solvent: water, T = 25 °C)

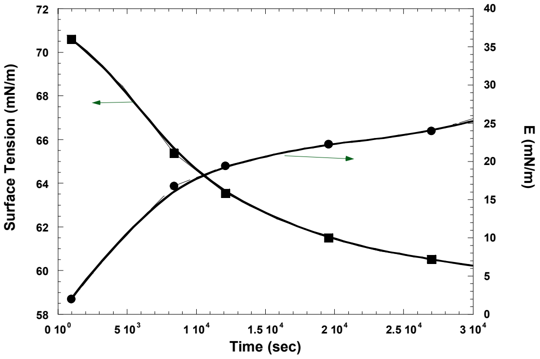


Figure 6: Evolution of surface tension (■) and elasticity modulus (●) with time for sodium decylsulfonate in water (C = 10^{-4} mol·L^{-1}; T=25 °C; frequency: 0.42 rd·s^{-1})

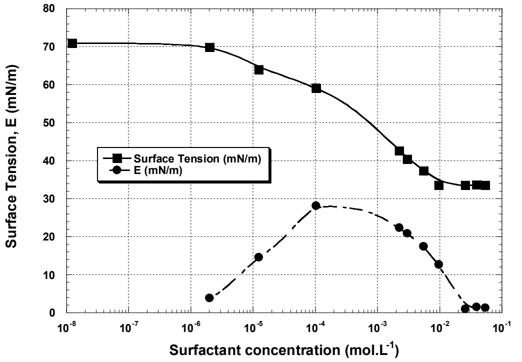


Figure 7: Evolution of equilibrium surface tension (■) and elasticity modulus (●) with sodium decylsulfonate concentration (solvent:water; frequency: 0.42 rd·s^{-1})

Conductimetric study

As carried out for surfactant solutions, the conductivity of a chitosan solution can be measured when a surfactant solution is added (Fig. 8).

Conductimeric curves are more complex than those of pure chemicals. A slope appears at a surfactant concentration around 10^{-3} mol/L, which is much lower than the CMC of surfactant in water ($4 \cdot 10^{-2}$ mol/L). This critical concentration is considered as the critical aggregation concentration (CAC) between surfactant and polyelectrolyte. Before reaching this threshold concentration, the slope decreased, comparatively with that of the surfactant alone. This can be explained by the decrease of surfactant molecules from solution through electrostatic association with polyelectrolytes. This binding continued until the saturation of chitosan with surfactant. The concentration stoichiometric ratio of ionic charges Z = [TA]/([Chit] x (1-DA)) (concentrations being expressed as mol·L^{-1} for surfactant and monomol·L^{-1} for chitosan) was very close to 1 (Table 3), demonstrating that the major part of the ionic charges of the polyelectrolyte was compensated by the surfactant. Under such conditions, when polymer concentration was high enough, the precipitation of the complex was observed. It has already been noticed that the ionic "equivalence point" (for Z = 1) occurs before CAC[15] and also that the maximum of turbidity or of precipitation does not occur in these systems at the equivalence point, as in simpler mixtures of surfactants of opposite electrical charges. Indeed, in the bulk, the surfactant does not only screen the polymer charges, but it is likely to start interacting with the polymer chains. After reaching CAC, the slope increases and the curve tends to converge with the pure surfactant curve.

This CAC value is lower than CMC by several orders of magnitude,[18,43] because the polyelectrolyte stabilizes the charge on the micelle surface and no counter-ions are required to condense either on the micelle or on the polymer section associated with the micelle.[43] This regime of very small addition of surfactants is an important domain for all interfacial mechanisms involved in the stabilization of emulsions and foams.

From the slopes of the different linear parts of the curves, the association degree between chitosan and surfactant was calculated. For TA concentrations lower than CAC, the added TA molecules associate with the chitosan macromolecular chains, the slope of the conductivity curve being given by (5):

$$p_1 = (\lambda^0_{TA^-} + \lambda^0_{Na^+}) + \theta\left[\lambda^0_{Cl^-} - \lambda^0_{TA^-} - f(\lambda^0_{Chit^+} + \lambda^0_{Cl^-})\right]$$

where $\lambda°_i$ is the mobility of ion i, θ the association degree between chitosan and surfactant molecules and f the transport coefficient of polymeric ionic charges given by the Manning theory[44] (Table 1). For pure components, the observed slopes are:

$$p_{TA} = (\lambda^0_{TA^-} + \lambda^0_{Na^+}) \qquad [6]$$

$$p_{Chit} = \left[f(\lambda^0_{Chit^+} + \lambda^0_{Cl^-})\right] \qquad [7]$$

From these equations, one may obtain:

$$\frac{p_1}{p_{TA}} = 1 + \frac{\theta}{p_{TA}}\left[\lambda^0_{Cl^-} - \lambda^0_{TA^-} - p_{Chit}\right] \qquad [8]$$

and

$$\theta = \left(\frac{p_1}{p_{TA}} - 1\right)\frac{p_{TA}}{\left[\lambda^0_{Cl^-} - \lambda^0_{TA^-} - p_{Chit}\right]} \qquad [9]$$

Considering that, at 25 °C, $\lambda°_{Cl^-} = 76.35$ $S\cdot cm^2\cdot mol^{-1}$, $\lambda°_{TA^-} = 19.45$ $S\cdot cm^2\cdot mol^{-1}$, the θ values were calculated (Table 3), the values of the degree of association, which correspond to the fraction of ion pairs present in the complex, are high. Hence, there is a strong associative electrostatic interaction between polymer and surfactant and, the lower molecular weight, the higher the interaction (and the degree of association). It was already demonstrated[45] that the higher the charge density of the polyelectrolyte, the higher the degree of association is.

For TA concentrations higher than CAC, the slope of the linear parts of the curves is very close to the one obtained with surfactant alone, a value below CMC meaning the presence of independent TA molecules. For TA concentrations higher than CMC, the observed slope is that of the TA micelles.[14]

Interfacial properties – adsorbed layers

The adsorption kinetics of the TA–polyelectrolyte mixtures was performed at different surfactant and chitosan concentrations (Fig. 9). The composition of the mixed surfactant–chitosan solution was highly non-stoichiometric by the charges of the components that ensured the solubility of the formed dynamic associates (SPEC) in water, at surfactant concentration lower than the critical aggregation concentration (CAC) and approximately equal to 10^{-3} mol/L.

Cationic polyelectrolyte chitosan, as well as other polyelectrolytes, has no tensioactive properties,[17] which corresponds to the known property of the weakly hydrophobic polyelectrolytes – that of manifesting poor adsorption activity at both oil-water and air-water interfaces, at a relatively high degree of ionisation.[46,47] However, in mixed solutions of oppositely charged surfactants and polyelectrolytes, surface tension is reduced considerably at the same very low surfactant concentration in solution.[17] Chitosan forms cooperative electrostatic dynamic associations with the surfactant molecules, as previously demonstrated by conductimetric experiments, leading to co-adsorption of surfactant and polymer at the air-water interface.[48] As already demonstrated with various systems, the surface activity of these complexes is much higher than that of the polymer or surfactant alone,[49] due to the labile character of the alkyl chains of the surfactant.

The formation of the surfactant–polyelectrolyte complex makes easier the diffusion of tensioactive molecules towards the interface, as adsorption is quicker (lower induction times and accelerated kinetics), allowing more efficient processes for emulsion preparation. The calculation of the diffusion coefficients using relation [3] in the post-lag stage evidences an increase of the surfactant diffusion coefficient in the presence of the polyelectrolyte. As an example, it is equal to $9.5\cdot10^{-12}$ m^2/s in the 10^{-3} $monomol\cdot L^{-1}$ chitosan $1/10^{-4}$ $mol\cdot L^{-1}$ sodium decylsulfonate system, compared to

$0.27 \cdot 10^{-12}$ for pure surfactant – at the same concentration.

The higher the molecular weight of the polyelectrolyte, the more important the interfacial properties. Moreover, when molecular weight increased, the induction time decreased. Some previous studies[17,19] have demonstrated that the synergetic effects of the surface activity of SPECs increase with the length of the alkyl hydrophobic chains grafted onto the hydrophilic backbone. The present experiments show the influence of the macromolecular backbone size. Further experiments have to be carried out to give a correct interpretation of this observation.

Simultaneously with the decrease of surface tension during the formation of the adsorption layer, its mechanical characteristics evolve, the viscoelastic moduli increasing. The elastic moduli and surface tensions at equilibrium are given in Table 4. The total viscoelastic modulus E of the surfactant–polyelectrolyte complex was higher than those of the components alone, which may be related to the presence of an organized structure between chitosan and sodium decylsulfonate – as demonstrated for chitosan-SDS systems.[50] Building this structure increased the elasticity of the interfacial film and, hence, allowed an improvement in the emulsion stability. However, at very low polymer concentrations, polymers with different molecular weights behave similarly.

Stabilisation of emulsions

Emulsions are metastable dispersions made of two immiscible liquids, one being dispersed into the other by means of surface-active agents. Emulsions are of considerable industrial importance in a broad range of application domains, such as cosmetics, foods, paints and pharmaceuticals. Their stability depends on several parameters: drop size and polydispersity, drop volume fraction, solubility of the phase dispersed into the continuous one, etc. The lifetime of emulsions may vary from a few minutes to many years, depending on the surfactant and emulsion characteristics. Emulsion destruction occurs under the influence of several processes: sedimentation or creaming, Ostwald ripening (transfer of liquid from smaller drops to the larger ones by diffusion through the continuous phase) and coalescence (fusion of two droplets after rupture of the liquid film between them). It is currently accepted that the last process is mainly controlled by surface viscoelasticity. Ostwald ripening is mainly controlled by the solubility of the phase dispersed into the continuous one and by the dispersed-phase volume fraction. However, recent work suggested that surface elasticity also plays an important role in this process.[51] More recently, Georgieva *et al*. have demonstrated the correlation between emulsion stability and the elasticity modulus.[52]

Surfactant–polyelectrolyte complexes have been demonstrated to help in foam stability,[53] and their influence on water/oil emulsion stability was studied. It is known that the smaller the size of emulsion droplets, the more reduced the gravity forces and Brownian diffusion are, leading to sedimentation and creaming prevention.[54] Moreover, steric stability, due to the adsorption of the macromolecular chains at the interface, may prevent flocculation and coalescence of the emulsion droplets.[54]

An example of retrodiffusion spectra is presented in Figure 10. These spectra represent the macroscopic mark of emulsion at a given time. As reflectance R increases with the volume fraction of the dispersed phase when the droplet size remains constant, it may be observed that the oil droplets ride up to the emulsion surface (as the volume mass of the organic phase is smaller than that of the aqueous one). This phenomenon is called “creaming”. The addition of surfactant increases the stability of emulsions containing chitosan. The droplet diameter was calculated by the modified Stokes law (Table 5).

Stability duration was estimated from the retrodiffusion spectra, as time regained to reach a decrease in the migration rate of droplets (Table 5). The stability of emulsions was improved when the complex was used. When polymer concentration was close to the overlap concentration C* (of the $1/[\eta]$ order of magnitude, $[\eta]$ being the intrinsic viscosity of the polymer), the addition of surfactant does not notably modify the characteristics of the emulsions, while, for lower polymer concentration, the addition of surfactant causes a remarkable decrease of the migration rate and size of droplets, leading to an increased stability of the emulsion. This stability is observed even at very low surfactant concentration (100 times lower than the CMC of pure surfactant in water).

The use of a polymer concentration of the order of magnitude of the overlap concentration leads to a higher stability of the emulsions, even when using surfactant concentrations much lower than its critical micelle concentration. This may be of great interest when the use of low molecular weight surfactant appeared as a drawback, for example in body care formulations. Interfacial experiments were carried out on systems evidencing the best stability of emulsions (Tests 3 and 11, Fig. 10 and Table 5). The addition of polymer to surfactant improves the stability of emulsion by decreasing surface tension and by increasing the elasticity modulus. However, some difference may be observed: the elasticity modulus is higher when low molecular weight chitosan was involved. This is in relation with the concentration used: previously, the polymer concentration was lower than the overlap concentration contrary to the concentration used for emulsion stability tests. This aspect should be better investigated for defining the optimal formulation for stabilizing emulsions.

Table 3
Physico-chemical characteristics of chitosan-sodium decylsulfonate complexes

Parameters	Chitosan 1/TA	Chitosan 2/TA
CAC (mol.L^{-1})	$9.4 \cdot 10^{-4}$	$9.8 \cdot 10^{-4}$
Z	1.1	1.1
Association degree (θ)	0.95	0.83

Table 4
Surface tension and elastic modulus at equilibrium

System	Surface tension (mN/m)	Elastic modulus (mN/m)
Sodium decylsulfonate, 10^{-5} mol·L^{-1}	64.0	14.69
Sodium decylsulfonate, 10^{-4} mol·L^{-1}	59.5	28.21
Chitosan 1, 10^{-3} monomol·L-1	70.1	3.76
Chitosan 2, 10^{-3} monomol·L-1	71.6	0.99
TA 10^{-5} mol·L^{-1} – Chitosan 1 10^{-4} monomol·L^{-1}	59.1	49.17
TA 10^{-4} mol·L^{-1} – Chitosan 1 10^{-3} monomol·L^{-1}	55.9	54.14
TA 10^{-5} mol·L^{-1} – Chitosan 2 10^{-4} monomol·L^{-1}	52.9	45.49
TA 10^{-4} mol·L^{-1} – Chitosan 2 10^{-3} monomol·L^{-1}	44.9	72.68

Table 5
Emulsion characteristics from Turbiscan experiments

Test	Polymer	C_p (monomol·L^{-1})	C_{TA} (mol·L^{-1})	C_p/C_{TA}	Stability time	Migration rate (mm/min)	Droplet size (μm)
			$2.5 \cdot 10^{-4}$		40 min	0.52	21.5
1	Chitosan 1	$2.5 \cdot 10^{-2}$			44 h	$1.63 \cdot 10^{-2}$	13.9
2	Chitosan 1	$2.5 \cdot 10^{-2}$	$1.25 \cdot 10^{-4}$	200	32 h	$1.40 \cdot 10^{-2}$	12.9
3	Chitosan 1	$2.5 \cdot 10^{-2}$	$2.5 \cdot 10^{-4}$	100	47 h	$1.49 \cdot 10^{-2}$	13.3
4	Chitosan 2	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	100	4 h	0.26	39.7
5	Chitosan 2	$5 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	50	4 h	0.33	44.5
6	Chitosan 2	$1 \cdot 10^{-2}$			24 h	$5.9 \cdot 10^{-2}$	24.6
7	Chitosan 2	$1 \cdot 10^{-2}$	$5 \cdot 10^{-5}$	200	120 h	$5.7 \cdot 10^{-2}$	24.2
8	Chitosan 2	$1 \cdot 10^{-2}$	$1 \cdot 10^{-4}$	100	120 h	$4.2 \cdot 10^{-2}$	20.7
9	Chitosan 2	$2.5 \cdot 10^{-2}$			24 h	$2.8 \cdot 10^{-2}$	26.5
10	Chitosan 2	$2.5 \cdot 10^{-2}$	$1.25 \cdot 10^{-4}$	200	200 h	$1.9 \cdot 10^{-3}$	6.9
11	Chitosan 2	$2.5 \cdot 10^{-2}$	$2.5 \cdot 10^{-4}$	100	800 h	$3.8 \cdot 10^{-4}$	3.1

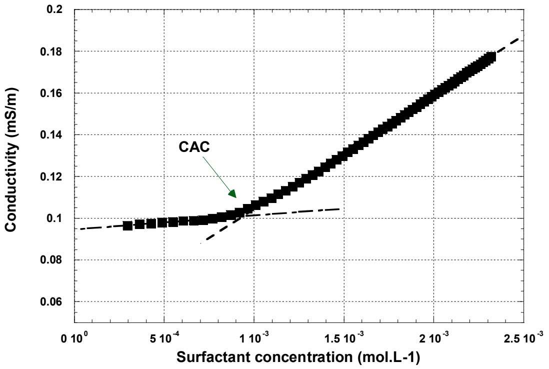
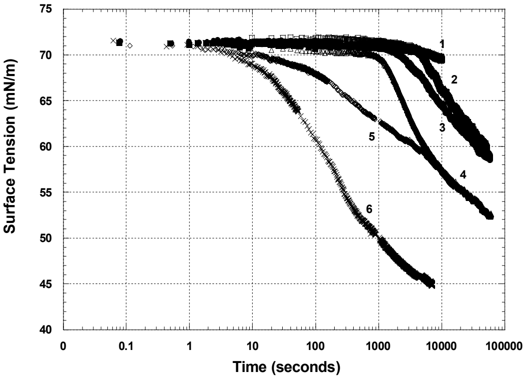


Figure 8: Evolution of conductivity of a chitosan solution with addition of a sodium decylsulfonate solution (Chitosan 1, 10^{-3} monomol·L^{-1}; T = 25 °C; solvent:water)



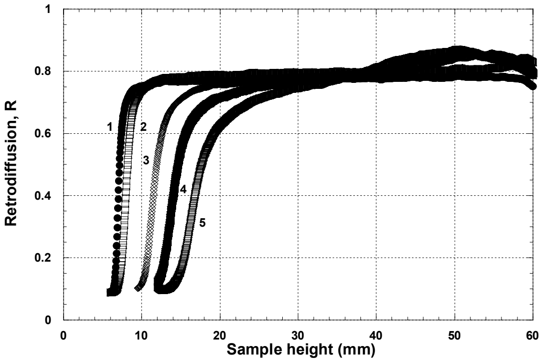


Figure 9: Dynamic surface tension curves of sodium dodecylsulfonate (TA), chitosans and complexes (curve 1: Chitosan 2 10^{-3} monomol·L^{-1}; curve 2: TA 10^{-4} mol·L^{-1}; curve 3: TA 10^{-5} – Chitosan 1 10^{-4}; curve 4: TA 10^{-5} – Chitosan 2 10^{-4}; curve 5: TA 10^{-4} – Chitosan 1 10^{-3}; curve 6: TA 10^{-4} – Chitosan 2 10^{-3})

Figure 10: Retro-diffusion curves using Turbiscan for emulsion 11 sample (Table 5) at different times (curve 1: 0 min; curve 2: 2 days; curve 3: 2 weeks and 1 day; curve 4: 3 weeks and 2 days; curve 5: 4 weeks and 2 days)

CONCLUSIONS

Cationic chitosan and anionic sulfonate surfactants may interact by electrostatic interactions. Such surfactant/polyelectrolyte complexes (SPECs) present very interesting surface-active properties, even at very low surfactant concentrations (much lower than the CMC of pure surfactant), influencing either surface tension or the viscoelastic properties of the adsorbed layers. This allows their use as emulsion stabilizers, while the very low surfactant concentration recommends them as potential candidates for cosmetic applications.

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