Carbohydrate Polymers 74 (2008) 648–658

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Study of the complex formation between sodium dodecyl sulfate and hydrophobically modified chitosan

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ARTICLE INFO

Article history:
Received 29 October 2007
Received in revised form 22 February 2008
Accepted 14 April 2008
Available online 22 April 2008

Keywords:
Chitosan
Hydrophobically modified polymer
Sodium dodecyl sulfate
Surfactant selective electrode (SSE)
Isothermal titration calorimetry (ITC)

ABSTRACT

The cationic biopolymer chitosan has many applications in the food, cosmetic and pharmaceutical industries. In this paper, grafted alkylated side chains on the chitosan backbone hydrophobically modify this water-soluble polymer. In this study, cationic HMP is characterized (acetylation degree and substitution degree) and polymer–surfactant complexes formed with anionic surfactant Sodium Dodecyl Sulfate (SDS) are investigated. Solvent is a pH 4 acetic acid solution $T = 25$ °C.

Binding isotherms and surface tension measurements have been made. The structure of the complexes in the bulk phase has been studied by turbidity and zeta potential measurements. Isothermal titration calorimetry (ITC) allowed some conclusions to be drawn concerning the extent of the hydrophobic interactions.

It is concluded from the determination of optimal ionic ratio shows that the alkylated chitosan/SDS system could be used as wall material for capsules using the coacervation process.

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1. Introduction

Chitin, the second most abundant natural polysaccharide after cellulose, is found in crustaceous shells. Chitosan is the main derivative water-soluble polymer: it is obtained by partially or fully N-deacetylation of chitin. Chitosan is interesting in many applications such as food, cosmetics or pharmaceutical industries because it is a non-toxic, biodegradable polymer and soluble in acidic conditions due to the protonation of amino groups (Ravi-Kumar, 2000; Rinaudo, Pavlov, & Desbrières, 1999).

Chitin and chitosan are copolymers of (1 → 4) linked 2-amino-2-deoxy-β-D-glucopyranose and 2-acetamino-2-deoxy-β-D-glucopyranose units (Fig. 1). These copolymers are characterized by their degree of acetylation (DA) that is the average molar ratio of *N*-acetyl-D-glucosamine units in the macromolecular chain. It is commonly accepted that chitosan has DA<0.5. At relatively low pH (<6.5), it is water-soluble and displays a polycationic character because of the protonation of amino groups (pK_a value equal to 6.5) (Rinaudo et al., 1999).

The introduction of alkyl side chains on the polymer backbone chemically modifies chitosan, thus forming a hydrophobically modified chitosan (alkylated chitosan).

Hydrophobically modified polymers (HMP) or so-called associative polymers, are widely used in technical formulations such as cosmetics or food due to their hydrophilicity, biodegradability and antibacterial properties. Because of the coexistence of both hydrophobic and hydrophilic parts, these associative polymers are amphiphilic: in an aqueous solution, hydrophobic parts assemble into micelle-like aggregates in order to avoid contact with water, whereas hydrophilic parts are exposed to water.

The interactions between polymers and surfactants in aqueous solutions have been a subject of intensive research as well as fundamental scientific studies. It is usually accepted that the main driving force for association in polymer-surfactant aqueous solution is the hydrophobic interaction (Onésippe & Lagerge, 2008). Previous studies have shown that chitosan can interact with anionic surfactants to form soluble or insoluble complexes (Thongngam & McClements, 2004; Vikhoreva, Babak, Galich, & Gal'braikh, 1997). These complexes are stabilized by electrostatic and hydrophobic interactions and can be formed when the surfactant concentration is well below its critical micelle concentration (CMC).

Few studies are dedicated to surfactant complexation with oppositely charged hydrophobically modified polyelectrolytes (Babak et al., 2000; Guillemet & Piculell, 1995; Magny, Iliopoulos, Zana, & Audebert, 1994). In general, these systems exhibit similar characteristics to surfactant/oppositely charged polyelectrolyte one.

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doi:10.1016/j.carbpol.2008.04.021

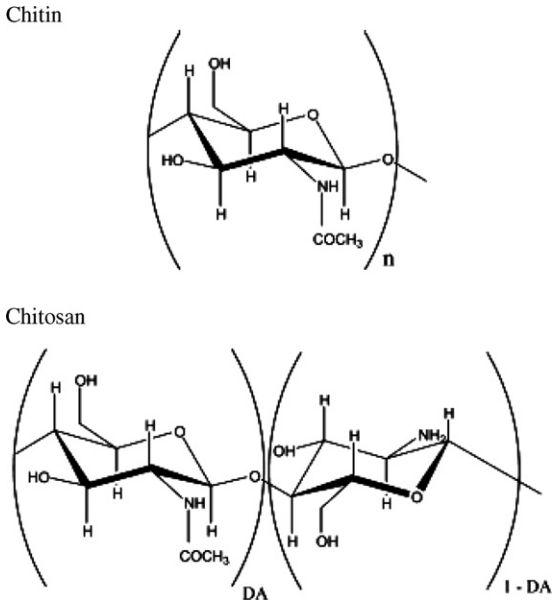


Fig. 1. Chemical structures of chitin and chitosan. DA is the degree of acetylation.

They form Surfactant Polyelectrolyte Complexes (SPECs). There are two critical concentrations: the critical aggregation concentration (CAC), which is usually well below the critical micelle concentration (CMC) of the surfactant (Chu & Thomas, 1986).

CAC is the concentration of the beginning of the hydrophobic interactions between surfactant molecules electrostatically bound to polymer according to Bai, Santos, Nichifor, Lopes, and Bastos (2004). In surfactant/polyelectrolyte of opposite changes, the CAC is generally identifiable as the beginning of the plateau in the surface tension isotherms (Ritacco & Kurlat, 2003). A saturation concentration C_2 can also be determined: it corresponds to the surfactant concentration when free micelles start to form after the polymer is fully saturated with bound surfactant (Prado, Macedo, Dias, & Dias, 2004). As described by Guillemet and Piculell (1995) the binding isotherms of oppositely charged polymer/surfactant system have a shape that may be divided into three parts: (1) a non-cooperative (electrostatic) high-affinity binding of surfactant, (2) an extended region of anti-cooperative binding and then (3) a region of cooperative binding.

This paper reports the study of interactions and nature of interactions between SDS and oppositely charged alkylated chitosan. The anionic surfactant SDS is involved in many studies of complexation with polyelectrolytes (Li et al., 2001; Thongngam & McClements, 2004; Vikhoreva et al., 1997). In our conditions (pH 4 medium; acetic acid solution is used as solvent), alkylated chitosan is a cationic polyelectrolyte because of the protonation of amino groups.

Results obtained by several methods such as turbidity measurements, surfactant selective electrode (SSE), zeta potential coupled with surface tension, isothermal titration calorimetry (ITC) are presented in order to better to explain the nature of interaction between hydrophobically modified chitosan and oppositely charged SDS.

2. Experimental

2.1. Materials

Alkylated chitosan (C12 alkyl chains), have a viscosity-average molar mass of about 300,000 g/mol. It was obtained by reductive amination according to the protocol defined by Yalpani and Hall (1984) and improved by Desbrières, Martinez, and Rinaudo (1996). The structure of the modified unit is shown in Fig. 2. The degree of acetylation (DA) and degree of substitution (DS), determined by ^{1}H NMR technique, are found to be equal to 0.25 and 0.068, respectively.

A preliminary study allows the calculation of C^* (critical covering concentration i.e., limit between the dilute and semi-dilute regimes): C^* was found equal to 0.0148 wt%. Beyond C^* (semi-dilute regime), HMP forms intermolecular hydrophobic domains but it happens sometime that these domains are present slightly before this critical concentration (Philippova et al., 2001).

Analytical grade surfactant, Sodium Dodecyl Sulphate (SDS) with a purity exceeding 99%, and acetic acid solution were purchased from Fluka (France). The water used throughout was distilled and deionized with a Millipore "Super Q" system.

2.2. Preparation of solutions

Water, buffered to pH ≈4 by acetic acid solution (1 mol/l), has been used as the solvent without any other reagent. The pH-measurements were performed with a Tacussel 3000 pH-meter with a glass electrode. Before use the solvent is filtered with a Minisart 0.45 μm cellulose acetate filter.

A polymeric stock solution was prepared by dissolving a mass of alkylated chitosan, to the desired concentration, in the acidic solvent. The solution was maintained under gentle magnetic stirring overnight at 25 °C, then the pH of the polymeric solution was adjusted to 4.0 using very small aliquots of 1 mol/l acetic acid solution. Finally the solution was kept under relaxation for one day before any use. pH value was checked and eventually adjusted as above described before any use. Concentrations are given in weight percent (%).

Surfactant solutions were prepared using the same procedure. Concentrations are expressed in mol/l.

2.3. ^{1}H NMR characterization of alkylated chitosan

As described by others (Desbrières et al., 1996), a 5 g/l alkylated chitosan solution is prepared in deutered water (D_2O) buffered with deutered acetic acid (AcOD) solution such as pH is equal to 4. After freeze-drying, the recovered product is redissolved in a deutered water solution in the presence of AcOD then is freeze-dried again. This stage is repeated three times to allow the exchange of the unstable protons of the hydroxyl groups of the polymer by deuterium atoms. The hydroxyl groups unstable protons vibrate at the same frequency, their exchange by deuterium atoms makes it possible to minimize the residual signal of light water (H_2O).

Fig. 3 represents a typical spectrum of ^{1}H NMR of a sample of purified hydrophobic chitosan obtained from a Bruker spectrometer advances DRX 400 at a frequency of resonance of 400.13 MHz

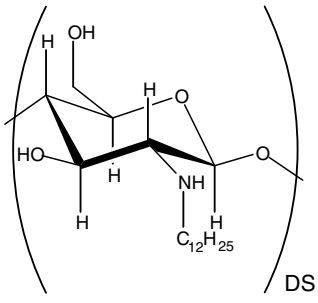


Fig. 2. Chemical structure of the modified unit of alkylated chitosan. DS is the degree of substitution.

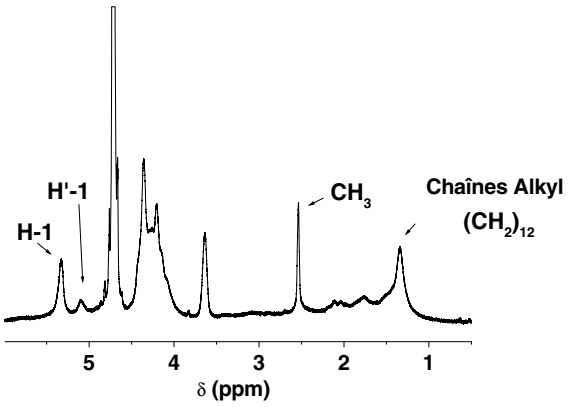


Fig. 3. ^{1}H NMR spectrum of hydrophobically modified chitosan at 80 °C.

and at 80 °C. It allows the evaluation of DA and DS (DS is the percentage of alkylated chains grafted onto the polymer backbone).

Pulses of 45° (5 ms) are applied with a time (DS) 40 s between accumulations and 256 accumulations to ensure of quantitative measurements. The calculation of DA is based on H-1 and H′-1 protons as internal reference (Rinaudo, Milas, & Le Dung, 1993); H-1 are the anomeric protons of D-glucosamine units and H′-1 those of *N*-acetyl-D-glucosamine units:

$$DA = \frac{\frac{I_{CH_3}}{3}}{I_{H-1} + I_{H'-1}} \quad (1)$$

$I_{H-1}, I_{H'-1}$ and I_{CH_3} represent the integrals of the signals of, respectively, H-1, H′-1 and CH_3 protons.

^{1}H NMR measurements were made at 80 °C: the resolution of the signals of the H-1 and H′-1 protons is not obstructed by resonance of water (H_2O). Table 1 reports the integration of the signals corresponding to the various protons. These values give an approximate DA of 25%. By using the following expression (Esquenet, 2003),

$$DS = \frac{\frac{I_{(CH_2)12}}{24}}{I_{H-1} + I_{H'-1}} \quad (2)$$

where $I_{H-1}, I_{H'-1}$ and $I_{(CH_2)12}$ represent integrations of the signals of, respectively, H-1 protons (anomeric protons of D-glucosamine units), H′-1 (anomeric protons of *N*-acetyl-D-glucosamine units) and protons of grafted alkyl chain. Thus, we calculate DS ≈ 6.8%.

The determination of DA and DS allow the calculation of the proportions of the various types of units for hydrophobic chitosan, values that are useful to determine polymer concentrations in monomol/kg for the estimation of ionic ratios.

2.4. Isothermal titration calorimetry (ITC) measurements

Enthalpy and kinetic data relating to SDS/alkylated chitosan binding can be obtained by direct calorimetric measurement, which is a valuable and independent experimental method. We used a new "Calostar" batch microcalorimeter, which is an improved version of "Montcal 3" microcalorimeter (Partyka, Lindheimer, Zaini, Keh, & Brun, 1986). Aliquots (50 μl) of the surfactant stock solution with concentration of 0.02 mol/l were injected stepwise, using an external syringe, into the calorimetric cell containing 8 g of solvent (blank experiment) or 8.0 g of polymeric solution (binding experiment). The differential molar enthalpies associated with these steps and thereby corresponding to any structural change of the SDS/alkylated chitosan complexes during their formation were calculated from the experimentally measured enthalpies changes occurring while injecting SDS solution. The measured heat effects are the sum of the heat of binding of SDS to polymer and the heat of dilution of the SDS stock solution. Consequently, a correction term arising from the dilution of the SDS injected into the calorimetric cell should be subtracted from the total enthalpic effect. Dilution enthalpies of the SDS stock solutions used for complexation were therefore also determined in order to correct the values measured during the complexation experiments for the heat of dilution. Data analysis by means of enthalpy and thermodynamic aspects of formation of surfactant–polymer complexes have been discussed in the literature (Prado et al., 2004; Thongngam & McClements, 2004).

Table 1
Integrations of protons in alkylated chitosan

	H-1	H′-1	$-CH_3$	$-(CH_2)_{12}$
Integration	100	16.68	87.18	190.34

The apparent differential molar enthalpies of dilution ($\Delta_{dil.}\dot{h}$) and complexation ($\Delta_{com}\dot{h}$) corresponding to a given dilution or complexation step were evaluated by means of the following equations:

$$(\Delta_{dil.}\dot{h}) = \frac{\Delta_{exp.}H}{\Delta n_2^i} \quad (3)$$

$$\Delta_{bind}\dot{h} = \frac{\Delta_{exp.}H - n_2^i \Delta_{dil.}h}{\Delta n_2^a} \quad (4)$$

Where $\Delta_{exp.}H$ is the experimentally measured enthalpy change, $\Delta_{dil.}\dot{h}$ is the differential molar enthalpy of dilution for the equilibrium concentration C of SDS in the calorimetric cell, n_2^i is the number of moles of SDS injected into the calorimetric cell, Δn_2^a is the change in the number of moles of SDS bound to the polymer and is determined graphically from the binding isotherm, and $\Delta_{dil.}$ h is the molar integral enthalpy of dilution for the equilibrium concentration of SDS in the calorimetric cell. All the adsorption experiments were conducted at T = 25 °C.

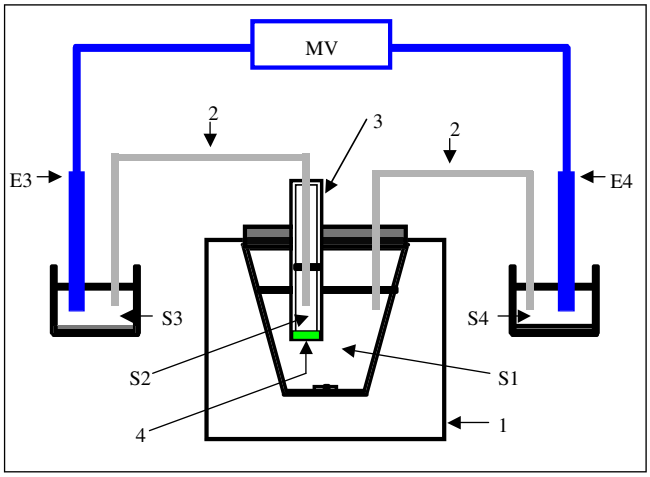
2.5. Turbidity measurements

Observation of turbidity provides information about the formation of insoluble complexes. Turbidity measurements were made using a spectroscopic technique (Metrohm 662 photometer at 600 nm) at 25 ± 0.1 °C. Aliquots (50 μl) of surfactant solution (0.04 mol/l) were injected, using an external pump, into a beaker initially containing 20 ml of polymeric solution at the desired concentration. After each injection, the system was kept under agitation for 5 min before measuring the turbidity change. Measurements were carried out three times and the change of turbidity was followed by measuring the spectrode tension (U) after each injection. This tension U is normalized by the initial tension U_0. Thus typical solubilization curves could be constructed by plotting normalized tension according to SDS concentration, $U/U_0 = f(C_{SDS})$.

2.6. Surfactant selective electrode (SSE) measurements

Surfactant ion specific electrodes have been proved useful to follow the evolution of the binding between surfactant and polymer (Li & Kwak, 2003; Magdassi & Vinetsky, 1995; Thongngam & McClements, 2005a, 2005b; Vinetsky & Magdassi, 1996) by measuring variation in the electromotive force (emf) due to the changes in SDS concentration in solution.

In this study, it was possible to estimate the binding isotherm of SDS with alkylated chitosan: it is a graph depicting the amount of SDS bound onto the polyelectrolyte as a function of free SDS concentration in solution. A SDS selective electrode was elaborated following the procedure described in the literature (Carlsson, Lindman, Watanabe, & Shirahama, 1989) and a concentration cell (Fig. 4) was constructed in our laboratory (Onésippe & Lagerge, 2008).



MV: Millivoltmeter
S1: Studied solution
S2: internal reference (SDS solution)
S3 and S4: NH_4Cl saturated solutions
E3 and E4: Calomel electrodes
1 = Thermostated cell
2 = Electrolytic bridges
3 = PVC tube
4 = PVC membrane with plasticizer.

Fig. 4. Concentration cell for the determination of binding isotherms.

This surfactant selective electrode allows accurate measurements of SDS concentrations only in a limited concentration range of 1×10^{-5} mol/l – 6×10^{-3} mol/l.

Binding measurements were carried out in duplicate, using a potentiometric titration technique (Metrohm Titrino 751 GPD) at $T = 25 \pm 0.1$ °C. Small aliquots (100 μl) of micellar solution of SDS (0.04 mol/l) were injected stepwise, using an external syringe, into a beaker initially containing 25 ml of either acetic acid solution, pH ≈4.0 (blank experiment) or an homogeneous hydrophobically modified chitosan solution at various weight percent in acetic acid (binding experiment). After each injection, the system was kept under stirring for 4 min before measuring the emf relative to a commercial Calomel electrode connected through a NH_4Cl bridge. Changes in free SDS concentration were followed by measuring the emf after each injection. Typical binding curves could be constructed by plotting changes in emf according to free SDS concentration, $E = f([SDS])$. The free SDS concentration in aqueous chitosan solution was determined from the linear range of the calibration curve.

2.7. Surface tension measurements and Zeta potential measurements

Surface tension was measured at 25 °C using the Wilhelmy plate method with K-12 tensiometer (Krüss, Germany) with the accuracy of ±0.3 mJ/m^2.

The zeta potential was calculated by measuring the electrophorectic mobility, using the Smoluchowsky approximation:

$$\mu = \frac{\varepsilon\zeta}{\eta} \tag{5}$$

where

ζ is zeta potential
μ is electrophoretic mobility
ε is dielectric constant
η is viscosity.

The of microelectrophoresis apparatus used is a Malvern Zeta-Sizer HS3000.

For both measurements, we have investigated alkylated chitosan/SDS solutions of fixed polymer concentration and variable surfactant concentrations (these solutions were left to mix during one week at 25 °C before any measurement).

3. Results

3.1. ITC measurements

Thermodynamic aspects of polyelectrolyte/surfactant interactions are investigated by this method. Enthalpies associated with the binding of surfactant onto the polyelectrolyte are directly measured.

The experiment is a series of 60 consecutive injections of a concentrated SDS solution (0.02 mol/l) in the measuring cell containing either pure solvent (blank experiment), either a polymeric solution at the desired concentration (binding experiment).

Variations of observed (apparent) differential molar enthalpy during the binding process between SDS and a 0.01 wt% (< C^*) alkylated chitosan solution are presented in Fig. 5a. This curve is not corrected by the dilution effect nor normalized by the quantity of bound surfactant. At the lowest SDS concentrations (< 0.5 mmol/l), there is a very strong exothermic peak (while dilution of SDS into solvent is endothermic) that reaches the endothermic values for intermediate SDS concentrations (∼0.5–8 mmol/l). The exothermic peak corresponds to CAC value (see Fig. 5b) and the increase of enthalpy towards endothermic values is related to the appearance of hydrophobic interactions (beyond the CAC value). Finally enthalpy values decrease (but remain endothermic) for SDS concentrations higher than 5.3 mmol/l (C_2, end concentration of interaction), where the two curves are similar.

Fig. 5c represents the observed differential molar enthalpy of complexation according to total SDS concentration for various alkylated chitosan/SDS systems (HMP concentrations ranging from 0.01 wt% to 0.05 wt%). The curves are similar and can be described as previously. The exothermic peak is more accentuated when polymer concentration increases and CAC values are not proportional to HMP concentration. We define the value ΔH^0_{int} as the enthalpy change between CAC value and C_2 concentration. This value tends to be the same in the semi-dilute regime whatever the polymeric concentration.

Table 2 reports isothermal titration calorimetry results.

3.2. Turbidity measurements

Results for 0.01 and 0.02 weight percent (wt%) alkylated chitosan solutions are showed in Fig. 6a. In the absence of chitosan or alkylated chitosan, SDS solution remains transparent: no sufficiently large aggregates to diffuse the light are formed. In the presence of alkylated chitosan, there is a decrease of the transmittance to a minimum ($C_{SDS} = 0$ to $C_{SDS} = 3.2$ mmol/l) and then a slight and progressive increase. Complexation of SDS and oppositely charged alkylated chitosan produces an insoluble complex (large enough to scatter the light), which in turn increases the turbidity. The fact that the normalized tension reaches a minimal value suggests that the HMP is saturated with SDS. Fig. 6b highlights the beginning of the experiment and shows a horizontal part then a break. This break corresponds to the concentration when SDS has neutralized a given fraction of the positive charges of HMP; hence it is possible to find $n_{SDS}/n_{alkylated\ chitosan}$ ratio corresponding to the precipitation of the SPECs.

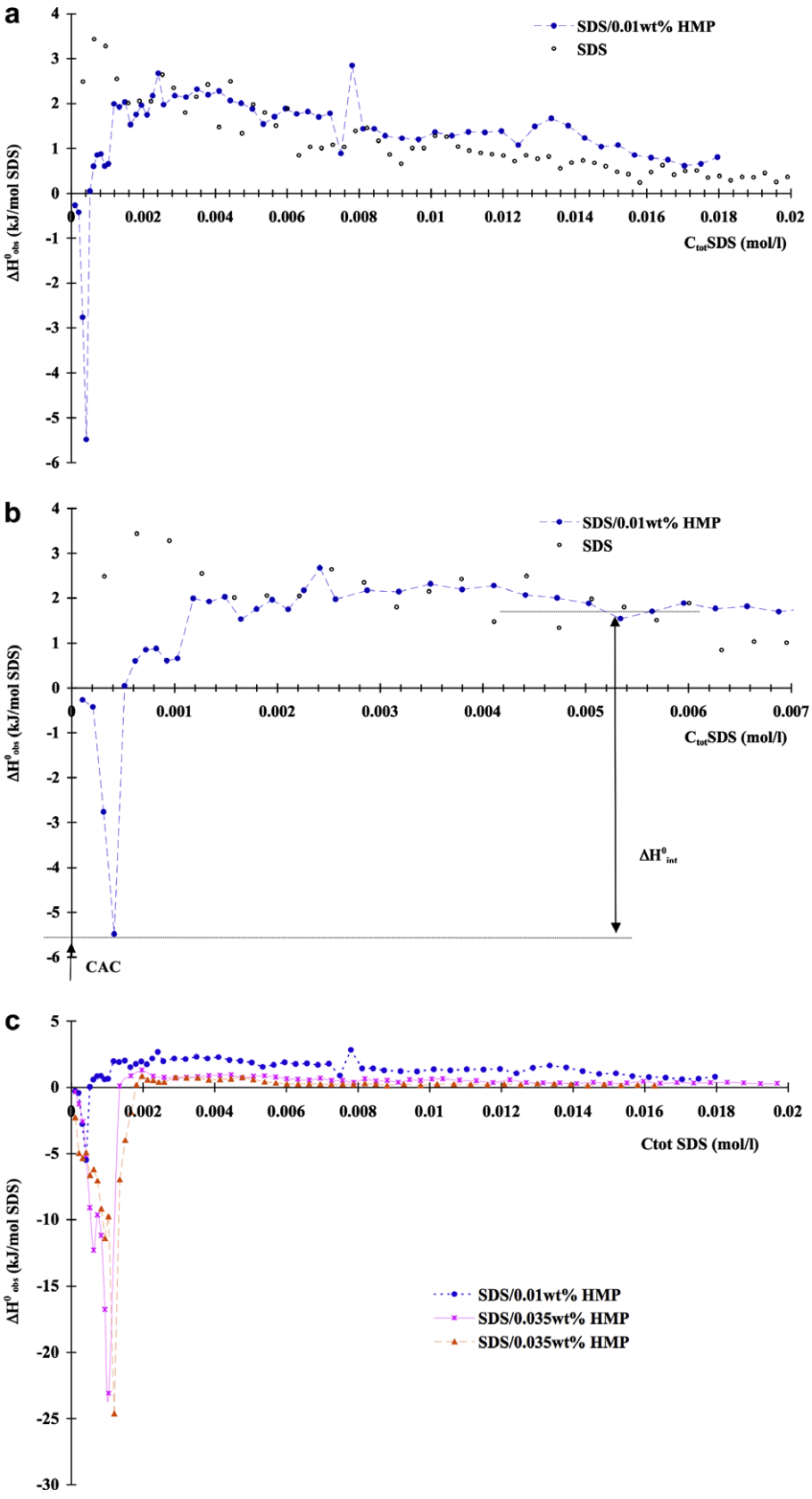


Fig. 5. (a) Enthalpic curve of dilution of a micellar SDS solution in 0.01 wt% HMP solution. (b) Expansion of (a). (c) Effect of HMP concentration on the variation of observed enthalpies occurring when a micellar SDS solution is diluted into HMP solution.

Table 2
Calorimetric results for various HMP/SDS systems

C_{HMP} (wt%)	CAC (mmol/l)	ΔH^0_{int} (kJ/mol)	ΔG^0_{int} (kJ/mol)	$T\Delta S^0_{int}$ (kJ/mol)	C_2 (mmol/l)
0.01	0.41	−7.4	−13.9	6.5	5.5
0.035	1.03	−24	−9.7	−14.3	5.7
0.05	1.2	−24.8	−9	−15.8	5.7

3.3. Binding isotherms

Fig. 7 shows the changes in emf, when SDS was titrated into solvent in the absence (calibration curve) and the presence of HMP 0.01 wt%. In the absence of HMP, there is an approximately linear decrease in EMF with increasing SDS concentration. The difference between the two types of curves is due to the surfactant/polymer interactions (Thongngam & McClements, 2004). In the presence of alkylated chitosan, the highest emf is observed at low SDS concentrations where the amount of free SDS is low. Added SDS interacts electrostatically with the polyelectrolyte. There is a continuous decrease up to a second region where the decrease is much more pronounced, starting about 0.8 mmol/l. We associate the CAC with the beginning of the change of slope.

Free SDS quantities according to total SDS quantities are presented in Fig. 8. This curve is similar to those observed by others (Thongngam & McClements, 2004) for similar system. It is composed of two distinct parts: a segment where free SDS quantities remain close to zero and a second segment where free SDS quantities increase with total SDS concentration.

Binding isotherm of 0.01 wt% alkylated chitosan/SDS is presented by Fig. 9a. It is a representation of bound SDS per gram of polymer according to free SDS concentration in solution. Its shape is similar to the one observed by others (Guillemet & Piculell, 1995; Lynch, Sjostrom, & Piculell, 2005). Effect of HMP concentration is shown in Fig. 9b. All binding isotherms have similar trend than 0.01 wt% HMP/SDS one.

3.4. Surface tension and electrophoretic mobility measurements

Behavior of polymeric solutions at liquid/gas interface is presented in Fig. 10a. The surface tension of acetic acid (solvent) is 70 mN/m (Esquenet, 2003) It is obvious that alkylated chitosan solutions show an amphiphilic character because the hydrophobic side chains tend to locate at the interface (Babak, Lukina, Vikhoreva, Desbrières, & Rinaudo, 1999).

Surface tension isotherms of HMP/surfactant systems were elaborated with volume-to-volume SDS/alkylated chitosan solutions, the constant polymer concentration was chosen to be 0.01 wt% (Fig. 10b). At this concentration, pure alkylated chitosan solution does not have any surface activity. For a better understanding, the surfactant solutions isotherm is also presented in Fig 10b. At low ionic strength (pH 4, AcOH) and without any polymer, the critical micelle concentration (CMC) of SDS is observed around 8 mmol/l, a value that is consistent with literature data (Aniansson et al., 1976). The difference between SDS and SDS/alkylated chitosan curves is characteristic of systems containing an associative polymer as described for alginate amphiphilic derivatives/SDS system (Babak et al., 2000).

This synergistic effect is due to the formation of highly surface-active SPECs. CAC is found at $C_{SDS} \approx 0.4$ mmol/l (break in the curve).

Fig. 10c is a comparison of electrophoretic mobility measurements to adsorption isotherm at liquid/gas interface for 0.01 wt% alkylated chitosan/SDS system. Electrophoretic mobility μ is correlated to particles charge. SPECs are almost neutral between the beginning of the experiment (lower SDS concentrations) and concentrations around CAC value. Charge inversion occurs at C_{SDS} = 0,6 mmol/l. Beyond this value, the global charge of the complexes tends towards an excess of negative charges.

4. Discussion

ITC measurements allow a thermodynamic study of complexation between SDS and alkylated chitosan and the determination of CAC and C_2 concentrations (Table 2). Polyelectrolyte/surfactant interactions are shown by the difference between the two curves (Fig. 5): SDS interacts with the polymer in two stages because there is a pronounced exothermic peak followed by an endothermic shoulder. These two stages are well identified in the literature and are characteristic of oppositely charged polymer/surfactant systems (Thongngam & McClements, 2004; Wang & Tam, 2002). As long as SDS dilution curve in solvent is not merged with polymer dilution one, it means that the lately injected micelles are disturbed by the presence of polymer or SPECs.

As explained by others (Thongngam & McClements, 2004), this switch from exothermic to endothermic values suggests that the polymer is saturated by the surfactant; there is no longer a hydrophobic interaction between them. These endothermic enthalpy values are correlated with demicellization of SDS in aqueous solution (Thongngam & McClements, 2005b).

ΔG^0_{int} values are negative; consequently the formation of SPECs at CAC value is a thermodynamically favorable process. The following relation $\Delta G = \Delta H - T\Delta S$ allows us to calculate the entropy change associated with the interaction. This change shows that the interaction is governed by a gain of entropy.

The results from turbidity measurements provide valuable insights into the formation of insoluble complexes between SDS and alkylated chitosan. Complexation between SDS and HMP processes in two steps as explained previously (Magny et al., 1994): first, there is an electrostatic interaction an then hydrophobic interactions.

The EMF curve is composed of two distinct segments (Fig. 7). The first segment means that all the SDS injected into the medium is bound onto chitosan or that there is no measurable free SDS in the solution. It is the first way of complexation characterized by electrostatic interactions: there is few free SDS in solution because it is a region of strong affinity between surfactant and polymer. The second segment characterizes the second way of complexation i.e. hydrophobic interactions (beyond the CAC), which are weaker. The slope of this second part is higher than the first part one: we presume an incorporation process of freshly added surfactant molecules in already formed aggregates.

The isotherm describing the binding of SDS to alkylated chitosan (Fig. 9) is composed of three parts. (1) The non-cooperative binding is very strong up to charge neutralization. (2) At $\Gamma = 9.10^{-3}$ mol/g, there is a plateau where bound SDS quantity does not change over a large range of SDS concentrations. The beginning of the plateau has to be correlated to the point where free SDS concentrations increase in Fig. 8. The plateau indicates a region of anti-cooperative binding because free SDS concentration increases while binding is quasi-constant. In this domain, added surfactant hardly incorporates into negatively charged mixed micelles. At the end of the plate ($C_{freeSDS}$ = 1.05 mmol/l thus C_{totSDS} = 2 mmol/l), anti-cooperative binding is done. Then, the cooperative binding begins when adding SDS in the medium. Freshly added SDS monomers have hydrophobic interactions with already bound monomers onto alkylated chitosan. The beginning of the second plateau indicates end of cooperative binding and moreover the end of interactions between HMP and SDS.

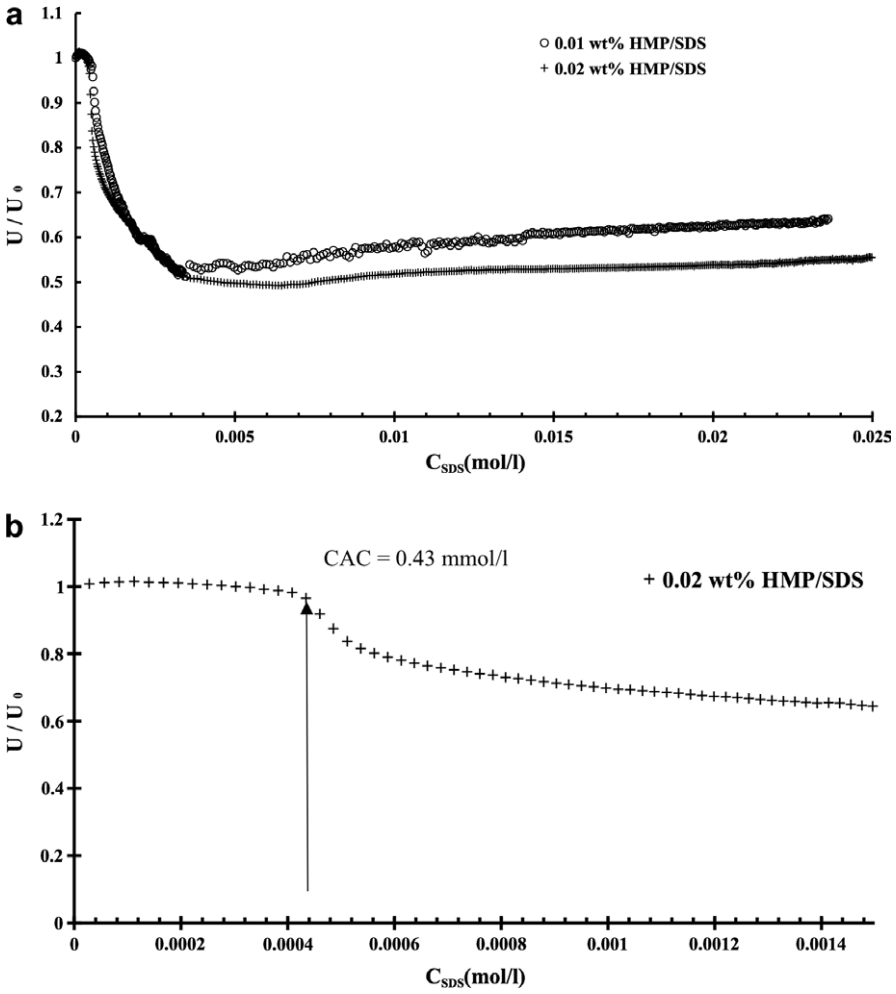


Fig. 6. (a) Change in turbidity according surfactant concentration. (b) Expansion of the beginning of the turbidity curves.

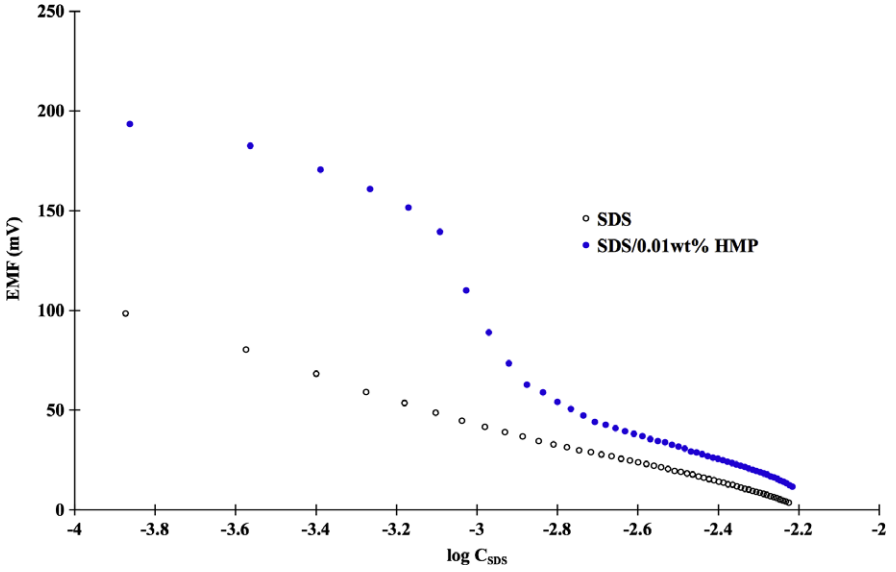


Fig. 7. Variation of SDS solution emf in the presence and absence op HMP.

While increasing polymeric concentration, bound SDS (plate region) decreases (Fig. 9b). Actually, 0.02 wt% and 0.035 wt% concentrations belong to the semi-dilute regime where we think there a decrease of surfactant affinity for HMP probably due to the presence of intermolecular hydrophobic inaccessible nano-domains in the polymer.

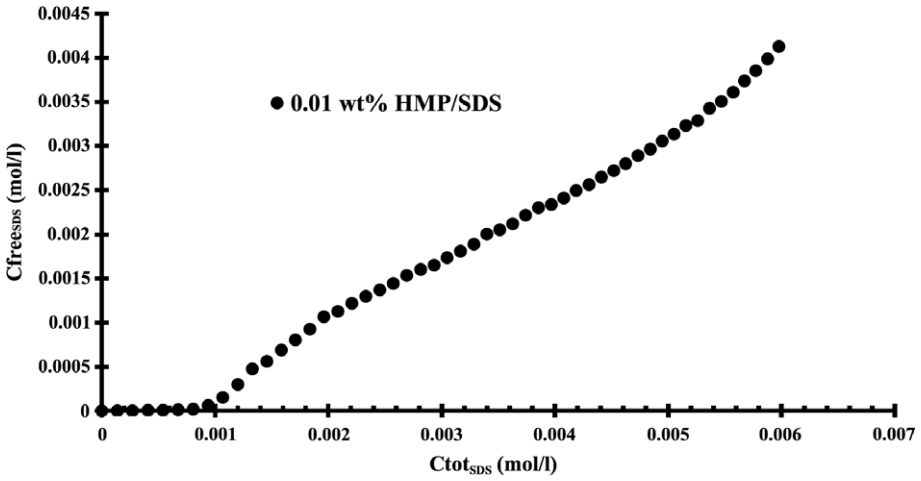


Fig. 8. Variation of amount of monomers according to total SDS concentration.

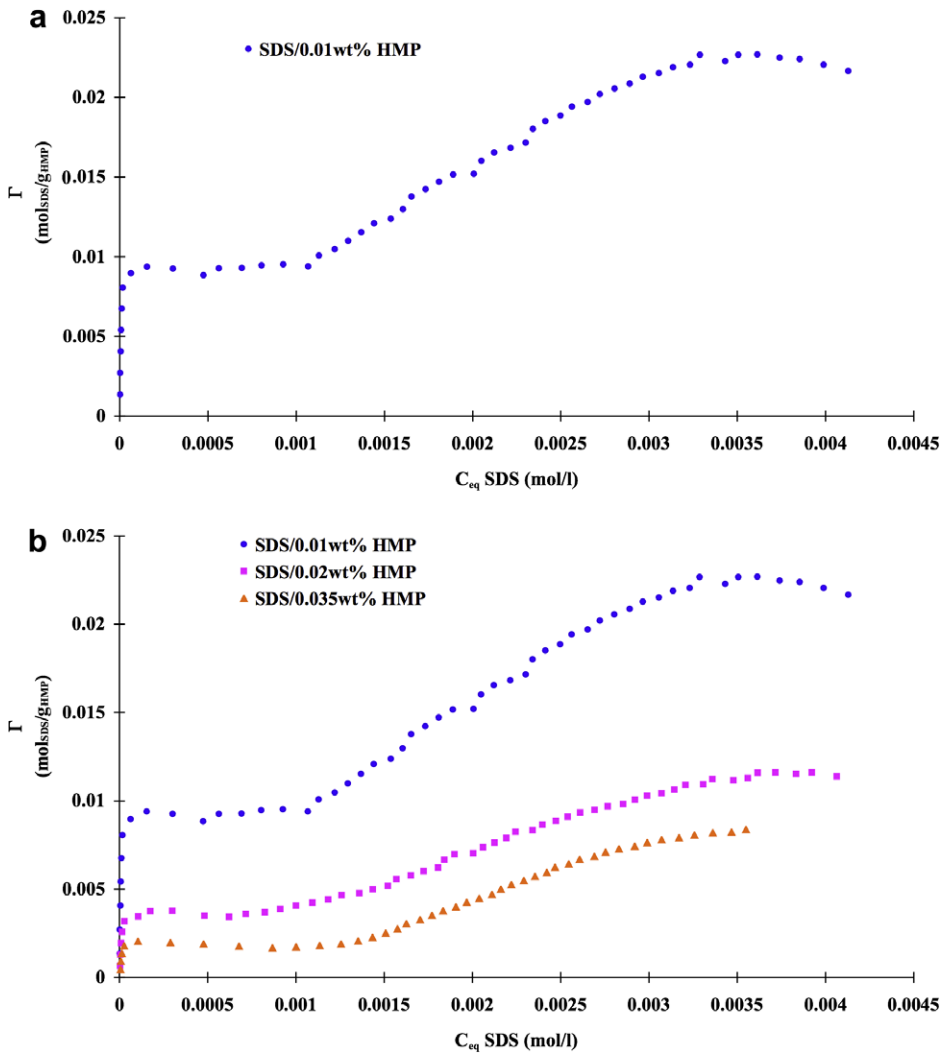


Fig. 9. (a) Binding isotherm for 0.01 wt% HMP/SDS system. (b) Binding isotherms for different concentrations of HMP in HMP/SDS systems.

Surface tension measurements give the information about surface properties of SPECs. At concentrations above the CAC, there is formation of surfactant aggregates (bound on the polymer) by a cooperative process. As explained by Magny et al. (1994), this binding is supposed to occur close to the polyelectrolyte alkyl side chains and some mixed hydrophobic clusters form and start to

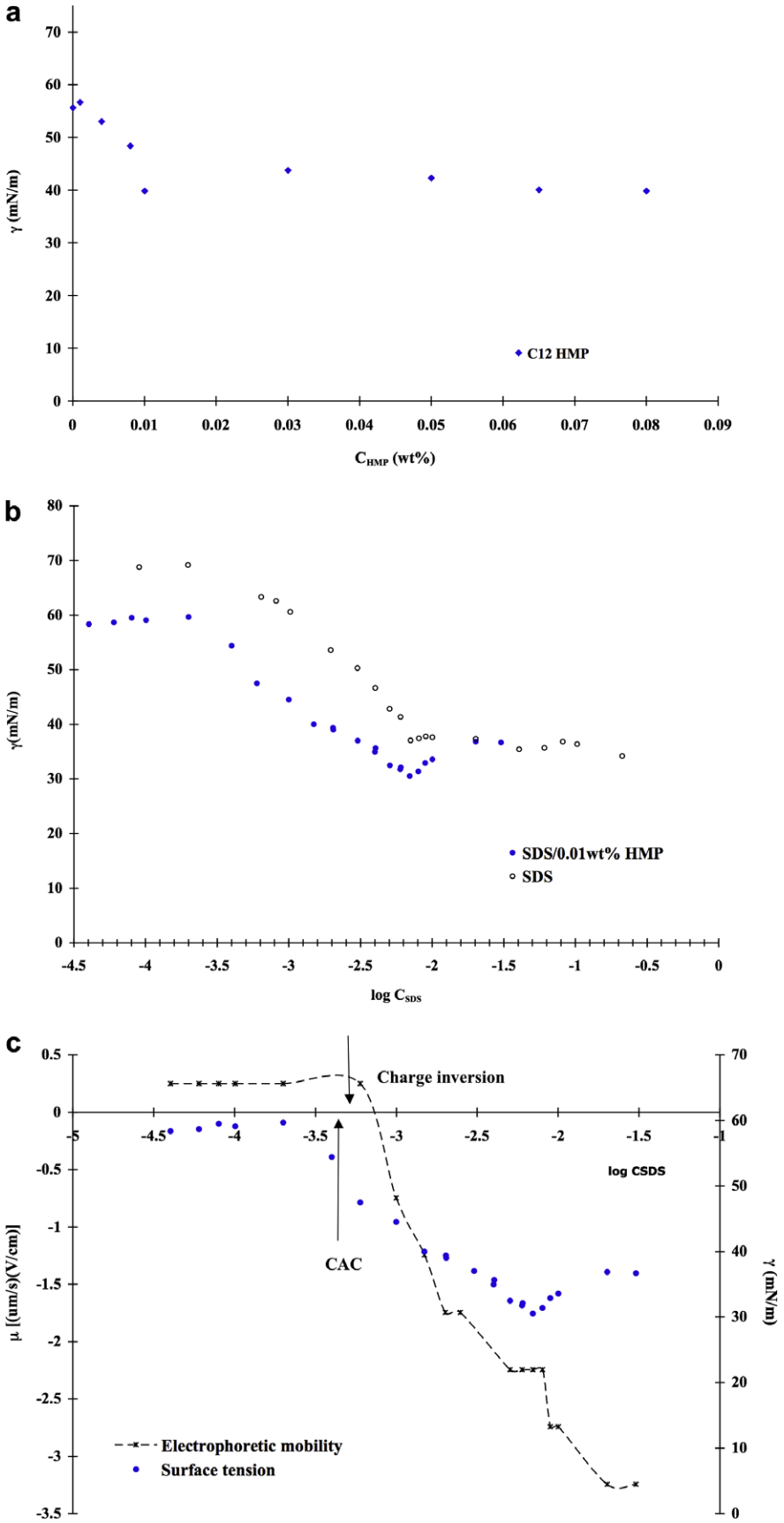


Fig. 10. (a) Adsorption isotherm of alkylated chitosan at liquid/gas interface. (b) Adsorption isotherm of 0.01 wt% HMP/SDS complexes at liquid/gas interface. (c) Comparison of adsorption isotherm at liquid/gas interface and variation of electrophoretic mobility according to SDS concentration for 0.01 wt% HMP/SDS system.

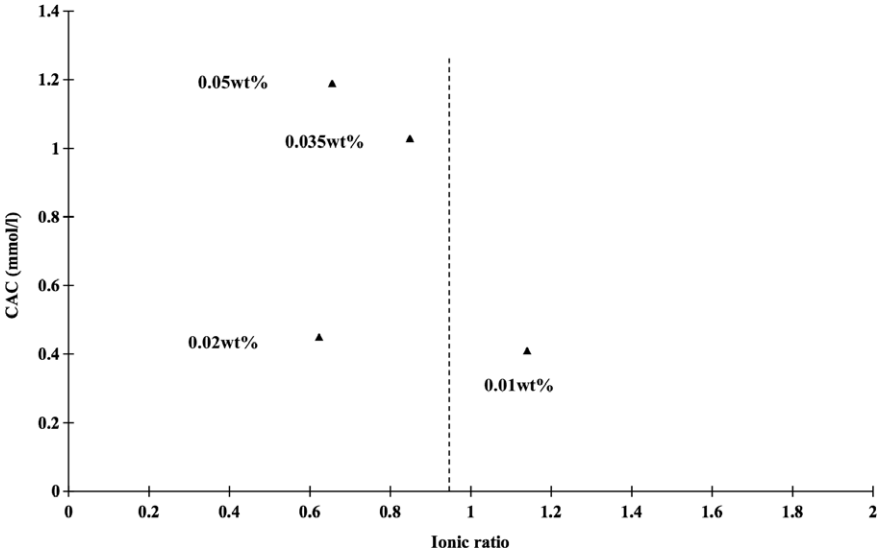


Fig. 11. Evolution of CAC values according to ionic ratios.

cross-link the polymer chains. Upon increasing SDS concentrations, the surface tension of alkylated chitosan solutions gradually decreases, giving evidence of the formation of high surface activity aggregates.

We explain the small rise in the surface tension before the two curves by the fact that up to a certain value of the SDS/chitosan ratio, the complexes are more amphiphilic than SDS alone. At $\log C_{SDS} \approx -2.2$, SDS aggregates form about the macromolecule and the complexes become more hydrophilic. They are therefore displaced from the interface by SDS molecules, up to the concentration where the bulk SDS activity does not increase any more, at the CMC where the two curves merge ($\log C_{SDS} \approx -1.8$). At the end of the experiment, binding and blank experiment curves merge because surfactant molecules saturate the water/gas interface; all SPECs are located in bulk. Electrophoretic mobility measurements indicate that beyond the CAC value, the SPECs are neutral.

4.0.1. Determination of optimal ionic ratio of alkylated chitosan/SDS system

In order to apply alkylated chitosan/SDS complexes to the encapsulation process of hydrophobic molecules, it is necessary to investigate the conditions of neutrality and thus express polymer and surfactant ionic concentrations.

One mole of SDS carries a negative charge while it is not the case of the polymer because of the acetylation and substitution degrees. According to previous calculations, a macromolecular chain of alkylated chitosan contains 1095 D-glucosamine units, carriers of positive charge by protonation in acid medium.

The charge neutrality is obtained when the ionic ratio $\frac{[SDS]}{[\text{alkylated chitosan}]}$ is equal to 1 (with [SDS] and [alkylated chitosan], respectively, representing the ionic concentrations of surfactant and monomer).

From turbidity measurements results, Fig. 11 shows the ionic ratio values. The ionic ratio is close to 1 when polymer concentration is around 0.01 wt% (dilute regime), that is to say that one HMP charge is compensated by one surfactant charge. When HMP concentration is 0.01 wt%, surface tension isotherm probes that SPECs are amphiphilic until CAC. Thus, this system seems to be eligible for the desired encapsulation process.

5. Conclusion

In our conditions of solvent and pH, surfactant/polyelectrolyte interactions start before CAC value. SDS bounds strongly onto oppositely charged and hydrophobically modified chitosan in two stages as probed by binding isotherms and ITC measurements. First, there is a very strong electrostatic binding, followed by a non-binding region and then there is a cooperative binding. When polymeric concentrations are getting greater, there is a non-proportional increase of CAC values; we explain this behavior as due to the conformation change of HMP when it is in semi-dilute regime. More particularly, hydrophobic domains those are inaccessible to SDS, limit CAC values in semi-dilute regime. As cited in literature CAC value is 1–2 orders of magnitude lower than CMC (Magny et al., 1994).

A focus is made on 0.01 wt% HMP/SDS system. The SPECs formed are closer to the neutrality according to ionic ratios and are almost neutral at CAC value according to electrophoretic mobilities measurements. Surface tension isotherm of 0.01 wt% alkylated chitosan/SDS system establishes that, moreover neutrality, formed SPECs are amphiphilic until this CAC value. With regard to encapsulation process, this insoluble system (0.01 wt% HMP/surfactant) is eligible as a wall material for capsules made by complex coacervation, for example.

Acknowledgements

This work was supported by Ministère de l'Enseignement Supérieur et de la Recherche (France). The authors thank Valery Babak for providing the alkylated chitosan.

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