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Original Scientific paper

An investigation of chitosan and sodium dodecyl sulfate interactions in acetic media

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Abstract: A polymer/surfactant association is a cooperative phenomenon in which the surfactant binds to the polymer in the form of aggregates, usually through electrostatic or hydrophobic forces. As is already known, polyelectrolytes may interact with oppositely charged surfactants through electrostatic attraction that results in polymer/surfactant complex formation. This behavior could be desirable in wide range of application of polymer/surfactant mixtures, such as improving colloid stability, gelling, emulsification and microencapsulation. In the present study, surface tension, turbidity, viscosity and electrophoretic mobility measurements were used to investigate the interactions of the cationic polyelectrolyte chitosan (Ch) and the oppositely charged anionic surfactant sodium dodecyl sulfate (SDS) in buffered water. Obtained results show the presence of interactions that lead to Ch/SDS complexes formation at all investigated pH and for all investigated polymer concentrations. Mechanisms of interaction, as well as characteristics of formed Ch/SDS complexes, are highly dependent on their mass ratio in the mixtures, while pH has no significant influence.

Keywords: polymer/surfactant complexes; cationic polyelectrolyte; anionic surfactant; surface tension; viscosity; electrophoretic mobility.

INTRODUCTION

The field of polymer/surfactant interactions has attracted a lot of attention both from the theoretical and practical points of view. Although the subject has been studied over a period of several decades, the perspective of the application of polymer/surfactant mixtures in the chemical, food and pharmaceutical industries determines its further extensive research.[1] The effects of polymer/surf-

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actant interactions are useful in practice to achieve emulsification, colloidal stability, viscosity enhancement, gel formation and solubilization.[2–4]

Polymer/surfactant interactions in the mixtures can be relatively weak, between the polymer chain and the surfactant head group, or strong, electrostatic interactions between oppositely charged polymers and surfactant head groups. However, hydrophobic interactions between the polymer and the surfactant chains are also always present and, in some systems, could be the predominant attractive forces. In particular, oppositely charged polymer/surfactant systems that includes polyelectrolytes and amphiphilic polyelectrolytes, have been widely studied by means of variety of techniques, such as tensiometry,[5,6] conductometry,[7–9] isothermal titration calorimetry,[10,11] neutron refractometry[6] and some others. Strong interactions within these systems, usually caused by electrostatic attraction and hydrophobic interaction, lead to the formation of complexes with various structures and characteristics and, in some cases, to coacervate formation and phase separation.[8,12] The interaction in oppositely charged polymer/surfactant systems is generally accepted as an ion-exchange process in which the electrostatic forces of interaction are reinforced by aggregation of the alkyl chains of the bound surfactant molecules.[10,13]

Chitosan (Ch) is a nontoxic, natural, biodegradable polysaccharide that currently receives a great deal of attention for applications in food and pharmaceutical products. Some authors have indicated the ability of ingested Ch to decrease oil absorption or lipase activity in the digestive tract of human or animal, which enables its application in functional food products.[14,15] In addition, due to its antibacterial and antiviral activities, biocompatibility and bio-adhesive nature, Ch has been used for different biomedical applications.[7,16–20]

Ch is a linear copolymer composed of *N*-acetyl-d-glucosamine and d-glucosamine units that is usually obtained by partially or fully *N*-deacetylation of chitin.[21] The solubility, rheological properties and surface adsorption of aqueous Ch solutions depend on the average molecular weight, degree of deacetylation, and the distribution of the acetyl and amino groups along the polymer chain, as well as on the pH and ionic strength of the solution.[15,22] Namely, Ch is readily soluble in dilute acidic solutions below pH 6 due to the protonation of the amino groups that have a pK_a value of 6.3.[23] At low pH values, these amines are protonated, become positively charged and make Ch a water soluble cationic polymer. On the other hand, at pH values higher than 6, Ch is less charged (protonation of amines is restricted) and it becomes insoluble. When positively charged, the amine groups are promising sites for electrostatic interactions with oppositely charged surfactants and polyelectrolytes, thus inducing numerous changes in their aqueous mixtures.[24,25,27] Such changes in the bulk solution, as well as at interfaces, could be useful for various applications of Ch/surfactant and Ch/polyelectrolyte mixtures, such as emulsification and microencapsulation.

The aim of this study was to investigate the interaction mechanisms between the cationic polysaccharide Ch and sodium dodecyl sulfate (SDS), by determining the surface and bulk properties of their aqueous mixtures. SDS is a well studied anionic surfactant that commonly interacts with both non-ionic and ionic polymers through different mechanisms.[3,4,24] Previous studies showed that chitosan can interact with anionic surfactants to form either soluble or insoluble surfactant/polymer complexes.[8,9,11] It was proposed that Ch/SDS complexes are stabilized by a combination of electrostatic, ion–dipole and hydrophobic interactions and can be formed even when the surfactant concentration is below its critical micelle concentration.

In this study, a wide variety of methods, including surface tension, electrophoretic mobility, turbidity and viscosity measurements, were used to provide more information about Ch/SDS interactions. The influence of pH and Ch concentration on the behavior of Ch/SDS complexes at interfaces and in the bulk was investigated in detail. In addition, the study gives information about the optimal mass ratio of Ch and SDS that may be used as a material for microcapsule formation suitable for food and pharmaceutical applications.

EXPERIMENTAL

Materials

Low molecular weight Ch was obtained from Sigma–Aldrich (China). The degree of deacetylation of the Ch, determined by potentiometric titration according to the procedure described by Yuan *et al.*,[28] was found to be 81.8 %. SDS, purity >99 %, was purchased from Merck (Germany). In all experiments, buffered water was used as the solvent, and the pH was adjusted using an aqueous 0.2 M solution of acetic acid (Zorka-Pharma, Serbia) and an aqueous 0.2 M solution of sodium acetate (Centrohem, Serbia).

Preparation of solutions

The experiments were performed at pH 4, 5 and 6. The pH values were measured using an 827 lab pH-meter (Metrohm, Switzerland). Stock solutions of 1 mass % Ch were prepared by dissolving the required amount of polymer in buffered water of the chosen pH under stirring and after relaxation at room temperature for 24 h, the pH value of the solution was checked. SDS stock solutions (2 mass %) were prepared using the same procedure. Ch/SDS mixtures were prepared by mixing the required volumes of the stock solutions. Turbidity measurements of Ch/SDS mixtures were performed at a Ch concentration of 0.1 mass %. For the surface tension measurements, the concentrations of SDS were varied from 0.00001 up to 1 mass %, while the Ch concentrations were kept constant at 0.005, 0.01 or 0.05 mass %. Electrophoretic mobility measurements of Ch/SDS mixtures were performed on a series of mixtures at a Ch concentration of 0.01 mass %. Viscosity measurements were performed on a series of mixtures containing 0.01, 0.05, 0.1, 0.2, 0.5 mass % Ch. The mixtures were left for 24 h at room temperature and then the pH value of the solutions was checked.

Turbidity measurements

The changes in the turbidity of Ch/SDS mixtures were determined by measuring the transmittance at 600 nm in 1 cm path length cuvette against buffered water at room temperature using a Halo DB-20S UV–Vis spectrophotometer (Dynamica, UK). Transmittance of the mixtures where phase separation occurred was measured in the supernatant phase. Turbidity of the samples was calculated as:

$$\text{Turbidity} = 100 - \text{transmittance (\%)}$$

All measurements were performed in triplicate.

Electrophoretic mobility measurements

The electrophoretic mobility of Ch/SDS complexes at pH 4 was determined using Zetasizer Nano ZS (Malvern Instruments, UK). The viscosity (0.88 mPas) and refractive index (1.33) of the solvent at 25 °C were used for data analysis. All measurements were performed in triplicate.

Surface tension measurements

Surface tension measurements were realized on a Sigma 703D tensiometer (KSV Instruments, Finland) using the *Du Noüy* ring method at 30±0.1 °C. Prior to the measurements of surface tension, the ring was immersed in the liquid (below the surface) and the surface was left for 15 min to equilibrate. Surface tension of buffered water at pH 4, 5 and 6 that was used as a solvent, was 69.55 mN m^{-1} (measured under the same conditions), meaning that the pure electrolyte solution revealed no surface activity. The reported values of the surface tension were average values of at least three measurements.

Viscosity measurements

Viscosity measurements were performed on Cannon capillary viscometer 50 E599 (Cannon Instrument Company, USA) immersed in thermostatic bath at 30±0.1 °C. Flow time for solvents at pH 4 was 198.71 s. The flow times of the Ch/SDS mixtures were measured and the results are expressed as η_{rel} *vs*. SDS concentrations, where η_{rel} is given by:

$$\eta_{\text{rel}} = \frac{t}{t_0}$$

where t and t_0 are the flow times for the solution and pure solvent, respectively.

The viscosity of the supernatant phase was measured for mixtures where phase separation occurred.

For each solution, three viscosity measurements were taken and the average values were calculated.

RESULTS AND DISCUSSION

Phase separation in Ch/SDS mixtures

As already mentioned, interactions are most pronounced in systems consisting of a polyelectrolyte and an oppositely charged surfactant and they are often accompanied by phase separation. Considering that Ch and SDS bear opposite charges in buffered water, at pH lower than 6, the investigations commenced with the preparations mixtures containing 0.1 mass % Ch with different concentrations of SDS at pH 4. The Ch/SDS mixtures 24 h after mixing are presented in Fig. 1a.

It was noticed that introducing SDS to the Ch solution at concentrations lower than 0.01 mass % did not induce any visually observable changes in the mixtures. With further increase in SDS concentration, the

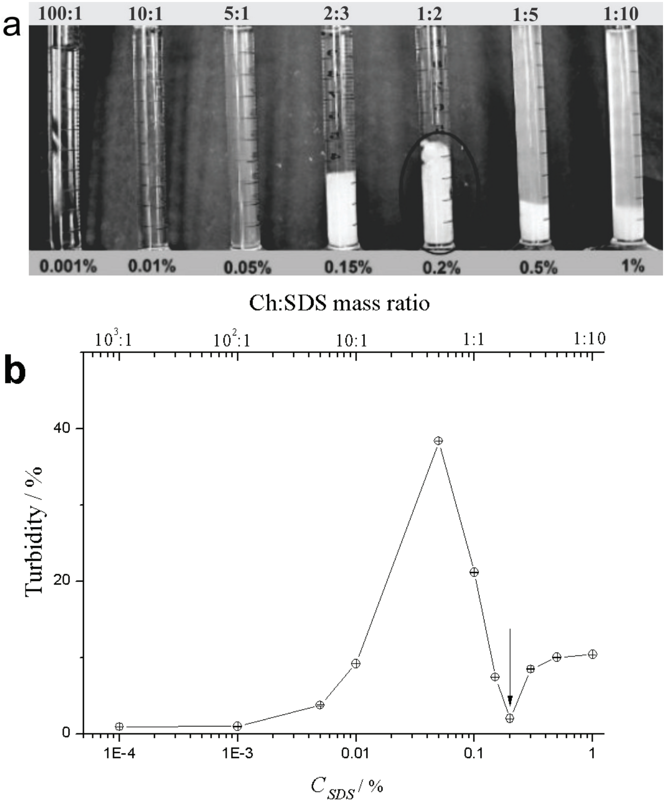

Fig. 1 Phase separation (a) and the turbidity measured at 600 nm (b) of 0.1 % Ch mixtures containing various SDS concentrations at pH 4.

mixtures become turbid and phase separation occurred at an SDS concentration of 0.15 mass %, *i.e.*, insoluble Ch/SDS complexes precipitated at the bottom as a coacervate phase (Fig. 1a). In order to quantify the visually observed changes, the turbidity of the Ch/SDS mixtures at pH 4 were measured and the results are presented in Fig. 1b. The solution of chitosan in water at pH 4 was clear (turbidity 0.80 %) and mixtures of Ch containing less than 0.005 mass % SDS did not show changes in turbidity. However, further addition of SDS caused an increase in the turbidity of the mixtures. Namely, the gradual binding of the negatively charged polar heads of the SDS molecules onto the positively charged amino groups on the Ch molecules led to the formation of complexes that were less charged and thus, less soluble in water. The turbidity reached a maximum at an SDS concentration of 0.05 mass % and decreased after this concentration, which could be due to the beginning of the phase separation process. The minimum in turbidity of the supernatant phase (marked with arrow in Fig

1b), *i.e.*, complete precipitation of the complexes occurred at 0.2 mass % SDS (Ch/SDS mass ratio 1:2), which could be explained by their neutrality. After this concentration, further addition of SDS led to an increase in the turbidity of the supernatant phase. The increase in the dispersibility of the coacervate phase might be due to an excess of complexes with a negative charge caused by the hydrophobic binding of SDS molecules.

Electrophoretic mobility of Ch/SDS mixtures

As is known, an electrical charge on particles influences their electrophoretic mobility. Measurements of electrophoretic mobility were performed in order to confirm the assumption that the precipitation of Ch/SDS complexes occurred because of changes in their electrical charge. The results are presented in Fig. 2.

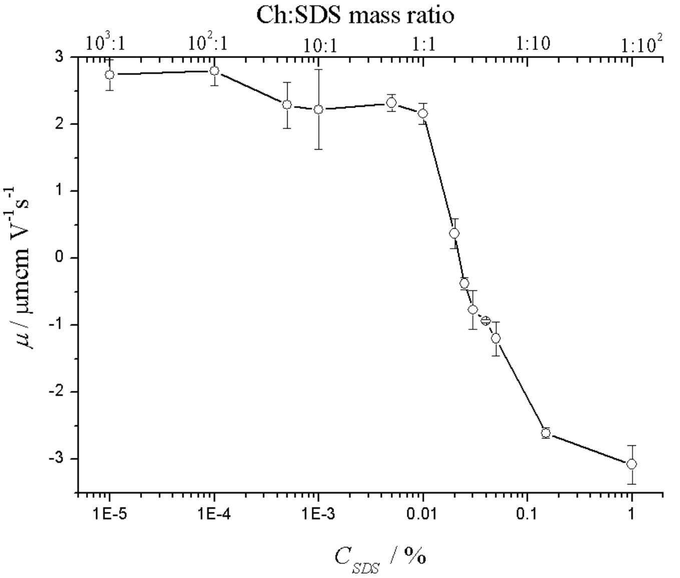

Fig. 2 Electrophoretic mobility of Ch/SDS mixtures at 25 °C and pH 4 as a function of the SDS concentration and the Ch:SDS mass ratio. The chitosan concentration was 0.01 mass %.

As a cationic polyelectrolyte, Ch molecules bear net positive charges in aqueous solution under acidic condition, at pH values lower than 6. This was confirmed by electrophoretic mobility measurements since electrophoretic mobility of 0.01 mass % Ch solution at pH 4 was 2.84 μm cm V^{-1} s^{-1}. The addition of oppositely charged SDS to the Ch solution induced the formation of complexes that bore a net positive charge, but it decreased the absolute value due to the gradual binding of SDS by electrostatic attraction. This gradual decrease in charge caused a decrease in the solubility of the Ch/SDS complexes and, consequently, turbidity occurred (Fig. 1b). After reaching an SDS concentration of

0.01 mass %, the charge of the complexes decreased rapidly and at an SDS concentration of 0.022 mass %, *i.e.*, at a Ch/SDS mass ratio of around 1:2, they became neutral. As the result, precipitation of the coacervate occurred in the mixture causing a decrease in turbidity. Further addition of SDS led to charge inversion and the total charge of the complexes tended towards an excess of negative charge. Electrostatic repulsion between complexes caused their slight redispersion from the coacervate phase and turbidity resulted (Fig. 1b).

Since tensiometric and viscometric measurements give important information about system behavior at the interface and in the bulk, these two techniques were used for detail examination of Ch/SDS interaction mechanisms.

Surface tension measurement of Ch/SDS mixtures

In the mixtures of polyelectrolytes and oppositely charged surfactants, interactions are strong and predominantly caused by electrostatic attraction between the charged groups of polymer chains and head groups of surfactant molecules. In this manner, they often show very different surface tension behavior than that of weak interacting system, such as hydrophobic interactions in nonionic polymer/surfactant systems.[3,4,6] The surface tensions of pure SDS and Ch/SDS mixtures in buffered water at 30 °C and pH 4 are presented in Fig. 3.

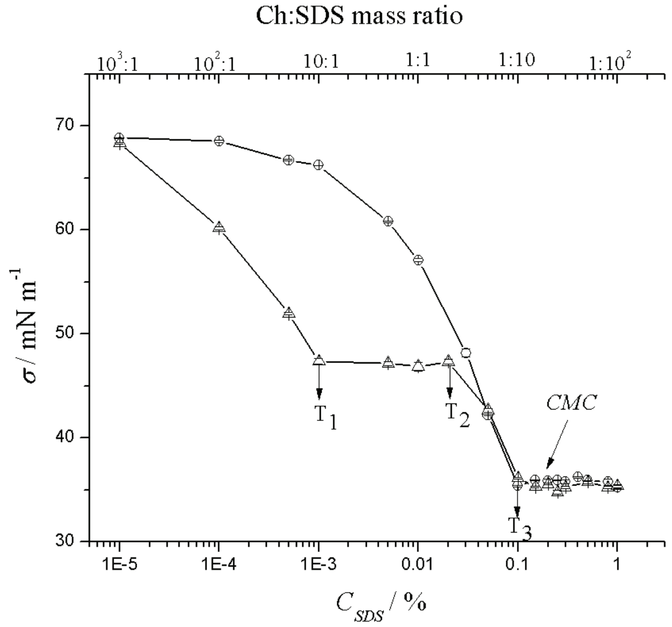

Fig. 3. Surface tensions of pure SDS (-○-) and Ch/SDS mixtures (-Δ-) as functions of the SDS concentration and the Ch:SDS mass ratio at 30 °C and pH 4. The chitosan concentration was 0.01 mass %.

Surface tension of pure Ch solution in buffer was 69.15 mN m^{-1}, indicating the absence of surface activity of the polymer, as is case of most strong polyelectrolytes.[6–8] Simultaneously, SDS induced a very large reduction in the surface tension at very low concentrations up to the critical micelle concentration (*CMC*), 0.18 mass %, after which the surface tension was practically constant. This large reduction in surface tension was due to the strong adsorption of SDS molecules at the liquid–air surface, typical for most surfactants in aqueous solutions.[1] As observed in Fig. 3, changes in the surface tension of Ch/SDS mixtures showed discontinuities at characteristic SDS concentrations, which correspond to changes in the turbidity and electrophoretic mobility. The overall pattern was different from those published by Onesippe and Lagerge, as they reported a gradual decrease in surface tension in the region of interaction with increasing concentration of SDS.[8,24]

The interaction between Ch and SDS at the surface was detected at very low concentrations of surfactant. Namely, a pronounced lowering of the surface tension in the Ch/SDS mixture occurred at 0.0001 mass % SDS, indicating the formation of surface-active complexes. With increasing SDS concentration, the surface tension of the Ch/SDS mixtures significantly decreased until the first discontinuation, T_1, was reached at an SDS concentration of 0.001 mass % (Ch/SDS mass ratio 10:1). At this mass ratio, as may be seen from Figs. 1b and 2, the turbidity in the mixture occurs, indicating that the complexes, although positively charged, less soluble but still surface active. Further addition of SDS did not lead to a change in surface tension until the second break point, T_2, was achieved at 0.02 mass % SDS (Ch/SDS mass ratio 1:2). In the SDS concentration region between T_1 and T_2, the positive charge on the Ch/SDS complexes decreased, the turbidity increased and precipitation of the coacervate occurred, but the surface tension still remained low. Such behavior could be attributed to the formation different kinds of Ch/SDS complexes that were formed in the bulk, amphiphilic in their nature and extremely surface active. After this concentration, further addition of SDS caused a significant decrease in surface tension until T_3, when the value was lower than that for the pure surfactant solution at the *CMC*. Once micelles of SDS abound in solution, Ch molecules are stripped from the interface and the surface tension becomes essentially equal to that of a micellar, polymer-free surfactant solution.[3] At this concentration the surface was saturated only with SDS molecules and further increase in SDS concentration led to the formation of regular SDS micelles in the bulk, *i.e.*, surface tension remained constant.

The influence of Ch concentration on surface tension behavior of the Ch/SDS mixtures is presented in Fig. 4.

Although the overall pattern looks similar to the one observed for weakly interacting systems, there are some important differences.[6] Namely, the initial pronounced decrease in surface tension at low SDS concentration and the position

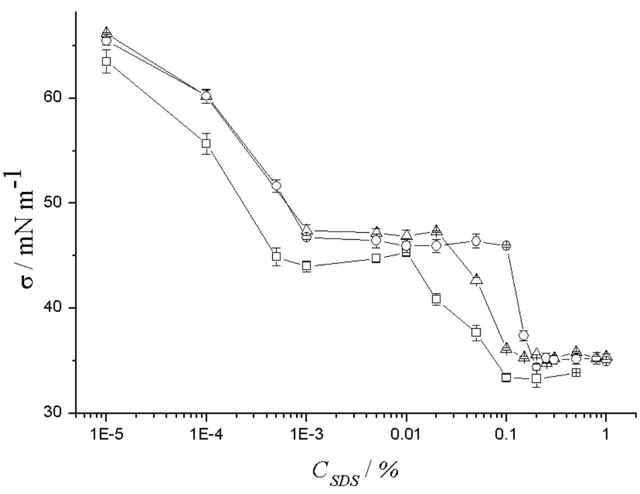

Fig. 4. Surface tension of 0.005 (-□-), 0.01 (-Δ-) and 0.05 mass % (-○-) Ch mixtures with SDS *vs*. the SDS concentration at 30 °C and pH 4.

of T_1 were dependent on the Ch concentration; T_1 occurred at higher SDS concentrations with increasing Ch concentration. Moreover, T_3, *i.e.*, the *CMC* for the mixed Ch/SDS system appeared to be similar to, or lower than, that for pure SDS, in contrast to the behavior for weakly interacting systems, when the *CMC* of the mixture was generally higher.[1] Such behavior could be attributed to the formation of polymer/surfactant complexes that differed in their structure depending on the concentration of surfactant, as already reported for some related polyelectrolyte/surfactant systems.[6,29] It could be assumed that at low SDS concentration, below T_1, single SDS molecules were bound to the Ch amino groups *via* electrostatic attraction and surface active Ch/SDS monomer complexes were formed. After reaching a certain SDS concentration at T_1, the cooperative adsorption of SDS molecules in form of some sort of aggregate on the Ch chain started in the bulk. Such bulk complexes do not affect the Ch/SDS adsorbed layer at the interface and as a result, the surface tension remained unchanged. The T_1–T_2 plateau appeared at characteristic polymer/surfactant mass ratios, between Ch/SDS mass ratio 10:1 and 1:2. Electrophoretic mobility measurements showed that the Ch/SDS complexes bear a net positive charge in the SDS concentration region between T_1 and T_2, although a gradual decrease in the absolute value was observed (Fig. 2). Considering this, the occurrence of turbidity and the gradual precipitation of the bulk Ch/SDS complexes, which were observed in the T_1–T_2 region, could be attributed to a reduction in charge and the simultaneous increase in hydrophobicity. At a Ch/SDS mass ratio of 1:2, the complexes were almost neutral in their charge (μ = 0.37 μm cm V^{-1} s^{-1}) and fully precipitated as a coacervate phase. A further increase in the SDS concentration led to a gradual deployment of the SDS molecules at the interface, which resulted in a significant decrease in the surface tension. At T_3, the phase interface was saturated with SDS molecules and after this concentration, regular SDS micelles were formed in the bulk. Simultaneously, the binding of SDS molecules to the Ch/SDS complexes continued *via* hydrophobic interactions and the total charge of the complexes tended towards an excess of negative charges (Fig. 2).

Considering that the pH value may affect the interactions in polyelectrolyte/ /surfactant systems, changes in the surface tension of Ch/SDS solutions at different pH values were examined. The results are presented in Fig. 5.

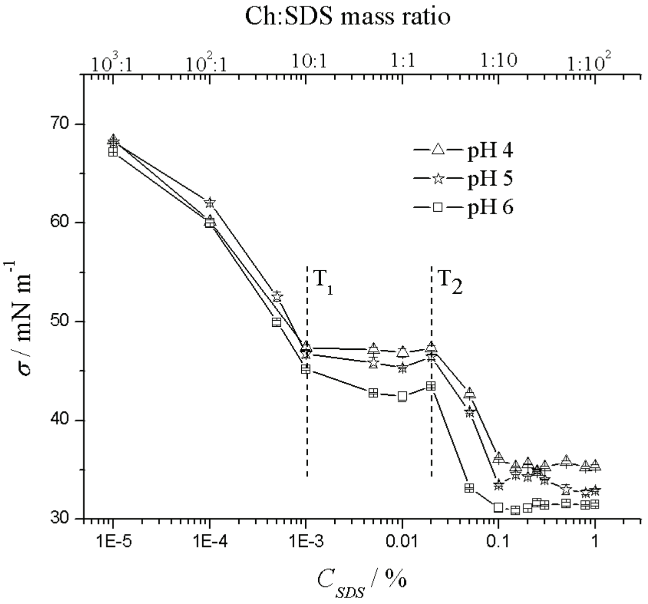

Fig. 5 Surface tension of Ch/SDS mixtures as a function of SDS concentration and Ch:SDS mass ratio at different pH values and at 30 °C. Chitosan concentration was 0.01 mass %.

As can be seen from Fig. 5, the Ch/SDS mixtures containing 0.01 mass % Ch showed characteristic break points, T_1, T_2 and T_3, at all the investigated pH values. The appearance of the curves at pH 5 and 6 appeared very similar to that at pH 4. Namely, the formation of soluble Ch/SDS complexes started at very low SDS concentrations causing a significant decrease in the surface tension. In addition, the positions of discontinuities were at the same SDS concentrations: T_1 appears at 0.001 mass %, T_2 at 0.02 mass % and T_3 at 0.1 mass % SDS, indicating that, in examined range, the pH had no significant influence on the interactions.

Viscometric investigation of the Ch/SDS interactions

In order to understand better the mechanisms of interaction between Ch and SDS, viscometric measurements of the Ch/SDS mixtures were performed. The relative viscosities of the Ch/SDS mixtures with various SDS concentrations at pH 4 are presented in Fig. 6.

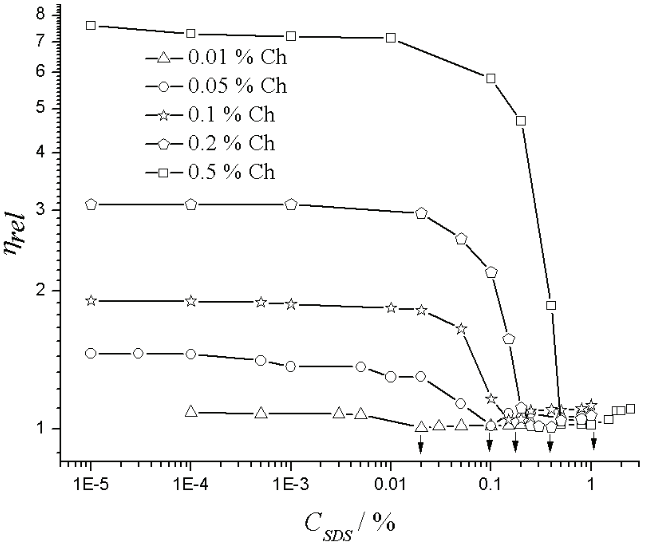

Fig. 6. Relative viscosity of Ch/SDS mixtures containing different Ch concentration *vs*. SDS concentration at 30 °C and pH 4.

The relative viscosity of pure Ch solutions at concentrations of 0.01, 0.05, 0.1, 0.2 and 0.5 mass % at pH 4 were 1.10, 1.52, 2.02, 3.10 and 7.84, respectively. The introduction of SDS to the Ch solutions did not affect the relative viscosity, indicating that the interactions between these two molecules occurred at the interface, which fully corresponded to the previous surface tension measurements. At SDS concentration of 0.01, 0.02, 0.05 and 0.1 mass % in the mixtures containing 0.05, 0.1, 0.2 and 0.5 mass % Ch, respectively, the precipitation of the Ch/SDS complexes started (Ch/SDS mass ratio of 5:1) and the viscosities of supernatant phases were measured. After these concentrations, further addition of SDS caused a decrease in η_{rel} of the supernatant phase leading to complete precipitation of the coacervate phases at 0.02, 0.1, 0.2, 0.4, 1.0 mass % SDS, respectively. These polymer-depleted phases showed a minimum in the viscosity (marked with arrow) that always appeared at a Ch/SDS mass ratio of 1:2. Further increase in the SDS concentration led to an increase in the relative viscosity of supernatant phase, indicating better dispersibility of the complexes due to their electrostatic repulsion.

It is evident that viscometric measurements fully corresponded to the turbidity, surface tension and electrophoretic mobility measurements of the Ch/SDS mixtures.

CONCLUSIONS

The results presented in this paper showed that the cationic polymer, chitosan and the anionic surfactant SDS interacted over a wide range of surfactant concentrations. The interactions started at very low SDS concentrations by electrostatic binding of SDS molecules, resulting in the formation of soluble and extremely surface active complexes. At a Ch/SDS mass ratio of 10:1 for all the investigated chitosan concentrations, the interactions occurred in the bulk and did not affect Ch/SDS adsorbed layer at the interface, *i.e.*, the surface tension remained unchanged until reaching a Ch/SDS mass ratio of 1:2. The bulk complexes carried a net positive charge (a gradual decrease in the absolute value was observed) and gradually precipitated from the solution with increasing SDS concentration. At a Ch/SDS mass ratio of 1:2, independent of the polymer concentration and pH, neutral complexes fully precipitated from the solution, while the polymer depleted phase showed a minimum in viscosity. A further increase in the SDS concentration led to weak hydrophobic binding of the SDS molecules to the Ch/SDS complexes, the total charge of the complexes tended towards an excess negative charge and, consequently, the coacervate phase became slightly redispersed.

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ИЗВОД

ИСПИТИВАЊЕ ИНТЕРАКЦИЈА ИЗМЕЂУ ХИТОЗАНА И НАТРИЈУМ-ДОДЕЦИЛ-СУЛФАТА У КИСЕЛОЈ СРЕДИНИ

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Повезивање полимера и сурфактанта је кооперативни феномен где се молекули сурфактанта везују за молекуле полимера у форми агрегата, обично електростатичким или хидрофобним силама. Као што је већ познато, полиелектролити ступају у интеракцију са супротно наелектрисаним сурфактантима електростатичким привлачењем, што доводи до формирања комплекса полимер/сурфактант. Ово понашање смеша полимер/сурфактант има широку практичну примену, како за побољшање стабилности колоидних система, гелирање, емулговање, тако и у процесима микрокапсулације. У циљу испитивања интеракције катјонског полиелектролита хитозана (Ch) и супротно наелектрисаног анјонског сурфактанта натријум-додецил-сулфата (SDS) у пуферу, мерени су површински напон, вискозитет, мутноћа и електрофоретска покретљивост. Добијени резултати указују на присуство интеракције која доводи до формирања Ch/SDS комплекса на свим испитиваним pH вредностима. Механизам интеракције, као и особине

формираних Ch/SDS комплекса у највећој мери зависе од њиховог масеног односа у смеши, док pH нема значајнији утицај.

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