

Formation of an ordered nanostructure in surfactant-polyelectrolyte complexes formed by interfacial diffusion

V. G. Babak¹, E. A. Merkovich^{1,2}, J. Desbrières³, M. Rinaudo^{3,*}

¹ A. Nesmeyanov Institute of Organoelement Compounds, INEOS RAS, 28 Vavilova St., Moscow 117813, Russia

² Moscow Textile University, 1, Malaya Kaluzhskaya, Moscow 117813, Russia

³ CERMAV - CNRS, associated with University Joseph Fourier, Grenoble 1, BP53, 601 Rue de la Chimie, 38041 Grenoble cedex 9, France

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Summary

This paper concerns the obtention of capsules stabilized by a shell formed by an electrostatic complex which also present an ordered nanostructure. The complex involves chitosan as a semi rigid positively charged polyelectrolyte and sodium dodecyl sulphate (SDS) anionic surfactant. The shell consists of a network in which anionic surfactant micelles crosslink the cationic polymer chains.

Keywords: Alkylated chitosan solution, ionic complex, polyelectrolyte-surfactant, nanostructure.

Introduction

Ionic surfactants (S) in mixed aqueous solutions with oppositely charged polyelectrolytes (PE) often form insoluble surfactant-polyelectrolyte complexes (SPEC) over a critical concentration value referred as the c.a.c. (critical aggregation concentration). This value is usually about two orders of magnitude smaller than the critical micelle concentration (c.m.c) of the same surfactant in absence of polyelectrolyte (1,2). Depending on the structure of the surfactant (its hydrophobic character) and on that of the polyelectrolyte (its charge density) the binding of ionic surfactants with oppositely charged polyelectrolytes has been often reported as cooperative (3,4). In moderate surfactant concentration, the polyelectrolyte complexes are demonstrated as stoichiometric relative to ionic functional groups of PE.

In this paper, we investigate the complex formed by interfacial diffusion between a cationic chitosan delivered as drops in a solution of excess of a negatively charged surfactant. The role of hydrophobic side chain on chitosan is discussed. Originality of this work consists as using a polyelectrolyte solution when usually a polyelectrolyte gel is used.

Experimental.

Chitosan (Mw= 195,000g/mol; degree of acetylation DA= 0.12) from Protan was purified and carefully characterised by SEC and nmr for Mw and DA respectively (5,6); it is perfectly soluble in acidic condition and its charge parameter when fully ionised is 1.2. Alkylated chitosan was prepared in our laboratory from this initial chitosan and C₁₂

* Corresponding author

Tel.: 33-476037627; Fax: 33-476547203; e-mail: marguerite.rinaudo@cermav.cnrs.fr

aldehyde. It is characterised by its alkylation degree ($\tau = 0.04$)(7). All the solutions were prepared in acetate buffer pH=4.6 and ionic strength 0.05M. The concentrations are expressed in monomol/L or in $-\text{NH}_3^+$ equiv./L taking into account the DA. Anionic surfactant sodium dodecylsulphate (SDS) was from Fluka.

Capsules with a diameter of nearly 1mm were formed by dropwise addition of the polymer solution into SDS solution. SDS solution was always at a concentration larger than the c.m.c in water (usually 0.05M).

Optical investigations were realised using a video camera attached to a microscope and alternatively recorded with a video printer.

SAXS (small angle X-ray scattering) measurements have been used to evidence the ordered nanostructure formed. The experiments were performed on a diffractometer AMUR- K (Institute of Crystallography -Russian Academy of Sciences) with a linear position-sensitive detector and a single crystal monochromator at a wavelength $\lambda = 1.542 \text{ \AA}$. Kratky-type geometry was used with a sample to detector distance 673 mm and a sample slit width 0.2 mm to cover the range of momentum transfer $0.012 < q < 0.55 \text{ \AA}^{-1}$. The capsules are placed in the sample holder in their swollen state; the windows of the sample holder consist of a 0.01mm thickness poly(ethylene terephthalate) film. The data were normalised to the intensity of the incident beam and corrected for the detector response following standard procedure.

Results and discussion.

It is known that ordered nanostructure is formed in SPEC sediments and it was attributed to side by side hydrophobic interactions between hydrophobic chains of the surfactants (8-11). A more pronounced ordering structure was found by SAXS on the complexes formed between covalently cross-linked polyelectrolyte gels and the oppositely charged surfactants (12-20). For the first time, this phenomena is studied from a solution of ionic polysaccharide which must be considered as a semi rigid polymer.

The experimental data given in this paper concern a development of our previous work on interaction of ionic surfactant with oppositely charged polyelectrolytes realised on chitin and its derivatives (1,2,7). Chitosan with a degree of acetylation of 0.12 is water soluble in acidic conditions and when fully ionised its charge parameter is 1.2 i.e. the distance between ionic sites along the chain is 5.85 \AA . It was previously demonstrated that it interacts cooperatively with SDS with a critical aggregation concentration in the range of 10^{-5} M , i.e. 100 times lower than the c.m.c of SDS in the same solvent and in absence of polymer (2). The alkylation of chitosan gives a surface active polymer which also interacts cooperatively with surfactant but giving a higher surface tension at the c.a.c compared with chitosan having the same DA. This can be attributed to a lack of cooperativity introduced by the interfacial orientation of the alkyl chains at the air-solution interface.

Drops of polymer solutions (0.1 equiv./L or a weight concentration around 19 g/L) introduced in a surfactant 0.05mol/L solution were shown to be stabilized by strong interaction at the interface of the two solutions. A capsule forms whose skin thickness increases progressively with time; it was previously tested for chitosan (21); it was suggested that the surfactant micelles progressively diffuse into the polymer solution to form a physical gel. Figure 1 shows the evolution of the capsule shell thickness with increasing time. Our aim is to investigate the role of alkyl chain on chitosan in relation with the shell formation and its structure.

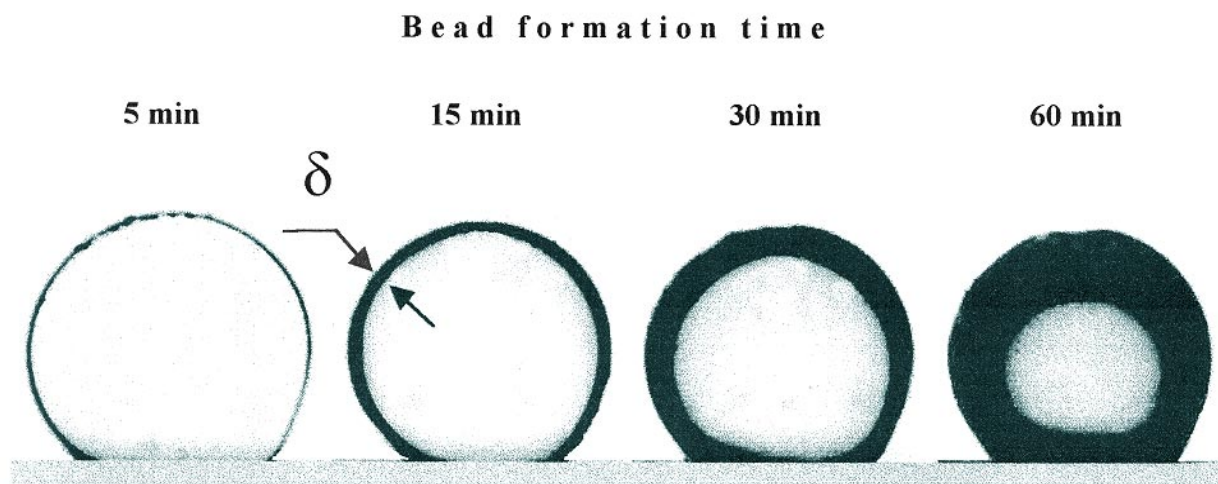


Figure 1. The thickness δ of the gel bead wall growing with time. $C_{\text{ch}}=0.1$ equiv./L; $C_{\text{SDS}}=0.05$ mol/L

In figure 2, the SAXS intensity profile is given; in this figure, a peak appears corresponding to the existence of an ordered structure formed at the interface. As comparison the signal obtained, in absence of surfactant, on the polymers just recovered from solution in alkaline conditions is monotonous indicating an amorphous structure. With the alkylated polymer the peak is broader indicating a distribution of the characteristic distances in the capsules i.e. less cooperativity.

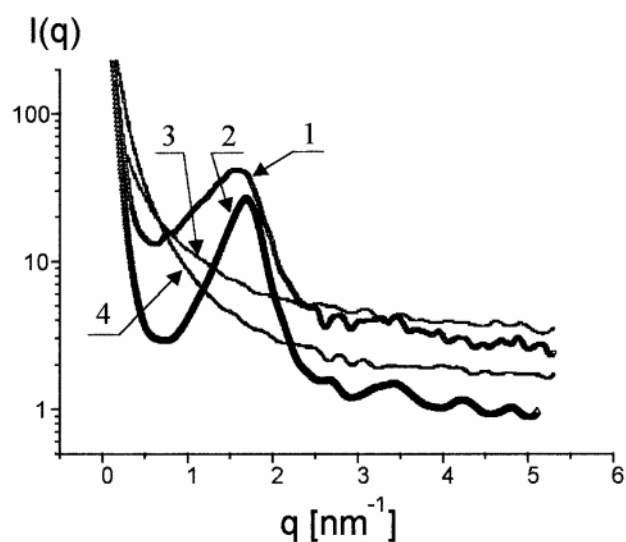


Fig. 2. X-ray intensity profiles for chitosan-SDS complexes : alkylated chitosan gel beads (curve 1) and parent chitosan gel beads (curve 2) ($C_{\text{chit}}=C_{\text{alkylChit}}=0.1$ equiv./L) in SDS solution ($C_{\text{SDS}}=0.1$ mol./L), chitosan gel bead (curve 3) and alkylated chitosan gel bead (curve 4) recovered in NaOH solution.

The characteristic periodicity of the ordered elements is estimated using the Bragg relation. Analysis of the SAXS curves shows two peaks slightly different for the two polymers. The values are given in the following :

Samples	q max	average d
Chitosan/SDS	1.66 nm ⁻¹	3.80 nm
Alkylated chitosan/SDS	1.59 nm ⁻¹	3.96 nm

It must be mentioned that the peaks are very reproducible in position and width; it is characteristic of the sample tested. In addition, ageing of the films never produced modification in the peak structure nor obtention of secondary order peaks

In a separated experiment, the complex was proved to be at charge stoichiometry in a swollen state with a complex volume fraction round 0.4 (21).

Conclusion.

This paper shows that electrostatic complexes are formed between ionic surfactant and oppositely charged polyelectrolytes. It demonstrated that a stable complex is formed from aqueous solution when usually it was studied on polyelectrolyte gels. The capsule shells obtained may be considered as physical network in which surfactant micelles form polycationic- multianionic electrostatic complexes as crosslink points even at relatively low concentration of both components. In addition, it was again shown that alkylation partially prevent the high degree of order of the nanostructure formed as observed at the air-liquid interface. The stronger film is formed for highly charged polyelectrolytes in presence of a strongly hydrophobic oppositely charged surfactant; the role of the semi-rigid character of polysaccharides is under investigation in complementary experiments.

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