Experimental Report

15/01/2014

Proposal:	**9-12-343**	**Council:**	10/2012
Title:	Structural characterization of mixtures of chitosan and oppositely charged alkyl ether carboxylates		

This proposal is a new proposal

Researh Area: Chemistry

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Samples: Chitosan/(C6H11NO4)1000
Alkyl ether carboxylic acids/CiEjCOOH
Heavy Water / D2O

Instrument	Req. Days	All. Days	From	To
D33	2	2	08/07/2013	10/07/2013

Abstract:

Mixtures of oppositely charged polyelectrolyte and surfactants are widely used in many applications and their aggregation is driven by several forces, ranging from electrostatic to hydrophobic interaction.
In our investigation we will study the effects of the addition of chitosan to three alkyl ether carboxylates, differing in their molecular structure and as a consequence showing very different micellar aggregates in solution. From the SANS experiments the corresponding mesoscopic structural picture shall be derived, which then allows for a detailed understanding of the correlation between surfactant structure, mesoscopic structure of these mixed hybrid materials and their properties.

Structural characterization of mixtures of chitosan and oppositely charged alkyl ether carboxylates

Introduction. Mixtures of oppositely charged polyelectrolytes and surfactant are used in a variety of fields, such as cosmetics, detergency, pharmaceutical formulations, etc.. For many purposes biocompatible and biodegradable compounds are needed, e.g., for medical or food industry. A large class of biopolymers which is intensively being studied is that of polysaccharides: chitosan, alginate or cellullose are three examples for natural polycations, polyanions and neutral polymers.
Chitosan, due to its low cost, antiinflammatory and antimicotic properties, is is employed as additive for fungicides, as hemostatic agent or for water filtration, just to mention few applications. However, a main limitation of chitosan is its low solubility in water at neutral and basic pH conditions. A way to overcome this problem is to chemically modify chitosan to make it a strong electrolyte, i.e., *via* quaternization of the amine group.

Results. In this experiment at D33 we have investigated solutions of 0.3 wt% of quaternized chitosan (with different degree of substitution, see Table 1) with $C_{18}EO_9CH_2COOH$ (RO90) at different pH (4.0 and 7.0) and mixing ratio Z = [Surfactant]/[Polyelectrolyte charges].

Table 1: Degree of N-Acetylation, N-methylation and O-Methylation as determined from ^{1}H-NMR.

	Acetylatation	N-methylation	N,N-Dimethylation	N,N,N-Trimethylation	O-Methylation
Q-Chito 1	0.16	0.01	0.41	0.42	0.27
Q-Chito 3	0.14	0.04	0.59	0.23	0.32
Q-Chito 4	0.16	0.00	0.02	0.83	1.65
Q-Chito 5	0.17	0.03	0.76	0.30	0.52

In a previous experiment we have shown that the pH has a surprisingly strong effect on the structure of complexes formed by non-quaternized chitosan and RO90[1,2]. On the contrary, an increase of pH from 3.4 to 5.9 has little effect on the internal structure of the complexes (see Fig. 1). In all cases, the scattering curves resemble those predicted by a pearl-necklace model (see Fig. 2). Also an increasing charge density on the polymer influences only the low-q part of the spectrum (see Fig. 3), i.e. the density of the complex at a large scale. In general, all sample show a similar behavior, typically observed in mixtures of surfactants and flexible polymers, and not expected in complexes of chitosan. These findings have to be interpreted considering not only the change in charge density of the polymer arising from a different degree of quaternization, but also considering the effect of the O-methylation. It is well known that polysaccharides have a strong tendency to form intermolecular hydrogen bonds, whit the consequent formation of microcristalline domains (in the case of cellulose) or giving rise to extremely high persistence lengths (up to several tens of nanometers). It is likely that the O-methylation disturbs the intermolecular hydrogen bonds, therefore strongly reducing the persistence length of the polymer, which now behaves more like a flexible polymer rather than a semi-rigid polysaccharide.

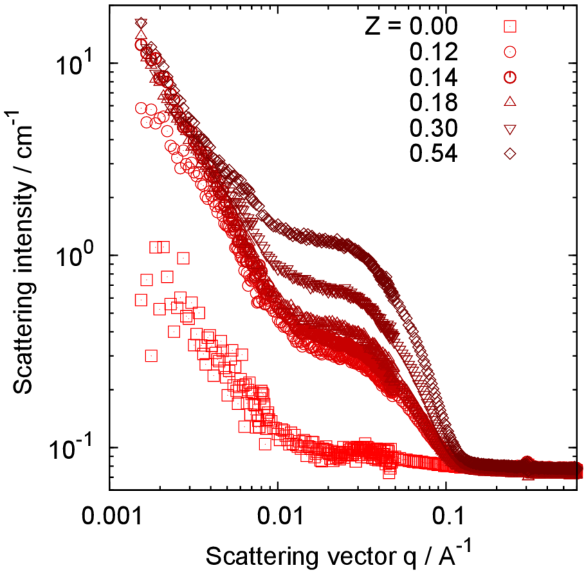

Fig. 1: SANS intensity as a function of the modulus of the scattering vector for mixtures of Q-Chito 3 at 0.3 wt% and RO90 with increasing pH and Z = 0.25.

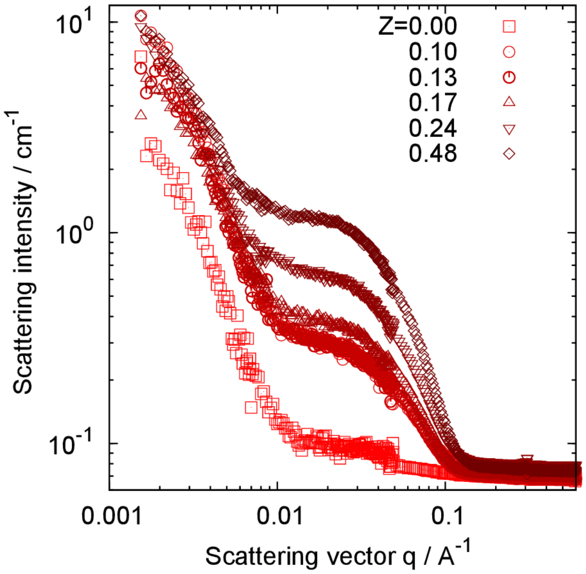

Fig. 2: SANS intensity as a function of the modulus of the scattering vector for mixtures of Q-Chito 5 at 0.3 wt% and RO90 at pH = 7.0 increasing Z.

References:

[1] Chiappisi, L.; Prévost, S.; Grillo, I.; Gradzielski, M. 2014 submitted.

[2] Chiappisi, L. Experimental report. Ex N°: 9-12-308

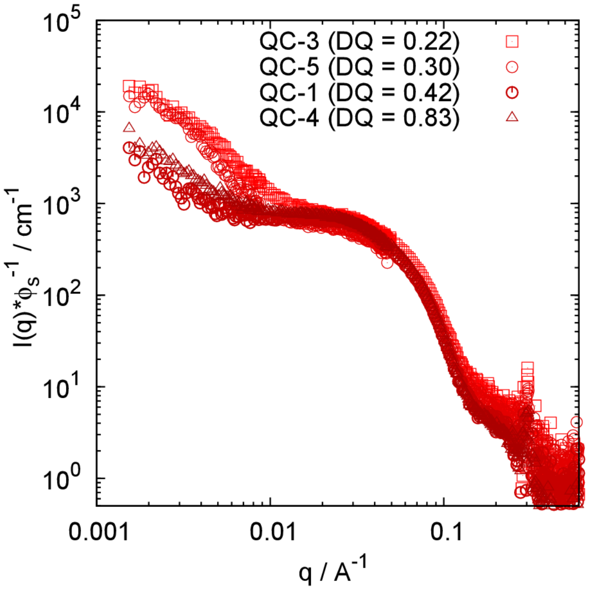

Fig. 3: SANS intensity as a function of the modulus of the scattering vector for mixtures of different modified chitosans at 0.3 wt% and RO90 at pH = 7.0 and Z = 0.13.