Experimental report

20/12/2016

Proposal:	**9-12-477**	**Council:**	4/2016
Title:	SANS study on pressure-induced structural transition in pH-responsivepolyelectrolyte surfactant complexes.		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: C11H23COO(CH2CH2O)4.5CH2COOH
Chitosan (C6H11NO4)n
C18H33COO(CH2CH2O)9CH2COOH

Instrument	Requested days	Allocated days	From	To
D11	3	3	20/06/2016	23/06/2016

Abstract:

In this proposal, we focus on the effect of hydrostatic pressure on the co-assembly behavior of strongly pH-responsive polyelectrolyte - surfactant complexes. The studied system is based on diluted solutions of chitosan, a cationic polysaccharide and oppositely charge ethoxylated fatty acids, whose behavior is strongly dependent on the degree of ionization of the surfactant. By applying an external pressure on the system, the effective pKa of the surfactant is systematically changed, and therefore its degree of charging. Accordingly, already small variations in external pressure are expected to have a deep impact on the resulting self-assembled colloids, as the strong pressure-dependence of the surfactant ionization is used as a lever to amplify the pressure effects on the self-assembly process.

Experimental Report for Proposal 9-12-477 on D11

“SANS study on pressure-induced structural transition in pH-responsive polyelectrolyte surfactant complexes.”

Introduction: With the performed experiments, we aimed at reavealing the effect of hydrostatic pressure on the co-assembly of pH-responsive polyelectrolyte surfactant complexes. The experiments, performed on D11 @ ILL, were performed on mixtures of the biopolymer chitosan (poly D-glucosamine) and alkyl oligoethyleneoxide carboxylic acids in the polymer excess regime. The system was previously been characterized at ambient conditions [1-2], and showed a remarkably strong response upon pH-changes, i.e., after the charge density of the surfactant aggregates is changed. Densitometric measurements predicted a volume change associated to the ionization of the surfactant of -30 mL/mol (see Fig. 1). Moreover, the volume of complexation between $C_{12}E_{4.5}CH_2COOH$ and Chitosan has been evaluated to range between -20 and -30 mL/mol surfactant at pH between 4.0 and 5.0. Accordingly, we expect the degree of ionization of the surfactant to increase with pH as well as the binding strength with the polymer.

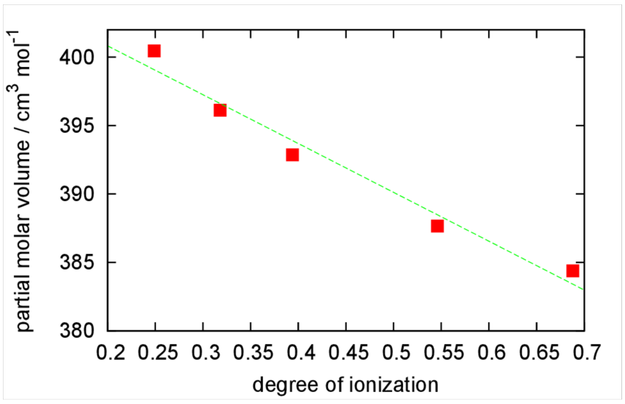

Fig. 1: Partial molar volume of $C_{12}E_{4.5}CH_2COOH$ *as a function of the degree of ionization. Linear fit was used for the determination of the volume of ionization.*

SANS-Experiments: Experiments were performed on complexes of chitosan with $C_{18:1}E_9CH_2COOH$ and $C_{12}E_{4.5}CH_2COOH$. The complexes between $C_{18:1}E_9CH_2COOH$ and chitosan showed a macroscopic phase separation at ca. 1.3 kBar, but no mesoscopic structural changes could be evidences before phase separation occurs. On the contrary, the complexes formed with $C_{12}E_{4.5}CH_2COOH$ show a highly interesting behavior.

Mixtures of chitosan and $C_{12}E_{4.5}CH_2COOH$ at pH 4.3 and mixing ratio $Z = 0.2 =$ [Surf.]/[Chitosan units] form multiwalled vesicles, with a clear interlamellar peak at $q^* = 0.9$ nm^{-1}. With increasing pressure two effects become clearly visible: the disappearence of the interlamellar correlation peak and a decrease of the forwards scattering intensity. A first quantitative analysis points towards the transition from multilamellar to unilamellar vesicles.

A similar effect is observed at pH 5.0, where, due to the increased degree of ionization of the surfactant globular micelles instead of vesicles are formed. At ambient pressure, a core-corona suprastructure is formed, with a core formed of densely packed micelles glued together by the polyelectrolyte chains, and sourrounded by a diluted chitosan corona. With increasing pressure, the correlation peak is lost, indicating the formation of a less ordered complex.

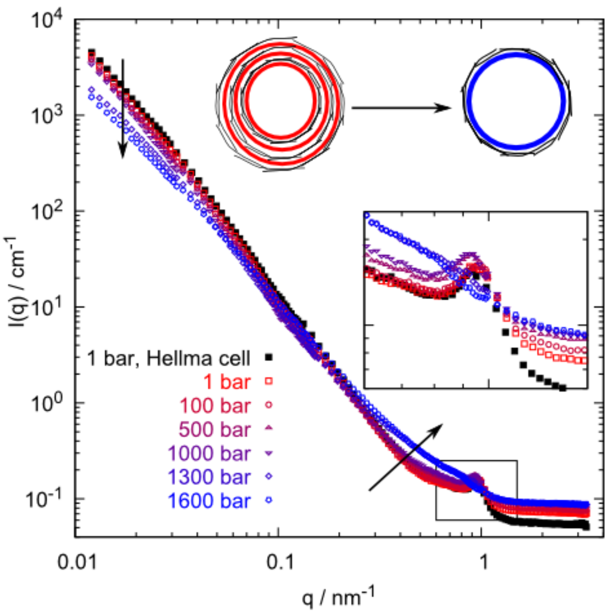

Fig. 2: SANS patterns from mixtures of chitosan and $C_{12}E_{4.5}CH_2COOH$ at pH 4.3, mixing ratio Z = 0.2, recorded at different hydrostatic pressures.

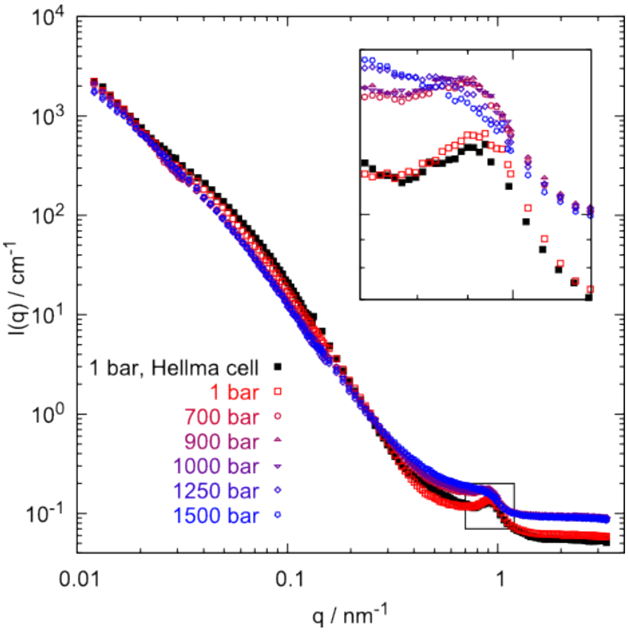

Fig. 3: SANS patterns from mixtures of chitosan and $C_{12}E_{4.5}CH_2COOH$ at pH 5.0, mixing ratio Z = 0.2, recorded at different hydrostatic pressures.

Summary: The complexes with the C18:1-alkyl chain surfactant did not show the expected structural transitions, while highly interesting results were obtained with the $C_{12}E_{4.5}CH_2COOH$ surfactant systems. The shorter alkyl chain allows for a higher solubility of the surfactant even at high pressures. For the latter case, a reduction of order is evidence at higher pressures, which could not be predicted by the densitometric measurements.

References

1. Chiappisi, L.; Prévost, S.; Grillo, I.; Gradzielski, M. Chitosan/alkylethoxy Carboxylates: A Surprising Variety of Structures. Langmuir 2014, 30 (7), 1778–1787.
2. Chiappisi, L.; Prevost, S.; Grillo, I.; Gradzielski, M. From Crab Shells to Smart Systems: Chitosan - Alkylethoxy Carboxylates Complexes. Langmuir 2014, 30 (35), 10608–10616.