Experimental report

17/02/2023

Proposal:	**9-12-546**	**Council:**	4/2018

Title: Pressure-indeced structural reorganization of polyelectrolyte-surfactant complexes

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: fatty acids
Chitosan

Instrument	Requested days	Allocated days	From	To
D11	2	2	26/09/2018	28/09/2018

Abstract:

Within the proposed experiment, we aim to further investigate the response of polysaccharide/surfactant complexes towards applied hydrostatic pressure. Previous experiments performed on mixtures of the biopolycation chitosan and oppositely charged ethoxylated fatty acids revealed strong structural transition upon application of hydrostatic pressure. However, the structural changes observed in SANS experiments are in contrast with the predictions based on thermodynamic predictions from molar volumes. Herein, we propose to perform a further set of experiments which will allow us to understand which are the driving forces governing the pressure responsiveness of these systems.

Experimental report for beamtimes 9-12-546 on D11 and CRG-2719 on IN15

Aim of the experiments was to probe the effect of hydrostatic pressure on the structure and the dynamics of multilayered polyelectrolyte-surfactant vesicles. Particular interesting are mixtures formed by the cationic polysaccharide chitosan and oppositely charged alkyl ethyleneoxide carboxylic acids (CiEjCH2COOH), which we have extensively studied by neutron scattering before[1–4]. In particular, depending on the pH – which controls directly the degree of charge of the surfactant – and the surfactant molecular architecture, the spontaneous formation of multilayered vesicles in solution is observed.

We have previously observed that the formation of multilayered vesicles formed in mixtures of chitosan and $C_{12}E_5CH_2COOH$ at pH 4.5 spontaneously assembles in vesicles with low multiplicity[1], and the formation of multilayered vesicles is associated to an increase in the membrane rigidity. We could thus conclude that the low multiplicity found in multilayered vesicles involving the rigid polysaccharide chitosan arises from the strongly coupled dynamics of the membrane layers.[1]

In experiment 9-12-546 we have further investigated the effect of pressure on the multilayered vesicular assemblies. A representative set of data is shown in figure 1. The decrease of the forward scattering intensity and the disappearance of the correlation peak, clearly and unequivocally indicate the disassembly of the multilayered structure. The data can be quantitatively described with a model of stacked membranes, allowing to extract valuable information such as the layer thickness, the average number of membranes in a stack, the number of non-correlated membranes, i.e., the number of unilamellar vesicles, and the membrane stiffness. In addition to a drastic reduction in the number of parameters at about 1.2 kBar, the analysis evidenced an increase in the membrane flexibility.

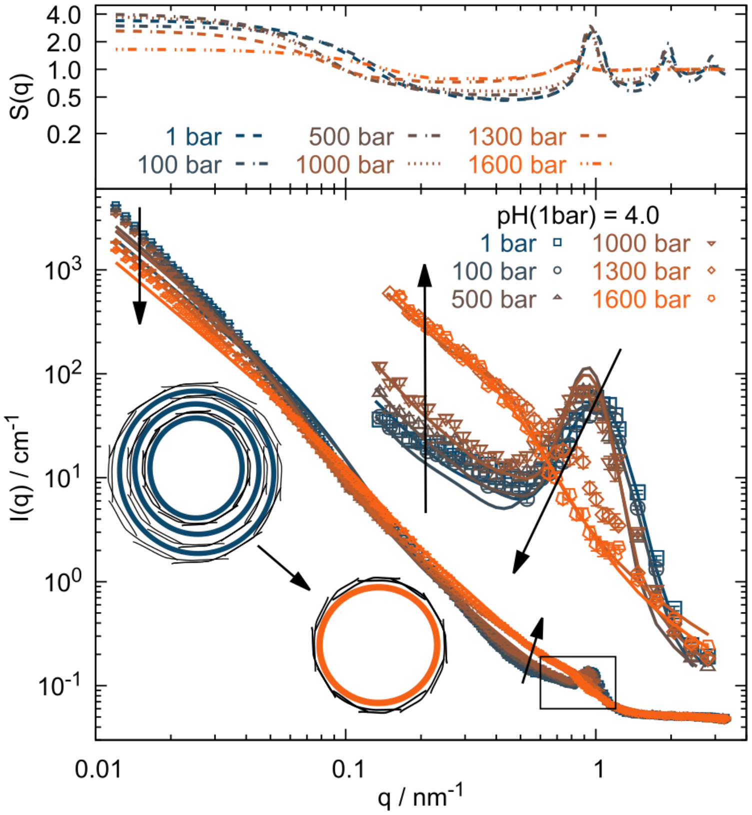

Figure 1: High-pressure SANS pattern recorded for mixtures of of chitosan and C12EO5CH2COOH, with a chitosan content of 0.3 wt% and a surfactant content of of 0.15 wt%, corresponding to a mixing ratio of Z = 0.2 in an acetic acid/sodium acetate buffer of total concentration of 0.2 M. On the left, the complexes were prepared with a pH value of 4.0, at ambient pressure. The experimental data represented by points, were fitted with a model of stacked layers, describing the large vesicles. Full lines are best fits according to the model, and S(q), shown on the top, represent the structure factor describing the interlamellar interferences.

The partial structure factor S(q, t) determined by NSE and recorded for the same mixtures was fitted with the Zilman-Granek model, which describes membrane undulations. The Zilman-Granek parameter, which is, to a first

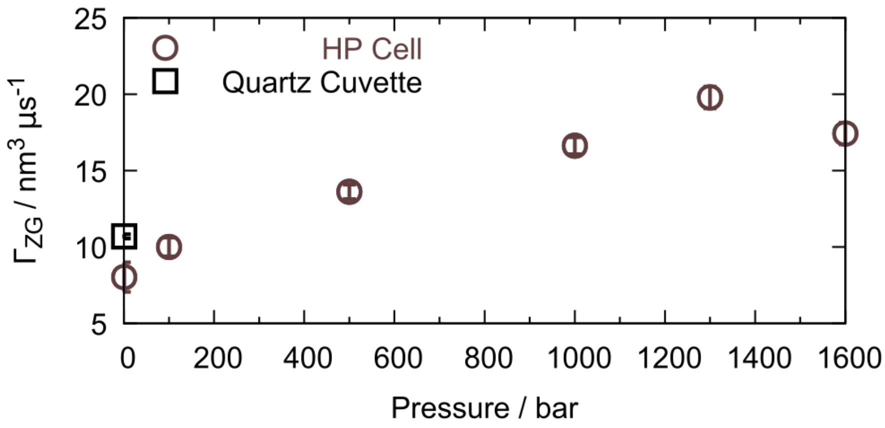

Figure 2: Dependence of the Zilman-Granek parameter from pressure, as determined from the analysis of the NSE data. For the sake of comparison, the same analysis was applied to data with higher quality recorded in conventional quartz cuvette at ambient pressure.

approximation, inversely proportional to the square root of the bending modulus, is shown as a function of pressure in Fig. 2. The analysis clearly indicates a softening the the lipid membrane with increasing pressure, with the Zilman-Granek parameter increasing from approx. 8 nm3µs−1 at ambient pressure to approx. 20 3µs−1 at 1400 bar. In contrast to the Caillé parameter determined from the analysis of the SANS data, which shows an abrupt increase around 1000 bar from 0.2 to 0.8, NSE shown an almost linear increase of Gamma_ZG with pressure.

The SANS and NSE experiments were complemented with density measurements, which allow the volume of complexation to be determined, and by pressure-dependent turbidity measurements, which also confirmed the transition from multilayered aggregates to unilamellar ones.

References

(1) Chiappisi, L.; Hoffmann, I.; Gradzielski, M. Membrane Stiffening in Chitosan Mediated Multilamellar Vesicles of Alkyl Ether Carboxylates. *J. Colloid Interface Sci.* **2022**, *627*, 160–167. https://doi.org/10.1016/j.jcis.2022.07.006.

(2) Chiappisi, L.; Prévost, S.; Gradzielski, M. Form Factor of Cylindrical Superstructures Composed of Globular Particles. *J. Appl. Crystallogr.* **2014**, *47* (3), 827–834. https://doi.org/10.1107/S1600576714005524.

(3) Chiappisi, L.; Prévost, S.; Grillo, I.; Gradzielski, M. Chitosan/Alkylethoxy Carboxylates: A Surprising Variety of Structures. *Langmuir* **2014**, *30* (7), 1778–1787. https://doi.org/10.1021/la404718e.

(4) Chiappisi, L.; Prévost, S.; Grillo, I.; Gradzielski, M. From Crab Shells to Smart Systems: Chitosan–Alkylethoxy Carboxylate Complexes. *Langmuir* **2014**, *30* (35), 10608–10616.

https://doi.org/10.1021/la502569p.