Experimental Report

09/04/2015

Proposal: **9-11-1693** **Council:** 4/2014

Title: Structural investigation of bio-polyelectrolyte – surfactant complexes

This proposal is a new proposal

Research Area: Soft condensed matter

Main proposer: **BUCHOLD Philipp**

Experimental Team: BUCHOLD Philipp

Local Contact: SCHWEINS Ralf

Samples: Hyaluron/TTAB-complexes

Instrument	Req. Days	All. Days	From	To
D11	2	2	22/09/2014	24/09/2014

Abstract:

Self-assembled complexes of oppositely charged surfactants and polyelectrolytes are widely used in many applications and their properties are controlled due to multiple parameters. In our SANS experiment we will derive a correlation between microscopic structure and the resulting macroscopic viscosity of complexes formed by the bio polyanion hyaluronan and a food-grade bactericide cationic surfactant. Specifically our aim is to investigate the influence on the structure by varying the ratio between the components, molecular weight of hyaluronan or the ionic strength of the solvent. Thereof we want to enhance the fundamental understanding, how the structural changes correlate with macroscopic behavior in viscosity in such complexes.

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INTRODUCTION:

The experiment was conducted to reveal the structure of complexes formed by the polyelectrolyte hyaluronic acid (HA) and oppositely charged surfactant. The complexes are self-assembling due to electrostatic attraction and the release of counter ions. Tetradecyltrimethylammonium bromide (TTAB) and lecithin, a phospholipid mixture, were used as charged or zwitterionic surfactants respectively. The focus was to investigate if structural differences occur, depending on the mixing ratio parameter Z (Z=[HA]/[surfactant]). Furthermore structural arrangements shall be related to the viscosity of the solution. For this all samples were studied complementarily by light scattering and viscometer.

SAMPLE PREPARATION:

Appropriate amounts of dry HA and dry surfactant were weighted and solved in either pure D_2O or 160 mM NaBr solutions. The samples were stirred at least 24 h and left for 2 days at room temperature for full equilibration.

RESULTS:

Samples with a mixing ratio in the range of Z= 2 to Z=0.05 at three different fixed HA concentrations (1, 0.4 and 0.3 wt%) were studied. For phase separated samples the dense gel phase were measured in sandwich cells. In the following SANS data of the three different sample sets are displayed (Fig. 1,2,5). In figure 1 and 2 one can clearly see, that the scattering curve (log-log plot) exhibits three major regions. At high q, a pronounced kink ($q \approx 0.1 – 0.12$ Å^{-1}), mid to low q, a slope of -1 followed by a kink to a slope of -3 at low q. In addition the scattering curves change systematically during small variation of the mixing ratio but evidently for the different phases. Comparing the polymer rich, the phase separated dense and surfactant rich phase, the mid q region indicating a cylindrical structure is extended in q range down to q=0.005 Å^{-1}. For a proper interpretation two different concepts of fit models were combined: A Core-Shell Cylinder and a fractal model. The cylinder model provides the form factor for a circular cylinder with a core-shell scattering length density profile. In this manner we can quantify the size of the cylindrical segments. Contrast variation experiments are already planned, to investigate the scattering contribution of HA and TTAB to these segments. Further the fractal model is a simplified concept of describing a disordered polymer network. The fits in figure 3 and 4 are taking into account all known constraints regarding the composition of the systems. In conclusion we find that the cylindrical segments causes the increase in viscosity. In the case of HA mixed with vesicles formed by lecithin, the samples showed precipitation after measurement. To prevent this precipitation temperatures above 60 °C are required at which thermal degradation occurs. Therefor we aren’t planning to investigate these system any further. For those samples the SANS-data (Fig. 5) show a q^{-3} dependence over nearly the whole spectrum except a pronounced peak at 0.1 Å^{-1}, which can be related to the lipid double layer of the phospholipid lecithin.

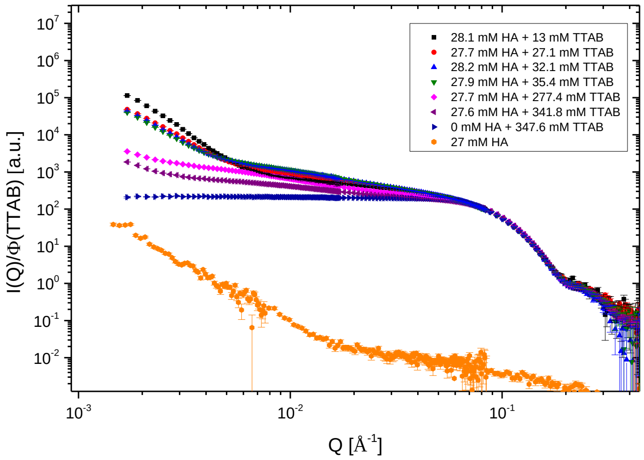

Figure 1: SANS-Data of HA (1 wt%)/TTAB complexes at different mixing ratios.

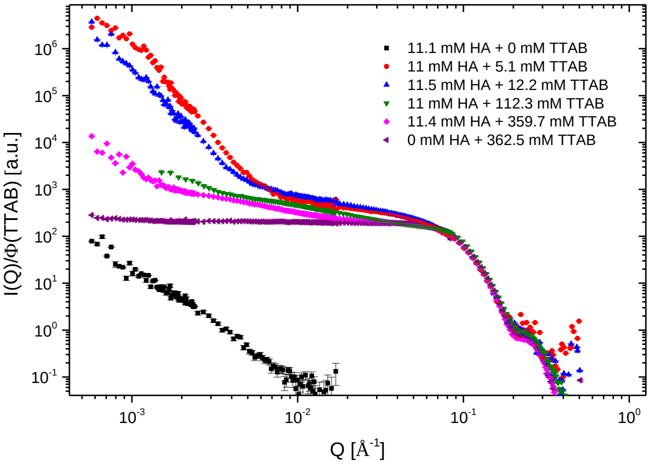

Figure 2: SANS-Data of HA (0.4 wt%)/TTAB complexes at different mixing ratios.

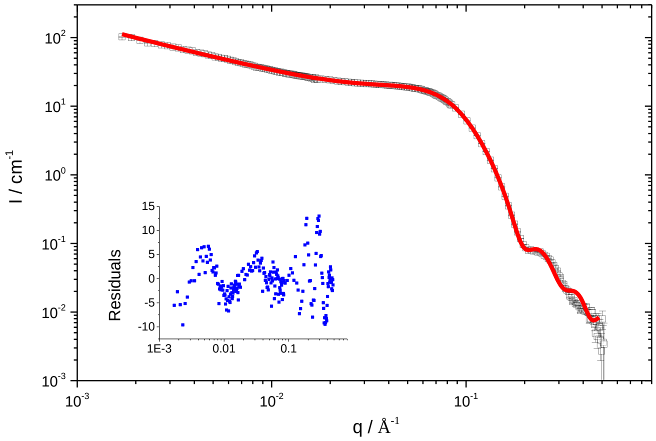

Figure 4: Fit model for SANS- data of HA/TTAB complex at Z = 0.05.

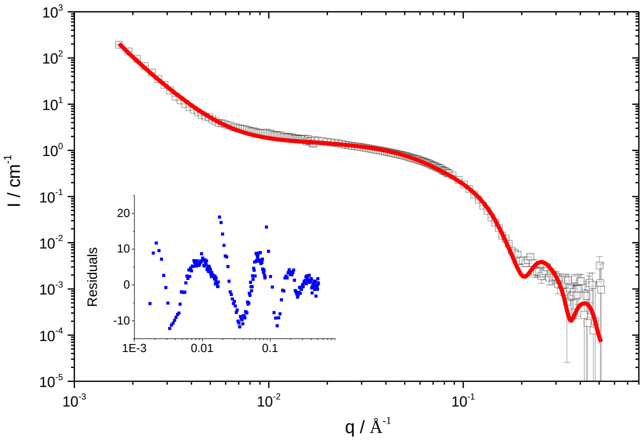

Figure 3: Fit model for SANS- data of HA/TTAB complex at Z = 2.

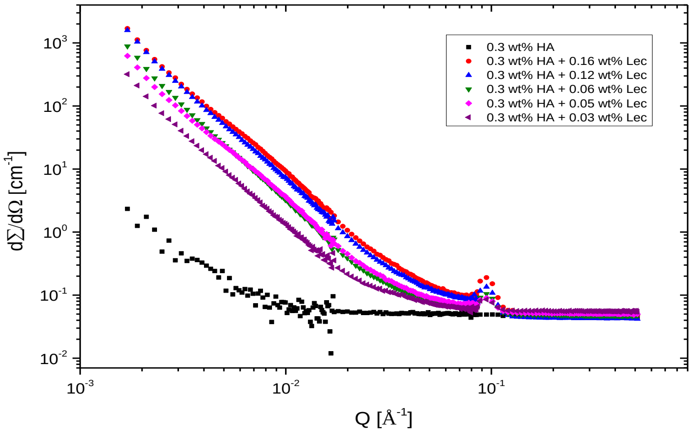

Figure 5: SANS-Data of HA/Lecithin complexes at different mixing ratios.