Experimental report

10/04/2020

Proposal: **9-12-545** **Council:** 4/2018

Title: Tuning Electrostatic Interactions in Uncommon Structures in Hyaluronate/Surfactant Complexes

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Sebastian BAYER**

Experimental team: Ozge AZERI
Sebastian BAYER
Miriam SIMON
Albert PRAUSE

Local contacts: Ralf SCHWEINS

Samples: TTAB
TDMAO
Hyaluronate

Instrument	Requested days	Allocated days	From	To
D33	0	2	31/08/2019	02/09/2019
D11	2	0		

Abstract:

In polyelectrolyte/surfactant complexes (PESCs) of hyaluronic acid (HA) and cationic surfactant tetradecyltrimethylammonium bromide (TTAB) we have observed the formation of rather large aggregates of low density, that remain constant in structure over a large range of charge ratios. By introducing tetradecyldimethylamine oxide (TDMAO), a nonionic surfactant that otherwise structurally resembles TTAB, into the system, we are able to vary the charge density of the micelles without changing their structure. This allows us to alter the charge conditions in the aggregate, which should have a strong impact on their structure, as experiments with a related system have shown. Additionally, varying the ionic strength allows us to tune electrostatic interactions, which gives us two additional parameters to shine light on the forces that guide the formation of these fascinating complexes.
This SANS/LS-study will deliver the structural details for the assembly conditions in this new type of PESCs. This is of fundamental interest, of relevance for biomedical applications because of the rich abundance of HA in the human body, and finally gives structural control over this novel type of PESC.

Introduction and Aim:

In this experiment, polyelectrolyte-surfactant complexes composed of anionic hyaluronan (Hy), cationic tetradecyltrimethylammonium bromide (TTABr) and uncharged tetradeclydimethylamine oxide (TDMAO) surfactants were studied with regards to their structural change close to the phase boundary. The system was also expanded to a microemulsion complex by addition of a co-surfactant (hexanol) and decane as oil. PBS buffer with 150 mM ionic strength and pH 7.4 served as buffer for all samples. The hyaluronan concentration was set constant at 1 wt%, which is well into the semidilute regime for the employed MW of 600 kDa. These parameters are similar to physiological conditions, which extends the application of our results for biological usecases.

We focused on the parameters charge density of the micelles/ microemulsion droplets, radius of the droplets, and temperature. These findings will add to a more rational design of PESCs in pharmaceutics and cosmetics.

Results:

While the scattering contribution of the polyelectrolyte network is mostly incoherent, and only at small-q a power-law increase in scattering intensity is seen, the micelles/ microemulsion alone can be modelled with a sphere model.

SANS on the mixed complexes shows that the spherical nature of the micelles/ microemulsion remains unaffected in the presence of the complexing polyelectrolyte, as can be seen from the unchanged spherical form factor at high-q. This is reported mor many PESCs. For $q < 1\,\mathrm{nm}^{-1}$, however, marked deviations of the sum of the scattering contributions of both single components are found in dependence of the sample composition/ temperature.

For samples with low charge density on the micelles and low temperature, a power law with an exponent between -1 and 0 is found at low-q, eventually leading to a plateau in the last datapoints. This is interpreted as linear arrangements of the droplets of finite length in a first analysis.

Samples with higher charge density and higher temperature showe q^{-1}-behaviour for $q < 1\,\mathrm{nm}^{-1}$. In addition, for very low q, the slope changes to q^{-4}. This is interpreted as spherical superstructures, and backed up by cryoTEM-measurements.

A systematic, quantitative study of the obtained data is underway.

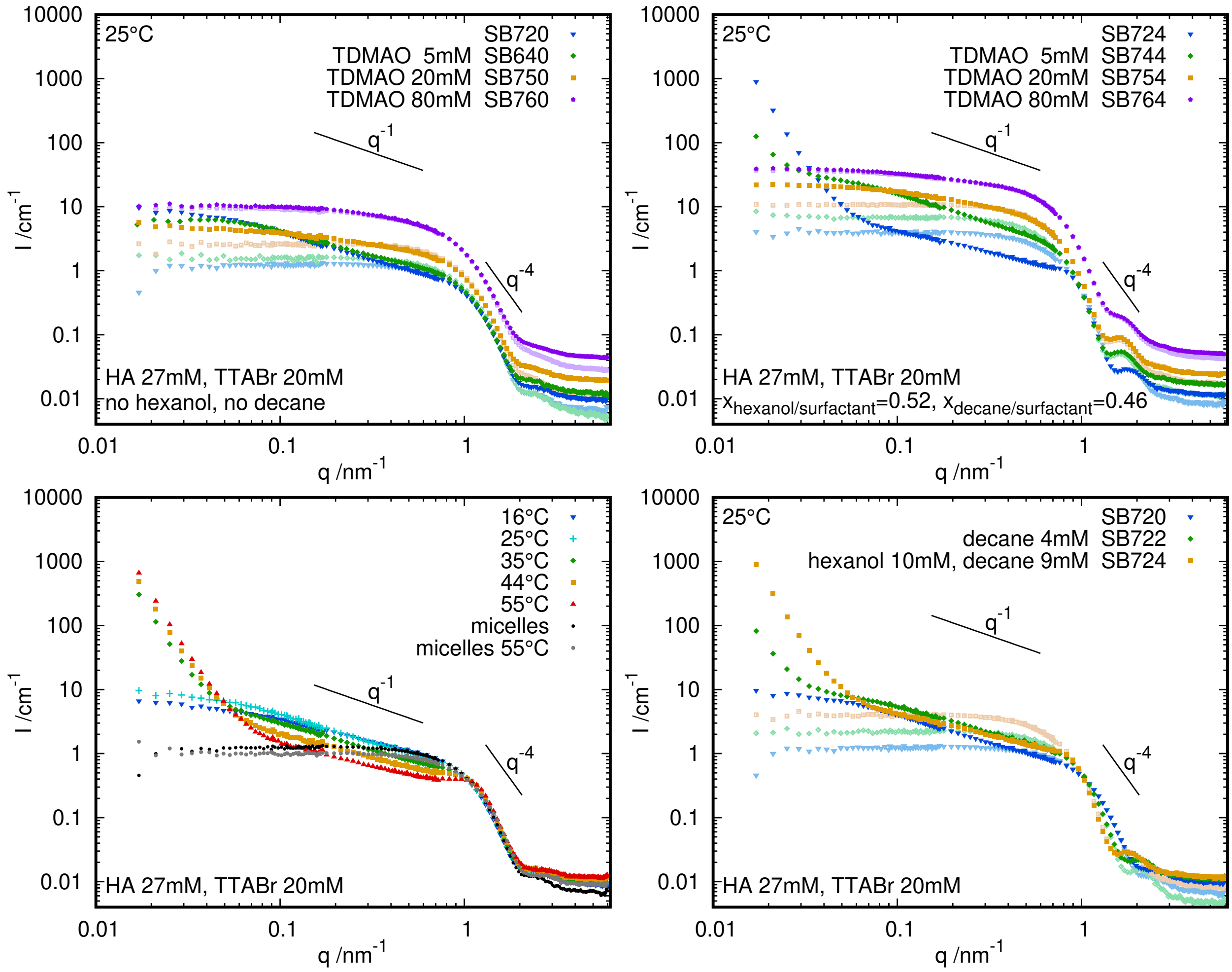

Figure 1: Exemplary datasets of measured series (pale colors: only microemulsion without Hy): top left: complexes with micelles with different charge densities. top right: the same series with microemulsion droplets (bigger size). bottom left: sample at temperatures from 16 to 55 °C. bottom right: series with maximum charge density in the microemulsion and increasing droplet radius.