Experimental report

11/01/2017

Proposal: **9-12-378** **Council:** 10/2014

Title: Hyaluronan/surfactant complexes – Connecting mesoscopic structure to macroscopic behaviour

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Philipp BUCHOLD**

Experimental team: Philipp BUCHOLD

Local contacts: Ralf SCHWEINS

Samples: $C_{14}H_{14}NO_{11}D_4$
$C_{17}H_{38}BrN$

Instrument	Requested days	Allocated days	From	To
D11	2	1	20/06/2015	21/06/2015

Abstract:

The biopolyelectrolyte Hyaluronan (HA) is known since nearly 90 years. Still the fundamental principles of its complexes with surfactants are not fully understood yet. In this experiment the structural changes upon varying the nominal charge ration Z between HA and surfactant (Z=[-]/[+]) shall be investigated. This will be done for comparing the cationic TTAB (tetradecyltrimethylammonium bromide) and the zwitterionic lecithin. For TTAB for $Z < 1$the viscosity compared to pure HA or TTAB solutions is increased possibly due to positively charged micelles interconnecting the HA network or inclusion of HA into a hexagonal structure. On the other hand in a polymer excess region ($Z > 1$) complexes with lecithin, a phospholipid, will be studied. These complex solutions show a lowered viscosity, potentially caused by lipid layers wrapping the HA. From the comparison of these experiments a more general picture of the structural behaviour of such complexes will be derived.

Experimental report

Proposal number: 9-12-378 / Test-24476

Main proposer: Philipp BUCHOLD

Introduction

Complexes formed by the bio-polyelectrolyte hyaluronan (HA) and oppositely charged surfactants have been studied since decades but the fundamental principles of their formation of mixed aggregates are not fully understood yet. For instance, the behaviour of HA in the presence of an excess of surfactant was not yet studied. Therefore, HA was investigated in this experiment in the presence of an excess of the cationic surfactant TTAB (tetradecyltrimethylammonium) in a solution with an ionic strength of 160 mM, similar to biological systems. In addition, we studied an amino acid derivate, lauryl arginine ethyl ester hydrochloride(LAE), to directly address the comparability between synthetic organic polymers and bio-mimetics.

Samples and sample preparation:

Appropriate amounts of dry HA and dry surfactant were weighted and solved in 160 mM NaBr in D_2O. The samples were stirred at least 24 h and left for 2 days at room temperature for full equilibration. Sample series consisted of 245 or 496 mM TTB and various amounts of HA to ensure an excess of surfactant. For mixtures of HA/LAE stock solutions of HA and LAE were prepared in pure D_2O and mixed at the right concentrations.

Results

The experiment showed that the presence of an excess of oppositely charged surfactant has only a marginal influence on the structure and behaviour (see Fig. 1 and 2) of the HA. Already at low concentrations of 2 mM HA the solutions become viscous compared to the solvent. This is interesting as normally the viscosity of polyelectrolytes/surfactant mixtures is dominated by the viscosity of the excess component. Here HA dominates the viscosity although TTAB is in nearly 100 times in excess. This behaviour could be explained by the formation of complexes composed of HA and TTAB micelles. The complexes are arranged in fractal fashion and incorporate the HA. A consequence of the complexation is, that no molecular dissolving or collapsing of the HA chain occurs. A full evaluation of the data and description of system is part of an accepted paper in soft matter (2017).

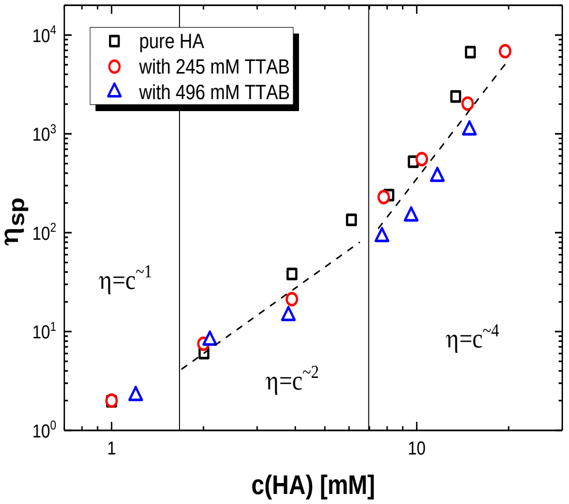

Fig. 1: The specific viscosities vs. concentration of HA as pure HA solutions (black squares), in mixtures with 245 mM TTAB (red circles) and 496 mM TTAB (blue triangles) (all samples in 160 mM NaBr in D_2O and at 25 °C; dashed line as guide for the eye).

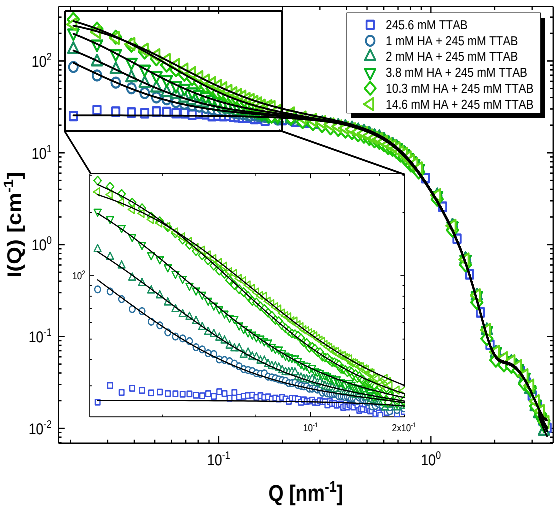

Fig. 2. Scattering intensities vs scattering vector Q for HA/245mM TTAB mixtures. Solid lines according to the described fit model.

Further two important conclusions could be drawn. The comparison to carboxymethyl cellulose showed, that a minimal derivation in the chemical structure of the polyelectrolyte does not only lead to a completely different mesoscopic structure (Fig. 3) but also increases the macroscopic viscosity. Here an interconnected superstructure of smaller micelle cluster seems to be present. The comparison to a HA mixture with the amino acid surfactant LAE revealed that the observed structures of HA/TTAB complexes are not unique but could be generalized for cationic surfactants. Already below 1 mM LAE in a mixture with 6 or 11 mM HA yields defined spherical clusters (Fig. 4). Accordingly our experiments show that the structure of polyelectrolyte/surfactant complexes depends subtley on the type of surfactant and even more so on that of the polyelectrolyte, thereby allowing to construct a large diversity

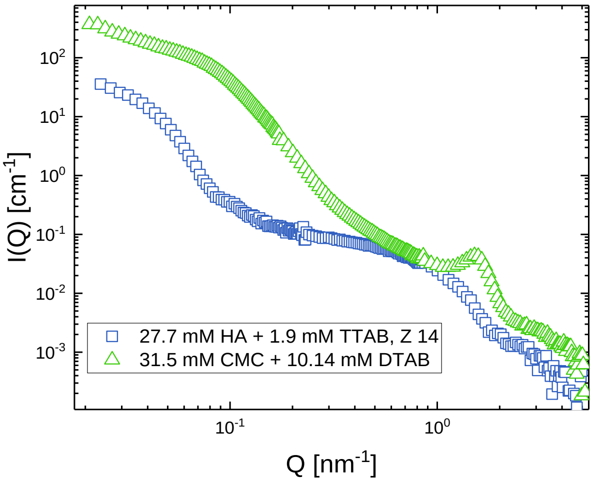

Fig. 3: SANS intensities of HA/TTAB and CMC/DTAB mixtures.

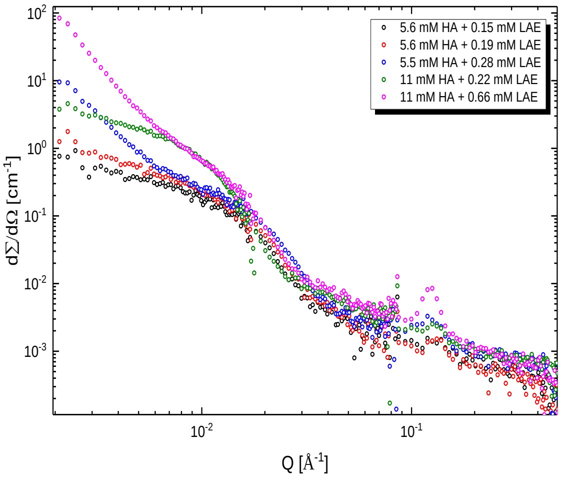

Fig. 4: SANS intensities of complexes formed by HA/LAE.

of structures in solution, with correspondingly varying properties.