Experimental report

11/01/2017

Proposal:	**9-12-435**	**Council:**	4/2015
Title:	Internal structure of hyaluronic acid(carboxymethylcellulose)/surfactant complexes – relation to rheological properties		
Research area:	Chemistry		

This proposal is a continuation of 9-11-1693

Main proposer:	**Philipp BUCHOLD**
Experimental team:	Philipp BUCHOLD
Local contacts:	Ralf SCHWEINS

Samples: $(C_{14}H_{21}NO_{11})_n$

Instrument	Requested days	Allocated days	From	To
D11	3	2	06/11/2015	08/11/2015

Abstract:

The polyanion hyaluronic acid (HA) and oppositely charged surfactant tetradecyltrimethylammonium bromide (TTAB) are interacting strongly in aqueous media due to electrostatic attraction and the release of counterions. The structure of the formed complexes depends on the mixing ratio and results in dramatic changes in viscosity. This structure-macroscopic behaviour relation shall be investigated by contrast matching either TTAB or HA, where both components will be employed in their deuterated version as well. Thereby the contribution of both components to the complex structure can be addressed in a unique fashion not possible by any other method. Further comparison to a structurally related polyanion (CMC) will then allow to address the question of the effect of polyanion architecture. This shall lead to a comprehensive structural picture for changes in viscosity in such systems based on their mesoscopic structure, in particular how they are controlled by structure and properties of the polyelectrolyte contained.

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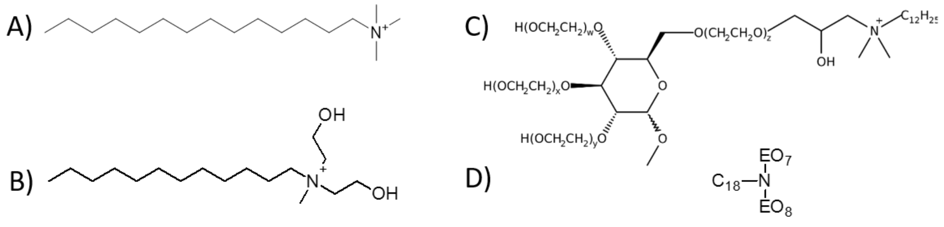
Introduction

Self-assembled complexes of polyelectrolyte and oppositely charged surfactants in aqueous solutions are versatile in macroscopic behaviour and mesoscopic structure and therefore are used in a wide scope of applications. The interactions between them are mainly caused by their electrostatic attraction and the release of counterions, and their properties can be controlled by several parameters. Important variables are the mixing ratio of both components, the ionic strength of the solvent and the chemical structure of the surfactant. However, the fundamental principles of the correlation between the macroscopic properties of the solution and the mesoscopic structural arrangements, and in particular the role of the architecture of the surfactant, are still unknown. For this reason, we investigated here the structure-properties relationship of the complexes formed by the polyanion hyaluronic acid (HA) and several positively charged surfactants. One goal is to distinguish between the contributions of polyelectrolyte and micelle to the structure of the formed complexes.

Samples and sample preparation:

Stock solutions of hyaluronic acid (600 kDa), tetradecyltrimethylammonium bromide (TTAB) (A) the positively charged surfactants Ethoquat (B), Glucquat (C) and Amiet (D) were prepared in phosphate buffered saline in D_2O (PBS) at appropriate concentration. Samples were made by mixing according volume of stock solutions together in the order of HA, solvent and then surfactant. The samples were stirred at least 24 h and left for 2 days at room temperature for full equilibration. HA was kept at 1 wt% and always in excess.



Results

The contrast match point of components and the surrounding medium was determined experimentally. In Fig. 1 the results of the contrast variation of a HA/TTAB system is shown. In this case the surfactant was matched to the solvent via deuteration of both the surfactant chain and the head group (d-TTAB). The matching was successful so that a pure surfactant solution showed nearly no intensities.

Interestingly also the mixtures of d-TTAB/HA showed low intensities and particularly also lower intensities as the pure HA solution; for comparison, also the mixture HA/TTAB in full contrast is included. It can be concluded that the intensity of the complex is mainly originated from the surfactant. Even further the complex must consist of HA and TTAB since the matched sample showed less intensities than the same concentrated pure HA solution.

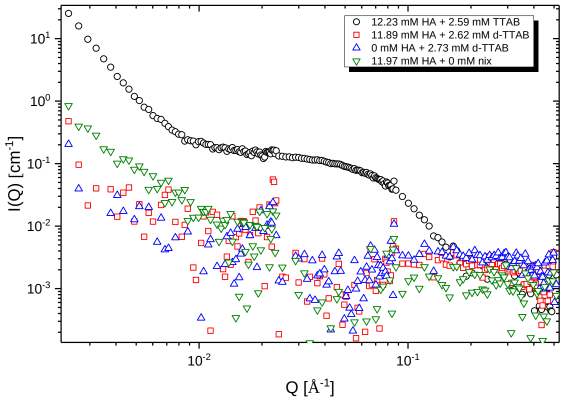


Figure 1: SANS Intensities of HA/deuterated TTAB mixtures. The according sample with full contrast is included.

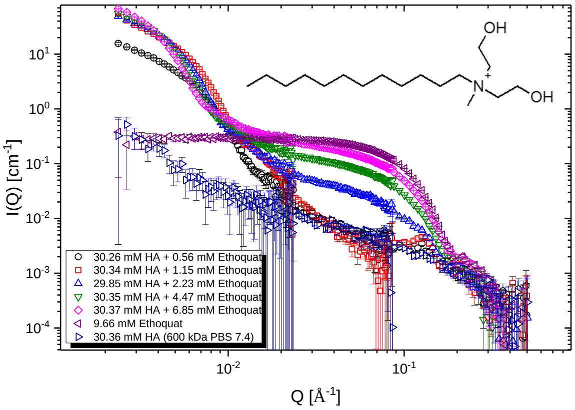


Figure 2: SANS Intensities of HA/Ethoquat in PBS. The chemical structure of this surfactant is given in the inset.

As a next step the hydrophilicity of the surfactant was systematically increased to investigate the role of the surfactant in the complex in more detail. Fig. 2-4 show, that HA forms a spherical superstructure as long as a positive charge remains on the surfactant. The absence of charge is macroscopically visible, since in this case no phase separation occurs as it is the case for HA/Amiet mixtures. In SANS, the uncharged surfactant (Fig. 4) shows no increased forward scattering, so that complexation can be excluded. Interestingly the TTAB (Fig. 1) and Ethoquat (Fig. 2) develop a substructure which is in a size range of 3 - 30 nm, detectable in the mid Q range in addition to the superstructure. It might be plausible that the substructure is build up by the micellar hydrophobic compartments formed by the tail of the surfactant, which are more or less strictly arranged in a cylindrical order yielding in a Q^{-1} dependence. Below the critical micellar concentration, the substructure is not present (Fig. 3), but the superstructure is. Consequently, one can conclude that HA and oppositely charged surfactant form clusters possessing a finite superstructure structure mainly determined by the HA itself. The substructure is determined by the chemical nature of the surfactant.

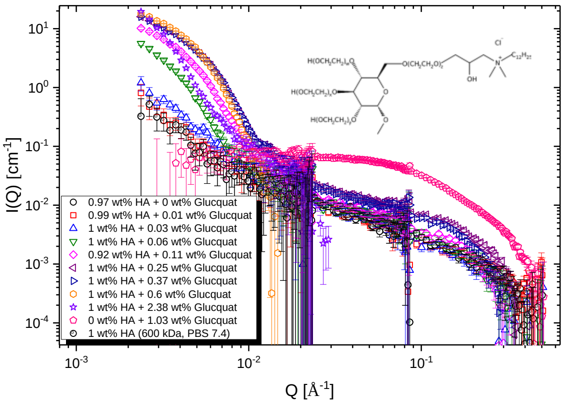


Figure 1: SANS intensities of HA/Glucquat complexes in PBS. The chemical structure of this surfactant is given in the inset.

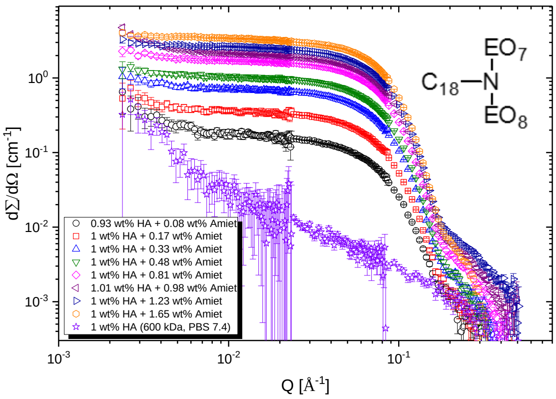


Figure 4: SANS intensities of HA/Amiet complexes in PBS. The chemical structure of this surfactant is given in the inset.