Experimental report

16/05/2019

Proposal: 9-11-1836 **Council:** 4/2017

Title: Experiment title: Dynamics of hydration water of hyaluronic acid / ionic surfactant complexes

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1771

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Samples: Hyaluronic acid
deuterated dodecyletrimehyleammonium bromide

Instrument	Requested days	Allocated days	From	To
IN13	7	7	15/03/2018	22/03/2018

Abstract:

Hyaluronic acid (HA) is one of the most important polysaccharide in biology. It is often associated with proteins (or other molecules) by specific interactions but also via electrostatic interactions, hydrogen bounding and hydrophobic forces. One important property of the HA is that its biological function can be opposite depending on its molecular weight and like any biological system, its functionality is related to the dynamics of hydration water. We already investigated the water dynamics of 2 hydration rates for long and short chain HA samples, in pure H2O, pure D2O and in the dry state. With the goal of understanding the mechanisms followed by this versatile biopolymer and in particular the associations effects, we propose to continue the characterization of the dynamics of its hydration water by elastic incoherent neutron scattering on purely electrostatic HA complexes. HA/ionic surfactants forming complexes that we observed by SANS in more dilute solutions will be used. For such experiments, the same hydration conditions as for HA solutions previously studied on IN13 will be considered, in order to investigate the effect of the complexation on the HA hydration properties.

Report of experiment 9-11-1836 on IN13

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Dynamics of hydration water of hyaluronic acid / ionic surfactant complexes

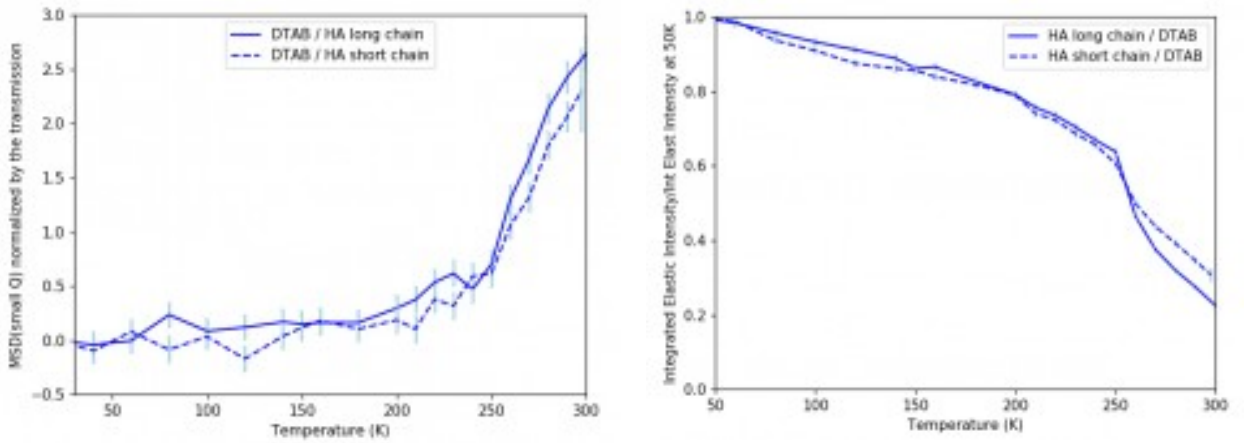
Biopolymers, in particular polysaccharides, have a great importance in biology. Among these polymers, hyaluronic acid (HA) has an important role in various biological processes, being largely present in the human body. It can associate with proteins by specific interactions but also via electrostatic interactions [Moss]. HA is supposed to have peculiar hydrodynamic properties which insure various functions in relation with the environment (water and other particles) : viscoelasticity in synovial joints, control of the tissue hydration etc. Within the group of substances known as glygoaminoglycan (GAG), HA is a linear polyelectrolyte with the repeating disaccharide structure poly((1→3)-β-D-GlcNAc-(1→4)-β-DGlcA). In addition, and in spite of its natural origin, HA is an excellent model for polyelectrolyte of the semi-rigid class [Buhler], able to associate via electrostatic forces but also via H-bonds. The understanding of the properties of this polysaccharide with complex behavior remains, nowadays, a soft matter subject including electrostatic, H-bond, and hydrophobic forces.

It is now well established that hydration water has a large importance in biological systems, being necessary for the system functioning. For example, protein fluctuations are indeed locked to water or solvent dynamics [Frauenfelder]. Very different situations occur: depending on the polymer surface, the water mobility can be either slowed down or enhanced. In most cases, the water at the protein surface presents the characteristics of confined water, with reduced mobility with respect to the bulk one [Bellissent-Funel]. However, in some situations, due to a subtle balance of hydrophilic and hydrophobic sites at the polymer surface, the water can be hypermobile [Kabir, Fichou]. HA is not an exception in this context. Several of the very important physiological roles that HA plays in living organisms are directly linked to the hydration water: maintenance of viscoelasticity, control of the tissue hydration, water transport... With the aim of understanding the mechanisms associated with HA (especially the role of the molecular weight) in the physiological conditions, complexed with other proteins or free in solution, it is therefore necessary to characterize the water dynamics at its surface as a function of its interaction with other molecules.

We recently performed a series of two IN13 experiments (See Exp. Reports CRG 2280 and 9-11-1771) on HA with a large and a small molecular weight showing that HA hydration in pure water does not depend on the chain lengths. In the present experiment we are characterizing the mobility of hydration water of the same 2 molecular weight HA samples as they interact electrostatically with ionic surfactant of dodecyletrimehyleammonium bromide (DOTA+ Br- or DOTAB) forming self-assemblies in water. Samples had the same hydration level as the one used for the first two experiments (approximately 0.67 g water/ 1g HA and 1 g water/ 1g HA) corresponding

to 15 water molecules per HA disaccharide unit. We already performed HA/DOTAB SAXS structural studies showing the complexation (unpublished results).

To check what is the effect of the complexation on the hydration water as a function of the HA molecular weight, molecular dynamics are characterized by monitoring the elastic incoherent neutron signal of HA - fully deuterated DOTAB complexes having a charge ratio r = 0.5. Small and large HA molecular weights were used for this experiment. Equivalent samples of HA-DOTAB in D2O as well as DOTAB in D2O and dry DOTAB samples were investigated in order to distinguish between H_2O and polymer or surfactant signals. Temperature scans between 20 and 300 K were performed for each sample.



The figures shows a first data analysis of HA/DOTAB complexes in H2O. A small difference appears between the MSD of the HA long and short chains in presence of DOTAB (at left). A transition in the integrated elastic intensity as a function of T (at right) that may be due to water in the bulk state is visible around T=250K for the long chains only.
A further analysis of these data compared to the previously obtained ones are under progress. They will also be compared to SAXS structural studies to better understand their functionality.

References

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