POLYELECTROLYTE/SURFACTANT COMPLEXES (PESCs) – VERSATILE SELF-ASSEMBLED SYSTEMS STUDIED WITH RESPECT TO THEIR STRUCTURAL, DYNAMICAL AND RHEOLOGICAL PROPERTIES

Michael Gradzielski, Technische Universität Berlin, Germany
michael.gradzielski@tu-berlin.de
Leonardo Chiappisi, Bin Dai, Miriam Simon, Technische Universität Berlin, Germany
Ingo Hoffmann, Sylvain Prévost, Philipp Buchold, Institut Laue Langevin (ILL), Grenoble, France

Key Words: PESCs, mesoscopic structure, SANS, rheology.

Mixtures of oppositely charged polyelectrolyte and surfactant are very interesting systems, as they allow to control the structure and properties of the self-assembled complexes over a very wide range. In our investigations we concentrated on biopolymers such as chitosan, hyaluronic acid or cationically modified cellulose and their combination with biofriendly surfactants. We studied several such systems comprehensively by means of static and dynamic light scattering (SLS, DLS), small-angle neutron scattering (SANS), neutron spin-echo (NSE), and rheology, in order to deduce systematic relations between the composition of the systems (as mainly controlled by the mixing ratio surfactant/polyelectrolyte), the mesoscopic structure and the macroscopic flow behavior. For instance one can produce highly viscous complexes of locally rodlike structure already at concentrations below 1 wt% by having these mixed PESC structures highly interconnected [1]. An interesting observation here is that the local dynamics of the polyelectrolyte chains, as evidenced by NSE, is only little reduced despite an increase of viscosity by more than 4 orders of magnitude [2].

For example for chitosan in mixtures with anionic surfactants one finds a pronouncedly pH-dependent aggregation behavior [3]. An interesting SPEC structure are locally rod-like aggregates and densely packed micelles of alkyloxy carboxylates in a chitosan matrix which can be present in globular or extended complexes, depending on the detailed composition of the system. This structural flexibility then was employed to use this system for selective separation of hydrophobic and hydrophilic organic compounds or sequestration of metal ions [4].

The local structure typically is determined by the surfactant self-assembly and for cases where the surfactant forms vesicles one can then have multilamellar vesicles (MLVs), where the number of lamellae is controlled by the amount of chitosan added (Fig. 1). Such MLVs are attractive for delivery purposes as they are fully composed of biocompatible components and their surface charge is controlled by the mixing ratio.

These are very interesting properties, but due to the intrinsic pH dependence of chitosan, which renders it insoluble above pH 6, we were also interested in extending this structural responsiveness of the SPECs to a much higher and larger pH-range. This was done by quaternizing the chitosan and for further amphiphilic modification we also introduced hydrophobic moieties (like dodecyl chains). In our experiments we studied how the modification of the chitosan (quaternization and hydrobization) affects the structure of SPECs formed.

From the combination of the structural properties with the release properties one can deduce in a systematic fashion what are the optimum conditions for designing SPECs for a desired delivery behavior, depending on the modification of the chitosan (or also by employing biopolyelectrolytes with other chain properties) and its content in the formulation. This renders SPECs very interesting self-assembled systems for a variety of applications.

Figure 1 – Scheme for transforming unilamellar to multilamellar vesicles by polyelectrolyte addition


Tuesday, August 1, 2017

Electrosta