Experimental report

18/02/2022

Proposal: 9-10-1626 **Council:** 10/2019

Title: Characterisation of pH responsive microgels at oil-water interface.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: [C6D7H4NO]n-co-C4H6O2

Instrument	Requested days	Allocated days	From	To
FIGARO	3	2	19/03/2021	21/03/2021

Abstract:

pH-sensitive soft materials are ubiquitous at oil-water interfaces in soft matter. Here we propose to study the pH-responsiveness of soft charged microgels at interfaces using the newly developed quartz-cell that allows to measure these microgels at oil-water interfaces and change the pH in situ. This study is fundamental to characterize the out-of-plane structure of charged microgels at oil-water interfaces. To date many ex-situ techniques reveal differences in the microgel arrangement at the interface due to microgel charges. Our study proposes to measure the microgel structure at different pH and charges condition in situ. The use of both deuterated monomer ([C6D7H4NO]n) and of a low neutron adsorbing oil (perfluoroctoane) will ensure data with high contrast for all experimental conditions. The data for the different contrasts will be fitted simultaneously using a multi-layer model (at least three layers needed). Despite the intrinsic scientific interest on the out-of-plane-behavior of microgels, this proposal is aimed to test the new quartz-cell and will open the possibility to perform experiments at the oil-water interface with the possibility to change the pH in situ.

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In this experiment, we set out to analyze the three-dimensional structure (out-of-plane density profile) of polyelectrolyte microgels adsorbed to oil-water interfaces *in-situ* as a function of their charge density. Therefore, p(D7-NIPAM-co-MAA) microgels were investigated with neutron reflectometry at water-perfluorooctane interfaces for three distinct conditions: uncharged state (pD 3, 0.1 mM KCl), charged state (pD 9, 0.1 mM KCl), and charge-screened state (pD 9, 100 mM KCl). Microgel stock solutions and aqueous subphases were prepared according to the respective conditions. Three distinct water-perfluorooctane interfaces were created (one for each condition). Adsorption of the microgels to the interface was observed in all of them. However, the reflectivity of the interfacial layer did not exhibit charge-dependent behavior as the curves were virtually identical between contrasting charge states. Changing the charge density of the microgels *in-situ*, i.e., through the addition of NaOD to the interface at pD 3 or, respectively, DCl to the interface at pD 9, led to no difference in the reflectivity curves either. Thus, the reflectometry results do not agree with dynamic light scattering studies conducted prior that clearly show a pH- and ionic strength-dependence of the microgels' swelling behavior in solution.

Consequently, it needs to be determined if the observed lack of a charge-dependence in the reflectivity curves is a feature of the microgels or due to experimental details (setup, sample preparation, etc.) We note that, unfortunately, we could not perform the reflectometry experiments in person because of the ongoing Covid-19 restrictions. However, we are in close contact with the instrument scientists to assess the possibility of potential experimental errors and plan to reapply for beamtime should it be determined that they are the cause for the contradicting results.