Experimental report

04/10/2019

Proposal: **9-11-1871** **Council:** 4/2018

Title: Thermo-responsive microgels at air-water interfaces: specular neutronreflectometry study to obtain out-fo-plane density profiles

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-1840

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Samples: (C6H11NO)n-(C7H13NO)m
C6H11NO)n-(C7H13NO)m

Instrument	Requested days	Allocated days	From	To
FIGARO	3	2	19/09/2018	21/09/2018

Abstract:

With specular neutron reflectometry it would be possible to determine the projected out-of-plane density profiles of microgels at air-water (D2O and ACMW) interfaces.
We would like to investigate p(NIPAM) and p(NIPAM-co-DEAAM) microgels adsorbed to the interface at temperatures below (swollen) and above (collapsed) their VPTT of 32 °C and 20 °C, respectively. The interfacial particle density or surface occupancy will be managed by spreading microgel suspension directly at the surface. We want to study if microgels change their structure adsorbed to the interface, similar to the reported transition from a fuzzy to a hard sphere in bulk. The data is fitted with a suitable model (three and two layers) using MOTOFIT and the scattering length density profiles are obtained. The polymer volume fraction as a function of the distance from the interface will be calculated. These profiles could be further connected to the structure and deformation of microgels at air-water interfaces as a function of temperature.

Our goal in the experiment was to measure NIPAM- and NIPAM-*co*-DEAAM- Microgels at air-water interfaces and their response to temperature at constant surface pressures. The microgels have the nearly the same size in solution and were synthesized with same cross-linker concentration (5 mol%). Due to the incorporation of DEAAM the volume phase transition temperature (VPTT) of the NIPAM-*co*-DEAAM microgels could be decreased to approx. 21˚C. In contrast to our proposal we conducted the measurements in a Langmuir trough.

Figure 1A and 1B show the reflectivity curves of the experiments for temperatures 10, 20, 30 and 40˚C at the air-D_2O interface for the NIPAM and NIPAM-*co*-DEAAM microgels, respectively. The surface pressure was controlled with compression of the interface in the Langmuir-trough to approx. 13 mN/m for all measurements.

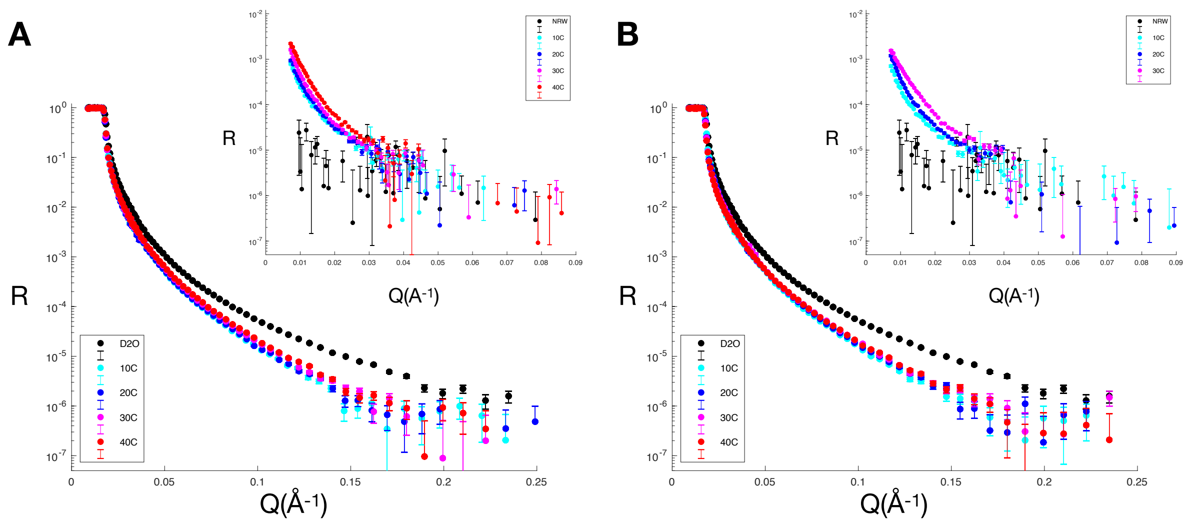

Figure 1: (A) Reflectivity curves of pNIPAM microgels at 13 mN/m at different temperatures in comparison to D_2O at the air-D_2O interface. Inset: Reflectivity curves of pNIPAM microgels at 13 mN/m at different temperatures in comparison to NRW at the air-NRW interface. (B) Reflectivity curves of pNIPAM-*co*-DEAAM microgels at 13 mN/m at different temperatures in comparison to D_2O at the air-D_2O interface. Inset: Reflectivity curves of pNIPAM-*co*-DEAAM microgels at 13 mN/m at different temperatures in comparison to NRW at the air-NRW interface.

In Figure 1A the pNIPAM microgel with a VPTT of 32˚C are shown. One can see the response of the microgel monolayer as a function of temperature directly from the reflectivity curves. The strongest change can be seen between 20 and 40˚C, whereas the curves at 10 and 20˚C do not show a strong difference. This is illustrated in particular by the curves at the air-NRW interface (inset of Fig. 1A)

In Figure 1B the pNIPAM-*co*-DEAAM microgel with a VPTT of 22˚C are shown. In contrast to the pNIPAM microgels, one can see the response of the microgel monolayer between 10 and 30˚C. The curves at 30 and 40˚C show only a slight difference. This is in agreement with the VPTT of the microgels in suspension. The inset of Figure 1B shows the reflectivity curves at the air-NRW interface. Unfortunately, measurements at 40˚C could not be conducted. Nevertheless, the strongest change can be seen between 20 and 30˚C.

The reflectivity curves for both microgel systems show that the monolayers react to change of temperature as expected from bulk. The strongest changes are observed when crossing the VPTT of the respective microgel.
To obtain a more robust fitting of the results the measurements were conducted at the air-D2O and –NRW interface. However, the protonated microgels display low reflectivity at the air-

NRW interface. In the following we want to conduct measurements of deuterated pNIPAM microgels to increase the contrast.