Experimental report

16/05/2022

Proposal:	**9-11-2067**	**Council:**	4/2021

Title: Swelling of ionic microgels embedded in a matrix of neutral microgels: a SANS with contrast variation study

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Andrea SCOTTI**

Experimental team: Andrea SCOTTI

Local contacts: Ralf SCHWEINS

Samples: $C_6H_{11}NO$
$C_6D_7H_4NO$

Instrument	Requested days	Allocated days	From	To
D11	1	1	15/09/2021	16/09/2021

Abstract:

Soft deformable microgels adapt their size and shape depending on the solution packing fraction. Studies on the response to crowding of both neutral and ionic microgels have been conducted using SANS with contrast variation to probe the form factor of individual microgels as a function of the solution concentration. The possibility to embed few ionic microgels in a majority of neutral microgels allows to study the swelling capability of the ionic microgels in crowded environment of neutral microgels. This is important to understand the role of electrostatic interaction in the deswelling/compression of an individual ionic microgel. Here we propose to study ionic hydrogenated microgels in a matrix of deuterated neutral microgels (contrast matched by the H_2O/D_2O mixture) in solutions at different pH. Since the ionic microgels will have a size of ~150 nm at pH = 3 and ~220 nm at pH = 9, we plan to use two families of deuterated neutral microgels with comparable sizes. We also plan to change the size ratio and see the effect on the deswelling of larger ionic hydrogenated microgels (~220 nm) embedded in a matrix of small neutral deuterated microgels (~150nm).

Background: Microgels are crosslinked polymeric networks swollen in a good solvent that are compressible and deformable [1]. The capability to be compressed allows large microgels to fit into an ordered lattice of smaller microgels without producing defects [2]. Therefore, size polydispersity does not suppress crystallization up to values of 18% [3], while for hard spheres the limit is 12%. Changes in the microgel shape and volume starts as soon as the solution osmotic pressure, π, is larger than the microgel bulk modulus, K. Recently we developed an elegant method to probe K using small-angle neutron scattering (SANS) [4]. Our method uses a partially-deuterated polymer, which exerts the required isotropic stress, and SANS with contrast matching to determine the form factor of the particles without any scattering contribution from the polymer. We have shown a clear difference in softness, compressibility and evolution of the bulk modulus between the shell of the microgel, and the rest of the particle, depending on the amount of crosslinker used in their synthesis. To date, more complex microgels possessing exotic internal architecture – e.g. hollow microgels – or with a charged polymeric network can be realized [5,6]. Their behaviour, as a consequence of their different compressibility, differs from both the regular microgels and hard colloids. To date, there is no quantitative information on how the presence of permanent charges within the polymeric network change the compressibility of individual microgels. This knowledge is fundamental for the further use of these different microgels as building blocks for macroscopic materials such as colloidosomes with well-defined properties. Furthermore, our data will shed light on the phase behaviour of very soft and deformable particles.

Aim: We want to use SANS with contrast matching to obtain the bulk moduli of charged microgels. By contrast matching partially-deuterated polyethylene glycol ($d_{83\%}$PEG) in a solution mixed with a few microgels, we can directly probe the form factor of these microgels. This gives access both to the total microgel size and to the other characteristic lengths, e.g. the radius of the cavity for the hollow microgels or the length of the fuzzy shell. Therefore, with these experiments, we will be able to characterize the different bulk moduli through the microgels and relate them to the polymer density profile.

Strategy: The different combinations of microgels we want to measure are: (i) charged microgels at pH 3 (collapsed, R = (103 ± 1) nm) and (ii) pH 9 (swollen, R = (133 ± 2) nm); (iii) hollow charged microgels at pH 3 (collapsed, R = (140 ± 2) nm, R_{cavity} = (40 ± 1) nm) and (iv) pH 9 (swollen, R = (187 ± 3) nm, R_{cavity} = (62 ± 1) nm). The synthesized $d_{83\%}$PEG is contrast matched in pure D_2O and has high molecular weight so that it cannot access the interior of the microgels [4]. We plan to realize solutions by mixing few microgels (volume fraction lower than 5%) with 10 different concentrations $d_{83\%}$PEG. Therefore, both the microgels will be measured at two different pH and at 10 different $d_{83\%}$PEG concentrations. This means that our experiment consists of 2 x 2 x 10 = 40 measurements. We have experimentally measured the course of the osmotic pressure as a function of the concentration of $d_{83\%}$PEG. Using concentrations of $d_{83\%}$PEG between 0 an 8 wt% we cover a range between 0 and 160 kPa [4]. The measured intensities will be proportional to the form factor of the microgels at different osmotic pressures. The form factors of these microgels will be analysed with the models we developed to describe the scattered intensities of these materials [2,3,6-8]. From the fitted values of the microgel radii and of the shell lengths, the changes in volume of all microgels, and of their fuzzy shells, can be obtained. Finally, the local slope of the variation of the osmotic pressure versus the changes in volume is proportional to the bulk modulus of the microgel at the different compression stages, and, therefore, can also be obtained directly [4]. The q-range of interest will be covered using three sample-to-detector distances (1.8, 6 and 18 m) [4]. Based on our previous experiment on SANS-I [4], we require 1 hour to perform a single measurement. Therefore, for all the measurements planned, we will require 40 hours of beamtime. Accounting for background measurements, sample changes, and detector movements, we ask for **2 days of beamtime**.

State of research: All the microgels and the deuterated polymer are already synthesized and characterized with SANS, SAXS, and DLS. The osmotic pressure of solution of $d_{83\%}$PEG with concentrations between 0.1 and 4 wt% have been measured using a membrane osmometer (Wescor 4420). Measurements of samples at higher concentration and, therefore higher viscosity, were not possible with the osmometer. The values of π versus the $d_{83\%}$PEG concentration are shown in Figure 1. The fit of the data is shown by the solid blue line and we obtain: $\pi = 217c + 451c^3$. This empirical equation is used to convert the $d_{83\%}$PEG concentration to osmotic pressure, even for concentrations larger than 4 wt%. The suspensions with microgels and $d_{83\%}$PEG cover a range between 0 and 160 kPa. A similar experiment has been conducted using SANS-I at PSI to obtain the bulk modulus of microgels synthesized with different amount of crosslinker [4]. As an example, we report the data of the compression of a 5 mol% crosslinked microgel in solution. The data are fitted using a fuzzy shell model, which is the same model we will use to fit the charged regular microgels.

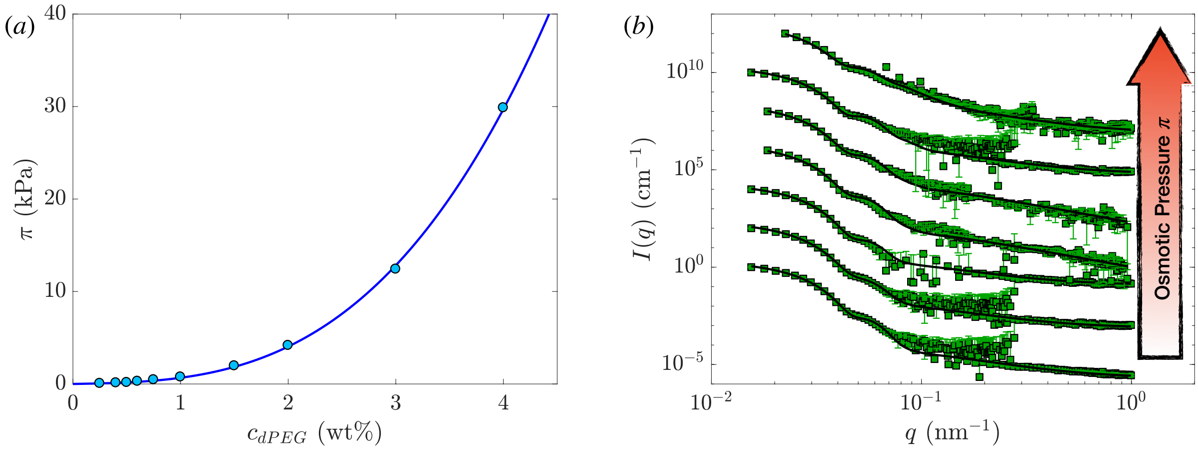

Figure 1 (a) Osmotic pressure vs $d_{83\%}$PEG concentration. Solid line is a fit with a polynomial function. (b) SANS form factors measured in samples with increasing $d_{83\%}$PEG concentration and, thus, osmotic pressure. The solid lines are fits with the model for a fuzzy sphere [2-4, 6-8].

References

1. M. Karg, A. Pich, et al., *Langmuir*, 2019, 35, 6231-6255.
2. A. Scotti, U. Gasser, et al., *PNAS*, 2016, 113, 5576-5581.
3. A. Scotti, U. Gasser, et al., *PRE*, 2017, 96, 032609.
4. J. E. Houston, L. Fruhner, et al., *Science Advances* (2022): Accepted. DOI: (10.1126/sciadv.abn6129)
5. M. M. Schmidt, S. Bochenek, et al., *Langmuir*, 2020, 36, 11079-11093.
6. S. K. Wypysek, A. Scotti, et al., *Macromol. Rapid Commun.*, 2020, 41, 1900422.
7. A. Scotti, S. Bochenek, et al., *Nature Commun.*, 2019, 10, 1418.
8. A. Scotti, A. R. Denton, et al., *Macromolecules*, 2019, 52, 3995-4007.