Experimental Report

16/03/2015

Proposal:	**9-10-1372**	**Council:**	4/2014	

Title: Concentration induced size and shape changes in ionic microgel systems

This proposal is continuation of: 9-10-1301

Researh Area: Soft condensed matter

Main proposer: **NOEJD Sofi**

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Samples: poly(N-isopropylacrylamide)-co-(acrylic acid)

Instrument	Req. Days	All. Days	From	To
D11	3	2	04/11/2014	06/11/2014

Abstract:

We use ionic microgel particles as model systems to understand interactions and phase behavior of soft colloids. To obtain precise information about the size and shape of individual particles, needed in the work on deriving the interaction potential, we propose to carry out small angle neutron experiments using the zero average contrast method. This will allow us to suppress intermolecular interaction contributions to the scattering intensity and only study the form factor in highly concentrated and interacting microgel systems.

Concentration Induced Size and Shape Changes in Ionic Microgel Systems

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1 Abstract

We use thermo-responsive negatively charged poly(N-isopropylacrylamide)-co-acrylic acid, PNIPAM-co-AA, particles as a model system to study the phase behavior of charged soft colloids from low to ultrahigh effective volume fractions ($\phi_{eff} >> \phi_{cp}$). Due to the repulsive, soft and deformable nature of the particles, it is still not yet clear how individual particles adapt themselves to a significant increase in number density. Here we further extended the investigated concentration range by performing zero-average contrast, ZAC, experiments on D11 in order to obtain crucial information on possible particle deformations. Measurements were performed for two particle softness and at two different temperatures. D11 allowed us to access the required spatial resolution and the very low q-values needed in this study. The results show that at ultrahigh packing fractions the microgels did not decrease their size due to compression effects for moderately cross-linked particles. For loosely cross-linked particles a reduction in size was seen above overlap concentrations.

2 Results

We used two sets of hydrogenated (Hm) and deuterated (Dm) ionic microgels (PNIPAm-co-AA) with a cross-linking density of 5mol% and 2mol%, respectively. To verify possible deformations of individual particles, small-angle neutron scattering measurements were performed under zero-average contrast, ZAC. In a previous experiment at D11, the ZAC solvents (e.g. the solvent at which the used equal number density mixture of Hm and Dm microgels have the same contrast) were determined. Working under ZAC conditions allowed us to resolve the concentration dependent form factors at volume fractions far above close packing, ϕ_{cp}. The obtained scattering curves and the corresponding fits, using the Fuzzy sphere model, for particles with a 5mol% cross-linking density at 20°C are shown in Figure 1 A). The absence of a structure peak clearly reveals that the measurements were performed fulfilling the ZAC conditions. For the highest concentrations, a small upturn at low q-values can be observed, which is most probably due to small aggregates present in the highly concentrated and viscous samples. As the temperature was increased the minima, as expected, shifted towards higher values of q as seen in Figure 1 B), here for a 4 wt% sample with a cross-linking density of 5 mol%. Fitting the curves gave a reduction in size from 77.9 nm at 20 °C to 69.8 nm at 27 °C. This is a clear indication of the thermo-responsive nature of the particles, which expel water from their interior when water starts to act as a poor solvent at high temperatures. Similar trends were seen for the sample with a cross-linking density of 2mol%, not shown in this report.

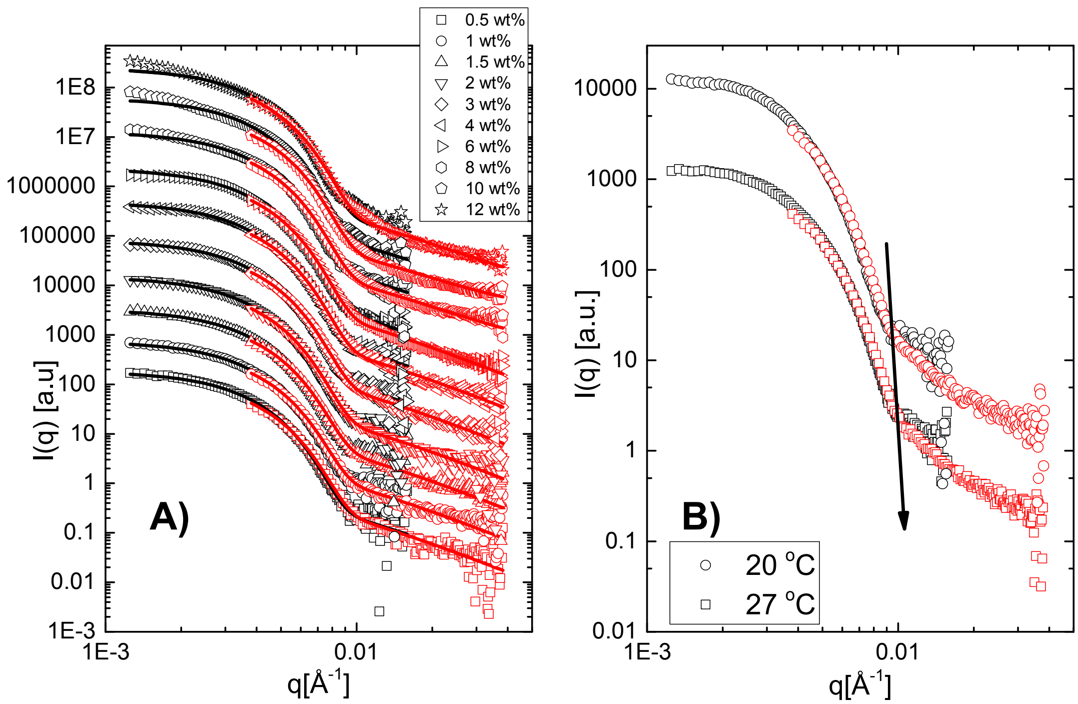

Figure 1: A) Form factors for an equal number density mixture of Hm and Dm with a cross-linking density 5mol% at a wide range of concentrations. Solid lines are fits based on the Fuzzy sphere model. B) Scattering data for an equal number density mixture of Hm and Dm with a cross-linking density of 5mol% at a concentration of 4 wt% at 20 and 27°C. Due to the thermo-responsive nature of the particles the minimum shifts towards a higher q-value due to particle shrinkage.

The fits of the scattering curves shown in Figure 1 A) allowed determining the particle size as a function of concentration. The obtained radii normalized by the radius at the lowest measured concentration are plotted in Figure 2. The evolution of the normalized SANS radii as a function of concentration show no significant decrease, which reveals that particles with a cross-linking density of 5mol% do not change their size in the studied concentration range. Even when the temperature was increased no change in size as a function of concentration was seen. Based on previous small-angle x-ray data the overlap concentration for the two temperatures was shown to between 3 and 5 wt%. This observation indicates that these soft particles most probably interpenetrate rather than deform at such high effective volume fractions. For the particles having a cross-linking density of 2mol% a decrease in size was observed for both temperatures above the overlap concentration. Due to the ultra-soft nature of these particles together with the electrostatic repulsion between the particles thus results in a reduction in particle size just above shell overlap. Due to the limitation in neutron flux, we however need further light scattering studies at lower concentrations in order to conclude on the de-swelling behavior of ionic microgel systems in the full concentration range.

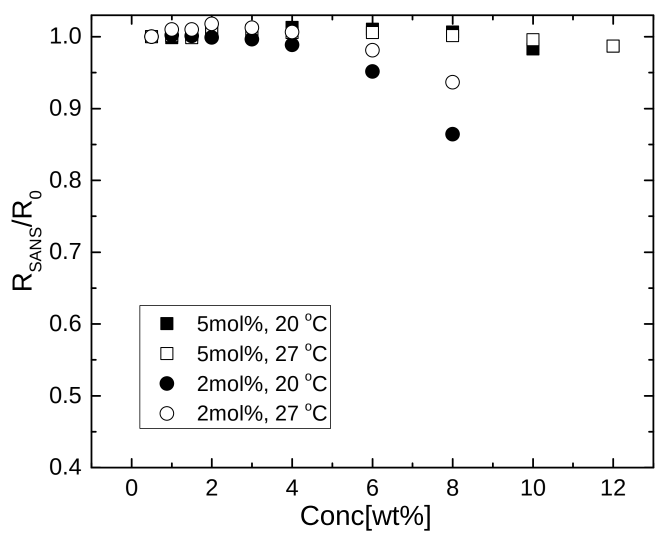

Figure 2: Normalized SANS radii as a function of concentration. R_0 is taken as the SANS radius for the lowest measured concentration.