Experimental Report

Proposal: **9-10-1301** **Council:** 10/2012

Title: Concentration and Temperature Dependent Swelling Behavior of Thermoresponsive Ionic Microgels Using ZeroAverage Contrast

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: poly(N-isopropylacrylamide) co poly(acrylic acid) (PNIPAm co PAA) microgels, deuterated and hydrogenated, in D2O and H2O

Instrument	Req. Days	All. Days	From	To
D11	3	2	25/02/2013	27/02/2013

Abstract:

Ionic microgels are a class of intriguing soft and deformable colloids with an effective pair potential that crosses over from Yukawa-like at large distances to a soft Hertzian repulsive interaction at short distances. A recent experimental-theoretical study using static and dynamic light scattering (PRL, 2012, 109, 048302) on ionic microgels of PNIPAM co PAA has provided evidence for significant changes in the swelling of microgel particle already in the fluid phase at much lower volume fractions than closed packing. These results are in contrast to our previous results from Zero Average Contrast (ZAC) experiments on neutral poly(N-isopropylacrylamide) (PNIPAm) microgels, where we have demonstrated that the size of the microgels remains almost constant in the fluid phase and only slightly decreases above closed packing. Given the importance of a detailed knowledge of the volume fraction and temperature dependence of the particle size and structure at high densities, we propose to perform SANS experiments under ZAC conditions using a mixture of hydrogenated and deuterated ionic microgels at different concentrations from the fluid to the glassy regime.

Concentration Dependent Swelling Behaviour of Thermoresponsive Ionic Microgels Using Zero Average Contrast

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Abstract

We used a cross-linked ionic poly(N-isopropylacrylamide)-*co*-poly(acrylic acid) (PNIPAm-*co*-PAA) microgel as a model system to study the behaviour of charged soft colloids at ultrahigh packing fraction ($\phi_{eff}>>\phi_{cp}$). We performed SANS experiments on D11 in order to access the required spatial resolution and the very low q-values using zero average contrast experiments. Detailed contrast variation studies allowed us to determine the match point of hydrogenated and deuterated microgels. Measurements performed at ZAC contrast allowed obtaining crucial information both below and above close packing. The results showed that at ultrahigh packing fractions microgels do not decrease their size due to compression effects.

Results

We used two sets of hydrogenated (H_m) and deuterated (D_m) ionic microgels of poly(N-isopropylacrylamide)-*co*-poly(acrylic acid) (PNIPAm-*co*-PAA) with a cross-linking density of 5mol%. We firstly determined the match point for the two sets of H_m and D_m microgels by carrying out experiments at different ratios of H_2O/D_2O under dilute concentration at 15ºC. The scattering curves for a representative sample, H_m and D_m ionic microgel with 5mol% cross-linking density, under different contrast conditions, are shown in Figure 1A and 1B, respectively. The corresponding extrapolated values of the scattering intensity to $q=0nm^{-1}$ are shown in Figure 1C, which allows to determine the match point.

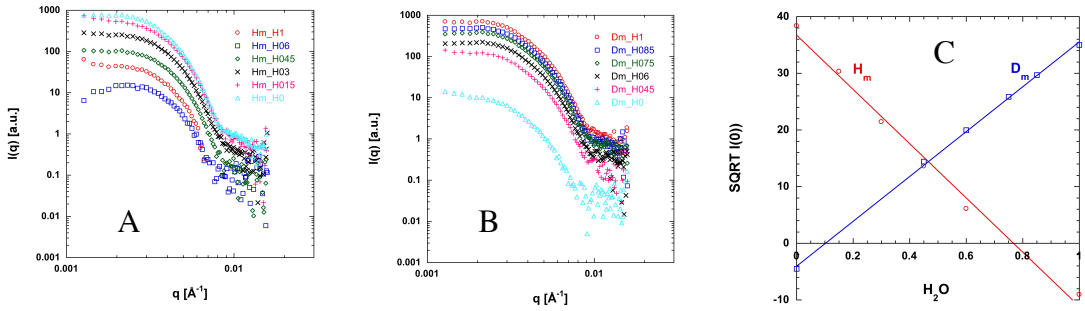

Figure 1. Obtained scattering curves of A) Hm and B) Dm microgels with 5mol% cross-linking density in various H_2O/D_2O mixtures. C) Square root of the forward scattering as a function of the H_2O content in the solvent.

In the next step, we measured equal number density mixtures of both hydrogenated and deuterated microgels at different volume fractions under zero average contrast. This allowed us to resolve the concentration dependent form factor at volume fractions above close packing, Φ_{CP}. The concentration normalized scattering data is shown in Figure 2a. The absence of the structure peak reveals that we performed the measurements fulfilling the zero average contrast conditions. The scattering curves and the corresponding fits using the fuzzy sphere model are shown in Figure 2b.

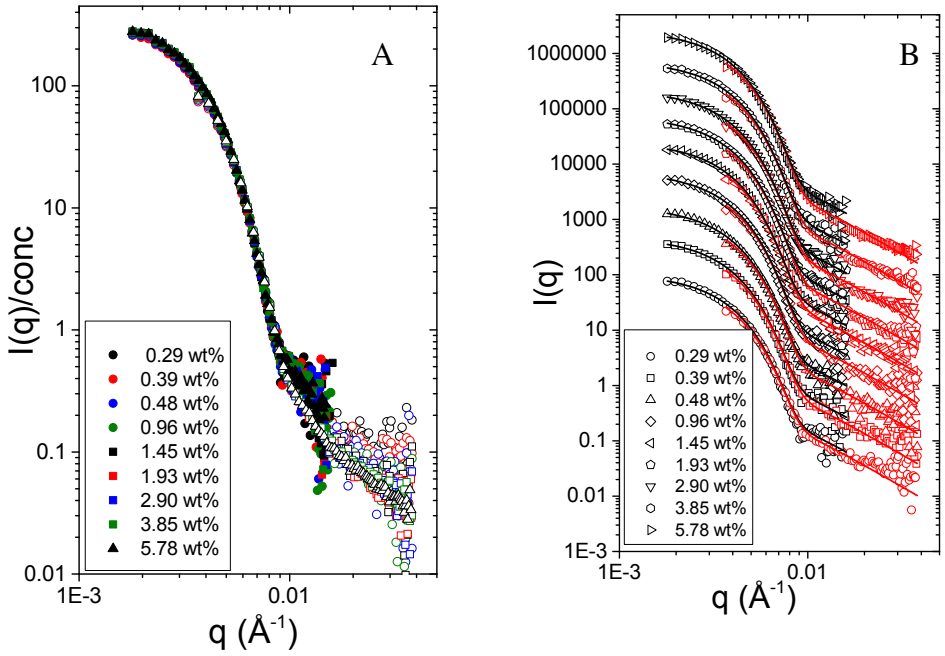

Figure 2. A) Normalized scattering curves of hydrogenated and deuterated microgel mixtures under zero average contrast. B) Scattering curves including, in solid lines, the fit using the fuzzy sphere model.

The fits to the scattering curves shown in Figure 2b allowed determining the particle size as a function of concentration. The SANS radius normalized by the SANS radius at the lowest measured concentration is plotted in Figure 3. For comparison the center-to-center distance, a_S, which is determined from the structure peak position using Static Light Scattering (SLS) and SAXS, is shown in the same figure.

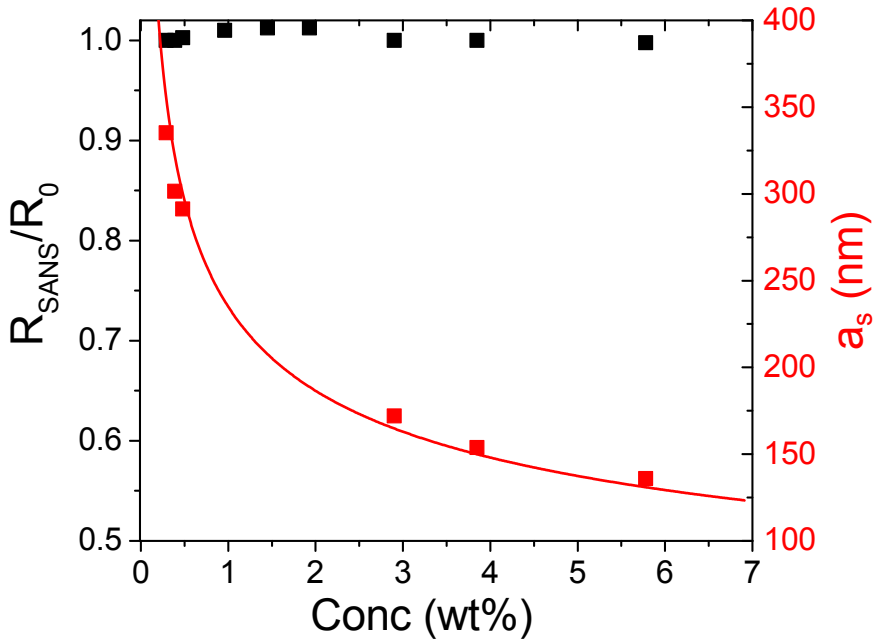

Figure 3. SANS radius normalized with the radius of the lowest measured concentration (black filled squares). For comparison the center-to-center distance, a_S, obtained by SLS and SAXS is plotted in the figure (red filled squares). The red solid line corresponds to the theoretical number density (n) dependence of the center-to-center distance $a_S \propto n^{-1/3}$ for colloidal systems interacting via a soft long range potential.

The evolution of the normalized SANS radii as a function of concentration show no significant decrease, which reveals that particles do not change their size in the studied concentration range. We however need further studies at lower and higher concentrations than those measured and also measurements with lower crosslink densities in order to conclude on the de-swelling behaviour of ionic microgel systems.