ESRF	**Experiment title:** Criticallity and phase behavior of PEGylated steric colloids	**Experiment number**: SC-4084
Beamline:	**Date of experiment**: from: 15.03.2015 to: 17.03.2015	**Date of report**:
Shifts:	**Local contact(s)**: Gudrun Lotze	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Malin Zackrisson Oskolkova, Division of Physical Chemistry, Lund University.

*Johan Bergenholtz Department of Chemistry and Molecular Biology, University of Gothen urg.

*Jeanette Ulama, Department of Chemistry and Molecular Biology, University of Gothenburg.

Report:

PEGylated spherical colloidal particles under marginal solvent conditions have been investigated using USAXS. The low q-range allowed for access to the comressibility regime of I(0) from which critical fluctuations and in particular the critical point can be allocated and the Widom line. This is regarded as a thermodynamic anomaly manifested as a maximum in thermodynamic response functions, such as the specific heat capacity (6). We have explored the possibility of core-softened potentials, where the potentials exhibit a repulsive core with a softening region i.e. a shoulder or a ramp, There results points to possible multiple critical points, however, the difficulty with measuring at shell-contrast due to the added salt calls for additional data collected at a different contrast far away from shell scattering.

Background

We set out to locate the critical point, by tracking and also determining the Widom line. It is found in the supercritical region of the phase diagram, due to the proximity of the critical point and the maximum is predicted to be prominent also far away from the critical point. Here, we wanted to determine the Widom line from the isothermal compressibility, which is determined from the intercept of the structure factor at, strictly speaking, zero angles.

Results

The particles, which have a polydispersity of 10–15% depending on batch synthesis, are composed of polystyrene cores with an in-situ PEG grafted layer. The PEG layer is usually providing a steric repulsive interaction. This can be manipulated by adding certain types of salts and by increasing the temperature. This is done in these experiments by adding Na_2CO_3 at a constant concentration of 0.4 M. The preliminary USAXS data of the normalized intensity collected at ID02 is shown in figure 1. Data is normalized with concentration in terms of volume fraction. Firstly, we observe a rather unusual contrast effect when salt is present believed to be due to close-to-shell scattering. This means that the polystyrene cores are

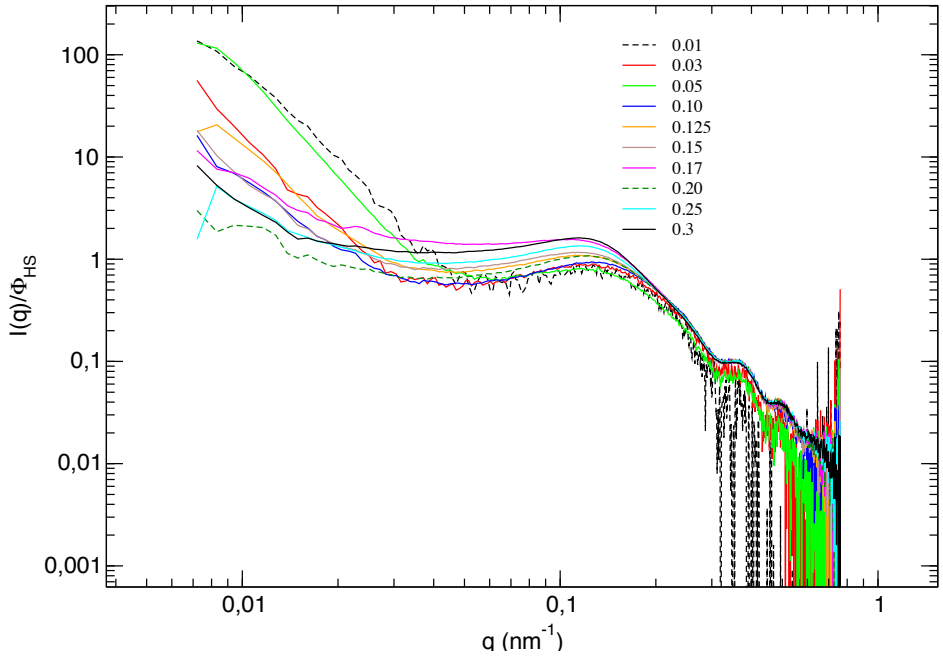
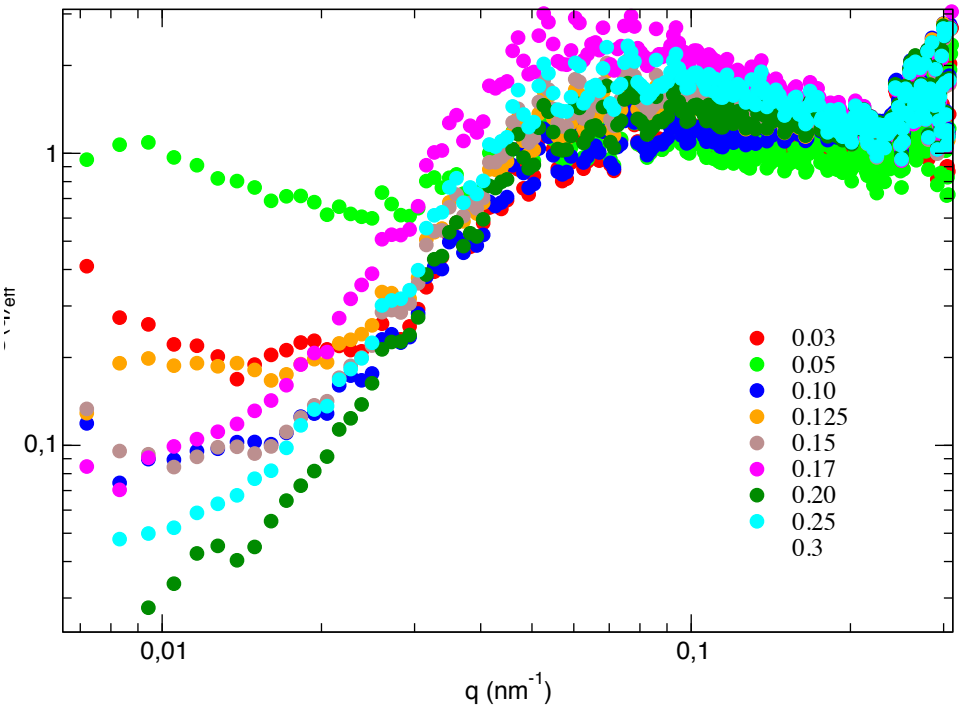


Figure 1. Scattered intensity vs. q (nm^{-1}) normalized with particle concentration for the PEG grafted polystyrene colloidal particlesd dispersed in 0.4 M Na_2CO_3 (aq) collected at the ID02 USAXS beamline. The legend show the particle volume fraction.

close to being index matched out. We suspect the strong upturn in the scattered intensity at the lowest conentrations comes from the close-to-shell scattering manifested as a very pronounced upturn at low q – values. This is apparent for the two lowest concentrations (0,01 and 0,03). This is a bit unfortunate since we are looking for increased low-q scattering as a sign of closeness to a critial point.

As we further increase the concentration we expect the low q intensity to increase if we are coming close to a critical point. In figure 2 we show effective structure factors as a function of q (nm^{-1}). There appears to be an upturn around 0,05 and also around 0,12 which is what we also observe in light scattering data (not shown).



Further conclusions will be drawn by modelling of data. There were experimental difficulites due to issues from cleaning since radiation damaged particles were sticking to walls and serious troubles with temperature control.

Figure 2.Effective structure factors, $S(q)_{eff}$, for the PEG grafted polystyrene colloidal particlesd dispersed in 0.4 M Na_2CO_3 (aq) collected at the ID02 USAXS beamline. The legend show the particle volume fraction.