



INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

Salting-out of Colloidal Latex Particles Grafted with Poly(ethylene glycol)

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ABSTRACT

Colloidal particles dispersed in a medium are important both in nature and in industry. The stability of colloidal particles is determined by the interactions between them and can be improved by steric stabilization. There is no conclusive understanding of how these sterically stabilized particles become unstable. In order to understand the loss of repulsion that leads to instability, model systems of well-defined dispersions are needed.

A semi-batch emulsion polymerization scheme has been used in this work in order to yield highly monodisperse, spherical core-shell particles in an aqueous medium. The cores of the particles are fluorinated, resulting in a refractive index close to that of water. By having the particles almost refractive index-matched, the core-core van der Waals attractions are minimized. This makes it possible to study the role of the grafted polymers.

In order to test the versatility of the synthesis scheme, crosslinked particles and particles with a polystyrene core, instead of the fluorinated core, have been synthesized. Moreover, syntheses with different lengths of the grafted polymer, yielding different thicknesses of the particle shell, have been performed. The stability of the colloids with respect to the addition of sodium carbonate has been tested. The results show that the particles with the shortest grafts are the most stable ones. For longer grafts, the stability limit, in terms of added salt, levels out. These experimental results have been fitted to a Flory-Huggins based model.

Both small-angle X-ray and neutron scattering (SAXS and SANS, respectively) measurements were performed on the particle dispersions employing two different kinds of salt in a range of concentrations. The SAXS measurements showed that the stability limit was independent of the particle concentration. This was explained by salt-induced, single-particle dewetting being the driving force for permanent aggregates to form. To investigate this hypothesis, the PEG layer was made more visible in the SANS measurements by changing the solvent to a H₂O:D₂O mixture. A decrease in the shell thickness was observed at salt concentrations close to where the particles start to aggregate, in support of the hypothesis. Also, at this point a peak at large scattering angles, corresponding roughly to the same length scale as the layer thickness, disappears in the SAXS measurements.

Moreover, dewetting of the PEG-layer was also indicated through structure determination, of the clusters formed in unstable dispersions, from SAXS measurements and computer calculations of the structure factor. The distance of closest approach of two particles in the clusters is smaller at higher salt concentrations, which could be explained by the grafted polymer layer contracting.

To further investigate the dewetting of the PEG-shell, interfacial tension (IFT) measurements were performed between aqueous dispersions with varying salt concentrations and toluene. A decrease of the IFT showed that the particles are surface active, even without salt. However, the IFT decreased more strongly in the presence of salt. A strengthening of the surface activity on adding salt supports the dewetting hypothesis.

Keywords: PEG, fluorinated colloids, monodisperse spheres, steric stability, emulsion polymerization, SAXS, crosslinking, salting-out, interfacial tension, SANS

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