Rheological studies on polymeric nanoparticle dispersions stabilized by a polyfructose-derivative surfactant

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The preparation of stable concentrated dispersions of latex particles is a very important subject due to technological interest in many applications. In this context, nonionic graft copolymer surfactants are commonly used because of their adsorption onto the particles forming strong steric barriers, highly insensitive to both temperature and electrolyte. We have studied a graft copolymer surfactant, consisting of an inulin (polyfructose) backbone on which several alkyl groups are randomly grafted [1]. The alkyl groups provide the anchor points for attachment at the solid/liquid interface, leaving the polyfructose loops in contact to the external aqueous solution. Previous results showed that particles covered by this surfactant possess very good stability at high electrolyte concentration [2, 3]. Colloidal dispersions stabilized by this inulin-derivative surfactant remain with no flocculation at high electrolyte (Na_2SO_4) concentration such as 1.5 mol.dm^{-3} [3] (Figure 1).

In the present work, a rheological behaviour study of polystyrene (PS) latex particles sterically stabilized with the polyfructose-derivative surfactant was carried out. The results of steady-state shear stress as a function of shear rate showed that could be used for determining the adsorbed layer thickness of the hydrophobically modified inulin polymeric surfactant. The surfactant layer thickness was determined by comparison of experimental data with the Dougherty-Krieger theoretical curve, which describes the relative viscosity as a function of the volume fraction assuming hard sphere systems [4]. The results proved that a graft copolymer layer was adsorbed onto the polystyrene particles reducing the maximum volume fraction from $\phi = 0.6$ assuming randomly packed hard spheres down to $\phi = 0.505$ (Figure 2). From these measurements, an adsorbed graft polymeric surfactant layer thickness of approximately 9.6 ± 2 nm was calculated. Moreover, viscoelastic measurements showed a change from mainly viscous to predominantly elastic response at low effective volume fraction, $\phi_{eff} = 0.24$. The latter indicates strong hydration of the polyfructose loops and tail, providing very strong steric repulsion, which indicates that soft interactions are present between the particles containing adsorbed surfactant.

The results of the layer thickness determination by rheology were consistent with those obtained in previous layer thickness determination studies carried out by means of Dinamic Light Scattering (DLS) [2] and Atomic Force Microscopy (AFM) [5]. Studies by DLS were carried out by post-adding the polymeric surfactant to a surfactant-free PS dispersion. The results showed an adsorbed layer thickness of approximately 10 nm. AFM measurements were carried out by means of a modified atomic force microscope apparatus [6]. The steric repulsions between two layers of the polymeric surfactant adsorbed onto a hydrophobic sphere and a plate were measured. The results showed that high steric repulsion was present even at high electrolyte concentration when approaching the two adsorbed layers. From these measurements, an adsorbed surfactant layer thickness of 9 nm approximately was obtained, confirming the rheological determinations.

References:

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Figures:

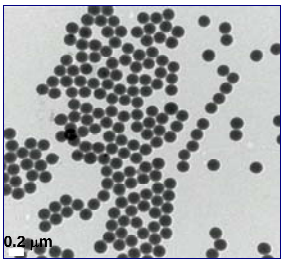

Figure 1. Polystyrene latex particles obtained by Transmision Electron Microscopy (TEM)

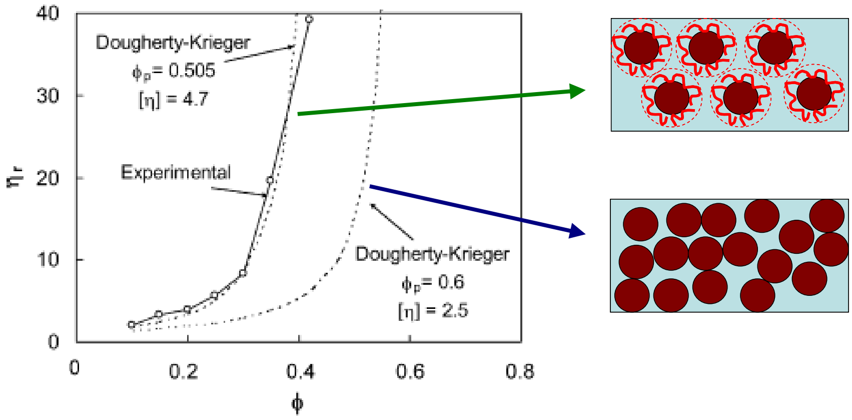

Figure 2. Relative viscosity as a function of particle volume fraction