Reduced Colloidal Repulsion in Fine Polymer-coated Colloidal Dispersions

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A large amount of polymer chains adsorbed onto colloidal particles typically act as a steric barrier to prevent colloidal flocculation and thus stabilize the dispersion. In contrast, the adsorption behavior, dynamic/structural features, and, in particular, particle interactions in dispersions consisting of *fine* colloidal particles with a normally low coverage of polymer chains remain little explored. Poly(ethylene oxide) (PEO) chains adsorbed onto polydisperse, fine silica colloidal particles (SAXS-determined radius ~7.4 nm; width of log-normal size distribution ~0.28; see Fig. 1) were considered as a standard system, where the impact of a small amount of polymer adsorption ($\leq 0.18\ \mathrm{mg/m^2}$) in controlling the interactions of the PEO-coated silica particles was systematically explored by analyzing the small-angle X-ray scattering (SAXS) data against three interaction potentials—the equivalent hard-sphere (EHS) potential, the Hayter-Penfold-Yukawa (HPY) potential, and the square-well (SW) potential. The present SAXS analysis was enforced by dynamic light scattering (DLS) characterizations for predetermining the adsorption behavior, when conventional separation protocols become ineffective for colloidal particles as small as presently studied. In addition, given a generally wide size distribution associated with small colloidal particles, the effect of polydispersity was consistently accounted for in fitting the form and structure factors extracted from the SAXS data. It is shown that, whereas the EHS potential is unable to resolve a definite trend as to the effect of a small amount of adsorbed PEO, the HPY and SW potentials consistently revealed an anomalous decrease of colloidal repulsions with increasing PEO coverage. The present findings were suggestive of a different possibility of fine-tuning the colloidal interactions of polymer-coated particles so as to regulate the self-assembly behavior in dense or condensed phases.

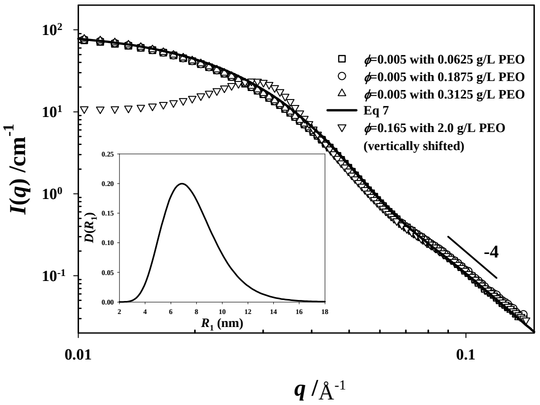

Fig. 1: SAXS data for sample solutions with silica volume fraction ϕ=0.005 at various PEO concentrations; line is fit to the core-shell model. The inset in shows the size distribution of silica particles determined from the form factor.

We have analysed the experimental structure factors for sample solutions with silica volume fraction ϕ=0.165 at various PEO concentrations using the three interaction potentials, i.e. the EHS, HPY, and SW potentials; the results are summaried below. In the EHS model, as expected, the effective volume fraction increases with increasing PEO coverage; therefore, it could be difficult to differentiate the sole impact of the shell material on the particle interaction. In the HPY model (see Fig. 2a), two important findings are: (1) the mean HPY radius increases with increasing PEO coverage, thus reflecting an increased geometric radius due to the PEO adsorption; (2) the mean potential strength and the decay constant both decrease with increasing PEO coverage (see Fig. 2b), suggestive of a less repulsive interparticle interaction in the effective range and in the strength. Finally, in the SW model, the retrieved geometric radius was found to decrease progressively with increasing PEO coverage, and, in particular, the depth of attractive potential increases accordingly, consistent with the trend suggested by the HPY analysis.

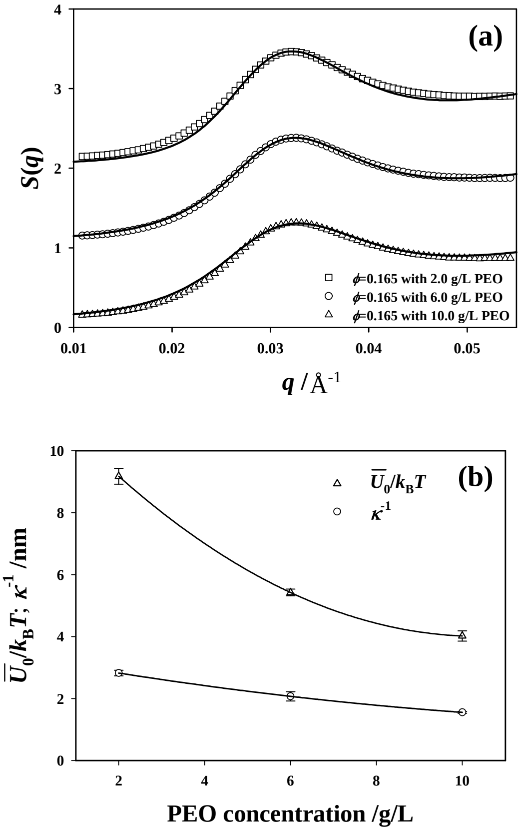

Fig. 2: (a) Experimental structure factors for sample solutions with silica volume fraction ϕ =0.165 at various PEO concentrations; lines are fits to the HPY potential. (b) The mean potential strength and the decay constant as functions of PEO concentration; lines are guides to the eye.