Structure of a Model Colloid-Polymer Mixture

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Introduction

Many industries today rely on mixtures of polymers and colloids to achieve desired material properties. Examples are paints, inks, and personal care products. Polymers are added to suspensions to stabilize the particles against aggregation, to induce aggregation or to alter the flow properties of the suspension. In many cases, polymers that are added do not adsorb to the particle surface and are thus free in solution. These free polymers can give rise to attractions between the particles due to excluded volume effects known as depletion attraction. The strength of the attraction is governed by the polymer concentration and the range by polymer size (molecular weight). Depending on the range and strength of the attraction, the suspension can gel or phase-separate. Hence, it is of utmost importance to first characterize the interactions between the colloidal particles in the presence of polymer before the suspensions are processed. The main focus of this work is to systematically characterize depletion interactions in a model colloid-polymer system as a function of polymer concentration and molecular weight by measuring the structure using ultra-small-angle x-ray scattering (USAXS). Quantitative comparisons of the structure[1] are then made with standard models in the literature[2] to see which model best describes the experimental system. These comparisons help us in identifying a model with which we will be able to predict the phase behavior, as well as macroscopic properties such as viscosity.

Materials and Method

The model colloid-polymer system consists of octadecyl silica particles suspended in toluene in the presence of polystyrene (PS). Particles were sized using transmission electron microscopy (TEM) and dynamic light scattering, yielding a size of 100 ± 5 nm. Polystyrene of three different molecular weights was used: 2.43×10^3 (radius of gyration $R_g = 1.29$ nm), 2.93×10^4 (5.74 nm) and 1.88×10^6 (69.77 nm) g/mol, respectively. Liquid cells specifically designed for USAXS, with a 1-mm x-ray path length and polyimide windows, were used to hold the suspensions. Scattering measurements over a scattering vector range from q = 0.0002 1/A° to 0.1 1/A° were taken from the suspensions at a fixed colloid volume fraction (ϕ) as a function of polymer concentration (polymer volume fraction, ϕ_p).

Results

Results from one set of measurements for the 2.93×10^4 g/mol PS are shown in Fig. 1. The intensities have been desmeared using the Lake program. Three curves are shown: (1) octadecyl silica in toluene with no added polymer and colloid volume fraction $\phi = 0.018$, (2) Octadecyl silica in toluene with $\phi = 0.29$ and (3) Octadecyl silica in toluene with added polymer - $\phi = 0.29$ and $\phi_p = 0.087$. Curve (1), known as the form factor, gives information about the particle size and is required to calculate the structure factor $S(q,\phi)$ for (2) and (3). $S(q,\phi)$ gives information about how the particles are spaced with respect to each other and hence is an indication of the interactions between the colloidal particles. The results of the S(q,f) calculations are shown in Fig. 2. Shown in the same figure are comparisons with a recently developed polymer reference interaction site model (PRISM)[3] to predict the structure of colloid-polymer mixtures. The data and the comparisons are shown only up to a q*(2R) of 8 because of the difficulties involved in the calculation of the structure factor. The peak in the structure factor occurs when there is a minimum

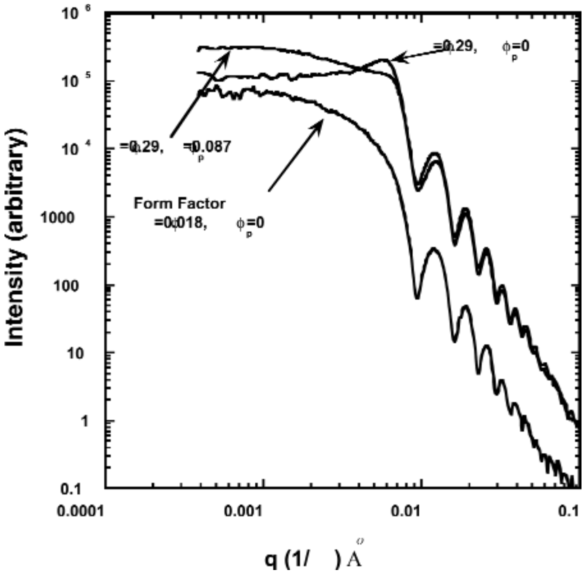

FIG. 1. Desmeared intensity as a function of wave vector for three different samples: ϕ is the colloid volume fraction and ϕ_p is the polymer volume fraction.

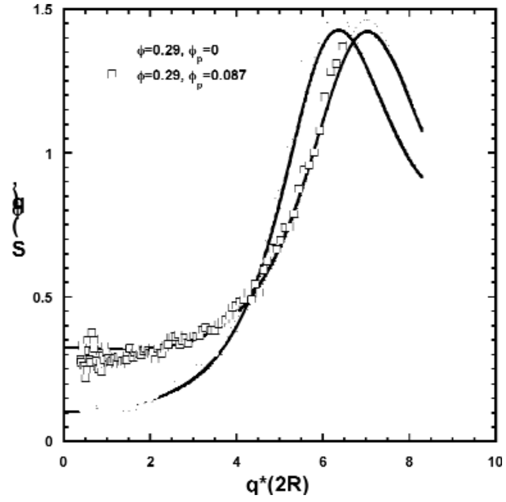

FIG. 2. Structure factor as a function of wave vector for two different samples at a fixed colloid volume fraction. The open symbols are USAXS data: $\phi = 0.29$, $\phi_p = 0$ (squares) and $\phi = 0.29$, $\phi_p = 0.087$ (circles). The solid curves are calculations using PRISM.

in the form factor (curve 1 in Fig. 1) and, hence, the structure factor data is very noisy around the first peak. We are currently working on newer methods of calculating S(q,ϕ) from the intensity data.

Discussion

The structure factor in the zero wave vector limit. S(0,ϕ), is known as the osmotic compressibility and is an indication of the strength of the attraction in the system. As can be seen from Fig. 2, S(0,ϕ) is higher when one adds polymer to the system, indicating attractions come into play. PRISM predicts the structure well right up to the first peak, where we run into difficulties in calculating S(q,ϕ). These results have helped us in confirming the fact that PRISM does much better than standard models in the literature in predicting the structure of colloid-polymer mixtures, and we are currently working on predicting the phase behavior of the experimental system using PRISM.

Acknowledgments

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