Experimental report

01/07/2016

Proposal: **9-12-395**

Council: 10/2014

Title: Probing evolution of interactions leading to clustering of charged nanoparticles dispersion.

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Sugam KUMAR**

Experimental team: Sugam KUMAR
Sumit MEHAN

Local contacts: Ralf SCHWEINS

Samples: SiO2 nanoparticles and polymers

Instrument	Requested days	Allocated days	From	To
D22	0	1	13/07/2015	14/07/2015
D11	2	0		

Abstract:

We have observed a re-entrant phase behavior in nanoparticle (silica) and polymer (PEG) system where nanoparticles (silica) undergo particle clustering and back to individual nanoparticles as a function of polymer (PEG) concentration. The phase behavior is believed to be governed by the interplay of different interactions (i) electrostatic repulsion between nanoparticles, (ii) polymer-induced attractive depletion between nanoparticles and (iii) repulsive polymer-polymer interaction present in the system. We propose to carry out SANS measurements to model these interactions and determining the possibility of equilibrium cluster phase under the influence of these short/long range opposing forces.

Experimental Report:

Title: Probing evolution of interactions leading to clustering of charged nanoparticles as induced by polymers

Abstract: A re-entrant phase behavior in nanoparticle (silica) and polymer (PEG) system where nanoparticles (silica) undergo particle clustering and back to individual nanoparticles as a function of polymer (PEG) concentration has been observed. The phase behavior is believed to be governed by the interplay of different interactions present in the system such as electrostatic repulsion between nanoparticles, polymer-induced attractive depletion between nanoparticles and repulsive polymer-polymer interaction. We carried out small-angle neutron scattering measurements to model these interactions and determining the possibility of equilibrium cluster phase under the influence of these short/long range opposing forces.

Introduction: The understanding of cluster phase charged colloids such as nanoparticles, proteins, polyelectrolytes etc have gained sufficient scientific interest due to its multitude applications ranging from molecular biology to food science [1-2]. It is generally believed that the cluster phases arise because of the competition between the short/long range attractive and repulsive forces at different length scales [3]. The charge stabilized silica nanoparticles in the matrix of polymer provides a model systems to investigate these interactions. The system shows a reentrant phase behavior where the charged stabilized nanoparticles (silica) undergo particle clustering and back to individual nanoparticles with increasing polymer [Polyethylene glycol (PEG)] concentration [4]. The phase behavior may be tuned by varying the degree of the different attractive and repulsive interactions present in the system and an equilibrium cluster phase may be achieved. Small-angle neutron scattering (SANS) have been used to investigate the role of different interactions during the re-entrant phase behavior and possibility of equilibrium cluster phase with varying solution conditions.

Experiments: Charge stabilized colloidal suspensions of 30 wt% silica nanoparticles (size = 16.0 nm) in water and PEG (radius of gyration = 2.8 nm, M.W. = 6 K) were obtained from Sigma-Aldrich. Samples were prepared by dissolving known amount of silica nanoparticles (2 wt%) and varying PEG concentration in a 15/85 H_2O/D_2O solvent for which polymer is contrast-matched. A small amount of salt (0.15 M NaCl) has been added in all the systems in order to reduce electrostatic repulsion so that under depletion attraction particle clustering can be observed. SANS experiments were performed at the D22 facility, Institu Laue Langevin, France. The mean wavelength of neutron beam used was 6 Å and the data were collected in the wave vector transfer (Q) range of 0.003 to 0.3 $Å^{-1}$.

Results and Discussion: The phase behavior of silica nanoparticles in the polymer solution as shown in Fig. 1 has been obtained by measuring the transmission of light through the system. The figure shows first a decrease in transmission from 1 to 0 and then increase in it from 0 to 1 with increasing polymer concentration. This variation of transmission reflects the evolution of the structure in the system, where the greater scattering of the light from larger structures decreases the transmission. This suggests that the charge stabilized nanoparticles forms large particle clusters and comes back to individual nanoparticles as a function of polymer concentration. Such phase behavior can be explained in terms of interplay of opposing attractive (polymer induced depletion) and repulsive (nanoparticle-nanoparticle electrostatic and polymer-polymer interaction) forces present in the system. At low polymer concentrations, total interaction potential is dominated by electrostatic repulsion while as the polymer concentration increases, the polymer induced depletion attraction between nanoparticles leads to the nanoparticle aggregation. Further increase in polymer concentration enhances the polymer-polymer repulsion which is believed to be responsible for the reentrance to one-phase behavior. The phase behavior depicts two narrow regions [I and II] of polymer concentration where the transmission is in between 0 and 1 indicating the presence of structures of intermediate sizes. SANS measurements were performed to model these cluster phase and the responsible interactions.

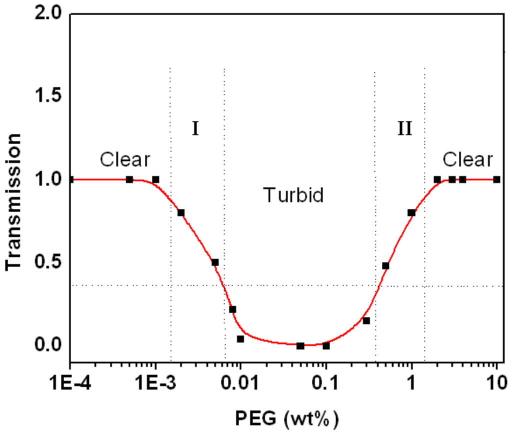

FIG. 1. Phase behavior of 2 wt% silica nanoparticles, with varying PEG in presence of 0.15 M NaCl.

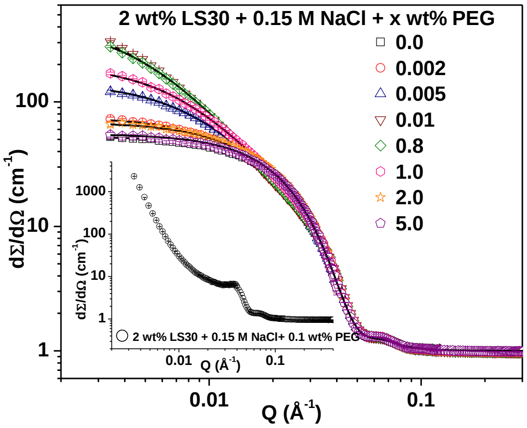

FIG. 2. SANS data of 1 wt% silica nanoparticles with varying concentration of PEG in the two regions shown in phase behavior. Inset shows SANS data for a two phase system (2 wt% LS30 + 0.1 wt% PEG).

Fig. 2 shows the SANS data of 2 wt% silica nanoparticles with varying polymer concentration in regions I and II of phase behavior. The SANS data of 2 wt% LS30 + 0.1 wt% PEG where system is in two-phase (Fig. 1) is depicted in the Inset. The inset data highlights typical features of permanent clusters e.g. large linear scattering in the low Q combined with a Bragg peak at intermediate Q values. The large low Q intensity arises from the overall cluster size whereas static interaction between the particles tightly bound within the clusters contributes in the appearance of Bragg peak. On the contrary, the SANS data in the Fig. 3 do not show either of these features but show a systematic scattering increase in the low Q region up to a critical polymer concentration (0.01 wt%). On further addition of polymer, fall of scattering intensity have been observed. Finally data of 5 wt% polymer almost matches to that of pure nanoparticles reflecting the re-entrant behavior (Fig. 1). The above observations suggest that there is a systematic evolution and devolution of attraction leading to a dynamic clusters phase. Unlike permanent cluster phase where the particles are tightly bound together, in dynamic clusters, particles move together under the influence of an attractive interaction but may escape from the clusters after a certain time [5].The evolution of attraction under which these dynamic clusters are formed can be treated based on colloidal fluid model where particles are considered to be trapped in an attractive potential well. The preliminary analysis of the data using square well attractive potential shows that the volume fraction of the particles increases as the system approaches to two-phase formation indicating the formation of the dynamic clusters under the depletion attraction [6]. The depth of the well increases in the region I indicating the increase in the depletion attraction with increasing polymer concentration. Further addition of polymer in region II decreases the strength due to enhanced polymer-polymer repulsion.

TABLE 1. Fitted parameters of 1 wt% nanoparticle system with varying polymer concentration.

Polymer conc. (wt%)	Depth of the Well (ε)	Volume Fraction of the particles
Prior to two-phase formation (region I)		
0.0	-	0.01
0.002	2.4	0.03
0.005	3.4	0.035
0.01	4.0	0.045
After two-phase formation (region II)		
0.8	4.0	0.05
1.0	3.6	0.04
2.0	2.3	0.024
5.0	-	0.01

References:

1. Z. Lu and Y. Yin, Chem. Soc. Rev. 41, 6874-6887 (2012)

2. R. Mezzenga, P. Schurtenberger, A. Burbidge, and M. Michel, Nature Materials 4, 729 (2005).

3. Y. Liu, E. Fratini, P. Baglioni, W.-R. Chen and S.-H. Chen, Phys. Rev. Lett. 95, 118102 (2005).

4. Sugam Kumar, D. Ray, V. K. Aswal and J. Kohlbrecher Phys. Rev. E 90, 042316 (1-10) (2014).

5. L. Porcar, P. Falus, W.-R. Chen, A. Faraone, E. Fratini, K. Hong, P. Baglioni and Y. Liu, *J. Phys. Chem. Lett.* **1**, 126–129 (2010).

6. Sugam Kumar, S. Mehan, V. K. Aswal and R. Schwein, AIP Conf. Proc. 1731, 040013 (2016)