Micelle-induced depletion interaction and resultant structure in charged colloidal nanoparticle system

D. Ray,¹ V. K. Aswal,^{1,a)} and J. Kohlbrecher²

¹*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*

²*Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 PSI Villigen, Switzerland*

(Received 7 February 2015; accepted 17 April 2015; published online 29 April 2015)

The evolution of the interaction and the resultant structure in the mixed system of anionic silica nanoparticles (Ludox LS30) and non-ionic surfactant decaethylene glycol monododecylether (C12E10), undergoing phase separation, have been studied using small-angle neutron scattering and dynamic light scattering. The measurements have been carried out for a fixed concentration of nanoparticle (1 wt. %) with varying concentration of surfactant (0 to 1 wt. %), in the absence and presence of an electrolyte. It is found that the micelles of non-ionic surfactant adsorb on the nanoparticle in the absence of electrolyte (form stable system), whereas these micelles become non-adsorbing in the presence of electrolyte (show phase separation). The phase separation arises because of C12E10 micelles, causing depletion interaction between nanoparticles and leading to their aggregation. The interaction is modeled by double Yukawa potential accounting for attractive depletion as well as repulsive electrostatic forces. Both the interactions (attraction and repulsion) are found to be of long-range. The nanoparticle aggregation (phase separation) is governed by the increase in the magnitude and the range of the depletion attraction with the increase in the surfactant concentration. The nanoparticle aggregates formed are quite large in size (order of micron) and are characterized by the surface fractal having simple cubic packing of nanoparticles within the aggregates. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919359>]

I. INTRODUCTION

Nanoparticle-surfactant complexes are an important class of functional conjugates having great practical relevance in the fields of colloidal stability, detergency, oil recovery, corrosion inhibition, composite nanostructures, etc.^{1–5} Most of these applications require the understanding of the interactions of nanoparticles with surfactants and strongly depends on their individual characteristics.^{6–14} Much research has therefore been devoted for the better realization of these understandings, required for numerous purposes, for example (i) to govern the interfacial processes, such as flocculation/dispersion and wetting,¹⁵ (ii) insight into the binding characteristics (anchoring strength, curvature of the adsorbing surface, etc.), their dynamics and functionality,^{16,17} (iii) design of the tailor-made conjugates,¹⁸ etc. Surfactants self-assemble to form micelles in aqueous solution. However, in the presence of nanoparticles, they can remain in the solvent as free micelles, form aggregates/flocs, adsorb on nanoparticles, or show some other phenomena, where the resultant structure depends on how these micelles and nanoparticles interact with each other.^{14,19–22}

A number of studies have been performed to visualize the interaction of charged nanoparticles (e.g., anionic) with anionic, cationic, or non-ionic surfactants. It has been observed that similarly charged nanoparticles and surfactant micelles do not interact directly, and both remain freely in the mixed system. On the other hand, a strong interaction between nanoparticles, mediated by the micelles, leads to the

nanoparticle aggregation when the nanoparticle and the surfactant present are oppositely charged. In the case of non-ionic surfactants, it is found that they adsorb on the surface of the nanoparticle either through bilayer formation or micellar decoration. The strength of the interaction between the surfactant head groups and nanoparticle surface in this case is considerably weaker than the coulomb interaction between an oppositely charged surfactant-surface pair. However, the presence of non-adsorbing surfactants in a colloidal dispersion affects the colloidal stability. When nanoparticles (larger) dispersed in a solution of non-adsorbing surfactant micelles (smaller), and the gap between two nanoparticles becomes smaller than the diameter of the micelles, depletion force arises between these two nanoparticles. At a small gap, the micelles are expelled from the gap, and an attraction between the two nanoparticles is generated due to the increase in the entropy, resulting in the decrease in the free energy.^{23–25} Experimentally as well as computationally, several groups have demonstrated that even at relatively lower surfactant (or polymer) concentrations, the depletion attraction can be significant enough to introduce phase transitions in an otherwise stable colloidal dispersion.^{26–36}

In this work, the depletion-induced attraction of nanoparticles, depending on the concentration of surfactant in the nanoparticle-surfactant mixed system, has been studied. It has been achieved in a system of anionic silica nanoparticles (Ludox LS30) and non-ionic surfactant decaethylene glycol monododecylether (C12E10) in aqueous electrolyte (NaCl) solution. It has been earlier observed that the silica nanoparticles in the presence of C12E10 give rise to a micelle decorated core-shell structure of nanoparticles through the formation of hydrogen bonds

^{a)}Author to whom correspondence should be addressed. Electronic mail: vkaswal@barc.gov.in.

between the ether head groups of the C12E10 molecule and the surface silanol (Si-OH) groups of silica. On the other hand, in the presence of electrolyte, the adsorption of surfactant micelles on the nanoparticle completely gets suppressed due to the weakening of the hydrogen bonds, leading to the depletion-induced aggregation of nanoparticles.³⁷ Herein, a systematic study has been carried out to observe the role of the surfactant micelles on the evolution of the interaction and the resultant structure with varying surfactant concentration. These systems have been characterized using small-angle neutron scattering (SANS) as this technique provides the information on the structure as well as the interaction, and due to its unique advantage of contrast variation to examine such multi-component systems. The different components (nanoparticle or surfactant) can be made selectively contrast-matched (invisible) by taking a mixture of hydrogenous (H₂O) and deuterated (D₂O) solvent to understand the role of individual components in the mixed system. SANS data are modeled using a combination of two Yukawa potentials accounting for both repulsive electrostatic and attractive depletion interactions between the nanoparticles. The choice of the Yukawa potential gives the range as well as the strength of the individual parts in the total potential.

II. EXPERIMENT

A. Materials

Electrostatically stabilized 30 wt. % colloidal suspensions of silica nanoparticles (Ludox LS30) and surfactant C12E10 were purchased from Sigma Aldrich. Distilled deionized water from Milipore MilliQ unit and 99.9% pure D₂O were used for the sample preparation. Samples were prepared by dissolving a weighted amount of silica nanoparticle (1 wt. %) and surfactant (0 to 1 wt. %) in a mixed D₂O/H₂O solvent in presence of an electrolyte (NaCl). The solvents H₂O and D₂O provide different contrasts for the particles because of very different neutron scattering lengths for H and D.

B. Methods

Small-angle neutron scattering experiments were performed at the SANS-I instrument at the Swiss spallation neutron source, SINQ, Paul Scherrer Institut, Switzerland.³⁸ The mean wavelength (λ) of the incident neutron beam was 6 Å with the wavelength resolution of approximately 10%. The scattered neutrons were detected by using a 96 × 96 cm² detector. The experiments were performed at two sample-to-detector distances of 2 and 8 m, respectively, to cover the data in the scattering vector [$Q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle] range of 0.006–0.25 Å⁻¹. All the measurements were carried out for a fixed concentration (1 wt. %) of silica nanoparticles and varying the concentration of surfactant in the range of 0 to 1 wt. %. Freshly prepared samples were held in quartz cells having thicknesses of 2 mm, and temperature was kept constant at 30 °C during the measurements. The data were corrected and normalized at absolute scale using a standard procedure. All the nanoparticle-surfactant systems were studied with the three contrast conditions: (i) no component is contrast-matched, (ii) silica nanoparticles are contrast-matched, and (iii) surfactants are

contrast-matched. The fact that the scattering length densities of H₂O and D₂O are very different from each other, and the contrast-match point is obtained by mixing them in a ratio where scattering length density of H₂O/D₂O mixed solvent match with the particular component to be contrast-matched. The contrast-match point depends on the chemical composition of the particles. The contrast-match point of silica nanoparticles is around 62 vol. % of D₂O in the D₂O/H₂O mixed solvent, while in the case of C12E10 micelles the value of contrast-match point is around 13 vol. % D₂O.

C. Small-angle neutron scattering analysis

In SANS, one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of wave vector transfer Q ($= 4\pi \sin(\theta/2)/\lambda$, where λ is the wavelength of the incident neutrons and θ is the scattering angle). For a system of monodisperse particles in a medium, $d\Sigma/d\Omega$ can be expressed as

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = nV^2(\rho_p - \rho_s)^2 P(Q)S(Q) + B, \quad (1)$$

where n denotes the number density of particles, ρ_p and ρ_s are, respectively; the scattering length densities of particle and solvent, and V is the volume of the particle.^{39–41} $P(Q)$ is the intraparticle structure factor and $S(Q)$ is the interparticle structure factor. B is a constant term representing incoherent background, which is mainly due to the hydrogen present in the sample.

Intraparticle structure factor $P(Q)$ is decided by the shape and the size of the particle and is the square of single-particle form factor $F(Q)$ as determined by

$$P(Q) = \langle |F(Q)|^2 \rangle. \quad (2)$$

For a spherical particle of radius R , $F(Q)$ is given by^{42,43}

$$F(Q) = 3 \left[\frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right]. \quad (3)$$

$S(Q)$ describes the interaction between the particles present in the system, and it is the Fourier transform of the pair correlation function for the mass centers of the particles. For dilute systems, $S(Q) \sim 1$. In the case of an interacting isotropic system, $S(Q)$ can be written as

$$S(Q) = 1 + 4\pi n \int [g(r) - 1] \frac{\sin Qr}{Qr} r^2 dr, \quad (4)$$

where $g(r)$ is the radial distribution function. It is the probability of finding the particle at a distance r from a reference particle centered at the origin. The $g(r)$ is governed by the form of the potential $V(r)$. The interactions in nanoparticle-surfactant mixed system may be attractive or repulsive or combination of both and has been calculated using the double Yukawa potential under mean spherical approximation (MSA) closure relation.^{44,45}

The double Yukawa potential (V_{2Y}), having four dimensionless parameters (K_1 , K_2 , Z_1 , and Z_2), is expressed by

$$\frac{V(r)}{k_B T} = \infty \quad \text{for } 0 < r \leq \sigma$$

$$= \frac{V_{2Y}}{k_B T} \quad \text{for } r > \sigma, \quad (5)$$

where k_B is Boltzmann constant, T is temperature, σ is the hard sphere diameter of the nanoparticle, and

$$\frac{V_{2Y}(r)}{k_B T} = -K_1 \frac{\exp\left[-Z_1\left(\frac{r}{\sigma} - 1\right)\right]}{\frac{r}{\sigma}} + K_2 \frac{\exp\left[-Z_2\left(\frac{r}{\sigma} - 1\right)\right]}{\frac{r}{\sigma}}. \quad (6)$$

In the case of interaction leading to the adsorption or decoration of micelles on the nanoparticles, the scattering cross-section comprises of four terms: two terms correspond to the scattering from nanoparticles and micelles, the third term is a cross-term between the adsorbed micelles and the nanoparticles, and the last term represents the cross-term between different adsorbed micelles on the nanoparticle surface. The contributions from the nanoparticle and the interference term between the nanoparticle and micelles cancel out when the nanoparticles are contrast-matched to the solvent. The scattering from the remaining two terms (micelles and the micelle–micelle interference) can be simplified as

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = n_m V_m^2 (\rho_m - \rho_s)^2 P_m(Q) S_{mm}(Q) + B, \quad (7)$$

where $P_m(Q)$ is the intraparticle structure factor of the micelles.^{46,47} $S_{mm}(Q)$ is the interparticle structure factor and is numerically calculated as

$$S_{mm}(Q) = 1 + \frac{1}{N} \sum_{i=1}^N \sum_{j>i}^N \frac{\sin\{Q(r_i - r_j)\}}{Q(r_i - r_j)}, \quad (8)$$

where $(r_i - r_j)$ is the distance between the centers of the two micelles adsorbed on the same nanoparticle, and N is the number of micelles adsorbed on the nanoparticle surface.^{47,48}

In the case particles are undergoing aggregation, which is usually described by the fractal structure, the scattering from such structures is given by

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = n_a V_p^2 (\rho_p - \rho_s)^2 P_b(Q) S_f(Q) + B, \quad (9)$$

where n_a and V_p are the number density and volume of an individual scatterer in the aggregates.⁴⁹ $P_b(Q)$ is the intraparticle structure factor of the building block in aggregated structures. The structure factor for mass fractal structure $S_f(Q)$ can be expressed as

$$S_{mf}(Q) = 1 + \frac{1}{(Qr_0)^{D_m}} \frac{D_m \times \Gamma(D_m - 1)}{\left[1 + \frac{1}{(Q\xi)^2}\right]^{\frac{D_m-1}{2}}} \times \sin\{(D_m - 1) \times \tan^{-1}(Q\xi)\}, \quad (10)$$

where D_m is the mass fractal dimension, ξ is the overall size of fractal aggregate (the maximum length up to which the fractal microstructure exists), and r_0 is the characteristic dimension of individual particles. Γ represents a gamma function. However, for $Q \gg 1/\xi$, $S_{mf}(Q)$ simplifies to $S_{mf}(Q) \sim Q^{-D_m}$, where $1 < D_m < 3$.⁵⁰

For surface fractal, $S_{sf}(Q)$ is given by

$$S_{sf}(Q) = Q^{-1} \Gamma(5 - D_s) \times \xi^{5-D_s} [1 + (Q\xi)^2]^{\frac{D_s-5}{2}} \times \sin[(D_s - 1) \tan^{-1}(Q\xi)], \quad (11)$$

where D_s is the surface fractal dimension. However, for $Q \gg 1/\xi$, $S_{sf}(Q)$ simplifies to $S_{sf}(Q) \sim Q^{-(6-D_s)}$, where $2 < D_s < 3$.⁵¹

The polydispersity in the size distribution of the particles is incorporated using the following integration⁵² in Eq. (1) as:

$$\frac{d\Sigma}{d\Omega}(Q) = \int \frac{d\Sigma}{d\Omega}(Q, R) f(R) dR + B, \quad (12)$$

where $f(R)$ is the particle size distribution and usually accounted by a log-normal distribution as given by

$$f(R) = \frac{1}{\sqrt{2\pi}R\sigma} \exp\left[-\frac{1}{2\sigma^2} \left(\ln \frac{R}{R_{med}}\right)^2\right], \quad (13)$$

where R_{med} is the median value and σ is the standard deviation (polydispersity) of the distribution. The mean radius (R_m) is given by $R_m = R_{med} \exp(\sigma^2/2)$. For simplification, the integration in Eq. (12) is carried out over $P(Q)$ whereas $S(Q)$ is calculated for the mean size of the particles.

The data have been analyzed by comparing the scattering from different models to the experimental data. Throughout the data analysis, the corrections were made for instrumental smearing, where the calculated scattering profiles smeared by the appropriate resolution function to compare with the measured data. The fitted parameters in the analysis were optimized using nonlinear least-square fitting program to the model scattering.⁵³

III. RESULTS AND DISCUSSION

The SANS data for the nanoparticle (LS30)-surfactant (C12E10) mixed systems prepared in D₂O are expected to have the contributions from both the components. To know the role of the individual components in their mixed system, SANS measurements were performed under different contrast conditions. Figure 1 shows the SANS data of LS30-C12E10 (1 wt. % each) mixed system without and with the electrolyte (0.1 M NaCl) in two different contrast conditions, where (a) C12E10 surfactant are contrast-matched (13% D₂O) and (b) LS30 silica nanoparticles are contrast-matched (63% D₂O). It is clearly seen that for both the contrast conditions the scattering profiles of the mixed system are very different without and with NaCl. In the case when the surfactant is contrast-matched, the data of mixed nanoparticle-surfactant system in the absence of electrolyte exactly overlaps with that of the pure nanoparticle system (without C12E10) as shown in Figure 1(a). This is a clear

FIG. 1. SANS data of silica nanoparticle (LS30)-nonionic surfactant (C12E10) system without and with electrolyte (NaCl) for (a) C12E10 surfactant micelles are contrast-matched (13% D₂O) and (b) LS30 silica nanoparticles are contrast-matched (63% D₂O).

confirmation that there are no changes in nanoparticles (structure and/or interaction) with the surfactant in absence of electrolyte. The scattering is governed by that from the individual nanoparticles. The data show typical features of the form factor scattering as the interparticle structure $S(Q)$ contribution can be neglected for 1 wt. % (0.4 vol. %) solution of LS30 nanoparticles. The analysis using Eqs. (12) and (13) gives the mean radius of silica nanoparticles 83 Å with a polydispersity of 0.17. There are dramatic changes in the scattering intensity in the presence of electrolyte, where the scattering increases sharply in the low- Q region of the data ($Q < 0.02 \text{ Å}^{-1}$) followed by a Bragg peak around $Q = 0.035 \text{ Å}^{-1}$. This kind of behavior can be expected when the nanoparticles (surfactant is contrast-matched) have undergone aggregation. The low- Q scattering represents the scattering from these fractal aggregates, and the Bragg peak arises due to the ordering of nanoparticles within the aggregate. The aggregation of nanoparticles is also supported by the fact that the system shows turbidity.

The reason behind the different phase behavior of nanoparticle (LS30)-surfactant (C12E10) system without and with the electrolyte is examined by contrast-matching the silica nanoparticles and the SANS data are shown in Figure

FIG. 2. SANS data of silica nanoparticle (LS30)-nonionic surfactant (C12E10) system with varying surfactant concentration at different electrolyte (NaCl) concentrations (a) without electrolyte, (b) 0.05 M, and (c) 0.1 M. The surfactant is contrast-matched (13% D₂O). Insets show the enlarged view of the scattering in the low- Q region on nanoparticle aggregation.

1(b). In the absence of electrolyte, the data of nanoparticle-surfactant mixed system do not match with that of the surfactant alone. The enhancement of the scattering intensity in the low- Q region with significant humps of decreasing magnitude in the intermediate- Q region for nanoparticle-surfactant system can be interpreted based on the micellar decoration (core-shell structure) on nanoparticles. On the other hand, non-adsorption of micelles in the presence of electrolyte is

TABLE I. Fitted parameters of the interaction and structure of 1 wt. % silica nanoparticle (LS30) with varying concentration of nonionic surfactant (C12E10) in presence of electrolyte (NaCl). The parameters K_1 and Z_1 are fitted parameters of attractive interaction between non-aggregated nanoparticles, whereas D_s (surface fractal dimension) and f_{agg} (fraction) are fitted parameters of aggregated nanoparticles. The parameters of the repulsive interaction K_2 and Z_2 were kept fixed for each electrolyte concentration as determined from the pure silica nanoparticle systems.

(a) 0.05 M NaCl [$K_2 = 1.3$ and $Z_2 = 16.2$]				
Surfactant concentration C (wt. %)	K_1	Z_1	D_s	f_{agg}
(i) Set I (low surfactant concentration regime)				
0.01	11.7	2.5	...	...
(ii) Set II (intermediate surfactant concentration regime)				
0.05	16.8	2.3	2.9	0.41
0.1	18.5	2.3	2.9	0.73
(iii) Set III (high surfactant concentration regime)				
0.5	...	...	2.8	1.0
1.0	...	...	2.7	1.0
(b) 0.1 M NaCl [$K_2 = 0.9$ and $Z_2 = 19.2$]				
Surfactant concentration C (wt. %)	K_1	Z_1	D_s	f_{agg}
(i) Set I (low surfactant concentration regime)				
0.01	13.8	2.1	...	...
(ii) Set II (intermediate surfactant concentration regime)				
0.05	17.0	2.1	2.9	0.71
0.1	17.3	2.1	2.8	0.87
(iii) Set III (high surfactant concentration regime)				
0.5	...	...	2.7	1.0
1.0	...	...	2.7	1.0

expected to induce depletion interaction responsible for the aggregation of the nanoparticles. The data of non-adsorbed micelles in nanoparticle-surfactant system in such case should match with that of the pure surfactant. However, a fractal like build up of scattering intensity observed in the low- Q region could be from some of the micelles trapped in between the nanoparticles during their aggregation. The dimension of micelle is calculated using a model of a spherical core attached with Gaussian chains. The radius of the core and radius of gyration of the hydrophilic chain of C12E10 micelles are found to be 17.0 Å and 12.2 Å, respectively.

From Figure 1, it has been found that the non-adsorption of surfactant micelles on the nanoparticles in presence of electrolyte leads to the aggregation of nanoparticles. To examine the evolution of the interaction responsible for this aggregation, SANS data of 1 wt. % LS30 nanoparticles with varying C12E10 concentration in the absence and the presence of electrolyte (0.05 and 0.1 M NaCl) are shown in Figure 2. All these measurements have been carried out in 13% D₂O where surfactant is contrast matched and only the nanoparticles are visible. In the absence of electrolyte, there is no change observed in the SANS data [Figure 2(a)]. It is a clear indication of no change in the structure and/or interaction of the nanoparticles over a wide range of surfactant concentration in the absence of electrolyte. However, with the addition of electrolyte, the build-up of scattering in the low- Q region [Figures 2(b) and 2(c)] can be understood in terms of enhancement of the attractive interaction of nanoparticles

by the non-adsorption of micelles. The $S(Q)$ of the attractive interaction is known to diverge in the low- Q region with the increase in the magnitude of the potential. The attractive interaction increases with the surfactant concentration leading to the aggregation of nanoparticles. These aggregates are characterized by fractal structure followed by a Bragg peak arising from the ordering of nanoparticles within the aggregate.^{21,37} The interplay of attractive and repulsive interactions also strongly depends on the electrolyte concentration. The nanoparticle aggregation is caused at relatively lower concentration for higher electrolyte concentration [insets of Figures 2(b) and 2(c)].

The SANS data in the presence of electrolyte [Figures 2(b) and 2(c)] are fitted in three different sets of concentration of the surfactant. In the first set (low surfactant concentration), the net interaction of nanoparticle is undergoing change from repulsive to attractive. The nanoparticle aggregates coexist with the interacting non-aggregated nanoparticles with the increase in the surfactant concentration in set II. The third set (higher surfactant concentration) mostly consists of the nanoparticle aggregates. The evolution of interaction in sets I and II has been determined from the structure

FIG. 3. Variation of (a) structure factor and (b) corresponding total interaction potential responsible for the aggregation of 1 wt. % silica nanoparticles as a function of C12E10 surfactant concentration in presence of 0.05 M NaCl.

FIG. 4. The fitted contributions of intraparticle structure factor $P(Q)$ and interparticle structure factor $S(Q)$ for 1 wt. % LS30 + 0.05 M NaCl in three different regions of surfactant concentrations: (a) nanoparticles interacting with effective attractive interaction at the low surfactant concentrations, (b) the increase in attractive interaction leading a fraction of nanoparticles to form aggregates at intermediate surfactant concentrations, and (c) all the nanoparticles convert to aggregates at higher surfactant concentrations. $P(Q)$ for nanoparticles in each case is fitted with the polydispersed spheres. $S(Q)$ of the nanoparticles is calculated by double Yukawa potential. The nanoparticle aggregates are characterized by $S(Q)$ of surface fractal and the nanoparticles within aggregates are modeled by the $S(Q)$ of the hard sphere repulsion.

FIG. 5. SANS data of silica nanoparticle (LS30)-nonionic surfactant (C12E10) system with varying surfactant concentration at different electrolyte (NaCl) concentrations (a) without electrolyte, (b) 0.05 M, and (c) 0.1 M. The nanoparticles are contrast-matched (63% D_2O).

factor $S(Q)$ of double Yukawa potential accounting for the attractive interaction as well as the repulsive interaction in the system. The structure factor of these data as obtained through dividing the scattering data by the data of the nanoparticle without any surfactant. The double Yukawa potential comprises of four parameters K_1 , K_2 , Z_1 , and Z_2 , which give the strength (proportional to K) and range (proportional to $1/Z$) of the interaction potentials. K_1 and Z_1 are the parameters

FIG. 6. Schematic of structures formed in silica nanoparticle-C12E10 surfactant micelle system without and with electrolyte. Micelles are adsorbed on the nanoparticles in absence of electrolyte, whereas micelle non-adsorption leads to depletion-induced nanoparticle aggregation. Some micelles get trapped in between the nanoparticles in the aggregates.

of the attractive potential, whereas K_2 (related to effective charge) and Z_2 (related to ionic strength) are the parameters of the repulsive potential. To minimize the number of the fitting parameters, the parameters of the repulsive potential (K_2 and Z_2) have been estimated from the pure concentrated solution of the nanoparticles, since it is difficult to see the significant $S(Q)$ contribution from the repulsive interaction in 1 wt. % LS30 nanoparticle system. The SANS data are taken at higher concentrations of nanoparticle, and the parameters for 1 wt. % are obtained through the extrapolation of the fitted parameters of higher concentrations.⁵⁴ These repulsive interaction parameters are kept fixed in the analysis of the data, and only the parameters of the attractive interaction are obtained as fitted parameters. The parameters K_2 and Z_2 change with electrolyte concentration as determined by the ionic strength.⁵⁵ The fitted parameters are given in Table I. It is found that the attractive interaction is of long-range. Similar results were also obtained in other systems.^{36,54} The magnitude and the range of the attractive interaction increase with the increase in the surfactant concentration. The increase in the attractive interaction leads to the nanoparticle aggregation (set II). The evolution of the calculated interaction potential is given in Figure 3. The aggregates are formed when the attractive interaction at the nearest approach of the nanoparticles overcomes the average kinetic energy ($1.5 k_B T$) of the nanoparticles. The variation of the fraction of aggregated nanoparticles with the surfactant concentration is given in Table I. Set III represents to the SANS data where all the nanoparticles have been aggregated. The slope of these data in the low- Q region is found between 3 and 4, suggesting the surface fractal nature of these aggregates observed in the Q -range of measurements. The data are fitted by a power law behavior of surface fractal $\sim Q^{-(6-D_s)}$ (D_s is fractal dimension) in the low- Q region along with the structure factor by employing a hard-sphere potential in the

Percus-Yevick (PY) approximation for the Bragg peak. The contributions of different modeled structure factors leading to surfactant-induced nanoparticle aggregation are summarized in Figure 4. The aggregates have a surface fractal dimension of about 2.8. It is also found that the average distance between the nanoparticles within the aggregate ($d \sim 2\pi/Q_p \sim 180 \pm 10 \text{ \AA}$) is similar to the particle diameter, suggesting a simple-cubic (SC) packing of the nanoparticles within the aggregates. The similar kind of cubic packing of nanoparticle aggregates has also been reported.^{20,56-58}

The role of surfactant in tuning the nanoparticle-surfactant system without and with the electrolyte is examined by contrast matching the nanoparticle in their mixed

FIG. 7. Variation in the average hydrodynamic radius of silica nanoparticle (LS30)-nonionic surfactant (C12E10) system as a function of surfactant concentration without and in presence of electrolyte (NaCl). Inset shows the variation in corresponding polydispersity index on average hydrodynamic radius.

system. Figure 4 shows the SANS data of LS30–C12E10 system in the solvent of 63% D₂O (nanoparticles are contrast matched) without and in presence of the electrolyte. There is also corresponding differences in the physical appearances of these systems. The mixed system is transparent without any electrolyte whereas turbid in the presence of electrolyte. The data in Figure 5(a) represent a system where micelles have rearranged themselves when mixed with the nanoparticles. The data are fitted with a core-shell structure of micelles-decorated nanoparticles coexisting with the free micelles. The analysis shows that there are about 53 micelles adsorbed on each nanoparticle and the fraction of overall adsorbed micelle is 81%. In the presence of electrolyte, micelles become non-adsorbing on nanoparticles, which means their scattering without and with the nanoparticle should match. However, there is a clear deviation of the SANS data in low- Q region [Figures 5(b) and 4(c)]. The fact that the nanoparticles are contrast-matched and the individual micelle cannot give such a build-up of scattering in the low- Q region, while the only possibility to explain the data is that some of the micelles get trapped in the nanoparticle aggregates. The micelles can be trapped in the gaps between the nanoparticles in the aggregates because of the significant size difference between the nanoparticle and the micelle. These trapped micelles are fitted with the mass fractal distribution [$I(Q) \sim Q^{-D_m}$]. The fractal dimension, irrespective of the surfactant and the electrolyte concentration is found to be 2.9. The schematic of structures formed in the silica nanoparticle–C12E10 surfactant micelle system without and with the electrolyte is shown in Figure 6.

Dynamic light scattering (DLS) has been further used to complement the SANS results. In DLS, one measures the signal generated by the light scattered from the diffusing particles and is analyzed by the intensity autocorrelation function $g^2(\tau)$, following a simple exponential decay with decay constant Γ ($= DQ^2$) as:

$$g^2(\tau) = 1 + \exp(-2\Gamma\tau). \quad (14)$$

The hydrodynamic radius is calculated from the diffusion coefficient (D) using Stokes-Einstein equation.⁵⁹ The larger width of the autocorrelation function is because of the slower diffusion and corresponds to the larger size of the diffusing particle. The data have been analyzed by the method of cumulants. The surfactant micelles get adsorbed on the nanoparticle surface providing stability to the nanoparticles in the absence of electrolyte. This is also reflected in the increase in the average hydrodynamic radius (from 110 Å without surfactant to 196 Å with surfactant) of the particles. The variation in the hydrodynamic radius of silica nanoparticles mixed with C12E10 (in varying concentration) in the absence and the presence of NaCl is shown in Figure 7. The turbid systems wherever present were diluted to minimize the effect of the multiple scattering. The hydrodynamic radius remains almost same with the surfactant concentration in absence of electrolyte, whereas shows a dramatic increase with the surfactant concentration in presence of electrolyte. This sharp increase in the hydrodynamic radius is consistent with the formation of nanoparticle aggregates as observed in

SANS. The radius of the nanoparticle aggregates is about 1500 Å. It is also found that the polydispersity index increases with the nanoparticle aggregation (inset of Figure 7).

IV. CONCLUSION

The evolution of the interaction and the resultant structure in the mixed system of anionic silica nanoparticles with non-ionic surfactant C12E10 without and with the electrolyte has been studied by SANS and DLS. It is found that in the absence of electrolyte the surfactant micelles adsorb on the nanoparticle, giving rise to micelle decorated core-shell structure of nanoparticles. However, the micelles become non-adsorbing in presence of electrolyte and induce depletion interaction between the nanoparticles leading to their aggregation. The interaction has been modeled by double Yukawa potential accounting for both attractive depletion and repulsive electrostatic interactions between nanoparticles. The depletion interaction is found to be long-range whose magnitude and range can be varied by surfactant and/or electrolyte concentrations. The nanoparticle aggregates are characterized by the surface fractals having simple cubic packing of nanoparticles within the aggregates.

- ¹S. Paria and K. C. Khilar, *Adv. Colloid Interface Sci.* **110**, 75 (2004).
- ²L. K. Limbach, R. Bereiter, E. Muller, R. Krebs, R. Galli, and W. J. Stark, *Environ. Sci. Technol.* **42**, 5828 (2008).
- ³G. Auernhammer, *Surface and Interfacial Forces—From Fundamentals to Applications: Progress in Colloid and Polymer Science* (Springer, Heidelberg, 2008).
- ⁴N. Veronovski, P. Andeozzi, C. L. Mesa, M. S. Smol, and V. Ribitsch, *Colloid Polym. Sci.* **288**, 387 (2010).
- ⁵R. Zhang and P. Somasundaran, *Adv. Colloid Interface Sci.* **123–126**, 213 (2006).
- ⁶J. Penfold, E. Staples, and I. Tucker, *Langmuir* **18**, 2967 (2002).
- ⁷M. K. Matsson, B. Kronberg, and P. M. Claesson, *Langmuir* **20**, 4051 (2004).
- ⁸P. G. Cummins, J. Penfold, and E. Staples, *J. Phys. Chem.* **96**, 8092 (1992).
- ⁹J. Penfold, E. Staples, I. Tucker, and P. Cummins, *J. Phys. Chem.* **100**, 18133 (1996).
- ¹⁰S. Mehan, V. K. Aswal, and J. Kohlbrecher, *Langmuir* **30**, 9941 (2014).
- ¹¹D. M. Lugo, J. Oberdisse, A. Lapp, and G. H. Findenegg, *J. Phys. Chem. B* **114**, 4183 (2010).
- ¹²S. Kumar and V. K. Aswal, *J. Phys.: Condens. Matter* **23**, 035101 (2011).
- ¹³B. Bharti, J. Meissner, U. Gasser, and G. H. Findenegg, *Soft Matter* **8**, 6573 (2012).
- ¹⁴K. P. Sharma, V. K. Aswal, and G. Kumaraswamy, *J. Phys. Chem. B* **114**, 10986 (2010).
- ¹⁵A. K. Arora and B. V. R. Tata, *Adv. Colloid Interface Sci.* **78**, 49 (1998).
- ¹⁶K. Ohbu, T. Tamura, N. Mizushima, and M. Fukuda, *Colloid Polym. Sci.* **264**, 798 (1986).
- ¹⁷D. P. Norwood, E. Minatti, and W. F. Reed, *Macromolecules* **31**, 2957 (1998).
- ¹⁸J. Singh, P. Yang, D. Michel, R. E. Verrall, M. Foldvari, and I. Badea, *Curr. Drug Delivery* **8**, 299 (2011).
- ¹⁹T. Thurn-Albrecht, G. Meier, P. Muller-Buschbaum, A. Patkowski, W. Steffen, G. Grubel, D. L. Abernathy, O. Diat, M. Winter, M. G. Koch, and M. T. Reetz, *Phys. Rev. E* **59**, 642 (1999).
- ²⁰S. Kumar, D. Ray, V. K. Aswal, and J. Kohlbrecher, *Phys. Rev. E* **90**, 042316 (2014).
- ²¹E. Venugopal, V. K. Aswal, and G. Kumaraswamy, *Langmuir* **29**, 9643 (2013).
- ²²S. Ahualli, G. R. Iglesias, W. Wachter, M. Dulle, D. Minami, and O. Glatter, *Langmuir* **27**, 9182 (2011).
- ²³H. N. W. Lekkerkerker and R. Tuinier, *Colloids and the Depletion Interaction* (Springer, Heidelberg, 2011).
- ²⁴S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1255 (1954).

- ²⁵J. M. Mendez-Alcaraz and R. Klein, *Phys. Rev. E* **61**, 4095 (2000).
- ²⁶H. N. W. Lekkerkerker, W. C. K. Poon, P. N. Pusey, A. Stroobants, and P. B. Warren, *Eur. Phys. Lett.* **20**, 559 (1992).
- ²⁷X. Ye, T. Narayanan, P. Tong, J. S. Huang, M. Y. Lin, B. L. Carvalho, and L. J. Fetters, *Phys. Rev. E* **54**, 6500 (1996).
- ²⁸R. Verma, J. C. Crocker, T. C. Lubensky, and A. G. Yodh, *Phys. Rev. Lett.* **81**, 4004 (1998).
- ²⁹E. Allahyarov, I. D'Amico, and H. Löwen, *Phys. Rev. Lett.* **81**, 1334 (1998).
- ³⁰H. N. W. Lekkerkerker and E. H. A. de Hoog, *J. Phys. Chem. B* **103**, 5274 (1999).
- ³¹M. Dijkstra, R. van Roij, and R. Evans, *Phys. Rev. E* **59**, 5744 (1999).
- ³²R. Roth, R. Evans, and S. Dietrich, *Phys. Rev. E* **62**, 5360 (2000).
- ³³A. Jusufi, J. Dzubiella, C. N. Likos, C. von Ferber, and H. Löwen, *J. Phys.: Condens. Matter* **13**, 6177 (2001).
- ³⁴R. Tuinier, J. Rieger, and C. G. de Kruif, *Adv. Colloid Interface Sci.* **103**, 1 (2003).
- ³⁵X.-Z. Cao, H. Merlitz, C.-X. Wu, and J.-U. Sommer, *Phys. Rev. E* **84**, 041802 (2011).
- ³⁶S. Kumar, M.-J. Lee, V. K. Aswal, and S.-M. Choi, *Phys. Rev. E* **87**, 042315 (2013).
- ³⁷D. Ray and V. K. Aswal, *J. Phys.: Condens. Matter* **26**, 035102 (2014).
- ³⁸J. Kohlbrecher and W. Wagner, *J. Appl. Crystallogr.* **33**, 804 (2000).
- ³⁹J. B. Hayter and J. Penfold, *Colloid Polym. Sci.* **261**, 1022 (1983).
- ⁴⁰S.-H. Chen and T. L. Lin, *Methods of Experimental Physics* (Academic Press, New York, 1987), p. 489.
- ⁴¹E. W. Kaler, *J. Appl. Crystallogr.* **21**, 729 (1988).
- ⁴²J. S. Pedersen, *Adv. Colloid Interface Sci.* **70**, 171 (1997).
- ⁴³D. Ray, V. K. Aswal, and J. Kohlbrecher, *Langmuir* **27**, 4048 (2011).
- ⁴⁴Y. Liu, E. Fratini, P. Baglioni, W.-R. Chen, and S.-H. Chen, *Phys. Rev. Lett.* **95**, 118102 (2005).
- ⁴⁵Y. Liu, W.-R. Chen, and S.-H. Chen, *J. Chem. Phys.* **122**, 044507 (2005).
- ⁴⁶G. Despert and J. Oberdisse, *Langmuir* **19**, 7604 (2003).
- ⁴⁷D. Lugo, J. Oberdisse, M. Karg, R. Schweins, and G. H. Findenegg, *Soft Matter* **5**, 2928 (2009).
- ⁴⁸J. Teixeira, *J. Appl. Crystallogr.* **21**, 781 (1988).
- ⁴⁹V. K. Aswal, P. S. Goyal, and P. Thiyagarajan, *J. Phys. Chem. B* **102**, 2469 (1998).
- ⁵⁰A. P. Radlinski, E. Z. Radlinska, M. Agamalian, G. D. Wignall, P. Lindner, and O. G. Randl, *Phys. Rev. Lett.* **82**, 3078 (1999).
- ⁵¹D. F. R. Mildner and P. L. Hall, *J. Phys. D: Appl. Phys.* **19**, 1535 (1986).
- ⁵²J. S. Pedersen, *J. Appl. Crystallogr.* **24**, 893 (1991).
- ⁵³P. R. Bevington, *Data Reduction and Error Analysis for Physical Sciences* (McGraw-Hill, New York, 1969).
- ⁵⁴I. Yadav, S. Kumar, V. K. Aswal, and J. Kohlbrecher, *Phys. Rev. E* **89**, 032304 (2014).
- ⁵⁵A. J. Chinchalikar, V. K. Aswal, J. Kohlbrecher, and A. G. Wagh, *Phys. Rev. E* **87**, 062708 (2013).
- ⁵⁶A. Demortière, P. Launois, N. Goubet, P. A. Albouy, and C. Petit, *J. Phys. Chem. B* **112**, 14583 (2008).
- ⁵⁷K. Kanie, M. Matsubara, X. Zeng, F. Liu, G. Ungar, H. Nakamura, and A. Muramatsu, *J. Am. Chem. Soc.* **134**, 808 (2012).
- ⁵⁸D. Sen, J. Bahadur, S. Mazumder, G. Santoro, S. Yu, and S. V. Roth, *Soft Matter* **10**, 1621 (2014).
- ⁵⁹P. Lindner and T. Zemb, *Neutrons, X-Rays and Light Scattering Methods Applied to Soft Condensed Matter* (North-Holland, Amsterdam, 2002).