

Hetero-aggregation of oppositely charged nanoparticles

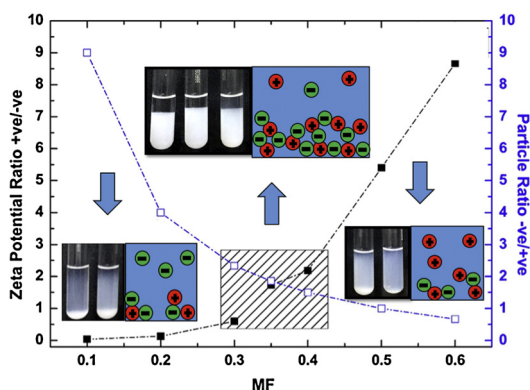


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GRAPHICAL ABSTRACT

A representation of state of dilute oppositely charged particle mixtures at different mixing fraction



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ABSTRACT

Hetero-aggregation refers to aggregation of particles that are not identical i.e. particles of different physical-chemical properties. The investigation of this phenomenon is important because of the fascinating structures that can be formed and their application in several fields including the synthesis of porous materials and particle stabilized emulsions. We report an experimental study of hetero-aggregation behaviour of oppositely charged nanoparticles of similar size. In this study, the hetero-aggregation phenomenon is investigated using a combination of visual observation, zeta potential measurements, dynamic light scattering, scanning electron microscopy and rheology measurements. We report details of aggregate size, structure, flow properties to provide understanding of hetero-aggregation by a careful examination of different phases formed upon mixing oppositely charged particles. The experiments were carried out at different mixing fraction (defined as the mass of positive particle in the dispersion divided by total mass of particles in the dispersion) varying from 0 to 1 with total concentration of particles ranging from 0.05 to 30 wt% (0.023–13.82 vol%). At low total particle concentration, four different states of the mixture were observed which includes sediment with turbid supernatant, sediment with clear supernatant, turbid sample with no sediment and a clear dispersion. However, at higher concentration above ~7.5 wt% (3.45 vol%), the mixture of oppositely charged particles form – a particulate gel with turbid supernatant at low mixing fraction (from 0.1 to 0.3), a solid-like gel at intermediate mixing fraction (from ~0.3 to 0.7) and a turbid sample at high mixing fractions from 0.7 to 1.0.

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Abbreviations: OCP, oppositely charged particle; SEM, scanning electron microscope.

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1. Introduction

An understanding and control of aggregation of particles is relevant to many product formulations such as - paint, ink/toner [1] and is of interest to several industries - for example, pharmaceutical [2], paper [3] and ceramic processing. A systematic study of aggregation phenomena in particular is important in the stabilization of emulsions [4–6], rheology of mixed suspensions [2,7], separation technology and in preparation of advanced materials [8–10]. The aggregation of colloids in a stable dispersion is usually achieved by the addition of polymers [11,12], electrolytes [13] or by changing the solution conditions (either pH or temperature). The phenomena of bridging flocculation and depletion flocculation in the colloid-polymer mixtures are well studied [14,15]. In charge stabilized suspensions, the addition of salt is known to decrease the electrical double layer repulsion thus leading to aggregation at low particle concentration and gelation at sufficiently high particle concentration. Generally, in salt induced aggregation of electrostatically stabilized suspensions, the aggregates formed contain particles of identical characteristics. This is termed as homo-aggregation. Alternatively, it is possible to induce aggregation in stable colloidal dispersion by an addition of particles with different physical or chemical characteristics, a phenomenon known as the hetero-aggregation [HA]. In here, the aggregates contain particles that differ in either physical or chemical characteristics. For example, the particles may differ either in surface chemistry, surface roughness, size, surface charge or shape. In this article, we focus on the hetero-aggregation of oppositely charged particles.

The hetero-aggregation phenomena in colloidal dispersions can be classified into four different categories on the basis of type and size of particle. The oppositely charged particles can be of (a) same type (for example polystyrene-polystyrene or gold-gold) and same size (b) same type but different size (c) different type (for example polystyrene-silica or silica - alumina coated silica) and similar size, and (d) different type and different size. One of the advantage of using particles of same type is that light scattering techniques can be used to probe kinetics and structure of aggregates. With dissimilar type of particles, it is possible to selectively etch or remove one of the particle using a suitable post processing method. This feature has been exploited in the preparation of porous ceramic material [16]. When the particles involved are of similar size, but of either same type or different type, the nature of aggregation is same. The aggregation phenomena in these systems (case (a) and (c)) depends on the mixing fraction (ω_f) and on the surface charge density of particles. At extremes mixing fractions, where one type of particle is present in clear majority, the aggregation process terminates at an early stage. Whereas at intermediate mixing fractions, large percolating clusters have been observed [17,18]. In dilute concentration regime, linear chain-like aggregates with ultra-low fractal dimension have been identified [13,19]. Recently, the hetero-aggregation process in oppositely charged anisotropic gold nanorods which are similar in size has been reported [20]. The hetero-aggregates with nanorods connected in side-to-side and end-to-end configuration were observed due to particle shape anisotropy. Using computer simulations, it has been shown that at a total particle concentration of 6% by volume and at volume ratio of 0.5, the OCP mixtures form a percolating network of particles across the entire simulation volume i.e., a colloidal gel with solid-like behaviour [21]. In these simulations, the interaction between particles were modelled by the DLVO theory [17,21–24]. When the size of the oppositely charged particles are very different from one another (case (b) and (d)), then the small particles can completely cover the surface of large particle [11]. This provides a methodology for the manipulation of surface charge and the stability of colloidal dispersions.

The experimental studies to date on the electrostatic hetero-aggregation (EHA) of oppositely charged particle mixtures are at very low volume fraction from 0.1 to 3 vol% \sim (0.5–6 wt%) which results in the formation of loose aggregates that have open structure with low fractal dimension [6,19,23]. Rheological studies on oppositely charged particle mixtures at low and high volume fraction (from 0.18 to 0.53) have shown a transition from colloidal gels to glassy state [25]. However, these studies are performed at equimolar composition (i.e., 1:1 mixing ratio). In this study, we investigate the EHA phenomena at low and high concentrations to identify their phase behaviour and their mechanical response, which would be of interest to develop processing routes for the fabrication of novel materials. We provide a comprehensive study of hetero-aggregation in very low to concentrated suspensions mixtures i.e. from 0.05 to 30 wt% (0.023–13.82 vol%) total concentration at mixing fractions from 0 to 1.

2. Experimental section

Materials: In this study, commercially available - LUDOX[®]-HS suspension containing mono-disperse spherical silica particles (negatively charged, pH 8–9, surface area \sim 220 m²/g, density-1.21 g/mL ($\rho_{\text{suspension}}$) at 25 °C and LUDOX[®]-CL suspension containing alumina coated silica particle (positively charged, pH 4–5, surface area \sim 230 m²/g, density-1.23 g/mL ($\rho_{\text{suspension}}$) at 25°C were used. Here after Ludox-HS and Ludox-CL are referred as $L_{\text{SiO}_2}^-$ and $L_{\text{Al}_2\text{O}_3}^+$ respectively. The counter ions in the negative and positive Ludox dispersions are Na^+ and Cl^- respectively, while the co-ions are OH^- and H^+ , respectively. These are available as 30 wt% aqueous particle dispersions from Sigma Aldrich. The average particle size of $L_{\text{SiO}_2}^-$ and $L_{\text{Al}_2\text{O}_3}^+$ are 14.5 ± 0.5 nm and 14.7 ± 0.3 nm respectively as determined by dynamic light scattering, these sizes are consistent with literature reports [6]. Therefore, both the particles are considered to be of similar size.

Preparation of oppositely charged particle (OCP) mixtures: The behaviour of OCP mixtures is strongly influenced by the composition of particles in the mixture. In this study, the composition is expressed as mixing fraction, ω_f , defined as the ratio of the mass of $L_{\text{Al}_2\text{O}_3}^+$ particle in the dispersion to the mass of total particle in the dispersion and can also be expressed as number ratio which is number of $L_{\text{SiO}_2}^-$ particles to number of $L_{\text{Al}_2\text{O}_3}^+$ particles:

$$\omega_f = \frac{\text{mass of } L_{\text{Al}_2\text{O}_3}^+}{\text{Total mass of } (L_{\text{Al}_2\text{O}_3}^+ + L_{\text{SiO}_2}^-)} \quad (1)$$

$$N_r = \frac{N_n}{N_p} \quad (2)$$

In order to analyze hetero-aggregation at a wide range of total particle concentration from 0.023 to 13.82 vol%, a total of 156 samples were prepared at different mixing fraction ranging from 0 to 1 shown in Table 1. Where, $\omega_f = 0$ denotes sample containing only $L_{\text{SiO}_2}^-$ and $\omega_f = 1$ denotes sample containing $L_{\text{Al}_2\text{O}_3}^+$ alone. The desired particle concentration suspension was prepared using de-ionized water (18.2 M Ω cm) from milli-Q system (Millipore, U.S) at 25 °C without any pH adjustment. All dispersions after this dilution process are stable against sedimentation and aggregation during the entire period of experimental observations. Starting with $L_{\text{SiO}_2}^-$ and $L_{\text{Al}_2\text{O}_3}^+$ dispersions of equal, but known concentrations, mixtures at different mixing fractions were prepared. The glass test tubes of 10 ml volume were used for the preparation of mixture of oppositely charged suspensions. The resulting dispersion was homogenized with a vortex mixer (CM101plus, Remi Laboratory Instruments, India) at 1000–1500 rpm for 1 min.

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