

Influence of structural forces and contact hysteresis on flow-induced aggregation and breakage of polymer nanoparticles.

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ABSTRACT

Small angle static light scattering was used on-line to monitor the flow-induced aggregation of surfactant-free polystyrene latexes in a stirred tank. Behavior of latexes with different primary particles diameters, different charge groups, and different surface densities of charge groups were investigated by performing a series of aggregation experiments at various pH values. For all experiments the solid volume fraction, the rotation speed and the salt concentration, well above the critical coagulation concentration, were the same. It was observed that average aggregate size at steady state, as characterized by the root-mean-square radius of gyration, $\langle R_g \rangle$, increases when pH decreases. Moreover, qualitatively different behavior of the time evolution of the $\langle R_g \rangle$ was observed when pH decreases below certain critical value. Similar trend can be observed when latex with smaller surface charge density is used. The experiments suggest that structural forces, in particular hydration repulsive force, and contact hysteresis play an important role in flow-induced aggregation and breakage.

Keywords: Aggregation; Breakage; Surface chemistry; Hydration repulsion force; Aggregate strength.

1. INTRODUCTION

Flow-induced aggregation and breakage are two phenomena frequently encountered in processes comprising flowing colloidal dispersion such as flocculation, flotation, crystallizations, and emulsion and suspension polymerization. Most of the research carried out on these two phenomena focused on the influence of various physical parameters such as the shear rate, solid volume fraction, primary particle size and equipment geometry [1-10] on the behavior of aggregating dispersions. However, to address the effect of surface chemistry on flow-induced aggregation is nearly impossible since most of the studies do not report data such as type and density of the surface charge groups [1, 5-7, 11, 12].

Based on these experimental data according to the Derjaguin, Landau, Verwey and Overbeek theory (DLVO) theory [13, 14] it is often assumed that for flow-induced aggregation in aqueous media with ionic strength well above the critical coagulation concentration (CCC) no electrostatic repulsion forces exist between primary particles and their interaction is solely affected by the combination of attractive van der Waals force and Born repulsion. However, this view is based on observations of aggregation in quiescent condition and is valid for systems

where DLVO theory can represent the interparticle interactions. Thus, the outcome of aggregation above the CCC should be universal at least for the same bulk material. However, it was shown [15-18] that chemical aspects of the interacting surfaces are of great importance. Consequently the structure of the double layer, i.e., depth and coverage of the counter-ions, co-ions and hydration water molecules adjacent to the surface, can still influence the interparticle forces within the aggregate above the CCC through various mechanisms such as: hydration repulsion [19-23], hydrophobic attraction [15], steric hindrance, and ion bridging [24], which might influence flow-induced breakage of aggregates, a phenomena that is absent in quiescent systems. Nonetheless, research work on surface chemistry effects in flow-induced aggregation of polymer colloids is relatively scarce [25, 26].

The objective of this work is to investigate the presence of non DLVO interaction and their effects on aggregation and breakage of polystyrene particles in turbulent flow. This was done by studying the influence of two surface attributes: the degree of ionization of surface groups and the surface charge density. The first attribute was studied by carrying out aggregation experiments of surfactant-free carboxyl latex at various pH values in salt concentration well above the CCC; in a fixed flow field and solid volume fraction. The second attribute was studied by repeating the experiments at various pH values for another surfactant-free carboxyl-modified latex with a smaller area per charge group albeit with smaller primary particle diameter. A sulphate latex with particle size similar to the carboxyl latex but with much larger area per charge group was also investigated. The bulk material of the three latexes is polystyrene.

2. EXPERIMENTAL

All latexes used in this study were while polystyrene latexes purchased from Interfacial Dynamics Corporation (IDC), Portland, OR (USA); Product-No. 7-300, CV = 3.2%, Batch-No. 2440, solid content = 4.3 % with primary particle diameter, d_p , equal to 300 nm and an area per carboxyl group on the surface was 162 \AA^2 , Product-No. 1-300, CV = 5.6%, Batch-No. 1919, solid content = 8.8 % with primary particle diameter equal to 320 nm and area per sulfate group on the surface was 1073 \AA^2 , and Product-No. 2-100, CV = 5.8%, Batch-No. 1909-1, solid% = 4 with primary particle diameter equal to 107 nm and an area per carboxyl-modified group on the surface was 82 \AA^2 . All of them exhibit narrow distribution of primary particles as

measured by light scattering in agreement with data provided by vendor.

Batch experiments were carried out employing the same equipment, experimental procedure and light scattering measurement technique as described in details in our previous papers [8-10]. Experimental procedure was as follows. Diluted dispersion of stable primary particles with desired solid volume fraction, prepared by diluting original latexes, was fed into the stirred tank. After the tank was filled completely, application of the high speed of the impeller double was used to check its stability and to destroy any loose aggregates that might exist. After few minutes the desired rotation speed was set. Aggregation was begun with the injection of 60 ml of 4.9 molar aqueous solution of $MgCl_2$ into the tank, along with the necessary amount of HCl or NaOH to reach the desired pH. The resulting salt concentration in the tank was always about five times the CCC. On-line light scattering measurements was started once the salt, and the acid or base, solution was injected [9]. Obtained cluster mass distribution (CMD) was characterized by root-mean-square radius of gyration $\langle R_g \rangle$. Moreover, the scaling exponent (SE) of the power law region in the structure factor of the light scattering signal [9] and perimeter fractal dimension as obtained from image analysis of clusters [10] were used to characterize the cluster structure.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on aggregation and breakage of carboxyl latex

Let us examine first the series of experiments at various pH values carried out using the carboxyl latex at solid volume fraction equal to 2×10^{-5} and stirring speed of 200 rpm as presented in Fig. 1. It can be seen that size of aggregates at steady state, as characterized by $\langle R_g \rangle$, is consistently larger as the pH decreases ($pH < 8$) with no further change below $pH < 5$. Another noticeable feature is the dramatic change in the shape of the time evolution of $\langle R_g \rangle$. In particular, for $pH > 6$ the shape is sigmoidal similar to that observed in our earlier work [9, 10]. At pH 6 a hump appears in the time evolution curve that becomes a clear peak in the size attained during experiments at $pH < 6$. We note that similar trend with significant increase of $\langle R_g \rangle$ with decreasing pH was obtained also for size of primary particles equal to 100 nm.

An important feature of the experiments illustrated in Fig. 1 is that initial aggregation kinetics, the first 5-7 minutes, where only pure aggregation is taking place [9] shows no dependency on pH. This observation of no dependency of the pure aggregation from the pH was confirmed in static aggregation experiments at different pH values and a fixed salt concentration same as that one used in flow-induced aggregation experiments.

The absence of pH effect on pure aggregation, either in flow or in quiescent system, suggests that the observed dependency of $\langle R_g \rangle$ on the pH is due to the effects of pH on the breakage of aggregates. As the system is fully

destabilized, primary particle aggregate immediately upon collision mainly due to the van der Waals forces. On the other hand, when their size starts to be affected by breakage, the strength of aggregates is influenced by the cohesive forces between particles upon contact which are dependent on the particle separation distance.

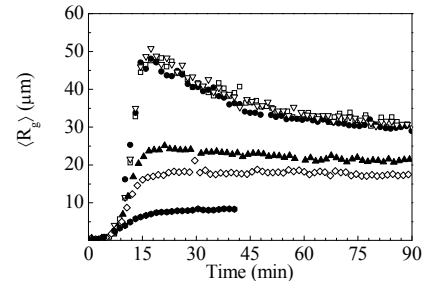


Figure 1 Time evolution of average radius of gyration $\langle R_g \rangle$ during aggregation of carboxyl latex with $d_p = 300$ nm in batch experiments using a solid volume fraction of 2×10^{-5} and a stirring speed of 200 rpm, at various pH values; (\bullet) pH 8, (\diamond) pH 7, (\blacktriangle) pH 6, (∇) pH 5, (\bullet) pH 4 and (\square) pH 3

As measured by Healy et al. [27] for amphoteric latex particles or by Pashley and Pashley and Israelachvili [19, 28, 29] for mica surfaces, where in the presence of salt hydrated cations bind to the negatively charge surfaces, existence of strong repulsion hydration force was observed. Due to the existence of this force, particles or mica surfaces cannot come closer enough as the van der Waals attraction force was not strong enough to dehydrate these cations. According to this observation, together with known strong hydration of Mg^{2+} and fact that amount of salt used for our experiments was significantly above CCC, we assume that presence of repulsion hydration force was affecting the steady-state values of $\langle R_g \rangle$ at high pH leading to larger separation distance between primary particles and therefore lower aggregate strength. By reducing pH, more surface carboxyl groups were neutralized by H^+ which as weakly hydrated cation allow closer contact of primary particles and therefore due to the stronger cohesive force leading to the higher aggregate strength. Finally, no dependency of the $\langle R_g \rangle$ for $pH < 6$ is related to the complete neutralization of the surface carboxyl groups with H^+ .

If this hydration mechanism hypothesis is controlling the steady-state aggregate sizes, similar effect as that done by reduction of pH can be achieved by using latex with significantly smaller number of surface groups per particles, i.e., larger area occupied by one surface group. To verify this hypothesis we examined the aggregation of a sulfate latex with an area per surface group equal to 1073 \AA^2 using $pH = 6$ using the same solid volume fraction and stirring speed mentioned above. The results are shown in Fig. 2 illustrated by solid squares along with experiments using the carboxyl latex with area occupied one surface group equal to 162 \AA^2 at the same pH (solid triangles). As it can be seen, due to nearly the same size of primary particles

the initial kinetics is the same for both latexes however with significantly different time evolution of $\langle R_g \rangle$ as well as steady-state sizes. This suggests that above mentioned mechanism is correct and latex with large area per group exhibited much larger sizes. Plotting the experiment obtained for carboxyl latex at pH = 3 in the same figure reveals an interesting feature. It can be seen that time evolution of $\langle R_g \rangle$ for the latex of area per sulfate group = 1073 \AA^2 measured at pH = 6 and that with area per carboxyl group = 162 \AA^2 measured at pH = 3 are perfectly overlapping. This means that under these conditions for both latexes is the effective area per surface group the same which further support our explanation about existence of hydration repulsive force for the system under investigation.

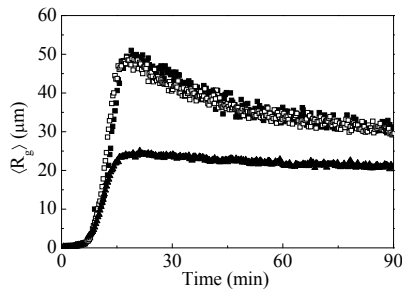


Figure 2 Comparison of the time evolution of $\langle R_g \rangle$ during aggregation in batch experiments using a solid volume fraction of 2×10^{-5} and a stirring speed of 200 rpm (\blacktriangle) carboxyl latex with $d_p = 300\text{nm}$ at pH 6, (\blacksquare) sulfate latex with $d_p = 320\text{nm}$ at pH 6, and (\square) carboxyl latex with $d_p = 300\text{nm}$ at pH 3

3.2 Restructuring and evidence of contact hysteresis

Now we focus on the qualitative change in the time evolution of aggregates sizes. As we have seen, in some experiments the time evolution follows a sigmoidal behavior that is well understood and can be directly modeled. On the other hand, in other experiments, the aggregates grow to maximum sizes in relatively short time. Then slow decay ensues after this maximum is reached.

Earlier works which encountered this behavior attributed it to restructuring [7], defined as reorganization of primary particles within the aggregate under hydrodynamic stresses. They suggest that aggregating particles form initially an open structures, thus they reach large sizes. These large open aggregates are later compacted gradually by sliding and rolling of aggregate parts. To test this hypothesis we performed the measurement of the aggregate structure either through light scattering or by image analysis of 2D aggregate pictures sampled at various times of the process. It was found that both method show very small variation of the aggregate structure with fractal dimension around 2.6, in agreement with our previous work using various size of primary particles [8, 10]. Based on this we can conclude that restructuring alone cannot interpret the overshoot behavior observed in Fig. 1.

In this work we propose a new hypothesis to explain the overshoot which is based on the observation that appearance of the overshoot occurs at the same conditions that lead to larger aggregate sizes, i.e., smaller separation distance between primary particles leading to the larger interparticle forces. On the other hand, after reaching maximum in $\langle R_g \rangle$ observed decay in the aggregate sizes can be accounted for by a gradual loss of the aggregates cohesive force. According to this we assume that due to short separation distance breakage event is characterized by the ductile separation of primary particles leading to the increase of the primary particle roughness and therefore gradual loss of aggregate cohesive force. Similar phenomenon was used for various systems in the literature [30-34]. Reitsma et al. [35] applied the analysis of Mauguis and Pollock derived for the contact between a deformable sphere and a rigid surface [36] to find out the load leading to full plastic deformation, P_p . For polystyrene particles of radius 115 nm pressed against silicon wafer it was found value of P_p around 81 nN. To determine whether also for conditions used in our experiments this situation could occur the value of load leading to plastic deformation was compared with the hydrodynamic force to which aggregates are exposed. According to the compact structure of aggregates and following our previous analysis [10] this force was approximated as the hydrodynamic force acting on a spherical particle in simple shear flow, which is equal to:

$$F_h = 5\pi\mu d^2G/8 \quad (1)$$

where μ is the dynamic viscosity, d is the aggregate diameter, and G is the shear rate related to the energy dissipation rate ε through $G = \sqrt{\varepsilon/\nu}$. Using largest value of the shear rate (located near the impeller blades) as obtained from CFD and aggregate diameter equal to $2\langle R_g \rangle$ the value of F_h around 120 nN was obtained. Based on this we can conclude that separation under this conditions is ductile.

To test whether the separation between primary particles is ductile leading to the increase of surface roughness a series of regrowth experiments was performed [10]. As it was shown by Soos et al. [10] when the system does not show any dependency of the steady state on the shear rate history, indicates that that interparticle forces do not change with aggregation and breakage events. An example of such experiment for carboxyl latex with $d_p = 300 \text{ nm}$ where stirring speed was varying between 200 and 400 rpm is presented in Fig. 3.

As it can be seen aggregates do not grow, upon reduction of the rpm, to the same sizes compare to the experiment obtained at the lower rpm without any rpm variation. The difference persists after many cycles of increase and decrease in the rotation speed. On the other hand, when applying 400 rpm from beginning, the overshoot is substantially smaller compare to the experiment at 200 rpm. Such behavior supports the description above where loss of the interparticle force after reaching maximum in $\langle R_g \rangle$ is

due to ductile separation which cause increase in surface roughness and contact hysteresis.

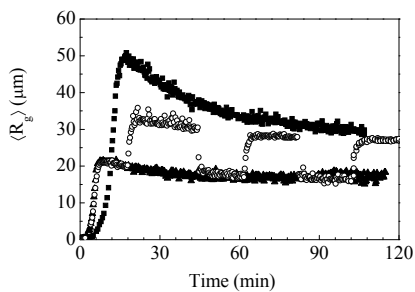


Figure 4 Response of the $\langle R_g \rangle$ to step changes in the stirring speed during aggregation of 300 nm carboxyl latex in batch experiments using a solid volume fraction of 2×10^{-5} and pH = 5; (■) 200 rpm, (○) 400-200-400-200-400-200 rpm, (▲) 400 rpm.

4. CONCLUSIONS

Evidence of the strong influence of the structural forces, i.e., hydration repulsion, on flow-induced aggregation and breakage above the CCC are given in this work. Their influence is mainly on the interparticle forces and minimum distance, which determine the aggregate cohesive forces. This can explain the increase in aggregate sizes with the decrease in pH. Similar trend can be obtained when latex with larger area per surface group is used. Time evolution of aggregate sizes with overshoot is related to the loss of aggregate cohesive force caused by ductile separation during breakage event. This sequence of aggregation-ductile separation- reaggregation of particles with rough surface causes the slow decay in aggregate sizes which stops when the interparticle forces and the aggregate sizes become small enough such that the hydrodynamic forces causing fragmentation are not large enough to induce ductile separation.

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