Bi-modal hetero-aggregation rate response to particle dosage

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The rate of flocculation of cationic polystyrene latex (PSL) particles by smaller, anionic PSL particles has been measured using a low-angle static light scattering technique. The rate of aggregate growth has been investigated as a function of particle size ratio and relative concentration of each particle species (for a constant dose of cationic particles). Contrary to many previous reports, two peaks in the flocculation rate were observed as a function of dose. It is speculated that the peak observed at the lower particle concentration coincides with the dose yielding maximum constant collision efficiency in the steady-state regime, a condition which is attained only after complete adsorption of the smaller particles onto the larger particle species. The peak at the higher particle concentration is believed to be related to the maximum collision rate constant upon reaching the steady-state regime, the value of which corresponds to maximum degree of aggregation and therefore the maximum mean collision efficiency prior to reaching this condition. From classical collision kinetics, the rate of aggregate growth may be represented as being proportional to the product of the collision rate constant and collision efficiency at any given time. Given then that the maximum value of these two variables coincides with different particle concentrations, the product of the response of each to particle dosage can in some cases yield a net bi-modal aggregation rate response to particle dosage. © 2005 American Institute of Physics. [DOI: 10.1063/1.2117027]

I. INTRODUCTION

The effectiveness of any particle aggregation process is dependent upon the desired outcome of the application for which it is employed. Usually it is the characteristics of the aggregates produced (particularly size, density, and strength) or the residual solid concentration after settling that determine the ultimate efficiency. For example, the rate of filtration through a sediment bed is maximized when the constituent aggregates are large and porous so maximizing these characteristics produces optimal efficiency.1

It has been suggested2 that in many situations the conditions required to achieve desirable aggregate characteristics, as well as those required for low residual solids concentration, coincide with the conditions required to achieve a maximum rate of aggregation. While this cannot be true for all cases, since some applications favor opposing characteristics, the link between aggregation kinetics and the efficacy of an aggregation process is irrefutable. Understanding the conditions required to optimize aggregation kinetics then is fundamental to effective practical application.

From the work of von Smoluchowski3 with later modification by La Mer and Smellie4 the rate of aggregation can be expressed in terms of a population balance equation. The rate of change of the total population of m-fold aggregates is given by the sum of all collision rates resulting in formation of such aggregates \((i+j→m)\) less the sum of all collision rates between these aggregates and any other species \((m')\),

\[
\frac{dN_m(t)}{dt} = \frac{1}{2} \sum_{i+j=m} K_{ij} N_i(t) N_j(t) E_{ij} - N_m(t) \sum_{m'=1}^{\infty} K_{mm'} N_{m'}(t) E_{mm'},
\]

where \(K\) is the collision rate constant of the subscripted species, which takes into account various physical properties related to the colliding species and the suspending medium. The term \(E\) is the so-called collision efficiency factor, which is simply the fraction of all collisions between species of the type denoted by the subscript that result in adhesion. For systems in which the initial suspended particle or aggregate concentration and the size of all species are constant, the aggregation rate is directly proportional to \(E\), this being some function of the relative amounts of each species present that are oppositely charged (or otherwise attractive).

Attempts have been made to quantitatively define \(E\) in terms of the concentration of flocculant (primarily, or perhaps exclusively, polymeric) added relative to the particle concentration,1,5 although none so far has proven generally

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applicable. The model proposed by La Mer and Smellie\textsuperscript{4} forms the basis of all other formulations to date as the underlying principle seems intuitively reasonable. Without focusing on specifics, this model predicts that the greater the heterogeneity of each particle-floculant system (that is heterogeneity across the entire system as opposed to individual species) the greater the likelihood of a collision occurring with a nonsimilar species: a collision that will result in adhesion. For example, if flocculation is facilitated by electrostatic attraction between the particle and polymer, maximum $E$ should coincide with maximum charge heterogeneity. Particle-floculant heterogeneity is maximized when equivalent amounts of each are present (the exact measure of this “amount” appears to be the sticking point in the current models of $E$). Consequently, there must be some optimum amount of floculant that corresponds to maximum collision efficiency and therefore aggregation rate.

The vast body of work in this area certainly supports the notion of a single optimum floculant concentration for maximum aggregation rate. An exception to this rule is the data presented by Walsh and Anderson\textsuperscript{8} for the flocculation of polystyrene latex particles with a cationic polyelectrolyte based on quaternized poly(dimethylaminoethyl methacrylate). Their results show a floculant dosage at which the floc formation rate is maximized followed by a decrease and another increase in rate at higher dosages. It is unclear whether there is another decrease at still higher dosages, thus forming a bimodal response, but nevertheless the data contradict the usual assumption of a monomodal response.

While the observations of Walsh and Anderson appear to be anomalous in the presence of other published data, it is possible that in many cases the resolution and repeatability of the data presented are too low to be able to detect fine structure in these dosage response curves. It is also possible that secondary peaks have been observed in the past but have been simply attributed to experimental error since it is assumed that only one peak should exist. Data are presented in this paper showing distinctly bimodal aggregation rate responses of cationic polystyrene latex (PSL) particles to dosage of anionic PSL particles. Aggregation rate measurements were made using a static light-scattering technique, a brief theoretical discussion of which is provided below.

\section*{II. LIGHT-SCATTERING THEORY}

Electromagnetic radiation incident upon a particle induces a dipole moment within the molecules of the particles due primarily to the motion of electrons. As the light wave passes, the oscillating electric field causes the electrons to oscillate also, the effective current producing an electromagnetic field of its own and radiating light at the same wavelength as the incident light: elastic scattering. The intensity of scattered light is dependent upon the shape of the particle and its size relative to the wavelength of the incident light as well as the refractive index of the particle relative to that of the surrounding medium. Interpretation of scattering patterns, by application of a suitable theory, therefore provides an effective, and widely used, means by which to gather information related to the physical properties of particles.

Although full Mie theory\textsuperscript{9} provides a means by which to determine an absolute aggregation rate, difficulties have been encountered applying Mie theory using the associated instrument software.\textsuperscript{10} Size distributions determined by this method show a lack of continuity in the time domain as the tolerance threshold of the optimization routine employed excludes valid data. If the aggregate size distribution is not seen to evolve in a smooth fashion then the aggregation rate, in terms of the rate of change of the mean aggregate size, determined from such size distributions will likewise be inconsistent. Aggregation rates were instead determined (albeit arbitrarily) by analysis of the measured scattering data at a single low angle, a technique that has proven reliable in previous studies.\textsuperscript{11-13}

According to the Rayleigh-Gans-Debye approximation,\textsuperscript{9} the intensity of light scattered $I(\theta)$ at a given angle $\theta$ by an aggregate may be expressed in terms of the Rayleigh scattering equation modified by a form factor $P(\theta)$ and structure factor $S(\theta)$,

$$I(\theta) = I_R(\theta)P(\theta)S(\theta),$$

where $I_R(\theta)$ is the Rayleigh scattering intensity, which for a single scatterer is given by the expression

$$I_R(\theta) = \frac{I_0}{\pi} \frac{8\pi^2 m^6}{\lambda^4} \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \left(1 + \cos^2 \theta\right),$$

where $I_0$ is the intensity of the incident radiation, $r$ is the distance to the detector, $a$ is the radius of the constituent particles, $\lambda$ is the wavelength of the incident light in the medium, and $m$ is the refractive index of the particle relative to that of the surrounding medium.

The form factor takes into account interference between waves scattered by different volume elements in the same particle: \textit{intraparticle} interference. It has been evaluated for a number of particle morphologies including spheres, cylinders, aggregates, and macromolecules.\textsuperscript{9} For homogeneous spheres the form factor is given by the expression

$$P(\theta) = \left[\frac{3(\sin(qa) - qa \cos(qa))}{(qa)^3}\right]^2,$$

where $q$ is the magnitude of the scattering wave vector (the vector sum of the incident and scattered wave vectors) and is given by the expression:

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}.$$

At scattering angles approaching zero ($\theta \rightarrow 0$) any phase delay caused by scattering elements within a particle being at different distances from the light source is almost entirely cancelled by the difference in distance of these elements to the observer. Consequently, intra-particle interference decreases dramatically at low forward scattering angles and the form factor approaches unity, as can be seen from Eq. (4).

The structure factor accounts for interference between waves scattered from volume elements within different particles: \textit{inter-particle} interference. The general form of the structure factor is given by the Fourier transform of the density autocorrelation function, $g(r)$, a measure of the probabil-
ity of finding a particle at a distance \( r \) from any other particle in the aggregate. For an isotropic + system the general form of the structure factor is

\[
S(\theta) = 1 + 4\pi N_p \int_0^\infty r^2[\langle g(r) - 1 \rangle_{\theta}] \frac{\sin(qr)}{qr} \, dr,
\]

where \( N_p \) is the number density of the particles. Sorensen shows that expansion of the integrand in Eq. (6) for values of \( q \) less than the reciprocal radius of aggregates \((R^{-1})\) yields the Guinier expression:

\[
S(\theta) = 1 - \frac{1}{3}(qR)^2; \quad q \ll R^{-1}.
\]

The region defined by \( q \ll R^{-1} \) is known as the Guinier regime. It can be seen from Eq. (7) that at very small \( q \langle q \ll R^{-1} \rangle, S(\theta) \) approaches unity; that is the intensity of scattered light from Eq. (7) is independent of aggregate structure. Recalling that the form factor also approaches unity at low \( q \), the intensity equation for aggregates at such angles is simply that for Rayleigh scattering [Eq. (3)].

Equation (3) describes the Rayleigh scattered light by a single particle. For multiple identical particles the total scattering intensity is given by the sum of the contributions of each individual particle. For \( n \) particles the total scattering intensity is thus given by

\[
I(\theta) = nI_R(\theta),
\]

assuming both \( S(\theta) \) and \( P(\theta) \) may be neglected as discussed above. This may be extended to a system of particles differing in size or refractive index such that the total intensity of scattered light is given by the total contribution of each species of particle of type \( i \) summed across all aggregates,

\[
I(\theta) = \sum_{i=1}^{\infty} n_iI_R(\theta).
\]

The summation of individual contributions in the manner of Eqs. (8) and (9) is limited to reasonably dilute systems; at higher concentrations multiple scattering may occur, whereby a significant amount of scattered light is subsequently scattered by other particles. Likewise, a cluster of particles must be treated as a single entity whereby multiple scattering within the aggregate is equivalent to intraparticle scattering, as described above.

Returning to Eq. (3), an important relationship between the size of scatterers and the intensity of scattered light is apparent: Rayleigh scattering intensity varies as the sixth power of the particle radius and therefore the square of the individual particle volume. From Eq. (9) the total scattering intensity for a system of particles is therefore proportional to the square of each particle (or aggregate) volume \( V_i \), summed across the entire system,

\[
I(\theta) \propto \sum_{i=1}^{\infty} n_i V_i^2.
\]

Differentiating this expression yields the rate of intensity change at a given angle for Rayleigh scattering [and the Rayleigh-Gans-Debye (RGD) scattering at low angles] as a function of time,

\[
\frac{dI_\theta}{dt} \propto \sum_{i=1}^{\infty} \frac{dn_i}{dt} V_i^2.
\]  

Thus, the rate of change in the intensity of light scattered by an aggregating system is proportional to the rate of increase in the total volume of aggregates (assuming that the volume of particles may not change). As a result of the fractal structure of aggregates, any collision involving an aggregate or particle resulting in adhesion necessarily results in an increase in the total aggregate volume. Therefore, any system of particles undergoing aggregation must exhibit a change in the overall volume of aggregates as time progresses. The rate at which the aggregate volume increases is thus indicative of the rate of aggregation and it follows from Eq. (11) that the rate of intensity change at a single low forward angle is also proportional to the overall rate of aggregation.

A further consideration with regard to single-angle analysis is that since the aggregation rate of particles is being related to the change in volume of aggregates with time it is important to ensure that for comparison of different systems this relationship remains unchanged. The mass \( M_R \) of a fractal aggregate is proportional to its radius \( R \) raised to the power \( d_F \),

\[
M_R \propto R^{d_F},
\]

where \( d_F \) is the mass fractal dimension, a non-Euclidean aggregate scaling exponent that defines the density profile of an aggregate. It follows then that the volume of an aggregate is related to the number of constituent particles \( i \) by the expression

\[
V_i \propto i^{3d_F}.
\]

The rate of intensity change at a given angle as a function of time, given by Eq. (11), may then be expressed in terms of \( i \) and \( d_F \) as

\[
\frac{dI_\theta}{dt} \propto \sum_{i=1}^{\infty} \frac{dn_i}{dt} i^{6d_F}.
\]

It can be seen from this relationship that the rate of intensity change is proportional to the mass fractal dimension so it must be ensured that this is constant when comparing different rates. The Guinier regime is bounded above by the so-called fractal regime \((R^{-1} < q \ll a^{-1})\) in which it can be shown that the scattered intensity is proportional to the magnitude of the scattering wave vector with the mass fractal dimension as the power-law exponent,

\[
I(\theta) \propto q^{-d_F}, \quad R^{-1} < q < a^{-1}.
\]

Applying this relationship, it is possible to determine \( d_F \) for a system of aggregates from the gradient of a log-log plot of the scattered intensity as a function \( q \) within the fractal regime.
The final volume fraction of the PSL species to be flocculated was $1.25 \times 10^{-5}$, corresponding to an approximate number concentration of $1.83 \times 10^{10}$ m$^{-3}$. This concentration was chosen as it is within the range found to give negligible multiple scattering for the static light-scattering technique. It is also a sufficiently low particle collision rate such that aggregate growth could be easily monitored with time. The concentration of flocculant was varied according to experiment requirements.

The dilute particles and flocculant were combined in a mixing vessel and a 10 s period of initial mixing was applied using a six-blade Rushton impeller driven by an overhead stirrer at 150 rpm. This brief mixing period was intended to rapidly achieve an even distribution of particles and flocculant while having minimal effect on the flocculation process, thus preserving perikinetic conditions.

Following the mixing stage, the aggregating suspension was transferred from the mixing vessel to the flow cell of the Malvern Mastersizer 2000 by means of a peristaltic pump, connected in-line after the Mastersizer cell. A flow rate of $1.4 \times 10^{-3}$ L s$^{-1}$ was maintained for 30 s to allow the flow cell to completely fill, at which time the pumping was discontinued and measurement of the light scattered by the sample was initiated.

### C. Light scattering

Aggregate growth was monitored using the Mastersizer 2000 (Malvern, UK), a low-angle static light-scattering instrument. The intensity of scattered light (supplied by a He–Ne laser with a wavelength of 633 nm) was recorded simultaneously for 10 s at multiple angles for a range of times. The intervals separating measurements were varied depending on the total length of the experiment. At most this required 24 h, for heteroaggregation of similarly sized particles.

The principal decision to be made when performing single-angle analysis is which angle is to be chosen. Data presented by Ofoli and Prieve suggest that at an angle of 2° (for He–Ne laser in an aqueous medium) the relationship between the intensity of scattered light and the square of the volume of scatterers is valid only below aggregate diameters of approximately 1 μm. Above this size they conjecture that the scattered intensity becomes dependent upon the shape of the aggregates and deviation from the volume-squared relationship is observed.

Unlike homoaggregation (coagulation of like-charged particles), in the early stages of heteroaggregation growth occurs simultaneously with adsorption. To avoid confusing the change in scattering intensity due to aggregation with that of adsorption, aggregation must be monitored at later times (corresponding to larger aggregates) to allow an adsorption equilibrium to be reached. A consequence of monitoring the later stages of aggregation is that the aggregates formed during experiments in this study grow far beyond 1 μm. In response to the size of aggregates observed for a given experiment it was necessary to analyze the data at an appropriately low scattering angle: larger aggregate sizes required lower angles. However, any decrease in scattering

### III. EXPERIMENT

#### A. Materials

All solutions and suspensions were prepared using Millipore “Milli Q Academic” grade de-ionized water and adjusted to pH 5 using analytical grade HNO$_3$ (Aldrich). Analytical grade KNO$_3$ (Aldrich) was used as a background electrolyte in all experiments at a concentration of 0.01 mol L$^{-1}$.

The model particle system used in all experiments was an aqueous suspension of cationic PSL particles (Interfacial Dynamics Corp., USA) with amidine functional groups. Sulfate functionalized anionic PSL particles (Interfacial Dynamics Corp., USA) were used to facilitate heteroaggregation. The concentration of these particles was varied as required to achieve the desired relative number concentration of anionic to cationic particles. The number-averaged radius and coefficient of variance of each particle species, determined by transmission electron microscopy as quoted by the manufacturer, are presented in Table I. These values were confirmed by dynamic or small-angle static light-scattering experiments (Malvern Zetasizer ZS and Malvern Mastersizer 2000). The zeta potential ($\xi$) of the PSL particles was measured (Malvern Zetasizer ZS) for all particles at pH 5 and a KNO$_3$ concentration of 0.01 mol L$^{-1}$. The sulfate and amidine functionalized groups were found to impart a negative and positive surface charge to the particles, respectively, for the conditions assumed in this (and indeed most) work.

#### B. Aggregation

The particles and flocculant employed for a given aggregation experiment were first diluted in separate containers to a concentration double that required after they are combined (i.e., equal volumes of each). Addition of a concentrated flocculant solution (or suspension) to a dilute particle suspension, or vice versa, will result in a localized concentration of one species. The aggregation kinetics in such circumstances will differ to that observed for an evenly interdispersed system of particles and flocculant, a condition that is assumed in this (and indeed most) work.

### Table I. Properties of polystyrene latex particles.

<table>
<thead>
<tr>
<th>$R$ (nm)</th>
<th>%CV</th>
<th>$\xi$ (mV)</th>
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<tr>
<td>310</td>
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<td>+33</td>
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<td>14.4</td>
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<tr>
<td>21.5</td>
<td>17.1</td>
<td>-52</td>
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<tr>
<td>40</td>
<td>8.3</td>
<td>-37</td>
</tr>
<tr>
<td>75</td>
<td>5.3</td>
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<td>111.5</td>
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<td>-43</td>
</tr>
<tr>
<td>152</td>
<td>7.9</td>
<td>-36</td>
</tr>
<tr>
<td>207.5</td>
<td>3.6</td>
<td>-45</td>
</tr>
</tbody>
</table>

The concentration of these particles was varied as required to cationic particles. The number-averaged radius and coefficient of variance for all particles at pH 5 and a KNO$_3$ concentration of 0.01 mol L$^{-1}$. The sulfate and amidine functionalized groups were found to impart a negative and positive surface charge to the particles, respectively, for the conditions assumed in this (and indeed most) work.
angle was observed to be accompanied by a decrease in the signal-to-noise ratio of the data. Deciding upon the most appropriate angle for a given experiment is not as straightforward as simply using the lowest possible angle to minimize shape effects.

The experiment has been performed based on the data on the measured size of the aggregates. By ensuring the angle chosen for analysis is sufficiently low and that at later aggregation times (when the total aggregate volume is largest) the corresponding $q$ is well within the Guinier regime, aggregate structural effects are minimized and the scattered intensity approximates Rayleigh scattering. Within this constraint the most appropriate angle for analysis can be chosen by observation of the signal-to-noise ratio.

IV. RESULTS AND DISCUSSION

A. Light-scattering measurements

Measurements of the intensity of scattered light at a single low angle as a function of time were used to determine the aggregation rate of cationic PSL particles destabilized by addition of anionic PSL particles. To ensure the rate of intensity change is truly indicative of the aggregation rate when making comparisons it is necessary to ensure that the scattering angle chosen for analysis is sufficiently low and the fractal dimension of aggregates formed at different dosages is constant.

The mass fractal dimension of aggregates may be determined from the scattered light intensity at a range of angles in the fractal regime. Plotting the logarithm of the intensity of scattered light at a given time (late in the aggregation process to allow sufficient aggregate growth) as a function of the logarithm of $q$, the slope of the linear region of the resulting curve is $-d_F$. By way of example, Fig. 1 shows the scattering curve for aggregates formed by heteroaggregation of the cationic PSL particles ($R_1=310$ nm) and anionic PSL particles of ($R_2=207.5$ nm) after approximately 19 h. A straight line fit by a linear least-squares optimization to the data points between $\log_{10} q$ equal to $-2.5$ and $-3.5$ (the fractal regime for these data) shows a gradient of $-1.82$ corresponding to a $d_F$ of 1.82.

Figures 2(a) and 2(b) show the fractal dimensions over the range of dosages, in terms of the relative ratio of small particles to large ($N_2/N_1$), investigated for heteroaggregation of the cationic PSL particles with anionic PSL particles of $R_2=207.5$ nm and $R_3=152$ nm, respectively. Clearly the fractal dimension in both cases is independent of the dosage anionic PSL particles showing a standard deviation from the mean value of only 0.03 and 0.02 for each case. The requirement that the mass fractal dimension is constant for all dosages for which an aggregation rate comparison is to be made is thus satisfied for these particular anionic particles.

Due to the aggregation time being less for the smaller anionic particles the aggregate size at the end of the experiment is too small to give a sufficiently large linear region for accurate fractal analysis. (The fractal regime merges into Guinier regime so there are insufficient points with which to fit a straight line.) However, since the fractal dimension is seen not to differ greatly for the larger sizes it is reasonable to assume that this will also be the case for the smaller particles.

An additional feature of Fig. 1 is the clearly defined plateau region, below $\log_{10} q$ equal to $-4$, corresponding to the Guinier regime. The angle analyzed for determination of the aggregation rate must correspond to a $q$ value [Eq. (5)] that lies within this region. The upper limit of this region will decrease with increasing aggregate size; so to compare aggregation rates for different dosages the angle must be chosen so as to lie within the lowest bounded Guinier regime. This angle needs not be the same for different anionic particle sizes as comparison of aggregation rates is made only for the same sized particles.

For the rate of intensity change to be truly proportional to the volume of the aggregates squared the angle chosen must be well within the Guinier regime ($q \ll R^{-1}$). This is often not practical due to a very low signal-to-noise ratio (a
problem when attempting to fit a line of best fit, as described below. However, even at the upper limit of the Guinier regime ($q=R^{-1}$) the structure factor from Eq. (7) reaches a minimum of $2/3$. Provided then that the angle is within this region, any deviation from the volume-squared relationship is likely to be sufficiently minimal to allow comparison of aggregation rates.

Analysis of the scattered light data at a single angle yields an intensity versus time plot such as those presented in Fig. 3 for the heteroaggregation of cationic PSL particles ($R_1=310$ nm) with different dosages of anionic PSL particles ($R_2=111.5$ nm). The scattering angle analyzed in this cases is 1.12°, corresponding to a $\log_{10} q$ value of $-3.6$. This angle lies within the Guinier regime for the larger aggregates formed by addition of these smaller anionic particles, unlike the anionic PSL particles of radius $R_2=207.5$ nm for which this angle is within the fractal regime (Fig. 1).

Each set of measured intensity data in Fig. 3 is fitted with a fourth-order polynomial using a linear least-squares method. While in reality the intensity of scattered light is not a polynomial function of time, the quality of the resulting fit using such expressions was found to be very good. This is exemplified by the correlation coefficient ($r^2$) values presented in Fig. 3 which in each case shows the fitted polynomial accounts for greater than 99% of the total variation in the data about the average. Lower-order polynomials yielded significantly lower $r^2$ values (the resulting curves were visibly a poor fit) while higher-order polynomials increase the likelihood of an artificial fine structure being introduced to the fitted curve that is not present in the data.

**B. Dosage response curves**

The instantaneous rate of intensity change ($dI/dt$) for a given dosage and time can be determined by differentiating the polynomial expression that has been fitted to the measured data and evaluating at the appropriate time. This allows the presentation of a dosage response curve for a given system of particle and flocculant, in which the value of $dI/dt$ at an arbitrary time is plotted as a function of dosage. Such dosage response curves for aggregation of the cationic PSL particle species in Table I by each species of anionic particle in the same table are shown in Figs. 4–6.

In Fig. 4(a) the early stages are shown for aggregation of the cationic PSL particles by the anionic PSL particles of radius equal to 111.5 nm. Interestingly $dI/dt$ initially appears to increase monotonically with dosage (aside from a slight inflexion between $N_2/N_1=6.5$ and 8) showing no sign of an optimum, at least for the dosages investigated. The distinct decrease in $dI/dt$ above $N_2/N_1=10$ is only observed after $t=4578$ s (approximately 76 min).

For any stable system of particles the rate of aggregation must be zero until the addition of a destabilizing species such as an oppositely charged particle or polymer. So given that addition of such a species takes place at $t=0$, the rate of aggregation of the system must initially be zero. Any initial change in the intensity of scattered light at $t\rightarrow 0$ must there-
fore be due to adsorption of the destabilizing species rather than aggregation of the actual particles (since the overall change in intensity is the sum of all changes in particle population). For heteroaggregation of oppositely charged PSL particles adsorption will certainly be reflected in the initial change in intensity of scattered light.

Given the adsorption of the anionic PSL particles onto cationic PSL particles is a collision process, which is described by Eq. (1), the rate of adsorption should be linearly proportional to $N_2/N_1$. Initially then $dI/dt$ should simply increase linearly with the dosage of anionic particles. This explains the apparent lack of an optimum dosage at the earlier times shown in Fig. 4(a). As adsorption of small particles progresses the larger particles become destabilized and aggregate. The linear relationship between $dI/dt$ and dosage of anionic particles thus breaks down as $dI/dt$ is then the sum of the population change due to both adsorption and aggregation. Thus, even at $t=30$ s in Fig. 4(a) the hint of a peak can be observed, corresponding to the dosage at which the maximum aggregation rate is taking place.

With continued adsorption of small particles and the resulting decrease in their population, the rate of adsorption should likewise decrease while the rate of aggregation increases. This is evidenced in Fig. 4(a) by the increasing departure from linearity with time due to the relatively rapid decrease in $dI/dt$ at higher dosages; the modal response of aggregation begins to superecede the linear response of adsorption. Upon complete adsorption of all small particles the rate of adsorption must be zero and the shape of the dosage response curve, as seen in Fig. 4(b), is indicative of the rate of aggregation alone.

The most notable feature of Fig. 4(b) is the distinctly bimodal aggregation rate response to dosage, in agreement with the findings of Walsh and Anderson but contrary to the generally held assumption of a monomodal response. This observation is echoed in the aggregation rate response curves for a number of other anionic PSL sizes, as seen in Fig. 5. Note that only later stage dosage response curves are presented in this case so as to ignore the effect of adsorption on the response curves.

In the case of the intermediate particle size ratios, $R_2/R_1$ equal to $0.36$ and $0.49$ [Figs. 4(b) and 5(b)], both peaks are easily distinguishable without the need for a particularly high data point resolution. It seems surprising that such noticeable bimodal behavior has only been reported once previously. However, much of the previous work in this area has been done with particles and flocculants (either particle or polymer) of greatly differing size. From Fig. 5(c) it appears that in such cases distinction between the two peaks is not as clear, the uppermost peak on the abscissa apparently being overshadowed by the lowermost peak such that the former could easily be overlooked.

For similar sized particles, $R_2/R_1$ equal to $0.67$ as seen in Fig. 5(a), the lower peak is overshadowed by the higher, opposite to the observations made for greatly differing particle sizes. Indeed, to this effect there is a general trend of increasing significance of the uppermost peak relative to the peak at the lower dose with increasing similarity of particle sizes.

For the heteroaggregation of almost identical PSL particles $(R_2/R_1=0.94)$ under perikinetic conditions, Stoll and Pefferkorn observed an optimum particle fraction $(N_2/(N_1+N_2))$ of 0.8, equivalent to an optimum dosage $(N_2/N_1)$ equal to 4. This was accompanied by a second peak aggregation rate at a particle fraction of 0.2, equivalent to $N_2/N_1$ equal to 0.25 or $N_1/N_2$ equal to 4. Rather than the bimodal response observed in our own data, these twin peaks can be considered in the first case to be the result of negative
particles flocculating stable positive particles and vice versa in the second case, hence their occurrence at equivalent dosages.

From collision efficiency considerations alone it is expected that for heteroaggregation of identical particles of equal but opposite charge the optimum dosage is 1 as this corresponds to the highest degree of species heterogeneity. Clearly for the data reported by Stoll and Pefferkorn another factor must be determining the optimum dosage. Given the observed optimum dosage in Fig. 3(a) for $R_2/R_1$ equal to 0.67 is approximately 5, it seems reasonable that this other factor combined with collision efficiency is responsible for the bimodal response observed in our own data. It is likely that Stoll and Pefferkorn did not observe a collision efficiency related peak at 1 because of the aforementioned trend of increasing relative significance of the uppermost peak with decreasing particle size ratio.

Figure 6 shows the dosage response curve for flocculation of the cationic PSL particles with anionic PSL particles of radius equal to 40, 21.5, and 9.5 nm. The latter two curves [Figs. 6(a) and 6(b)] show a monomodal dosage response although in each case the effective dosage range is quite broad, similar to that seen in Figs. 4 and 5. It is expected that if only a single peak is observed due to the lack of a second peak it would be of a similar breadth to one of the single peaks seen in Figs. 4 and 5. It is possible that in this case a monomodal response is seen, because with the significance of the uppermost peak being proportional to $R_2/R_1$, the two peaks are simply not resolved and thus they appear as a single broad peak. Evidence for this is provided by the 40 nm response curve [Fig. 6(a)] which, while having only one peak, appears to reveal the existence of a second unresolved peak at a higher dosage than the first in the form of a pronounced shoulder.

The possibility of convoluted peaks in Fig. 6 may provide an explanation to an inconsistency noted by Hogg$^5$ between current theory and experimental observations: the La Mer-Smellie model of collision efficiency$^{4,5}$ predicts a distinct optimum dosage, however, flocculation is commonly found to be close to optimal over a broad range of dosages. It seems reasonable to assume that one of the peaks in each of the dosage response curves in Figs. 4 and 5 is related to maximum collision efficiency, while the other peak must be due to some other factor.

C. Origin of bimodal response

It is usual to consider flocculation of particles as a sequence of separate processes, whereby adsorption of the polymeric flocculant to the surface of suspended particles for the most part precedes the actual flocculation process.$^{22}$ The same assumption could be made for the adsorption of small particles onto the surface of larger oppositely charged particles prior to the occurrence of any significant aggregation (formation of aggregates comprised of multiple large particles). If this assumption is correct, it implies a constant collision efficiency factor throughout the aggregation process, assuming an even distribution of flocculant or oppositely charged particles across the entire surface of the suspended particles.

If the collision efficiency factor is constant during aggregation then, assuming all other factors in Eq. (1) are constant or vary proportionally with $E$, the aggregate formation rate should be proportional to $E$ alone, as is usually assumed. However, as was discussed by Hsu and Lin,$^{23}$ the assumption that aggregation is negligible in the time span required for a constant collision efficiency factor to be reached (before complete adsorption of the flocculant) is questionable even for polymeric flocculants. One only needs to consider the case of similar sized oppositely charged particles, for which the collision rate of each species with any other given species present (particle or aggregate) must likewise be similar. In this case, it is likely that a constant collision efficiency factor will only be reached after significant aggregation has occurred.

Given sufficient time any aggregating system should eventually reach a steady-state regime in which collision efficiency is constant as a result of complete adsorption of flocculant. The degree of aggregation that occurs prior to reaching this steady-state regime should be a function of the concentration of added flocculant. As previously mentioned, Fig. 4(a) shows the reduction in adsorption rate at each dosage with time, revealing the aggregation response curve prior to the adsorption rate reaching zero. This is indicative of the fact that some aggregation must be taking place prior to a constant collision efficiency factor being reached. Thus it cannot be assumed that the size distribution at the onset of the steady-state regime is constant for all dosages and therefore the collision efficiency factor is not the sole variable in Eq. (1). One must also consider the collision rate constant $K$ which is sensitive to the aggregate size distribution, at the time when a constant collision efficiency factor is reached.

If it is assumed that the size of suspended particles is constant at $t=0$ for any flocculant dosage, the degree of aggregation prior to reaching constant collision efficiency should be proportional to the aggregate-aggregate collision efficiency $E_{mn}$ during this time. (Any variation in the value of $K$ prior to reaching the steady-state regime being reached must be in direct proportion to any change in $E_{mn}$.) At a single time $t$ the average collision efficiency per collision can be expressed as $E(t)$, that is the apparent collision efficiency of the system as a whole. [Here $dE(t)/dt$ is proportional to the rate of small particle adsorption.] This can then be averaged over some time period such that the time-averaged collision-averaged collision efficiency is expressed as $\bar{E}$. Within the steady-state regime $E_{mn}$ is the same as $E(t)$ which is also the same as $\bar{E}$ [assuming $E(t)$ is averaged only over the steady-state regime such that $dE(t)/dt=0$]. However, in the time period preceding the steady-state regime $\bar{E}$ may differ from the instantaneous value of $E(t)$ at a given time, which in turn may also differ from the collision efficiency of each individual collision, $E_{mn}$, at that time. A higher $\bar{E}$ prior to reaching the steady-state regime implies a greater degree of aggregation during this time.

Returning to Eq. (1), the collision rate constant for two
solid particles for which Brownian motion is the sole transfer mechanism (perikinetic collisions) is given by

\[ K_{ij} = 4\pi(D_i + D_j)R_{ij}, \]  

(16)

where \(D_i\) and \(D_j\) are the diffusion coefficients of particles \(i\) and \(j\), respectively, and \(R_{ij}\) is the collision radius of the particles, that is the distance at which collision between the particles is considered to be inevitable. In the absence of any long-range attractive forces \(R_{ij}\) may be approximated as the sum of the particle radii, \((R_i + R_j)\). The particle diffusion coefficients are given by the Stokes-Einstein equation,

\[ D = \frac{k_BT}{6\pi\eta r}, \]  

(17)

where \(k\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\mu\) is the dynamic viscosity of the suspending medium, and \(r\) is the hydrodynamic radius of the particle. The perikinetic collision rate constant may then be expressed as

\[ K_{ij} = \frac{2k_BT(R_i - R_j)^2}{3\mu R_i R_j}, \]  

(18)

if one assumes the radius of a particle is equivalent to its hydrodynamic radius.

During aggregation, collisions occur not only between particles but also of course between aggregates. The radius of an \(m\)-fold aggregate scales according to\(^24\)

\[ R_m = R_0 m^{1/d_F}, \]  

(19)

where \(R_0\) is the primary particle radius and \(d_F\) is the fractal dimension, a non-Euclidean scaling exponent. An analogous expression of the aggregate hydrodynamic radius can be derived by substitution of the hydrodynamic fractal dimension, \(d_{HF}\).\(^25\) Substitution of Eqs. (19) into (18) yields the perikinetic collision rate constant for fractal aggregates, \(m\) and \(m'\),

\[ K_{nm'} = \frac{2k_BT}{3\mu} \left( m^{1/d_F} + m'^{1/d_F} \right)(m^{-1/d_H} + m'^{-1/d_H}). \]  

(20)

Pusey and Rarity\(^25\) report light-scattering data that indicate the mass and hydrodynamic fractal dimensions are equivalent for aggregates formed by reaction-limited coagulation \((d_F = d_{HF} = 2.1)\). Meakin \textit{et al.}\(^26\) report a similar result for theoretical calculations of simulated diffusion-limited cluster-cluster aggregates; fractal dimensions of around 1.8 are found for both cases. The implication of these findings is that liquid contained within the perimeter of an aggregate is unable to flow into the bulk solution. Thus, according to these data, aggregates behave as solid spheres of equivalent physical radius and the collision rate constant can be described by the expression

\[ K_{nm'} = \frac{2k_BT}{3\mu} \left( mm' \right)^{1/d_F}. \]  

(21)

It was noted by Gregory\(^27\) that the permeability of aggregates increases with decreasing mass fractal dimension. Presumably then \(d_F\) must increase with decreasing mass fractal dimension such that the equivalence of these terms is limited to higher values of \(d_F\).

In the early stages of aggregation, aggregates are not strictly fractal and Eq. (18) holds quite well. However, Eq. (21) is required to describe the later stages when aggregates start showing fractal characteristics. It can be seen from Eqs. (18) and (21) that the collision rate constant is proportional to the size ratio of the colliding aggregates or particles. That is, the larger the difference in size between two species of particle or aggregate the more likely they are to collide. This is more prominent for aggregates than particles as with increasing radius they suffer less of a decrease in diffusion coefficient due their fractal nature.

As is the case for the collision efficiency factor, the collision rate constant may be averaged across all possible collisions such that at time \(t\) the mean collision constant is denoted \(K(t)\), the apparent rate constant for the system as a whole. It can be seen from Eqs. (18) and (21) that the perikinetic particle and aggregate collision rate constants are proportional to the size ratio of the colliding aggregates or particles. That is, the larger the difference in size between two species of particle or aggregate the more likely they are to collide. A greater degree of aggregation prior to reaching the steady-state regime, that is a higher value of \(E\) preceding this point in time, will result in a broader aggregate size distribution once it is reached. A broader size distribution in turn implies a greater average difference in size between any two aggregates so it follows that \(K(t)\) upon reaching the steady-state regime is proportional to the degree of aggregation, and therefore \(E\), prior to reaching the steady-state regime.

Already it is apparent that the collision rate constant upon reaching the steady-state regime is not independent of dosage. To further understand this relationship it is necessary to understand the relationship between dosage and collision efficiency. The adsorption rate of flocculant onto particles can be described by the von Smoluchowski approach to binary particle collisions such that the fraction of flocculant remaining in solution can be expressed as an inverse exponential function of time,\(^22\)

\[ \frac{N(t)}{N(0)} = e^{-at}, \]  

(22)

where \(N(0)\) is the initial number concentration of the flocculant particles and \(a\) is a constant. Bear in mind that this is only an approximation as it assumes no change in the collision efficiency or rate constant for flocculant adsorption. The adsorbed fraction of flocculant is thus given by

\[ x_A(t) = 1 - e^{-at}. \]  

(23)

Assuming an even distribution of flocculant across all particles at any given time \(\text{[such that } E_{nm'} = E(t) \text{ for all } m \text{ and } m']\), the fraction of each particle surface covered by flocculant at time \(t\) is given by

\[ \Theta(t) = x_A(t)\Theta_{\text{max}}, \]  

(24)

where \(\Theta_{\text{max}}\) is the fractional surface coverage once all the flocculant has been adsorbed, the steady-state surface coverage. The collision efficiency can be approximated as\(^5\)
This relationship implies that $E(t)$ has a maximum value of one-half when $\Theta_{\text{max}}$ is equal to one-half. Applying Eqs. (23)–(25), the collision efficiency factor can be calculated as a function of $(t/a)$ for any value of $\Theta_{\text{max}}$, as demonstrated in Fig. 7.

The value of $E(t)$ (or indeed $\bar{E}$) within the steady-state regime is a function of flocculant concentration, increasing until reaching that corresponding to maximum $E(t)$ (indicated by the solid line in Fig. 7). It follows then that the degree of aggregation prior to steady state likewise increases with concentration until reaching that required for maximum $E(t)$ in the steady-state regime. However, consider a system where the eventual value of $E(t)$ in the steady-state regime is below maximum due to an overabundance of flocculant adsorbed to the larger particles (indicated by the dashed line in Fig. 7). In this case $E(t)$ must first increase with the amount of adsorbed flocculant to the maximum possible value before decreasing to a constant value. This means that $\bar{E}$ prior the steady-state regime may, in fact, be higher for particle concentrations that ultimately result in a lower constant $\bar{E}$ (the mean collision efficiency from $t=0$ to the start of the steady-state regime) thus implying a greater degree of aggregation and therefore a greater value of $K(t)$ upon reaching constant $E(t)$. This is, in fact, the case in Fig. 7 where in the time frame shown the value of $E(t)$ in the steady-state regime for $\Theta_{\text{max}}$ equal to 0.5 is 0.439 while for $\Theta_{\text{max}}$ equal to 0.6 it is 0.444. Figure 8 schematically illustrates this effect in terms of the relative number concentration of oppositely charged particles. Roughly speaking, the need for the higher dosage to “pass through” the maximum collision efficiency (optimum surface coverage) before reaching equilibrium means, for the case depicted, that the mean collision efficiency prior to the steady-state regime is higher than for the case where the equilibrium collision efficiency is maximized.

It can be seen that for a given particle-flocculant system there may be a dosage, greater than that required for maximum constant $E(t)$, at which a maximum value of $K(t)$ is attained upon reaching the steady-state regime. Given then the aggregation rate for a given size ratio is, in fact, proportional to $KE$, from Eq. (1), any difference in $K(t)$ upon reaching the steady-state regime will be reflected in the aggregation rate response to flocculant dosage. A maximum value of $K(t)$ upon reaching the steady-state regime at a concentration above that required for maximum constant $E(t)$ (such as $\Theta_{\text{max}}=0.6$ in Fig. 7) has the potential to produce a secondary peak when the functions relating each variable to $N_2/N_1$ are multiplied together.

Although speculative in nature, the hypothesis presented regarding the origin of the observed bimodal response is supported by the noticeable decrease in significance of the uppermost peak with increasing difference in particle size. The rate of adsorption of small particles onto large relative to the rate of aggregation should be higher for a greater difference in particle size due to a higher collision rate constant of oppositely charged particles. Thus with decreasing size of the anionic particles there is a lower degree of aggregation prior to reaching the steady-state regime in the case of (b), which in turn is due to this system having to “pass through” the optimum surface coverage before reaching complete adsorption.

Since the peak lowest on the abscissa at any time must be related to the maximum value of $E(t)$ at that given instant, it is expected that the position of this peak (i.e., the dosage at which it occurs) will decrease with time as more small particles are adsorbed until a constant value of $E(t)$ is reached. This is indeed observed in Fig. 4(a) where the lower peak moves from $N_2/N_1=6.46$ to $N_2/N_1=5.03$ over the course of the adsorption stage, further supporting the presented hypothesis. Upon complete adsorption of all small particles the dosage corresponding to maximum $E(t)$ is no longer a function of time $[E(t) = \bar{E}]$ so it is expected to maintain a stable position. This too is observed for the lower peak in Fig. 4(b) where after reaching $N_2/N_1=5.03$ it maintains this position until the end of the experiment. This is the steady-state regime where the mean collision efficiency at each dosage remains constant with time.
By contrast, the position of the uppermost peak at any time is related to the maximum value of $E$ up to that given instant. So while it is expected that the position of this peak will also decrease with time, the shift should not be as dramatic as that for the peak lowest on the abscissa. Given then that the downward shift observed for the lower peak for the time frame monitored covered only a single increment between measured dosages, it is not surprising that no perceptible shift was observed in Fig. 4 for the upper peak.

Assuming the hypothesis presented is, in fact, correct, a final reason for the observation of only monomodal responses in studies to date is the fact that polymeric flocculants are by far more widely investigated than particle flocculants. The adsorption rate of a polymeric flocculant is much faster than for a particle of similar radius of gyration because the hydrodynamic radius of the former is much smaller. (Polymer chains exist as coils in solution rather than solid particles.) Thus for a particle and polymer flocculant of similar physical dimensions, the adsorption time of the polymer will be significantly less and therefore so to will be the degree of aggregation prior to reaching the steady-state regime. This is not to say that no aggregation takes place at all during this time, it is just less than would be expected for particle flocculants of similar dimensions.

V. CONCLUSION

The light-scattering data presented for the aggregation of cationic PSL particles by addition of smaller, anionic PSL particles as a flocculant (hetero-aggregation) are observed, in some cases, to demonstrate a distinctly bimodal aggregation rate response to the smaller particle dosage. This is in contradiction to the monomodal response typically reported and also expected from the assumption that aggregation rate is proportional to collision efficiency alone for a constant particle concentration and size. Other light-scattering data presented herein do show the expected monomodal response but only for smaller particle size ratios $R_2/R_1 < 0.13$. The bimodal response is most notable for intermediate particle size ratios, $R_2/R_1 = 0.36$ and 0.49 being the clearest.

It has been previously proposed that within the time frame required for complete adsorption of flocculant to suspended particles it is possible for some aggregation of these particles to take place. The temporal variation in the aggregate-aggregate collision efficiency during this time is a function of flocculant concentration and should result in differences in size distributions once complete adsorption has been achieved. This in turn implies a difference in the mean collision rate constant of different dosages upon complete adsorption of flocculant.

The dosage corresponding to a maximum collision rate constant upon complete adsorption (the start of the steady-state regime) will not necessarily coincide with that corresponding to the maximum constant collision efficiency factor. Rather it must occur at a lower concentration for any adsorption time greater than zero. Given then that the overall aggregation rate is proportional to the product of the collision efficiency and collision rate constant, the aggregation rate response curve is proportional to the product of two noncoinciding peaks: the collision rate constant and collision efficiency dosage response curves. As such, it is possible for a bimodal aggregation response to occur, as evidenced by the light-scattering data obtained in this study.

It can be seen that the likelihood of a bimodal response occurring is dependent upon the relative magnitude of the maximum collision rate constant and collision efficiency within the steady-state regime as well as the dosages corresponding to this rate constant and collision efficiency. More importantly perhaps is that, even in cases where a monomodal response is observed, the actual optimum dosage for the maximum rate of aggregation may coincide with either the maximum collision efficiency or collision rate constant dosage. Certainly it appears from the data presented that there is an increasing likelihood of the latter with greater similarity in the size of the oppositely charged particles. Further investigation into the effect of physical conditions such as solid concentration and fluid shear rate should provide insight into the defining parameter for optimum aggregation rate in practical systems, potentially leading to greater control of the aggregation process.

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