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An improved collision efficiency model for particle aggregation

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A generalized geometric model is presented which describes the collision efficiency factor of aggregation (the probability of a binary particle or aggregate collision resulting in adhesion) for systems comprised of two oppositely charged species. Application of the general model to specific systems requires calculation of the area of each species available for collision with a second species. This is in contrast to previous models developed for polymer-particle flocculation that are based on the fractional surface coverage of adsorbed polymer. The difference between these approaches is suggested as an explanation for previously observed discrepancies between theory and observation. In the current work the specific case of oppositely charged nondeformable spherical particles (heteroaggregation) is quantitatively addressed. The optimum concentration of oppositely charged particles for rapid aggregation (maximum collision efficiency) as a function of relative particle size is calculated and an excellent correlation is found with data taken from literature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2387172]

I. INTRODUCTION

Following the work of von Smoluchowski¹ it is usual to consider the rate of aggregate formation as proportional to the number of binary particle or aggregate collisions, per unit time and volume, resulting in adhesion (J). For two species, i and j , that may be either a particle or aggregate, this can be expressed as

$$J_{ij} = K_{ij}N_iN_jE_{ij}, \quad (1)$$

where N_i and N_j are the number concentration of each species, E_{ij} is known as the collision efficiency factor, and K_{ij} is a second order collision rate constant which takes into account the physical parameters of the system (particle size, temperature, etc.) as well as the transport mechanisms by which collisions are facilitated.

The term E_{ij} in Eq. (1) was introduced by Smellie and La Mer² to account for the possibility of a collision not resulting in adhesion and is simply equal to the fraction of collisions that do result in adhesion. It follows then from Eq. (1) that if the suspension properties and particle concentration are constant for all flocculant dosages, E_{ij} must be the determining variable for aggregate growth rate. Even in the face of temporal variations in the properties of an aggregating system prior to complete adsorption of flocculant, it has been shown³ that the collision efficiency factor is nonetheless central to determining the optimum dosage of flocculant

for rapid aggregation. Indeed, maximization of the collision efficiency factor is intrinsically connected to the effective application of flocculation and heteroaggregation techniques. Thus, understanding and controlling E_{ij} is of considerable importance not only for those who seek to understand the fundamental aspects of flocculation kinetics but also those who wish to apply this process to practical situations.

Some work has been done to try and develop a quantitative theory for E_{ij} ,^{2,4-13} specifically for the flocculation of particles by polymers, but to date no model has proven to be universally satisfactory. The goal of this work is to develop and implement a more robust quantitative model for E_{ij} based on the existing models.

II. THEORY

A. Background

Smellie and La Mer² noted that the rate of floc formation should be dependent upon the amount of flocculant adsorbed per particle (θ) as well as the surface area still open per particle ($1-\theta$). They proposed that E_{ij} (the collision efficiency factor for a collision between species i and j) could be quantitatively defined as the probability of collision between the bare fraction particle surface and the fraction of particle surface covered by polymer,

$$E_{ij} = P(\theta|(1-\theta)), \quad (2)$$

which was expressed quantitatively as simply the product of θ and $(1-\theta)$,

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$$E_{ij} = \theta(1 - \theta). \quad (3)$$

This probabilistic model implies a maximum collision efficiency of 0.25 (25% chance of any given collision resulting in adhesion) at an optimal fractional surface coverage of one half. Hogg⁵ later noted that the original Smellie–La Mer formulation does not take into account the probability of the opposite situation, that is the probability of polymer-bare surface interactions, $P((1 - \theta) | \theta)$. Assuming that these probabilities are equivalent (the colliding species have the same fraction of surface covered by polymer), the correct formulation of the Smellie–La Mer model should be

$$E_{ij} = [\theta(1 - \theta)] + [(1 - \theta)\theta] = 2\theta(1 - \theta). \quad (4)$$

According to Eq. (4), the optimum surface coverage remains one-half [as for Eq. (3)], but the maximum collision efficiency is 0.5 rather than 0.25 at this surface coverage. This is readily understood if one considers a situation where the polymer is oppositely charged to the particle, lies flat against the particle surface, and the size of each polymer patch is large relative to the total surface area of the particle. If the surface coverage is equal to one-half, the situation can be likened to flipping coins: half a coin is heads and the other half tails, so if two coins are thrown there is a 50% chance of getting two of the same side (25% chance each for two heads and two tails) and the same chance of getting two opposite sides. However, as was noted by Hogg⁵ and De Witt and van de Ven,⁹ despite the correction to the Smellie–La Mer model, the model fails to explain reported optimum flocculant concentrations corresponding to surface coverages of significantly less than one-half^{14,15} nor does it explain experimentally determined values of E_{ij} much greater than one-half, in some cases approaching unity.^{16,17}

Numerous attempts have been made to refine the model of Smellie and La Mer to account for the discrepancies between theory and experimental observations. Formulations have included terms for physical effects such as particle or aggregate rotation during interaction,⁵ fractional activation of surface function groups,⁶ the possibility of aggregation of like-charged surfaces,^{4,7,12} temporal variation of surface coverage,⁸ and multiple collisions during a single encounter.¹³ However, none of these modifications has successfully reconciled the noted discrepancies.

B. Proposed modification

All attempts at quantifying the collision efficiency factor to date have been based on the original Smellie–La Mer model. Our conjecture is that this model, while conceptually sound, is not sufficiently robust to allow refinement. This is not to say that the refinements themselves are not correct at least in a qualitative sense. All formulations of E_{ij} compare the fraction of particle surface covered by polymer to that which is bare. However, the fraction of particle surface area that is covered by flocculant (θ) is actually not available for particle-particle or particle-flocculant collisions because, by definition, it is covered. Therefore it should only be included in probability calculations for such collisions if the flocculant sits relatively flat against the particle surface, as exemplified by Fig. 1(a), such that θ equates to the area of flocculant

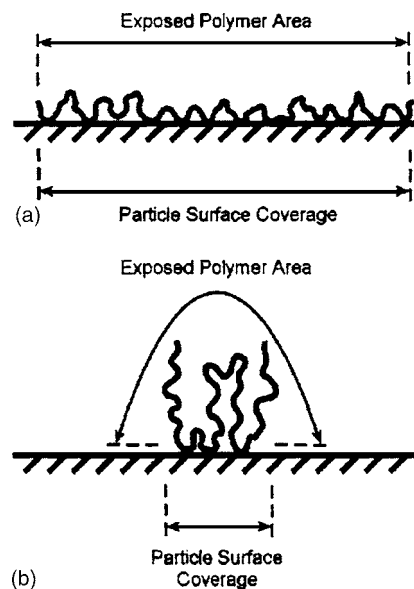


FIG. 1. Particle surfaces with adsorbed polymer (a) in a flattened conformation such that the area of exposed polymer is equivalent to the area of particle covered and (b) in an extended conformation such that the two areas do not equate.

exposed to the possibility of collision. So by applying the half surface coverage condition for maximum collision efficiency in the Smellie–La Mer model, it is implicitly assumed that the flocculant adopts a flat conformation during collisions.

It has been shown from theory¹⁸ and experiment¹⁹ that polymer chains adsorbed at low concentration on a substrate can adopt a relatively flat equilibrium configuration (the bound fraction at equilibrium nears 1 as surface coverage approaches 0). With increasing surface coverage the equilibrium bound fraction is found to decrease and the nonadsorbed polymer segments extend into the bulk phase as loops and tails. As already mentioned, surface coverage at optimum flocculation conditions is usually less than 0.5 so relatively flat configurations are possible given sufficient relaxation time and good affinity of the polymer for the substrate.

However, due to the increase in flocculation rate with increasing particle concentration²⁰ and shear rate,^{21,22} the total flocculation times too short for significant polymer relaxation are often reported giving rise to so-called nonequilibrium flocculation (NEF).^{23,24}

The effect of polymer extension on aggregation kinetics has been previously investigated.^{25,26} However, the frequently observed increased rate of aggregation with polymer extension is more commonly attributed to the effect of increasing collision radius on the collision rate constant (K_{ij}). It is important to note that while K_{ij} is a function of collision radius and therefore polymer extension, this does not preclude the collision efficiency from also being a function of the same variable. Indeed, it has been suggested previously^{23,27} that the morphology of relaxing polymer chains may be responsible for the observed discrepancies between theoretical and experimental collision efficiency factors, although no quantitative analysis has been undertaken.

The possibility of extended flocculant conformations affecting collision efficiency was first noted by Healy and La Mer.²⁸ They considered the effect such conformations have on the collision efficiency factor by calculating θ for Eq. (3) as a function of the number of adsorbing segments per polymer molecule. This simply means that nonadsorbing segments do not contribute to the surface coverage. The model of Swerin *et al.*¹¹ also considers polymer conformation, but rather than looking solely at the effect on surface coverage a direct enhancement to the collision efficiency factor is attempted. An extra term is included in their formulation additive with the probabilistic surface coverage term. The term describing the polymer conformation is entirely empirical and, as stated by the authors, should be regarded as a “rather crude attempt” at including flocculant extension in the collision efficiency formulation. Nevertheless, it does highlight the need to look beyond the effect of polymer conformation in terms of θ alone.

In addition to decreasing the fractional surface coverage for a given amount of adsorbed polymer, extended conformations will result in the exposed area of flocculant (the area of the imaginary surface outlining the general shape of the polymer) being greater than the area of the particle that it covers. This is exemplified by Fig. 1(b) where a polymer in an extended conformation (loops and tails) is adsorbed to a particle surface. The surface coverage in this case is significantly less than the exposed area of polymer, unlike the case in Fig. 1(a). Clearly it is the relative surface area of the particle and flocculant exposed to collision that dictates the chance of the two coming into contact rather than the surface coverage of flocculant on particle. This certainly explains the reported observations that optimum flocculation conditions are achieved at flocculant concentrations corresponding to a particle surface coverage of significantly less than one-half. It will be shown in Sec. III of this work that it is possible to define a generalized (system nonspecific) equation for collision efficiency as a function of the exposed area of flocculant and particle.

Application of the generalized model to specific systems requires calculation of the exposed areas of particles and flocculant (as a function of time in the case of transient morphology). Since it is difficult to know the exact dimensions of a polymer adsorbed at a surface, especially given that its conformation may change with time, calculation of the exposed area of flocculant is not trivial. However, if we consider the extreme case of NEF, where the collision rate of particles is infinitely fast, polymer chains are incapable of reconfiguration before collision with another particle. So, assuming adsorption of polymer chains from solution with minimal deformation until contact, a spherical coil configuration can be assumed as a limiting case in the same way as a completely flat conformation is the limiting case of equilibrium flocculation (EF). While it is likely that in most real systems some reconfiguration will occur during adsorption of polymeric flocculants and as such they are not ideally modeled as spheres when combined with the Smellie–La Mer model for a flattened configuration, these models describe limiting cases between which reality may lie. The more ap-

plicable model for a specific system will be determined by various physical factors affecting the relative rates of polymer relaxation and particle aggregation.

The clear benefit of assuming a spherical flocculant is that it is relatively simple to calculate exposed surface areas. Additionally, calculations of exposed area are readily applicable to aggregation of oppositely charged particles, the so-called “heteroaggregation.” Indeed, Stoll and Buffle²⁹ have described polymer bridging flocculation as a case of heteroaggregation in which macromolecular configurations and lengths play an additional role. Heteroaggregation then provides a means by which the generalized model presented in Sec. III can be experimentally tested, as will be shown in Sec. IV of this work.

III. COLLISION EFFICIENCY FACTOR MODEL

A. Probability equations

The collision efficiency factor for any two colliding systems (i and j), whether comprised entirely of particles, as in heteroaggregation, or polymer and particles, as in flocculation (or any other combination of charged species), is the summed conditional probability of a collision involving a positive or negatively charged area in i with a negative or positively charged area in j , respectively, and vice versa,

$$E_{ij} = \frac{1}{2} [P(j_+|i_-)P(i_-) + P(j_-|i_+)P(i_+) + P(i_+|j_-)P(j_-) + P(i_-|j_+)P(j_+)], \quad (5)$$

where $P(i_-)$, for example, denotes the probability of the negatively charged area in i being involved in a collision and $P(j_+|i_-)$ denotes the conditional probability of the positive area in j being involved in a collision once the negative area in i is involved.

If the involvement of an area in i in a collision has no effect on the probability of involvement of an oppositely charged area in j in a collision and vice versa then $P(j_+|i_-) = P(j_+)$, $P(j_-|i_+) = P(j_-)$, and so on. Thus Eq. (5) can be simplified to

$$E_{ij} = \frac{1}{2} [P(j_+)P(i_-) + P(j_-)P(i_+) + P(i_+)P(j_-) + P(i_-)P(j_+)], \quad (6)$$

which may be further simplified to

$$E_{ij} = P(i_+)P(j_-) + P(i_-)P(j_+), \quad (7)$$

if i and j contain the same relative areas of positive and negative charges. At least one of these generalized equations can be used to describe the collision efficiency factor for any system comprised of two oppositely charged species.

It is prudent at this point to note that Eqs. (5)–(7) consider only the chance of alignment of oppositely charged species during a collision, and in so doing they ignore several other possible effects that may result in some degree of deviation from predicted collision efficiencies. In particular, these equations do not take into account the possibility of collisions between like-charged species resulting in adhesion, as discussed by Ash and Clayfield⁴ and subsequent authors.^{7,9,10,12} Presumably the modifications these authors suggested for the Smellie–La Mer model of the collision

efficiency factor to account for this possibility could be adapted to the model presented herein. Introducing the terms for the sticking probability based on the potential and kinetic energies of interaction for negative-negative, positive-negative, and positive-positive interactions (α_1 , α_2 , and α_3 respectively), E_{ij} may be expressed as

$$E_{ij} = \alpha_1 [P(i_-)P(j_-) + P(i_-)P(j_+)] + \alpha_2 [P(i_+)P(j_-) + P(i_-)P(j_+)] + \alpha_3 [P(i_+)P(j_+) + P(i_+)P(j_+)]. \quad (8)$$

The energy of interaction terms are typically ascribed an arbitrary constant value or are chosen to reflect the collision efficiency of one species in the absence of the other (the stability of the separate dispersions). However, rather than being constant, these terms may actually vary with the relative surface area of opposite charge. Miklavic *et al.*³⁰ suggest that the rate of decay of interaction potential between two heterogeneous surfaces and therefore the probability of homoaggregation is a function of the periodicity (spacing) and size of the charged areas on each. However, at small Debye lengths (κ^{-1}), relative to the charge area and periodicity, the decay is less dependent on these parameters and is a primarily a function of κ^{-1} alone. It can be expected in such situations that the values of α_1 , α_2 , and α_3 are approximately constant for all dosages. So, provided that for the given κ^{-1} these particles are stable as separate dispersions ($\alpha_1 = \alpha_3 = 0$), the interaction energy terms from Eq. (8) can be ignored. A condition of considering only the alignment terms of the collision efficiency factor then (as is the case herein) must be that the size of the charged areas is large relative to κ^{-1} (or, perhaps more accurately, the distance of interaction).

Other deviations may arise from neglecting to include the other refinements mentioned in Sec. II A. It is expected that both rotation of particles⁵ and multiple collisions,¹³ for example, would somewhat increase the collision efficiency factor. Conversely, the so-called hydrodynamic (or viscous) effect,^{31,32} whereby particle collision is inhibited by resistance to displacement of the intervening liquid, may somewhat reduce the collision efficiency. However, for the purposes of this work only the alignment probability will be considered.

B. Collision efficiency factor

Application of Eqs. (5)–(7) to specific systems requires the calculation of the conditional and unconditional probability terms for the given system. The probability of a charged surface (solid or imaginary) within either colliding system being involved in a collision is the total area of the surface carrying that charge relative to the total area of the system.

For a collision between two single, oppositely charged particles, Eq. (7) may be reexpressed as

$$E_{ij} = \left(\frac{\Sigma A_{i+}}{\Sigma A_{i+} + \Sigma A_{i-}} \right) \left(\frac{\Sigma A_{j-}}{\Sigma A_{j-} + \Sigma A_{j+}} \right) + \left(\frac{\Sigma A_{i-}}{\Sigma A_{i-} + \Sigma A_{i+}} \right) \left(\frac{\Sigma A_{j+}}{\Sigma A_{j+} + \Sigma A_{j-}} \right), \quad (9)$$

where ΣA_{i+} and ΣA_{i-} are the total positive and negative surface areas in system i and so on (the Σ notation is used here

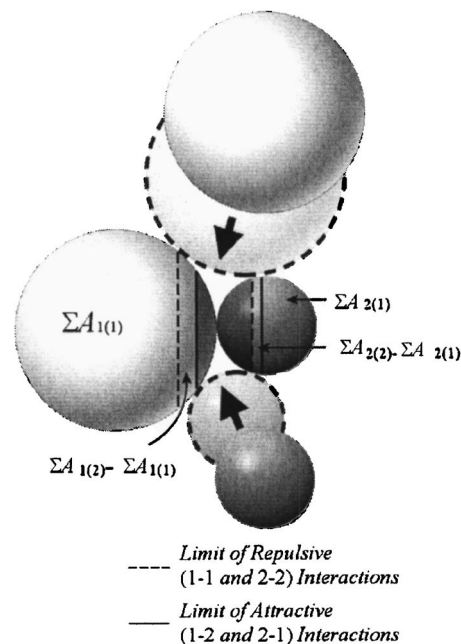


FIG. 2. Areas on particles within a binary aggregate exposed to and shielded from collisions with other particle species (note that the colliding particles depicted may be included within an aggregate).

to indicate that each area is the sum of all identical surface areas in a system). It is assumed that any point on the surface of each system can be described as either positive or negative. For a collision in which i is a positive particle and j is a negative particle, ΣA_{i-} and ΣA_{j+} are both equal to zero, so from Eq. (9) E_{ij} is equal to 1, as is expected for a collision between two oppositely charged particles. Likewise, if i and j are of the same charge Eq. (9) returns a value of zero for E_{ij} indicating that adhesion will never occur.

Extension of the model to collisions involving clusters of particles requires further qualification of surface areas. Consider a binary aggregate (m) comprised of two oppositely charged particles of different size radii (Fig. 2). The surface area in the interstitial region near the point of contact of the two particles is shielded from collisions with other similarly sized particles. So the area on each particle within the aggregate exposed to collisions will be less than the total surface area of the binary aggregate. If each aggregate contains some relative number of two oppositely charged species, the area on each species within each aggregate exposed to collisions with each other species must be defined. This is a total of eight different surface areas, four per aggregate, as opposed to the two areas discussed for a collision between two oppositely charged particles. The area on a small particle exposed to collisions with another small particle must be greater than that exposed to collisions with a large particle. Likewise the area on a large particle exposed to collision with another large particle must be less than that exposed to collision with a small particle. Consequently it is necessary to differentiate between oppositely charged particle species according to their size. The larger particle species, should a size difference exist, will be denoted as 1 and the smaller particle species as 2. For example, the total area of the larger species of particle

contained within an aggregate m exposed to collisions with any oppositely charged smaller species is denoted $\Sigma A_{m2(1)}$ and so on.

It is possible to derive an expression for the collision efficiency factor for two aggregates (m and q), each containing any number of equivalent or different sized oppositely charged particles (not necessarily the same for both aggregates). In this case, the probability of collision with a charged surface is dependent on the surface of the other system involved in the collision so the simplification made for Eq. (6) does not apply and Eq. (5) must be used.

To derive expressions for the conditional probabilities in Eq. (5) for cluster-cluster collisions we need to understand which collisions are precluded in the event of each particular area being involved in a collision. The interactions between certain sets and subsets that are precluded due to shielding are described by the expression

$$P(\Sigma A_{q1(2)} | \Sigma A_{m1(2)} - \Sigma A_{m1(1)}) \\ = P(\Sigma A_{q1(2)} | \Sigma A_{m2(2)} - \Sigma A_{m2(1)}) = 0. \quad (10)$$

This relationship is also applicable with the subscripts q and m interchanged. From this relationship and also Eqs. (A2) and (A3) (Appendix A), we are left then with a limited number of mutually exclusive interactions that are possible once a given area in one aggregate is assumed to take part in the collision, all of which are shown in Table I.

For any given row in Table I, the probability of each area in the second column being involved in a collision, conditional upon the area in the first column being involved, is the area in question in the second column relative to the sum of all areas in that column. Thus we can calculate the conditional probability terms from Eq. (5), yielding a general expression for the collision efficiency of cluster-cluster collisions,

$$E_{mq} = \frac{1}{2} \left[\left(\frac{\Sigma A_{q2(1)}}{\Sigma A_{q2(1)}} \right) \left(\frac{\Sigma A_{m1(2)} - \Sigma A_{m1(1)}}{\Sigma A_{m(T)}} \right) \right. \\ + \left(\frac{\Sigma A_{q2(1)}}{\Sigma A_{q2(1)} + \Sigma A_{q1(1)}} \right) \left(\frac{\Sigma A_{m1(1)}}{\Sigma A_{m(T)}} \right) + \left(\frac{\Sigma A_{q1(2)}}{\Sigma A_{q(T)}} \right) \\ \times \left(\frac{\Sigma A_{m2(1)}}{\Sigma A_{m(T)}} \right) + \left(\frac{\Sigma A_{m2(1)}}{\Sigma A_{m2(1)}} \right) \left(\frac{\Sigma A_{q1(2)} - \Sigma A_{q1(1)}}{\Sigma A_{q(T)}} \right) \\ + \left(\frac{\Sigma A_{m2(1)}}{\Sigma A_{m2(1)} + \Sigma A_{m1(1)}} \right) \left(\frac{\Sigma A_{q1(1)}}{\Sigma A_{q(T)}} \right) \\ \left. + \left(\frac{\Sigma A_{m1(2)}}{\Sigma A_{m(T)}} \right) \left(\frac{\Sigma A_{q2(1)}}{\Sigma A_{q(T)}} \right) \right], \quad (11)$$

where $\Sigma A_{m(T)}$ is the total area in m exposed to collisions and is given by

$$\Sigma A_{m(T)} + \Sigma A_{m1(2)} + \Sigma A_{m2(2)}, \quad (12)$$

the derivation of which is presented in Appendix A. The second bracketed term of each pair of multiplicative terms in Eq. (11) represents the chance of the area denoted by the numerator being involved in a collision. The first bracketed term represents the chance of this collision, should it occur,

TABLE I. Possible mutually exclusive collisions between areas of two particles.

Area in m aggregate	Possible collisions with q aggregate
$(\Sigma A_{m1(2)} - \Sigma A_{m1(1)})$	$\Sigma A_{q2(1)}$
$\Sigma A_{m1(1)}$	$\Sigma A_{q2(1)}, \Sigma A_{q1(1)}$
$(\Sigma A_{m2(2)} - \Sigma A_{m2(1)})$	$\Sigma A_{q2(1)}, (\Sigma A_{q2(2)} - \Sigma A_{q2(1)})$
$\Sigma A_{m2(1)}$	$\Sigma A_{q2(1)}, (\Sigma A_{q2(2)} - \Sigma A_{q2(1)}), \Sigma A_{q1(1)}, (\Sigma A_{q1(2)} - \Sigma A_{q1(1)})$

being with a particle of opposite type. For example, from the first two terms we see that if the attractive area not included in the repulsive area on a larger particle ($\Sigma A_{m1(2)} - \Sigma A_{m1(1)}$) is involved in a collision, this must result in adhesion because the only possible area on another particle that can collide with this area is the attractive area on a smaller particle, $\Sigma A_{q2(1)}$.

In the event that the two aggregates with the same relative number of 1 and 2 particles (m and m') such that the relative area of each is the same, $P(m'|m)$ is equal to $P(m|m')$, and Eq. (11) simplifies to

$$E_{mm'} = \left(\frac{\Sigma A_{m'2(1)}}{\Sigma A_{m'2(1)}} \right) \left(\frac{\Sigma A_{m1(2)} - \Sigma A_{m1(1)}}{\Sigma A_{m(T)}} \right) \\ + \left(\frac{\Sigma A_{m'2(1)}}{\Sigma A_{m'2(1)} + \Sigma A_{m'1(1)}} \right) \left(\frac{\Sigma A_{m1(1)}}{\Sigma A_{m(T)}} \right) \\ + \left(\frac{\Sigma A_{m'1(2)}}{\Sigma A_{m'(T)}} \right) \left(\frac{\Sigma A_{m2(1)}}{\Sigma A_{m(T)}} \right). \quad (13)$$

Equations (11) and (13) are reasonably system nonspecific inasmuch as they may be applied to any binary system of monodisperse species with an inherent net attraction. Transient morphology may be accounted for, provided a mean morphology may be assumed, if the values of ΣA are considered functions of time rather than simply constant. However, if the instantaneous morphology of either species varies greatly across the system (multiple polymer chains in various states of relaxation, for example) a more rigorous approach would be required. Note also that ΣA is based on effective collision radius, which may be somewhat larger than the actual radius of the particles in the presence of long range attractive and repulsive forces. For the work presented hereafter, the assumptions of a nondeformable spherical species in the absence of any long range forces will be invoked.

IV. APPLICATION TO HETEROAGGREGATION

A. Shielded area calculation

As mentioned earlier, we have chosen to work with a system comprised of two oppositely charged solid spherical particles as this is the simplest for calculation purposes. The species are denoted as 1 and 2 as before, where type 2 particles are the smaller (assuming a size difference exists). The particle and aggregate specific subscripts (i, m , etc.) will not be used in this section since only one aggregate needs to be discussed for demonstrative purposes.

Collision and adsorption of particles to form aggregates create areas on each particle within the aggregate that is

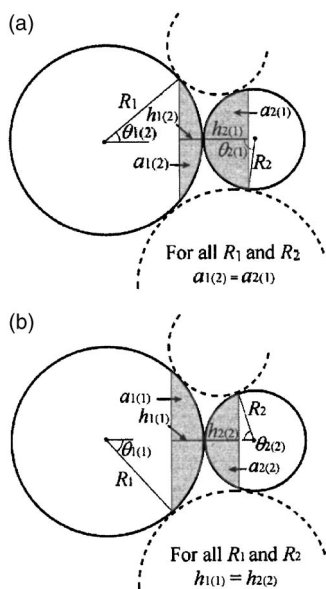


FIG. 3. Shielding of adsorbed particles from collisions with particles (indicated by the dashed line) of (a) *opposite* charge, the shielded areas on the large and small particle are denoted as a_1 and a_2 , respectively, and (b) *like* charge, the shielded areas on the large and small particles are denoted as $a_{1(1)}$ and $a_{2(2)}$, respectively.

shielded from further attractive collisions ($a_{1(2)}$ and $a_{2(1)}$) or repulsive collisions ($a_{1(1)}$ and $a_{2(2)}$), as illustrated in Fig. 2 and in two dimensions in Fig. 3. Using simple geometric and trigonometric relationships it is possible to determine this area for particles of known dimensions (Appendix B). For attractive collisions the shielded area is given by

$$a = 4\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right)^2, \quad (14)$$

where $a = a_{1(2)} = a_{2(1)}$, and for repulsive collisions

$$a_{1(1)} = 2\pi R_1 \left(\frac{R_1 R_2}{R_1 + R_2} \right) \quad (15)$$

and

$$a_{2(2)} = a_{1(1)} \left(\frac{R_2}{R_1} \right). \quad (16)$$

The remaining area on each particle accessible to a colliding species is simply the total area of the sphere less the value of a , such that

$$\Sigma A_{1(2)} = 4\pi R_1^2 - \frac{N_2}{N_1} a, \quad (17)$$

$$\Sigma A_{2(1)} = \frac{N_2}{N_1} (4\pi R_2^2 - a), \quad (18)$$

$$\Sigma A_{1(1)} = 4\pi R_1^2 - \frac{N_2}{N_1} a_{1(1)}, \quad (19)$$

$$\Sigma A_{2(2)} = \frac{N_2}{N_1} (4\pi R_2^2 - a_{2(2)}), \quad (20)$$

where (N_2/N_1) is the relative number concentration of particles present, which in a system of aggregates comprised of different particle ratios would require aggregate and particle specific subscripts (for example, N_{m1} is the number of type 1 particles in aggregate m). The value of (N_2/N_1) must be greater than or equal to 1 otherwise the large particles must be considered to flocculate the small particles and the numerical subscripts must be interchanged. It is assumed that the surface charge density of both particle species is greater than the packing density of oppositely charged particles, so that in any $\Sigma A_{1(2)}$ or $\Sigma A_{2(1)}$ there is at least one charged site.

Equations (17) and (19) assume a reasonably even distribution of small particles at the surface of each larger particle such that no overlap of the shielded areas on the surface of the latter occurs. This is a reasonable assumption given that adsorption of like-charged particles in close proximity is unfavorable due to their mutual repulsion. However, at high concentrations of the smaller species of particle relative to the larger, overlap of shielded areas will be unavoidable and accurate calculation of the exposed area requires a correction factor. For the work presented herein it is assumed that the correction factor has negligible effect on the calculated collision factor and can thus be ignored. It is intended that the overlap correction factor will be presented in a later paper for application of the model to the specific case of high (N_2/N_1) .

To test the validity of the proposed model it is necessary to investigate a system in which the collision efficiency factor is equivalent for all possible collisions and is not affected by any change in the system due to a collision resulting in adhesion. The most obvious system fitting this description is a system of aggregates, each comprised of the same ratio of positive and negative particles such that this ratio is constant irrespective of a collision resulting in adhesion. The individual collision efficiency factor can then be calculated for a given ratio of oppositely charged particles by substituting the appropriate area calculations into Eq. (13).

B. Collision efficiency and optimum dosage

Comparison of actual collision efficiency predictions with measured aggregation rates for different dosages is difficult since the aggregation rate is not solely dependent on the steady-state collision efficiency factor. Rather, the aggregation rate is dependent on both the steady-state collision efficiency factor and the mean collision efficiency factor up to the given point in time. This has been shown in some cases³ to produce a bimodal aggregation rate response to dosage rather than the expected monomodal response.

In previous work^{3,33} small-angle static light scattering data were presented representing the aggregation rate of oppositely charged polystyrene latex (PSL) particles in response to the relative concentration of each species (N_2/N_1 where N_1 is constant). These experiments were performed under perikinetic conditions at pH 5 and with a background electrolyte (KNO_3) concentration of 0.01 mol l^{-1} , corresponding to a κ^{-1} of approximately 3 nm. It was shown that

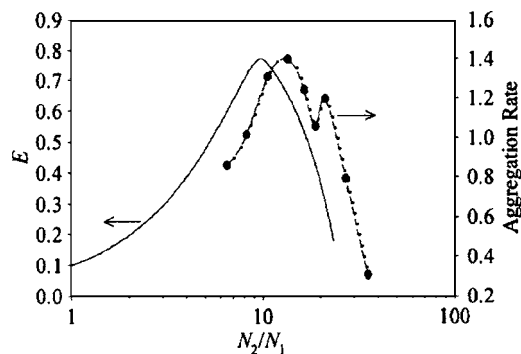


FIG. 4. Predicted (—) collision efficiency factor as a function of the number ratio oppositely charged particles (N_2/N_1) for a particle size ratio (R_2/R_1) of 0.24 compared with the measured (●) aggregation rate of anionic and cationic PSL particles ($R_1=310$ nm and $R_2=75$ nm) given in arbitrary units.

under these conditions a bimodal response to dosage was often observed, the significance of the uppermost peak on the abscissa (that related to the *mean* collision efficiency) decreasing with increasing difference in particle size.

Figure 4 shows the data presented for heteroaggregation of anionic and cationic PSL particles of radii of 75 and 310 nm, respectively. Note that both particle species are large compared with to κ^{-1} , as required in Sec. III A. As can be seen the lower (steady-state collision efficiency) peak is the dominant peak thus allowing the best possible comparison with the predicted collision efficiency factors, indicated by the solid line. While there is some offset between the predicted and measured values, the general shape of the curves are quite similar (ignoring the secondary peak in the case of the measured data of course). The offset may be due to the presence of the second peak shifting the apparent position of the lower peak upwards on the abscissa to some extent, or may simply be a result of error in the assumed particle sizes or concentration.

Data sets presented elsewhere³³ do not show such a dominant lower peak, however, and so comparisons with predicted collision efficiencies are much less successful: the greater the significance of the upper peak, the greater the distortion in shape of the lower peak. Nevertheless, the shift upwards of the actual position of the lower peak should not be so great as to disallow comparison with predicted optimum dosages (N_2/N_1) for maximum collision efficiency from Eq. (13).

Finding the value of (N_2/N_1) corresponding to the maximum value of Eq. (13) for a given particle size ratio requires an optimization routine, in this case a simplex search method using the MATLAB software package. It was noted that above certain values of (N_2/N_1), evaluation of Eqs. (17) and (19), prior to substitution into Eq. (13), yields negative values of $\Sigma A_{1(1)}$ and $\Sigma A_{1(2)}$, respectively. Negative values of surface area are clearly unphysical and so were assumed to be zero instead. It is likely that values of (N_2/N_1) yielding negative area values coincide with the prevention of large-large and large-small interactions due to the close proximity of adsorbed smaller particles.

Predicted optimum concentrations determined by optimization of Eq. (13) for a range of particle size ratios are presented in Fig. 5 (indicated by the solid line). Comparison

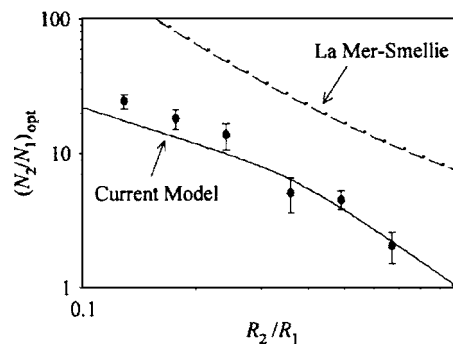


FIG. 5. Predicted (—) and measured (●) optimum ratios of anionic PSL particles to cationic PSL particles (N_2/N_1) for maximum $\langle E_{mm} \rangle$ for a range of particle size ratios (R_2/R_1) compared with the optima predicted by the Smellie–La Mer model (---). Error bars indicate the nearest dosage investigated.

of these predictions with those made using the half surface coverage condition (in this case, half the maximum packing density as calculated using the approximation suggested by Hansen and Matijević,³⁴ indicated by the dashed line) of the Smellie–La Mer model reveals a significant discrepancy, the predicted optimum being considerably less than that predicted by the Smellie–La Mer model.

The position of the lower peaks from the experimental data in literature^{3,33} is also presented in Fig. 5 compared with the predicted values from both the model presented herein and the Smellie–La Mer model. It can be seen that the measured optima (indicated by the closed circles) correlate very closely with the optima predicted by Eq. (13) (indicated by the solid line). By contrast, comparison with the optima predicted by the Smellie–La Mer model, indicated by the dashed line, shows the measured optima are at lower concentrations, in agreement with previously reported observations^{5,14,15} as mentioned.

A plot of the maximum collision efficiency factors, calculated using Eq. (13) at the predicted optimum dosage, for a range of particle size ratios is shown in Fig. 6. Unlike the Smellie–La Mer model, which predicts a maximum collision efficiency of 0.5 (after the correction made by Hogg⁵) at any optimum concentration irrespective of size ratio, the model presented herein predicts a maximum collision efficiency of 0.5 only if R_2/R_1 is equal to 1. With increasing difference in particle size the maximum collision efficiency asymptoti-

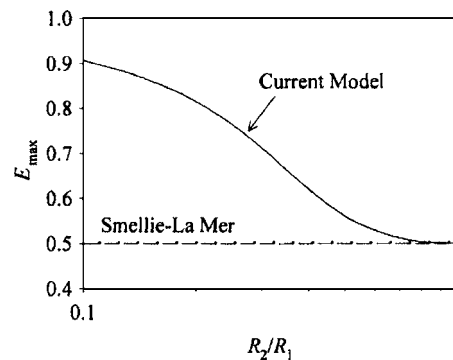


FIG. 6. Collision efficiency at optimum dosage for a range of particle size ratios predicted by the (—) current model and (---) Smellie–La Mer model.

cally approaches 1, accounting for the observation of Hogg that such collision efficiencies have been found experimentally.

While the above calculations work very well for heteroaggregation, making the assumption that a polymer chain adopts a coiled spherical conformation when adsorbed to a particle surface is probably oversimplifying the situation. Assuming a flat adsorbed conformation, however, as in the Smellie–La Mer model, is no doubt also an oversimplification. The true case probably lies somewhere between these two extremes, subject to the physical properties of the system that affect polymer conformation (e.g., particle collision time, the molecular weight of the polymer, and its affinity for the particle surface). Nevertheless, these models may allow us to can define upper and lower boundary conditions for optimum dosage, the current model being the upper boundary, and the Smellie–La Mer model being the lower, in terms of (N_2/N_1) . Obviously the flatter the conformation adopted by a polymer the closer the optimum should be to the lower boundary. However, given the widespread use of high molecular weight flocculants in concentrated suspensions of solid particles it is likely that in practice flattening will be minimal and the model presented herein will be more appropriate.

V. SUMMARY

A general quantitative theory has been presented relating the collision efficiency factor for a system of two oppositely charged species to the relative area of each exposed to the possibility of a collision. This differs from previous models, derived for polymeric flocculants, which relate the collision efficiency factor to the fractional surface coverage of polymer chains on particles. The theory has been applied to the specific case of a system comprised of two species of oppositely charged, nondeformable spherical particles as in heteroaggregation. Specific equations were derived for the collision efficiency factor for particle-aggregate and aggregate-aggregate collisions. Subsequent derivation of equations describing the shielded areas on particles within an aggregate allowed the calculation of actual collision efficiency factors for given particle size and number concentration ratios.

The validity of the model was tested by application to the prediction of the optimum number ratio of oppositely charged PSL particles for maximum aggregation rate. Comparison of the predicted optima with measured data from previous work shows an excellent correlation with the predicted values. The proposed model also accounts for previous observations^{16,17} of collision efficiency factors approaching unity, a phenomena that cannot be accounted for by the Smellie–La Mer model.

It is important to note that while a close correlation was observed, our model makes several assumptions that in many practical situations may not be correct. In particular, it is assumed that electric double layer interactions can be ignored. It is likely then that considerable deviation from predicted results would be observed if the same experiments were performed at a lower electrolyte concentration. Nevertheless, our model goes some way to explaining, at least

qualitatively, the discrepancies between the predictions of previous models based on particle surface coverage and experimental observations and provides a solid foundation from which models describing other systems (such as polymeric flocculants) may be developed.

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APPENDIX A: DERIVATION OF TOTAL EXPOSED AREA

The total area in m exposed to collisions, $\Sigma A_{m(T)}$, may be expressed as

$$\Sigma A_{m(T)} = \Sigma A_{m1(T)} + \Sigma A_{m2(T)}, \quad (\text{A1})$$

where $\Sigma A_{m1(T)}$ and $\Sigma A_{m2(T)}$ are, respectively, the total area of large and small particles in m exposed to collisions. Referring to Fig. 2, the area of attractive interaction on the smaller particles contained within an aggregate m , $\Sigma A_{m2(1)}$, forms a proper subset of (is entirely contained within) the area of repulsion, $\Sigma A_{m2(2)}$, which can be expressed as

$$\Sigma A_{m2(1)} \subset \Sigma A_{m2(2)}, \quad (\text{A2})$$

while for the larger particles the area of repulsion, $\Sigma A_{m1(1)}$, forms a proper subset of the area of attraction, $\Sigma A_{m1(2)}$, so

$$\Sigma A_{m1(1)} \subset \Sigma A_{m1(2)}. \quad (\text{A3})$$

Invoking Eqs. (A2) and (A3), $\Sigma A_{m1(T)}$ and $\Sigma A_{m2(T)}$ can be expressed as

$$\Sigma A_{m1(T)} = \Sigma A_{m1(1)} + (\Sigma A_{m1(2)} - \Sigma A_{m1(1)}) = \Sigma A_{m1(2)} \quad (\text{A4})$$

and

$$\Sigma A_{m2(T)} = \Sigma A_{m2(1)} + (\Sigma A_{m2(2)} - \Sigma A_{m2(1)}) = \Sigma A_{m2(2)}, \quad (\text{A5})$$

respectively. So Eq. (A1) can be expressed in its simplest form as

$$\Sigma A_{m(T)} = \Sigma A_{m1(2)} + \Sigma A_{m2(2)}. \quad (\text{A6})$$

APPENDIX B: DERIVATION OF SHIELDED AREA

The surface area of part of a sphere above the intersection of a plane (a spherical cap) is given by the equation

$$a = 2\pi R h, \quad (\text{B1})$$

where R is the radius of the sphere and h is the distance to the edge of the sphere perpendicular to the plane. Referring to Fig. 3(a), application of the law of cosines gives us

$$\cos \theta_{1(2)} = 1 - \frac{2R_2^2}{(R_1 + R_2)^2}, \quad (\text{B2})$$

and again for a right angle triangle,

$$\cos \theta_{1(2)} = \frac{R_1 - h_{1(2)}}{R_1}. \quad (\text{B3})$$

Equating (B2) and (B3) it can be shown that

$$R_1 h_{1(2)} = 2 \left(\frac{R_1 R_2}{R_1 + R_2} \right)^2, \quad (\text{B4})$$

which, by interchanging the numerical subscripts, must also be the solution to $R_2 h_{2(1)}$. So from Eq. (B1) $a_{1(2)}$ is equal to $a_{2(1)}$, both of which will be denoted as a for simplicity. So for all values of R_1 and R_2 , there is an equal area on each particle made unavailable for further adsorption of oppositely charged particles, given by the expression

$$a = 4\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right)^2. \quad (\text{B5})$$

The expressions for the shielded areas for repulsive interactions can be calculated using the same sequence of equations.

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