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A model of flocculation

Witold Brostow [a,*], Sagar Pal [b], Ram P. Singh [c]

[a] Laboratory of Advanced Polymers and Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, POBox 305310, Denton, TX 76203-5310, USA
[b] Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India
[c] Office of the Vice Chancellor, University of Lucknow, Lucknow 226 007, India

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Abstract

The phenomenon of flocculation in liquid suspensions has a variety of applications, including mineral processing, treatment of industrial effluents, and municipal sewage sludge purification. Obtaining metals from ores would not be possible without the slurry processing route. Flocculants play here a double role: limiting environmental contamination and also slowing down depletion of raw materials — including potable, industrial and agricultural water. Development of better flocculants requires improved understanding of the mechanism of their action. We propose a model of flocculation based on the assumption that effective flocculants pervade large volumes of liquids in the suspensions. Since many flocculants are polymers, good flocculants according to the model should have large radii of gyration R_G. We therefore assume a connection between R_G and settling velocities y of particles out of suspension. Four different types of aqueous suspensions are studied, containing in turn silica, coal, Mn ore and Fe ore. A unique relationship is demonstrated between R_G and y for several polymeric flocculants in each type of slurry. For each suspension type the corresponding equation has the form $y=aR_G^b$, where the two parameters characterize the suspended particles and the liquid medium. While polysaccharides from natural sources are used as flocculants, we show how their cationization enhances the flocculation efficiency in all media we have studied. Large effects are achieved for the flocculating agent concentrations in the range of 6–9 ppm.
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1. Introduction

Growing population causes a rapidly increasing consumption of raw materials on our planet, be they petroleum or water. Nuclear energy can be a substitute for petroleum; however, there is no substitute for water, possibly the most precious of all raw materials. In 2006 the Government of PR China has decided to spend US$41 billion on water purification in urban areas between 2007 and 2011 [1]. The main uses of water are in direct human consumption, in agriculture and also in a variety of industries. In the first two of these categories reusage is not possible, but in industry it is. Water is used, among other applications, in mineral processing, such as in bringing metal ores in the form of water slurries from their original location below the Earth surface to the surface and also in subsequent transport. Movement of coal from its deposits in coal mines and the subsequent surface transport similarly requires the use of water. To put it mildly, municipal sewage sludges deserve purification — the reason for the effort of the Chinese government just mentioned.

Reusage of industrial water and municipal sludges is based on getting the solid constituents out of suspension. With this task accomplished, the treated water can hardly be considered potable, but it can be reused by industry and in some cases (such as treated coal slurries) also as agricultural water. Two primordial objectives are accomplished at the same time: lesser contamination of the environment and slower depletion of raw water resources on Earth.

There is a difficulty in the basic process of getting the solid constituents out. Finely divided particulate matter *will not settle out of suspension* by gravity in an economically viable amount of time. The reason for slow gravity action is relatively small size of the particles, often with the diameter of ≈10 μm. We note that particle sizes in *emulsions* are still smaller, 0.05–5 μm

* Corresponding author.
E-mail addresses: brostow@unt.edu, vc@lkouniv.ac.in (W. Brostow).
URL: http://www.unt.edu/LAPOM/ (W. Brostow).

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[2], hence the removal of particles from emulsions (de-emulsification) is even more difficult.

Largely two processes are in use to accomplish the removal of particulate matter from suspensions: coagulation and flocculation. In the case of *coagulation*, destabilization of colloidal suspensions occurs by neutralizing the forces that keep the suspended particles separated [2,3]. The aggregates formed in the coagulation process are small and loosely bound; their sedimentation velocities are relatively low. Flocculation in liquid suspensions has been known for decades as a highly useful phenomenon [4]. In contrast to the process of coagulation, electric charge manipulation is not the dominant mechanism of action in *flocculation*. In fact, flocculation is possible without significant changes in the particle surface charges. Moreover, flocculation is much more effective than coagulation since the so-called flocs are larger and more strongly bound than the aggregates obtained by coagulation.

Better flocculants than the existing ones can be developed on the basis of improved understanding of flocculation. The already noted fact that electric charge variation is not the dominant type of behavior behooves us to explain the mechanism of the flocculation phenomenon, if possible, for a general case. That is, the proposed flocculation mechanism should not make appeal to the electric charge interactions. This situation is the starting point for the present paper.

2. Model development

In reviewing the literature on flocculation, it cannot escape one's notice that flocculating agents and drag reduction (DR) agents are often named in one breath [5]. In other words, a flocculating agent is expected to be also a DR agent. This poses an additional requirement on the model of flocculation we are now trying to develop: an explanation why a polymeric additive to a suspension causes flocculation has to include an explanation why the same polymer is also a drag reducer.

The new requirement actually helps us, since we do have a model of DR developed by one of us already in 1980 [6] and then further pursued by us [7–9].

The model is based on the assumption that each polymer chain pervades a volume in the liquid medium exceeding by far the dimensions of that chain. Among other observations, the fact that additives at concentrations as low as 10 ppm are effective as DR agents is thus explained. We note that flocculation agents are also effective at these very low concentrations. The original model of DR defined in [6] was provided with a direct experimental verification in 1999 [8]: the larger the solvation number of a polymer in a given liquid medium, the higher is the DR efficacy of that polymer. The solvation numbers have been determined by acoustic measurements.

As already noted, to explain the flocculation mechanism when an additive is placed in a suspension, we have to provide a model that explains the DR capability of the same polymer in the same base liquid. Since DR has been explained by large volumes pervaded by polymer chains in a given liquid, reconsider now possible measures of those pervaded volumes. The solvation number has served well the purpose [8]. However, the most often available measure of the pervaded volume is the radius of gyration. As discussed for instance by Gedde [10], the radius of gyration R_G is the root-mean-square distance of the collection of atoms from their common center of gravity:

$$R_G^2 = \Sigma_i m_i \mathbf{r}_i^2 / \Sigma_i m_i \tag{1}$$

Here m_i is the mass of the i-th atom while $\mathbf{r}_i$ is the vector from the center of gravity to that atom; the summations run over all atoms. As also discussed by Gedde [10], there are several methods of experimental determination of R_G, including light scattering and viscometry.

We now need a measure of the flocculation efficacy of a flocculating additive in a given type of suspension. There exists a so-called jar test in which the turbidity is measured as a function of polymer concentration. However, the experimental accuracy is not high. The resulting curves are often concave but in other cases they exhibit minima and/or maxima [11]. A better measure can be developed on the basis of settling times plotted as a function of the height of the interface. When flocculant is introduced into the container, an interface is formed. Above it is the supernatant liquid while below is the suspension containing the contaminants. Under the action of the flocculating agent, that is along with the progress of the flocculation process, that interface descends, until all contaminants are settled at the bottom. Curves of the interface height as a function of time are linear, except for the fairly short final parts which are concave. For instance, in the case of aqueous coal suspension the linearity is preserved over the first ≈20 cm fall of the interface height for all flocculating agents; see Fig. 1. The linear parts of such diagrams thus provide us with the *settling velocities* y which are used as a measure of the flocculant efficacy of an additive in a given suspension medium. Thus, the primary objective of the present work can now be restated as follows: we would like to define a quantitative relationship between y and R_G.

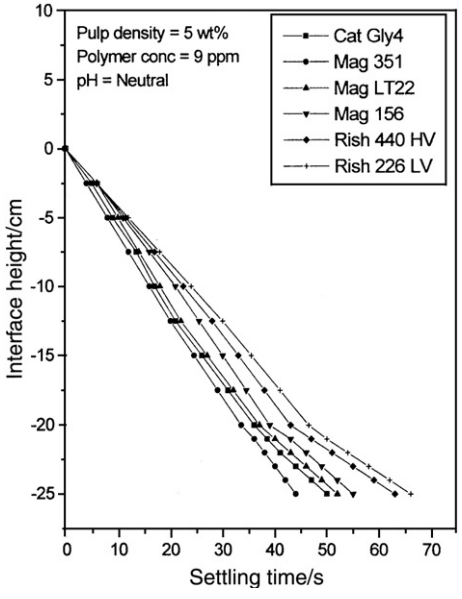

Fig. 1. Settling curves for coal suspension with addition of Cat Gly4 and several commercial flocculants (for the latter ones see the Materials subsection below).

3. Experimental

3.1. Materials

We have investigated polysaccharides, a widely used category of flocculants, available from a variety of natural sources and thus renewable, easily soluble in water, non-toxic, and with controllable biodegradability. Polysaccharides exhibit shear stability; in view of the model defined in the preceding section this fits with their flocculation capability. Cationization of polysaccharides has been known for more than 20 years [12]. There are a variety of applications; Zemaitaitiene and her colleagues have shown how textile dyes can be removed from solution by using an anionic flocculant [13]. It has been demonstrated in the laboratory of one of us that cationized polysaccharides have higher flocculation efficacy than the original ones [14] and their characterization has been provided [15]. Since one of the objectives of this work is also improvement of the flocculation efficacy, we have investigated several cationized polysaccharides — all with higher efficacies than the uncationized ones. Thus, amylopectin (AP), amylose (AM), glycogen (Gly) guar gum (GG, India is the largest exporter of GG in the world) and starch (St) have all been cationized by reacting each of them with *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC). Details of the synthesis are provided in [11] and [14]. Varying amounts of CHPTAC were used, and then for each starting polymer the cationized one with the best flocculation efficacy was characterized and studied more in detail. Those so studied are, in the obvious notation, Cat AP3, Cat AM, Cat Gly4, Cat GG4 and Cat St3. Radii of gyration in water of each of them have been determined [11] as described at the end of the present section.

Several commercial flocculants have also been applied, including three made by Ciba Specialty Chemicals Ltd., UK (Magnafloc 351, Magnafloc LT 22 and Magnafloc 156) and also by Rishabh Metals and Chemicals Ltd, Bombay (Rishfloc 440 HV and Rishfloc 226 LV). However, we were not able to include these materials in the present work since their R_G values are not available; possibly a given commercial flocculant consists of several materials since the chemical compositions of these flocculants are unknown.

3.2. Suspensions

To elucidate the flocculation mechanism, we have used four basic types of suspensions. Silica was supplied by Jyoti Chemicals, Mumbai, India. Coal sample (R-7 Jhanjra) was a gift from Coal Mines, Jharkhand, India. Iron and manganese ores were donated by Joda Mines, Jharkhand, India. The average particle sizes and specific gravities are listed in Table 1, along with the weight percentages of pulp used to create the suspensions. Concentrations of the polymeric additive were the same in each series of experiments: 6 ppm for the iron ore, 8 ppm for the silica, and 9 ppm for coal and for the manganese ore. These concentrations have been adjusted as follows. First, for each type of suspension we have started with 1 ppm only, then used 2 ppm, and so on. Initially the gradual increase of the flocculant concentration led to higher flocculation efficacy (determined as described below). However, for the iron ore suspension changing from 6 to 7 ppm of the flocculant has resulted only in a very small improvement in the flocculation efficacy. Therefore, for further more detailed studies of iron ore suspensions the 6 ppm concentration was retained. We have similarly arrived at the optimized flocculant concentrations for the other suspension types.

Table 1
Characteristics of suspended particles, parameters in Eq. (2) and goodness of the fit to the equation R^2

Medium	Pulp (wt.%)	Average particle size (nm)	Specific gravity (g cm^{-3})	*a*	b	R^2
Silica	3.0	102.3	3.10	1.138	0.222	0.967
Coal	5.0	79.6	1.40	0.539	0.120	0.977
FeO ore	10.0	105.7	3.45	0.632	0.174	0.985
MnO ore	3.0	86.9	2.50	1.181	0.291	0.983

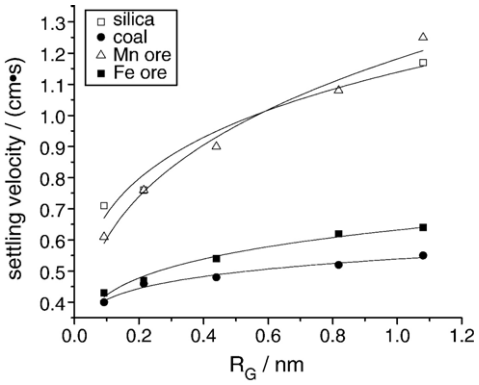

Fig. 2. Flocculation settling velocity for several suspension media as a function of the radius of gyration of the flocculating agent.

3.3. Determination of the flocculation efficacy

This has been accomplished as outlined above, see again Fig. 1.

3.4. Determination of the radii of gyration

R_G values have been obtained by using the static light scattering mode in the DLS-7000 Super Dynamic Light Scattering Spectrometer from Otsuka Electronics, Hirakata-City, Osaka, Japan. A procedure developed originally by Bruno Zimm and described for instance by Gedde [10] has been applied.

4. Model verification

We present the results graphically in Fig. 2. For every type of suspension investigated there is a one-to-one dependence between the settling velocity of the suspension and the radius of gyration of the flocculating additive applied.

For each medium the results shown in Fig. 2 can be represented as

$$y = a \cdot R_G^b \tag{2}$$

where a and b are parameters characteristic for a given suspension medium, that is both the dispersed phase and the majority liquid phase. Numerical values of these parameters are provided in Table 1 along with R^2 values. If the equation would fit the experimental data exactly, we would have R^2 equal to unity. We see in the table that the values of R^2 are close to one another while the lowest value is 0.967. Thus, Eq. (2) fits the experimental data within the limits of the experimental accuracy. As a corollary, lower R^2 values mean lower accuracy of experimental data for a given suspension class.

Once we have established the validity of Eq. (2), its use can also be inverted:

$$R_G = (y/a)^{1/b} \tag{3}$$

5. General overview

One of us has formulated the Easy Accessibility Model (EAM) [16,5,17]: the moiety grafted on a polysaccharide has more opportunity to form aggregates of the contaminants. Since grafting enlarges the pervaded volume and thus increases the radius of gyration, the model defined in Section 2 can be considered as an extension of EAM.

We recall the difference between coagulation and flocculation noted in Section 1: coagulation relies on a manipulation of electric charges. Flocculation does not, and our model does not consider electric charges. Needless to say, whatever is the electric charge interaction between the flocculation additive and the base liquid, it is reflected in the respective R_G value.

The data we have used pertain to aqueous solutions. However, the model of flocculation formulated in Section 2 makes no assumption on the nature of the liquid phase. We recall once again the flocculation–drag reduction connection and the fact that DR agents are used also in organic media. These cases include using polystyrene in toluene [6] as well as for instance the study by Choi and coworkers on polyisobutylene as a drag reducing agent in kerosene [18]. In the preceding paper [9] we have used amylopectin as a DR agent, while here its cationized form is a flocculating agent. Since large pervaded volume enhances both DR and flocculation, the condition for the flocculation mechanism explanation defined in the beginning of Section 2 is fulfilled as well.

We have began this article with the need for slower depletion of Earth's natural resources and also for at least slowing down contamination of the environment. As noted in Section 3, we have used flocculant concentrations in the 6–9 ppm concentration range. Thus, small indeed amounts of flocculating agents cause large desired effects. Since those agents are polysaccharides of natural origin, they are available worldwide, inexpensive, and by themselves do not cause environment contamination. Our own flocculating agents created by cationization of polysaccharides have higher flocculation efficacy than natural polysaccharides — while sharing with natural polysaccharides their other advantages.

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