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A Generalized Description of Aquatic Colloidal Interactions: The Three-colloidal Component Approach

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This paper describes several possible interactions among the different types of organic and inorganic aquatic colloids, based on our present knowledge of their size, electric charge, and conformation. The physicochemical properties of the different groups of colloids are described. Emphasis is placed on the various types of organic components, including fulvic compounds. Subsequently, the role of each colloid class is discussed with respect to homoaggregation (aggregation within a given colloid class) and heteroaggregation (aggregation among different colloid types). On the basis of a synthesis of literature reports, microscopic observations of natural colloids, experimental results obtained with model systems, and numerical simulations, it is concluded that the formation of aggregates in aquatic systems can be understood by mainly considering the roles of three types of colloids: (i) compact inorganic colloids; (ii) large, rigid biopolymers; and (iii) either the soil-derived fulvic compounds or their equivalent in pelagic waters, aquagenic refractory organic matter. In most natural aquatic systems, the small (few nanometers) fulvic compounds will stabilize the inorganic colloids whereas the rigid biopolymers (0.1−1 μm) will destabilize them. The concentration of stable colloids in a particular aquatic system will depend on the relative proportions of these three components.

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Introduction

In aquatic systems, the key role of submicron colloids in the transport of trace metals and organic compounds is now well documented. Through covalent, electrostatic, or hydrophobic interactions (*1, 2*), a large proportion (often 40−90%) of trace compounds may be adsorbed on marine (*3*) and freshwater colloids (*4*). Consequently, the properties and behavior of the submicron colloids will play key roles in the fate of trace compounds since colloids that are stable in solution may be transported long distances whereas coagulation or flocculation may facilitate colloidal elimination through sedimentation. In complex systems such as natural waters, colloid aggregation is ubiquitous due to the large number of colloid types and reactive sites. Indeed, size fraction analysis of natural aquatic colloids often demonstrates (*5*) a physicochemical uniformity among all fractions. This implies that, when making predictions on the circulation of trace compounds in natural waters, it is at least as important to understand the interactions of the major colloid groups as it is to determine the binding energies of trace compounds to each type of colloid. While the latter data have become available in recent years (*1, 2*), much work still remains to be done to determine the structural properties (*6*) and interactions of the colloids.

In this context, a key question to be resolved is related to the exact role of natural organic matter (NOM). It is generally accepted that NOM will stabilize inorganic colloids in natural waters (*7, 8*) as was discussed by Hahn and Stumm as early as 1970 (*9*). Nonetheless, the opposite phenomena has also been shown to occur with specific groups of NOM, in particular, the polysaccharides (*10, 11*). It is therefore essential that the specific behavior of the major groups of NOM be considered, by taking into account relevant physicochemical parameters such as molar mass, size, and electric charge density and conformational information such as the persistence length, gyration radius, or fractal dimensions (*12, 13*). This information is more difficult to obtain than the corresponding parameters that are necessary to model the behavior of inorganic colloids (mainly hydrodynamic radius and electric charge density; *14*). It is therefore not surprising that no generalized predictive model of colloidal interactions exists that includes the different types of organic biopolymers which comprise the majority of NOM. Nonetheless, it is possible to qualitatively classify the major inorganic and organic submicron colloidal components with respect to their structure and behavior, by comparing data obtained through (i) classical analysis, (ii) microscopic observations of aquatic colloidal components, (iii) studies of model experimental systems, and (iv) numerical simulations (*15, 16*).

The main objective of this paper is to gather information that is spread over the literature in order to facilitate its comparison, with the goal of understanding colloidal aggregation in natural systems. An important conclusion will be that a realistic description of colloidal systems in natural waters is possible by considering three colloid types: (i) inorganic colloids, (ii) fulvic compounds (pedogenic) or aquagenic refractory organic matter (pelagic systems), and (iii) biopolymers forming rigid fibrillar structures (hereafter referred to as rigid biopolymers). It is understood that the conclusions presented here are simplified and somewhat provocative; however, the purpose of this paper is to point out key aspects of the behavior and role of aquatic colloids in order to stimulate research in this area.

Experimental Considerations

It is out of the scope of this paper to discuss, in detail, the methodologies that were used to obtain the reported information. The reader is instead referred to the cited literature. Nonetheless, it must be noted that it is difficult to work with colloidal systems and that several precautions are thus required both to avoid artifacts during the collection, storage, and fractionation steps (*17*−*20*) and to properly prepare samples for microscopic observation (TEM: refs *19* and *21*−*23*; AFM: refs *17* and *22*). As no single technique is without potential artifacts, correct interpretation of colloid and aggregate structure must be based upon a large number of observations, using a combination of several techniques in parallel (*24, 25*).

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TABLE 1. Characteristics of Inorganic Colloids[a]

nature of solid	pH_{zpc}	site density[c] (nm^{-2})	specific surface area ($m^2\ g^{-1}$)
am-SiO_2	3.0−3.5	4.5−12	40−260
am-FeOOH	7.9−8.1	0.1−0.9 mol/mol of Fe	160−700
am-Al_2O_3	≈9.4	2−12[d]	
am-MnO_2	≈2.3	6−20[d]	260
allophanes		0.4−1.2	500−700
kaolinite	3.3−4.6[b]	0.6−3.6	10−20
chlorite		0.6−2.4	92−97
illite		0.9−2.7	90−130
smectites	≤2.5[b]	0.5−1.0	750−800
vermiculites		0.9−1.6	750−800

[a] Values are taken from refs *6* and *26*. Values are given for amorphous phases of metal oxides that should be more representative of natural colloids. [b] Values of pH at the isoelectric point and not at the zero point of charge (=pH_{zpc}). [c] Site density corresponds to the maximum negative charge density for $pH \gg pH_{zpc}$. [d] Values for crystalline forms of Al_2O_3 or MnO_2.

Nature and Morphology of Major Aquatic Colloids

The definition that we will employ for a colloid is any organic or inorganic entity large enough to have supramolecular structure and properties (e.g., possibility of conformational changes for organic colloids or a electrical surface field for inorganic colloids) but small enough not to sediment quickly (hours−days) in the absence of aggregation. This definition implies that the colloidal size range will typically be between 1 nm and 1 μm. Even though macromolecules such as the fulvic compounds have a size and properties on the lower limit of the colloidal size range, they clearly have colloidal properties and will be treated as such here. On the other hand, small organic molecules such as the amino acids, or monosaccharides will not be considered here.

The major inorganic colloids (IC) found in oxic waters include (Table 1; *1*, *6*, *26*−*28*) aluminosilicates (clays), silica, and iron oxyhydroxyde particles (Figure 1A,B). Calcium carbonate is usually found in larger particle sizes. Microscopic images demonstrate that waterborne iron oxyhydroxydes and some silica particles are near spherical although silica may also be found as irregularly shaped diatom-derived debris. Most aluminosilicates are angular, sheetlike particles. Other inorganic colloids can also be found, but they are usually minor components (e.g., aluminum or manganese oxides) or only present in anoxic waters (e.g., elemental sulfur or FeS). Despite their variable shapes, the major inorganic colloids are often "compact" particles. Apart from the iron oxyhydroxydes that are neutral or positively charged in the circumneutral pH range, the major inorganic colloids are negatively charged in water, due to their low zero point of charge (Table 1; *1*). It is therefore reasonable to represent the submicron inorganic colloids as compact, often negatively charged particles that cover the whole colloidal size range (*27*, *30*).

The nature of NOM has been reviewed previously (*6*, *31*). Three classes of aquatic organic compounds will be discussed here with respect to their colloidal properties (Table 2): the rigid biopolymers, the fulvic compounds, and the flexible biopolymers. Rigid biopolymers (RB) mainly include the so-called structural, fibrillar polysaccharides or peptidoglycans released from plankton as exudates or cell wall components (Figure 2A,B and Table 2, Section A; *6*, *34*, *38*, *46*). They constitute a significant proportion of NOM, varying seasonally between 10 and 30% in the surface waters of lakes (*6*, *11*, *31*) and likely comprise an even larger proportion in the surface waters of marine systems (*17*, *47*). They are refractory enough to be found in the deep ocean where they may have lifetimes of hundreds of years (*3*). Their intrinsic rigidity often comes from their associations into double or triple helices that may be stabilized by hydrogen or calcium bridges (*44*) or the fact

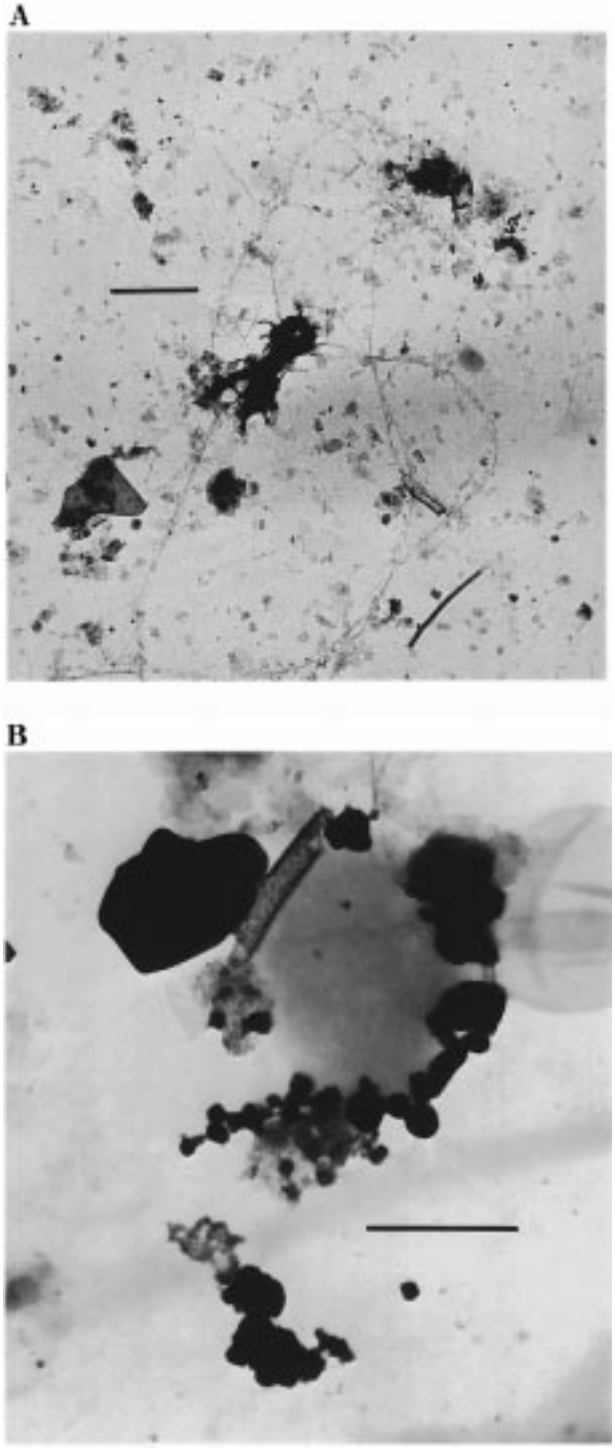

FIGURE 1. TEM image of inorganic colloids and aggregates with NOM carefully embedded in a hydrophilic resin (see ref *28* for experimental conditions). (Panel A) Colloids in the supernatant of mildly centrifuged Rhine River sample (centrifugation eliminates particles larger than a few micrometers). Images show isolated clay colloids and their compact aggregates as well as clay colloids associated within a fibril network (adapted from ref *29*). Scale bar corresponds to 1 μm. (Panel B) Compact heteroaggregate from Lake Bret, Switzerland (no fractionation before embedding colloids in resin). The picture shows a spherical silica particle (gray at center) aggregated with smaller iron hydroxide particles (black spheroids), a clay particle, and some biological debris. Scale bar corresponds to 250 nm.

TABLE 2. Characteristics of Major Groups of NOM[a]

nature (origin)	molar mass (Da)	dimensions (nm)	supramolecular structure	electrical charge for fully dissociated sites (mequiv g^{-1})	av age or degradation time
Section A: Rigid Biopolymers (RB)					
mucopolysaccharides, peptidoglycanes, hemicellulose, pectic compounds (microbial cell walls + extracellular products) (*32*−*34*)	10^4−>10^5	thickness: 1−3; length: 100−>1000 (*22*, *38*, *39*)	fibrillar structures based on double or triple helix formation (*44*); sometimes coils or gels depending on nature of cation, pH, or ionic strength (*45*)	minimum: 0; typically: −0.35 to −0.83; maximum: ∼−6	months (surface waters) to centuries (deep waters)
Section B: (Soil-Derived) Fulvic Compounds (FC)					
see Figure 3A for composition (fulvic fraction of soil leached out by rainfall)	500−5000 typically: number average = 2300; weight average = 1000 (*6*, *35*, *36*)	Stokes radius = 0.4−1.4 (pH 1−10) (*40*); gyration radius = 0.5−1.4 (different samples) (*41*, *42*)	spheroids; aggregates of spheroids; occasionally gels (*22*)	−6 to −11	∼450 years in soils
Section C: Flexible Biopolymers (FB)					
aquagenic refractory organic matter (AROM) (recombination of amino acids, sugars, etc. released by plankton)	500−800 (*43*)		flexible	−2.1 to −5.5 (*54*)	10−7000 years
reserve polysaccharides (internal cellular content)			flexible		hours to days (*6*, *34*)
proteic compounds	<a few times 10^4 (*37*)		flexible		hours to days (*6*, *34*)

[a] Unless otherwise stated, the information in this table has been taken from chapters 3, 4, and 6 of ref 6 and references therein. Values are representative; an exhaustive bibliography cannot be given here.

that the helices themselves may aggregate together. In addition, they are highly hydrated (up to 80%) and their rigidity results, in part, from a significant proportion of strongly bound water. TEM and AFM images of marine and freshwater biopolymers (Figure 2A,B) show that their total length may be larger than 1 μm, whereas their thickness is often only a few nm (Table 2, Section A). Table 3 gives examples of some of the important physicochemical parameters of purified, structural polysaccharides produced by microbes, with varying degrees of rigidities. Some polysaccharides have the capacity to form gels depending on the nature of bound cations (*48*). In addition to polysaccharides, RB may include biopolymers such as DNA released by plankton upon death, but these are generally minor components (*6*). The maximum charge densities of polysaccharides (when all the ionizable groups are deprotonated) are typically in the range 0 to −0.8 mequiv g^{-1} although polyelectrolytes such as alginates are exceptions (maximum charge density of ca. −6 mequiv g^{-1}).

Fulvic compounds (FC) generally represent the largest NOM fraction in freshwaters (typically 40−80%; *6*, *31*). Because they are primarily of pedogenic origin, they may also be present in the coastal waters of oceans but are absent from the pelagic zones (*6*, *17*, *31*). FC are chemically heterogeneous polymers (Figure 3A, Table 2, Section B) with a small molar mass (typically ∼1000 Da), high charge density at neutral or alkaline pH values, and typical average lifetimes of several hundred years. Soil-derived humic acids generally have higher molar masses and lower charge density than FC but have otherwise similar properties. In any case, they are generally minor components of NOM in waters (<5−10%). Due to the significant degree of branching of FC (Figure 3A), their high charge density at pH > 5 and degree of hydration (40% strongly bond water: 6): they are less flexible than linear biopolymers such as proteins (see below). Methods enabling either direct observations (TEM: Figure 3B; AFM: Figure 3C) or indirect measurements of size and shape (ultracentrifugation: 50; voltammetry: 51; fluorescence correlation spectroscopy: 25; fluorescence polarization: 52) suggest that, in dilute solutions (<10 mg L^{-1}) at circumneutral pH and low ionic strength ($\leq 10^{-2}$ M), FC behave as small rigid globules with diameters of 1−3 nm. Although FC are sometimes represented as linear polyelectrolytes, the linear representation of FC does not fit with either the experimental measurements discussed above or the more modern models that consider FC as highly branched molecules (see Figure 3A or ref *53* for a Monte Carlo based 3-D structure). Nevertheless, much remains to be learned about the structure of FC, in particular, at high concentrations and low pH and ionic strength.

Flexible biopolymers (FB) include three main groups of compounds: aquagenic refractory organic matter (AROM), reserve polysaccharides, and proteins (Table 2, Section C). AROM is composed of the chemically heterogeneous compounds produced in the water column, primarily by recombination of degradation products of microbial cells (see ref *54* for a model structure). AROM components are thus equivalent to the fulvic compounds produced in soils except that they are more aliphatic, have a slightly smaller charge density and molar mass (800 Da), and are less hydrophilic than FA (Table 2, Section C; *6*). The concentration of AROM rarely exceeds a few milligrams per liter. In streams, rivers, and small lakes, AROM normally represents a minor fraction of the NOM that is dominated by fulvics and, to a lesser extent, polysaccharides. In the pelagic waters of oceans and large lakes, AROM may represent up to 90% of the NOM.

Reserve polysaccharides are degraded within hours to days of their release in the water column (*6*, *34*). Proteins also form a part of the pool of intracellular material that is degraded within hours to days upon microbe death (*55*), consistent with the observation that the amino acid contents of sediment traps declines rapidly with depth (*56*) and data

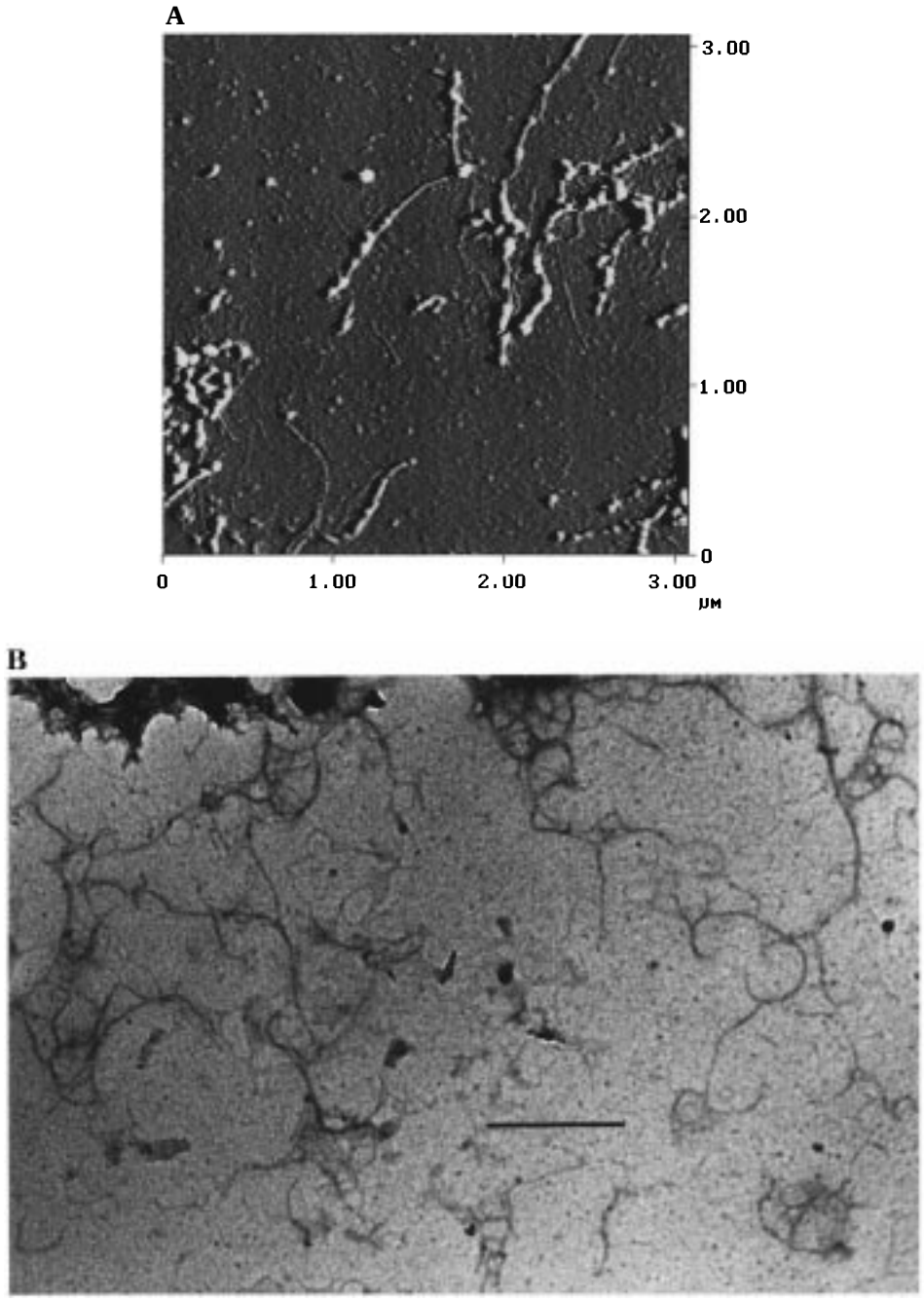

FIGURE 2. (Panel A) AFM pictures of fibrils extracted from the pelagic zone of the Gulf of Mexico (*17*). Compact colloids appear to be associated with most fibrils. Note that fibril thicknesses as read on the horizontal dimensions of AFM images are overestimated due to the nature of the technique (*22*); only vertical thickness measurements give realistic values. (Panel B) TEM images of fibrils (high polysaccharide content) extracted from Lake Bret (*11*). Scale bar corresponds to 250 nm.

which indicates that protease activity is high in aggregates found in surface waters (*57*). Since aquatic proteins generally have a molar mass that is in the tens of thousands and include a significant proportion of hydrophobic moieties, they will tend to form globules with diameters that are typically <3−4 nm (*6*).

A clear discrimination between polymers with rigid rod or coil structures is not possible. Alginic acid is an example of a semiflexible polysaccharide with intermediate properties to the biopolymers discussed thus far. It has larger molar mass than most of the flexible biopolymers (Table 3) and the highest maximum charge density of the natural polyelectrolytes (up to −6 mequiv g^{-1}). In principle, the conformation of ionizable polymers may change drastically with charge density (and therefore pH and ionic strength), passing from coil to rodlike conformation when going from low to high charge densities. For example, for polymethacrylate, the transition from a coil to a rod (*67*) is observed for a charge density of ∼4 mequiv g^{-1} (close to the maximum value of alginate). In natural waters, however, the charge density of polyelectrolytes may be significantly lower than their maximum value due to uneven distribution of charge because of polymer heterogeneity, partial protonation, complexation by metals or by an electrolyte screening, especially in seawater. It is therefore most likely that even the highly charged alginate would exist as extended coil rather than a rigid rod in natural waters (Table 3) and that electrostatic effects will not be sufficient to provide rodlike structure to any other natural biopolymers whose charge and size are usually smaller than those of alginate. In any case, because

TABLE 3. Representative Values of Physicochemical Parameters of Some Microbially Produced Polysaccharides

compound	molar mass (M_w)[a] (kDa)	gyration radius, R_G (nm)	persistence length (nm)[c]	comments	ref
schizophyllan	400−500	NA[e]	130−190	neutral, rigid, rod-like, triple helical structures	58
xanthan	100−2500	NA	100−140	single- or double-stranded structure; up to two carboxyl groups per five sugar repeating unit	59, 60
gellan	100−2000	NA	100−140	single-stranded or double-helical structure depending on conditions; negatively charged polysacharide	60, 61
alginate	200−2000	110[b,d]	9	negatively charged polyelectrolytes; extended random coils	62, 63
dextran	3−2000	20[b]	2.75	neutral; dense coil	64, 65

[a] Note that in general polysaccharides are polydisperse with respect to molecular weight since (i) they are not coded for in the DNA of the organism but are synthesized by polymerase enzymes and (ii) during extraction there is substantial depolymerization. For this reason, values given are representative only, designed to give the reader an idea of the natural variations of the molar masses. [b] Radius of gyration for molecule of $M_w = 500$ kDa. [c] The persistence length corresponds to the length of a statistically straight segment in the polymer chain and gives an indication of the rigidity of the polysaccharide. For example, schizophyllan has a total length of approximately 210 nm (*58*) of which ca.. 160 nm lies along a single axis. [d] Estimated from $R_G = 0.095 M_w^{0.54}$ (*66*). [e] NA, not applicable.

the exact concentration of these semiflexible polyelectrolytes is poorly known, their exact role can presently only be hypothesized.

Colloid Interactions

For most oxic waters, the size distributions of organic and inorganic colloids follow Pareto laws in the nanometer to micrometer range, with slopes between −2 and −3 (*27, 30*). These size distributions are not representative of isolated colloids but of the colloids plus their aggregates. Indeed, colloids of a given type (e.g., clays, fulvic acids, iron hydroxides) may aggregate together (homoaggregation) or with colloids of other types (heteroaggregation). General quantitative physicochemical theory exists only for the homoaggregation of compact particles, based on Smoluchowski equations and DLVO theory (*2, 14, 68−70*). These theories, combined with complementary hydrodynamic forces, have significantly contributed to our understanding of the behavior of particles larger than 0.1 μm in environmental systems (*1, 30, 69−71*). Nonetheless, there is no such general theory for heteroaggregation, especially for aggregation involving polymers, despite an important literature on the physicochemical properties of polymers and their interactions with compact colloids (*12, 13*). The section below summarizes our present understanding of the aggregation properties of the major aquatic colloids.

Homoaggregation of Major Colloids. According to DLVO theory, the interaction energy between two compact, spherical colloids results essentially from (i) their surface charge, which defines the electrical field around each particle, and (ii) the attractive van der Waals forces between them. The electrical field is always repulsive in homoaggregation, whereas it may be attractive or repulsive in heteroaggregation, depending on the nature of particles. The electric and van der Waals forces defines an energy barrier which, if overcome by the kinetic energy of particles moving in water, will lead to aggregation and an unstable suspension. It has been shown for submicron colloids that this kinetic energy results mainly from Brownian motion and little from hydrodynamic or gravitational forces (*30, 69, 71*).

Application of these principles to compact, inorganic colloids (IC) has provided the following information:

(i) In natural waters, IC include a large number of chemically different particles, so that in reality only heteroaggregation occurs. In practice, however, homoaggregation models that assume that all particles have similar surface properties have been reasonably successful. This is likely due, at least in part, to the fact that in natural waters most IC are covered by a similar adsorbed layer of fulvic compounds in freshwater (*8, 72*) and possibly AROM in seawater (see below). This adsorbed layer will fix the surface charge of the compact colloids. Therefore, to a first approximation, inorganic colloids can be treated as a single class of colloidal compounds, irrespective of their nature, for which only size polydispersity has to be considered (*30, 69, 71*).

(ii) The observed size distributions of inorganic colloids above 0.1 μm can be reasonably predicted by the classical Smoluchowski/DLVO theory combined with some additional hydrodynamic forces (*5, 30*). For inorganic colloids below 0.1 μm, organic matter, in particular the rigid biopolymers (RB), dominate aggregate structures (*15*) so that the above theory is no longer applicable.

(iii) Aggregates of compact inorganic colloids alone are usually formed slowly (reaction limited aggregation, RLA) because the collision efficiency between particles is low due to the significant repulsive charge of the inorganic colloids covered by fulvics. This results in compact aggregates (Figure 1B; Figure 4), which even after 1 week do not exceed 1 μm (Figure 4; *30*). Sedimentation of the submicron inorganic colloids is thus unlikely to occur by this aggregation process alone.

Homoaggregation of fulvics (FA) has been largely mentioned in the literature, but there is comparatively very little quantitative data. The data that are available have been obtained by viscosimetry, light scattering (*73*), fluorescence (*52*), ultrafiltration (*74*), and particularly TEM (transmission electron microscopy; *17, 22, 74, 75*) and AFM (atomic force microscopy; *22, 76, 77*) (Figure 3B,C). In these studies, homoaggregates of fulvics with similar structures as those formed by inorganic colloids (Figure 4) are observed in the pH range 5−8, for which COOH groups are dissociated (*6, 74*). Since under these conditions fulvics can be considered as charged globules (see above), it is likely that, as a first approximation, the Smoluchowski/DLVO theory is applicable, although for such small colloids, hydration effects and reversible aggregation must be considered (*78*). Furthermore, since a low collision efficiency is expected for low ionic strength waters, compact RLA-type aggregate structures should be observed. In high ionic strength marine systems, a loose aggregate structure is more likely to be observed due to a higher collision efficiency. Although no systematic study has been performed in this field, a few qualitative observations support the above assumptions for both freshwater and seawater (Figure 3; *22, 24, 74*). To the best of our knowledge, no similar information is available with respect to the possible homoaggregation of AROM.

Homoaggregation of rigid biopolymers (RB) has mainly been examined with respect to the gelling properties of the rigid polysaccharides. For example, it is known that double

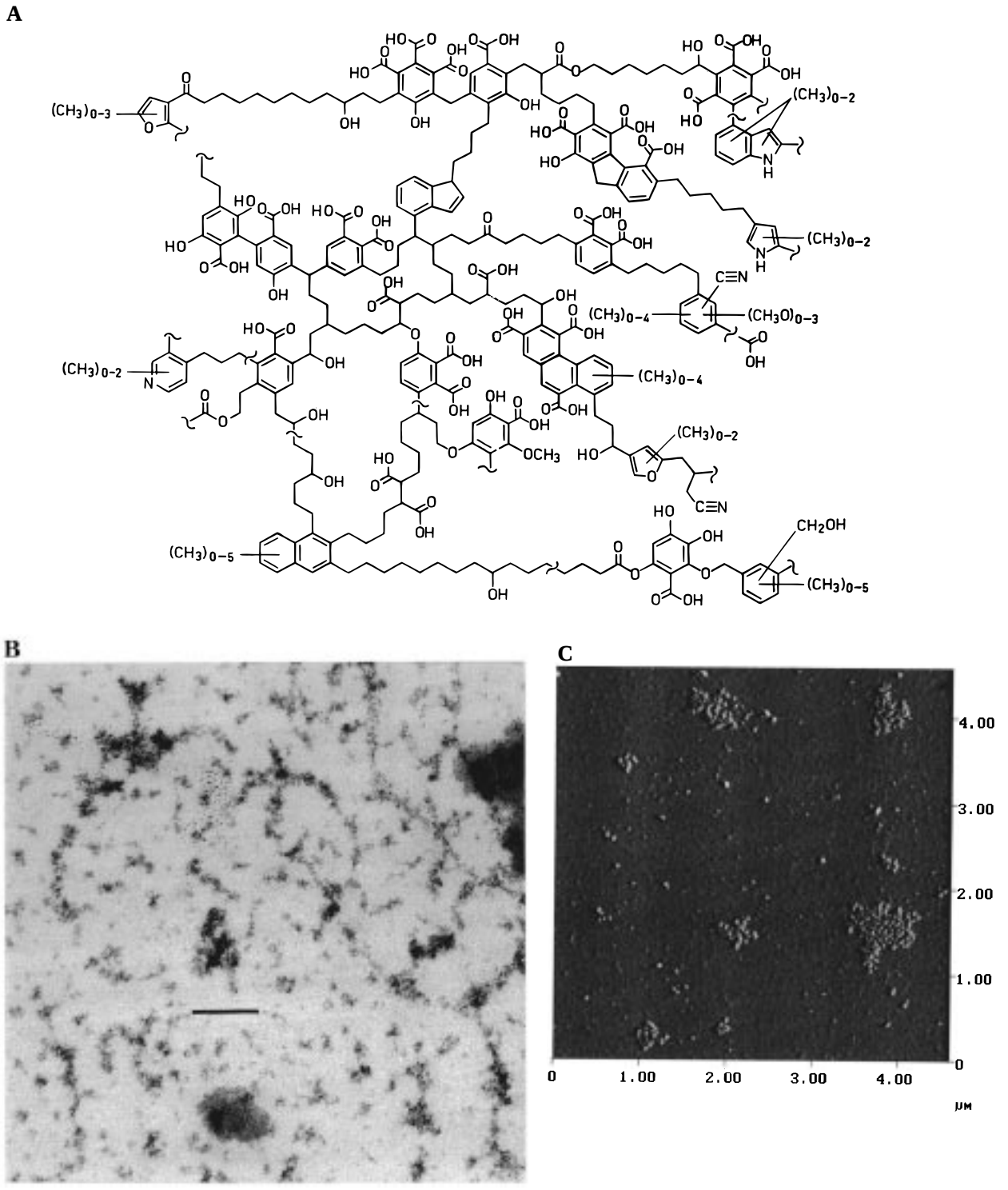

FIGURE 3. (Panel A) Proposed chemical formula for fulvic compounds (*49*). (Panel B) TEM image of FC-rich NOM from a Lake Bret sample (pH 7.5; ionic strength $\sim 10^{-2}$ M). No fractionation was performed prior to embedding in resin. This image is interpreted as having individual FC macromolecules (the smallest black points), homoaggregates (association of black points) and FC associated with fibrillar compounds. Scale bar corresponds to 100 nm. (Panel C) AFM image of a Laurentian soil fulvic compound (pH = ~6.5; ionic strength = $\sim 10^{-2}$ M) showing isolated FC (individual points) and FC aggregates (*22*). The thickness of the adsorbed FC is typically 0.4−2 nm based on two studies on different humic substances (*22, 25*). Note that the horizontal AFM dimensions given in panel C are greatly overestimated for macromolecule widths which are much smaller than the radius of curvature of the AFM tip (~20−50 nm); see Figure 2A.

or triple helices can be formed by hydrogen bonds or cation bridging between individual polysaccharide chains. The fibrils formed in this manner are quite rigid (Tables 2, Section A, and 3) and can be further aggregated (Figure 2). In some cases, the helices once formed are very stable, but in others there may be a transition between a helical and random coil conformation (*79*) that is dependent upon temperature, pH, ionic strength, and calcium content.

Heteroaggregation of Small Organic Biopolymers (FC or FB) with Comparatively Large Inorganic Colloids (IC). As mentioned above, the hydrodynamic diameter of fulvic compounds is 0.8−3 nm (Table 2, Section B), so that for any

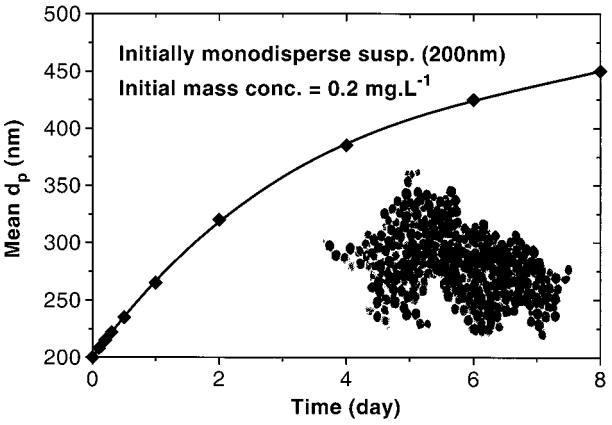

FIGURE 4. Time evolution of the mean diameter of compact colloid aggregates, based on DLVO−Smoluchowski theory, assuming an initial suspension of monodispersed colloids with size = 200 nm and typical lake or river water concentration = 0.2 mg L^{-1} (*5*). Note that 200-nm aggregates are formed almost instantaneously from a uniform size distribution of individual colloids in the size range of 1 nm−100 μm (*30*). The very slow size increase above 400 nm is due to the corresponding low values of diffusion coefficients. (Simulation conditions correspond to typical river water: see ref *5* for detail.) The inset shows a TEM micrograph of a compact homoaggregate of 50-nm hematite particles formed under conditions of slow, reaction limited aggregation.

inorganic colloid larger than 10−20 nm the interaction between FC and IC will correspond to the adsorption of the FC on the colloid surface (*2, 6, 80, 81*). The net result is mainly a modification of the surface properties of the colloid (surface potential and dielectric constant), both of which are included in the DLVO/Smoluchowski model. Indeed, as was discussed, inorganic colloids in contact with fulvics tend to have a similar negative surface charge (*8, 72*), irrespective of their intrinsic chemical nature. In the normal range of pH (5−8) and FC concentrations (0.5−10 mg L^{-1}) in freshwaters, this effect should stabilize a colloidal suspension (*70, 82*) due to electrostatic repulsion. Steric repulsion of IC by adsorbed FC would increase the stabilization effect as compared to the electrostatic repulsion alone. It is however unlikely to play a significant role, since the thickness of adsorbed FC molecules is small (AFM measurements typically give 0.4−2 nm; *22, 25*). These same AFM results suggest that multiple layers of FC do not form on mica by adsorption from dilute solution (<10 mg L^{-1}) at circumneutral pH. For fulvic concentrations larger than 5−10 mg L^{-1}, stabilization of IC by adsorption of FC aggregates on their surface or their embedding in a gel-like structure (*22, 76*) is possible; however, little information is presently available.

To our knowledge, there is also very little specific information on the interactions of the flexible biopolymers (FB) on inorganic surfaces in natural waters. On the basis of the properties of FB (Table 2, Section C), it can be inferred that reserve polysaccharides and many proteins will be quickly degraded and therefore play a negligible role. In pelagic waters, AROM and some recalcitrant proteins have the potential to play a role similar to that of FC in freshwaters since they are small (1−5 nm) polymers with hydrophobic moieties that will favor their adsorption on surfaces as thin films.

In summary, it is likely that the major influence of the fulvic compounds and the recalcitrant, flexible biopolymers on comparatively large inorganic surfaces will be a modification of the surface charge of the colloids. The net effect will depend on surface coverage of IC by FC or FB and the corresponding degree of charge neutralization of IC. For model compounds, it has been shown (*1, 2, 82, 83*) that adsorption of negatively charged FC or FB on positively charged IC (e.g., hematite) will result in destabilization only for surface coverages very close to charge neutralization. IC suspensions are thus stable at either lower or larger coverage. For the adsorption of such small polymers on comparatively large IC, surface coverage can be computed from the adsorption equilibrium constant and the maximum sorption capacity of IC (*1, 2*). Very little information is available on the adsorption properties of aquatic FB, and those of the FC have been studied mostly with model IC such as iron or aluminum oxides (*6, 8, 84*). Laboratory studies of both metal oxides and clays (*7, 8, 11, 85*) suggest that strong adsorption occurs and that very low concentrations of FC (≤1 mg L^{-1}) are sufficient to stabilize IC at colloid concentrations typical of natural waters (<10 mg L^{-1}). This result appears to be confirmed by macroscopic field studies (e.g., refs *69* and *86*).

More detailed information is still needed on the interactions of FB and FC with natural IC. Both natural surfaces and biopolymers are physically and chemically heterogeneous. Neighboring parts of a surface may have different charges or charge densities. Aggregation might then occur due to interactions of surface patches that do not necessarily represent the global surface characteristics. Conclusions drawn from studies using homogeneous polymers and colloids should therefore be used with caution when making predictions in environmental systems.

Heteroaggregation of Large Semiflexible Biopolymers (FB) with Inorganic Colloids (IC). The importance and role of large extended coil polymers such as alginate are largely unknown. For interactions with positively charged colloids such as iron oxyhydroxides or iron oxyhydroxide-coated particles, negative coil-like polymers will tend to collapse at the colloid surface due to the strong electrostatic attraction. This has been observed by electrophoretic mobility and light scattering measurements using model negatively charged flexible polymers [poly(acrylic acid) or hydrolyzed polyacrylamide, M_w of 10^6 Da] and positively charged colloids (hematite, 50 nm). The main conclusions of these studies are the following (*83*, *87*, *88*; Table 4):

(i) As for small polymers, charge neutralization of the inorganic colloid by adsorption of large polymers plays a key role in aggregate formation, irrespective of polymer size (Figure 5). The bridging of inorganic colloids by large flexible polymers (see below) is not significant.

(ii) At the particle−water interface, the adsorbed polymers may form very compact layers even for polymers with high molar masses (e.g., layers of 5−13 nm for molar masses of (1−2) × 10^6 Da; Table 4).

(iii) For very low polymer charge densities, charge neutralization may still occur, but contrary to small polymers, it does not lead to aggregate formation (Table 4) since the adsorbed layers are thick enough for steric repulsion to occur. In this case, the polymer layers prevent the particles from approaching to distances that would enable the van der Waals attractive forces to be efficient. Note that a polymer thickness of a few tens of nanometers is likely necessary for steric repulsion to occur (Table 4). In natural waters, this process is therefore unlikely to apply to FC. Furthermore, most flexible biopolymers in aquatic systems have molar masses that are too small to produce layer thicknesses greater than 5−15 nm.

In principle, the surface coverage concept (see above) is also applicable to large polymers adsorbed as thin layers and can be used to determine the degree of charge neutralization in order to make predictions with respect to IC stability. Equilibrium constants of large polymers on IC surfaces of opposite surface charge are not generally known but are usually large due to large entropic effects. This is confirmed by the observation that the molar mass of large polymers does not appear to affect the polymer/IC ratio

TABLE 4. Interaction between Hematite Particles (∅ = 50 nm) and Polyacrylic Acid Derivatives: Relationship between Polymer Charge, Molar Mass, Adsorption Layer Thickness (δ) on Hematite Particles, and the Occurrence of Flocculation (Adapted from ref *88*)

polymer[a,b]	electric charge density[c] (mequiv g^{-1})	molar mass (Da)	δ (nm) observed	δ (nm) calculated in the absence of charge[d]	flocculation with 10 mg L^{-1} hematite
PAM (pH = 4.5)	0	3.10^6	80 ± 7	80	no
0.4% HPAM (pH = 4.5)	0.028	2.10^6	58 ± 2	64	no
2.5% HPAM (pH = 4.5)	0.18	1.10^6	39 ± 3	44	no
6.1% HPAM (pH = 4.5)	0.44	2.10^6	13 ± 1	64	yes
PAA (pH = 3.0)	0.43	$1.4.10^6$	5 ± 1	53	yes
PAA (pH = 3.0)	0.43	$3.7.10^4$	2.1 ± 0.1	7	yes

[a] PAM = polyacrylamide; HPAM = hydrolyzed polyacrylamide (degree of hydrolysis in front of HPAM); PAA = poly(acrylic acid). [b] Solution pH values are given in parentheses. [c] Charge densities are estimations based on carboxyl group content, pH, and an intrinsic value of pK_a = 4.5. [d] Calculated based on eq 4 of ref *88*.

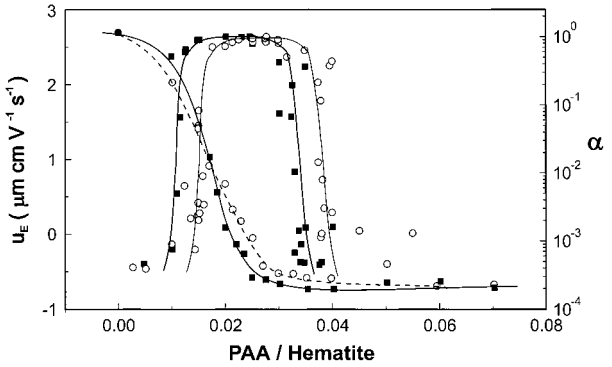

FIGURE 5. Electrophoretic mobility, u_E, and collision efficiency, α (proportional to aggregation rates), of a 10 mg L^{-1} hematite solution as function of the concentration of the poly(acrylic acid) (PAA) to hematite concentration ratio (w/w) at pH 3. The curves correspond to two molar masses of PAA (○, 3.7 × 10^4 Da; ■, 1.6 × 10^6 Da). In both cases, the coagulation rate (i.e., α) is at its maximum close to charge neutralization of hematite by the polymer (u_E ~0) and drops very quickly when particle becomes either positively or negatively charged (adapted from ref *83*).

required to induce aggregation (*83, 88*; Table 4). On the other hand, the surface coverage concept is not applicable to polymers forming thick layers for which steric effects between polymer/IC entities become predominant. This is the case for polymers with a low charge density adsorbed to oppositely charged IC (Table 4), of negatively charged polyelectrolytes bound to negatively charged IC by hydrophobic and/or covalent links, or of gel-like structures (*24*) into which IC may be embedded. More information is required to understand the significance of these processes in natural waters.

Heteroaggregation of Large Rigid Biopolymers (RB) with Comparatively Small Compact Colloids (IC or FC). TEM images of freshwater colloids (*15, 28*) often show small IC embedded in networks of fibrillar material (Figure 1A). In such cases, the small, compact colloids interact with a small part (hereafter called physical unit) of the fibrils, largely based on DLVO principles. The sticking of the compact colloid to the physical unit depends on the electric charge and van der Waals forces (as well as possible hydrogen or coordination bonds) of the two entities, as is the case for the interactions between two compact IC. Because of the secondary and tertiary structures of the RB (due to the formation and attraction of helices), the thickness and thus the van der Waals forces of fibril segments as well as the size of the reactive surface area may be significantly larger than for a corresponding segment of a single chain. Since most RB have a zero or slightly negative charge density (Table 2, Section A), aggregation with colloids is possible due to a minimal electrostatic repulsion. Because the fibrils may also be much longer than the diameter of the colloids, they can serve as rigid (or semi-rigid) long distance bridges between the colloids (Figure 1A). Attached, compact colloids may in turn serve as the binding unit among polymers that may lead to the formation of loose aggregate networks extending to very large dimensions. Although more studies are needed with respect to the processes involved, TEM and AFM images suggest that FC may also be aggregated as small spheroids along the fibrillar biopolymers (*15*). This suggests that, with respect to their interactions with fibrils, fulvic compounds might behave similarly to IC, i.e., as compact, charged, sphere-shaped colloids; an observation that is consistent with their semi-rigid structure (see properties of FC).

Such an aggregation process can be modeled by numerical simulation (Figure 6; *16*). RB are represented by a pearl necklace, with each pearl corresponding to a physical unit. The statistical conformation (or fractal dimension) of the necklace can be calculated with respect to its rigidity (or persistence length). Different values of sticking coefficients can be used to modify the probability of interaction between the small, compact colloids and the physical units of the RB. The important conclusions that are obtained by such simulations are the following:

(i) Because small colloids diffuse much more quickly than RB, the first step of the aggregation process is the formation of chains covered by compact colloids (Figure 6; cf. also Figures 1A and 3B). In a second, slower step, several fibrils may be associated to form a network (Figure 6) by attaching to the same compact colloid. This second step is slower not only because of the slower diffusion of RB with attached colloids but also because only a small proportion of aggregate collisions are successful; indeed in order to succeed, a collison must involve the compact colloid of one aggregate and the physical units of the biopolymer of another.

(ii) Aggregation kinetics can be expressed in terms of scaling laws (*16, 27*) over several orders of magnitudes (Figure 6), implying that under optimum conditions aggregates can be formed with sizes much larger than those obtained by coagulation of compact colloids only (Figure 4).

(iii) The key factors related to the optimal conditions for aggregation include (i) the normalized compact colloid to polymer concentration ratio, *x* (aggregates are not formed at extreme values of *x*; Figure 6B; *16*), and (ii) the RB rigidity [very large aggregates are only formed with rigid polymers, while aggregates formed with coiled chains are of limited size for reasons similar to those leading to Figure 4 (*89*)].

The above results (Figure 6; *16, 89*) are based on the assumption that compact colloids and physical units of RB can stick together whereas colloid−colloid collisions do not lead to stable aggregates. This simple situation, however, is rarely encountered in natural waters. In the more general

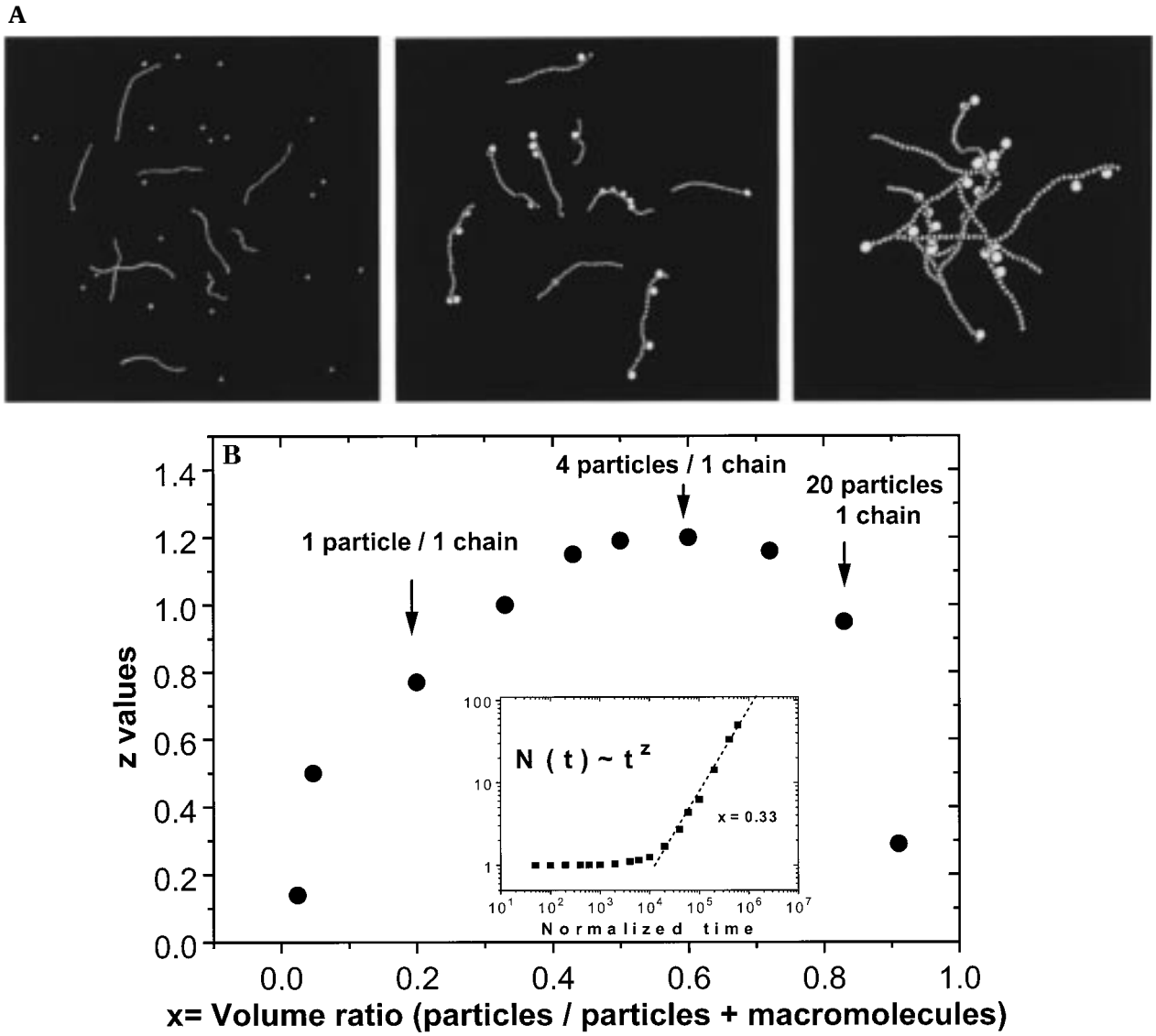

FIGURE 6. (Panel A) Numerical simulation of the successive steps of aggregate formation between IC and RB. Homocoagulation (IC−IC, RB−RB) is not allowed. The initial suspension is randomly dispersed and contains 10 chains and 25 particles. IC, RB, and their aggregates move freely according to their diffusion coefficient. Note that the scale increases from right to left. (Panel B, inset) Size evolution of aggregates [$N(t)$ = average number of RB chains per aggregate]. A power law is observed over several orders of magnitude of time and sizes. The slope is equal to z. This is a 3-D simulation using rigid chains. (Panel B) Aggregation kinetics: variation of the exponent, z, with the system composition, x [x-normalized concentration ratio = $V_{IC}/(V_{IC} + V_{RB})$ where V_{IC} and V_{RB} are the volumes of IC and RB in the solution]. The aggregation rate is the greatest for intermediate values of x (adapted from ref *16*).

situation, RLA aggregation of compact colloids occurs (Figure 4) concomitantly with colloid−RB aggregate formation. The net result is the formation of a network of RB connected together either by isolated or aggregated compact colloids (Figures 7, 1A and 3B).

It must be noted that the above simulations were performed by only considering the sticking coefficient between IC and RB and the size, conformation, and diffusion coefficient of the components and their aggregates. Aggregate stability will also depend on the shear forces in solution, the tensile strength of the RB, and the weight of the particles; all factors that will influence fragmentation. In addition, aggregate collapse must also be considered. Nonetheless, these effects are expected to play a significant role mainly for the larger IC (>50−100 nm), i.e., conditions for which the bridging role of NOM becomes less and less significant and the application of DLVO/Smoluchowski theory to compact colloids becomes more and more valid.

Discussion: The Three-Colloidal Component Approach

The interactions described above are summarized in Figure 8. A few, large, highly charged biopolymers such as alginic acid may have a complicated role in aggregation processes since, depending on their molar mass and the pH and ionic strength of the natural water of interest, they may behave as extended coils or form gels or coatings of variable thicknesses on the inorganic colloids. Nonetheless, as discussed above, such compounds seem to be the exception rather than the rule. Furthermore, the role of most of the flexible biopolymers is likely limited by their rapid turnover (*56*) and low concentration: proteins usually account for less than 15% of NOM in freshwaters and less than 6% of NOM in marine systems, and reserve polysaccharides are even less prevalent (*6*). For cases in which they do play a role, it is likely that it is similar to that observed for the FC (or AROM) in which the biopolymers form a thin organic coating on the inorganic colloidal surface (see Heteroaggregation of Large, Semiflexible

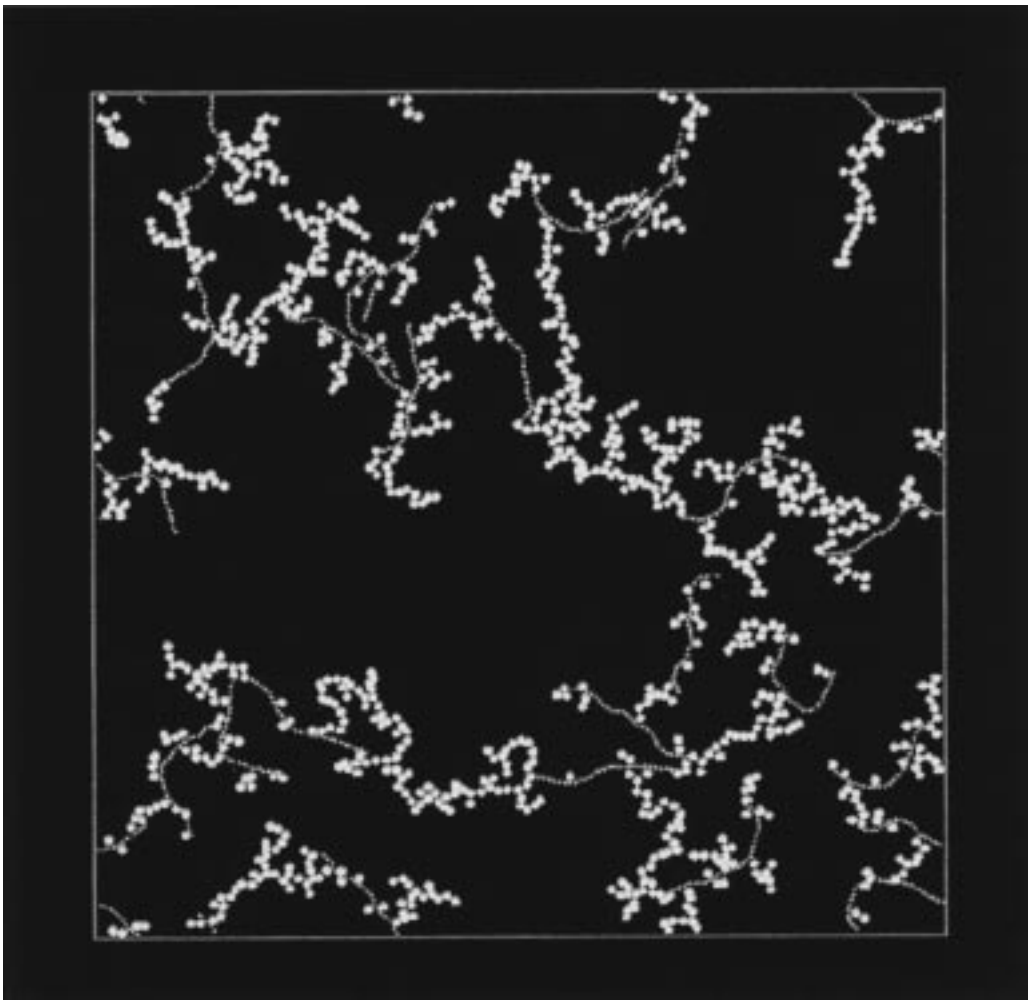

FIGURE 7. 2-D numerical simulation of IC−RB aggregate formation in a system where both IC−RB and IC−IC collisions lead to sticking. The initial suspension is randomly dispersed, and IC, RB, and their aggregates move freely according to their diffusion coefficients. The suspension contains 25 chains and 1000 particles. The sticking probability is 1 for both particle−particle and particle−polymer interactions.

Polymers ...). On the basis of the previous discussion, the following conclusions can then be made:

(1) To a first approximation, aquatic colloidal systems can be considered as being composed of three major types of components: (i) inorganic colloids (IC), (ii) fulvic compounds (FC) or aquagenic refractory organic matter (AROM), and (iii) rigid biopolymers (RB) for which the main interactions are summarized in Figure 8. A suspension containing only one of the components (IC, FC, AROM, RB) is stable for long periods of time, even when homoaggregation takes place. For instance, weeks or months are often necessary for FC or IC to reach aggregate sizes large enough to allow sedimentation (Figure 4). Although all interactions are dependent upon the physicochemistry of the medium, IC−FC and RB−FC interactions will not usually lead to destabilization, while IC−RB (or IC−RB−FC) interactions can promote aggregation.

(2) IC−RB interactions probably constitute a major pathway leading to sedimentation. Indeed, in surface waters, neither homoaggregation nor differential settling with large particles seem to play significant roles with respect to the sedimentation of the submicron colloids (*30*). On the other hand, computer simulation suggests that IC−RB aggregation can lead to large entities capable of either direct settling or orthokinetic coagulation (under the action of convective forces) with large quickly settling particles. Indeed, the IC aggregation and sedimentation rates have been shown in some cases to be largely dependent on the concentration of organic material released by plankton (*90*), specifically the fibrillar polysaccharides (*11*). Because RB are most likely to be released from plankton under specific ecological stimulus such as nutrient deficiencies (*46*) and since the formation of large, settlable aggregates requires an optimal IC/RB ratio (Figure 6), it is expected that aggregation rates will vary seasonally and from one ecosystem to another. According to this general picture, the aggregation of inorganic colloids in natural waters can therefore be seen as the result of two major but opposite effects: their stabilization by FC and their destabilization by RB.

(3) The aggregation rate between RB and IC is slow (11) and reaction limited for two major reasons:

(i) In most aquatic systems, IC and RB are coated with FC or AROM, which decreases the collision efficiency by imposing a quasi-uniform negative charge on the colloidal material.

(ii) Large aggregates are likely not formed by the addition of single colloids to an existing aggregates but rather by the collision of two aggregates (*16*). The attachment of two loose aggregates similar to those of Figure 6 is a low probability event that only occurs when free sites of the IC and the physical units of the RB of two aggregates are brought into physical contact during the aggregate collision. Typical rate constants of 0.05 to 0.1 h^{-1} have been observed for the aggregation of IC and RB in lake waters (*11*).

(4) Three concepts widely accepted by the scientific community should be reevaluated when considering colloidal systems:

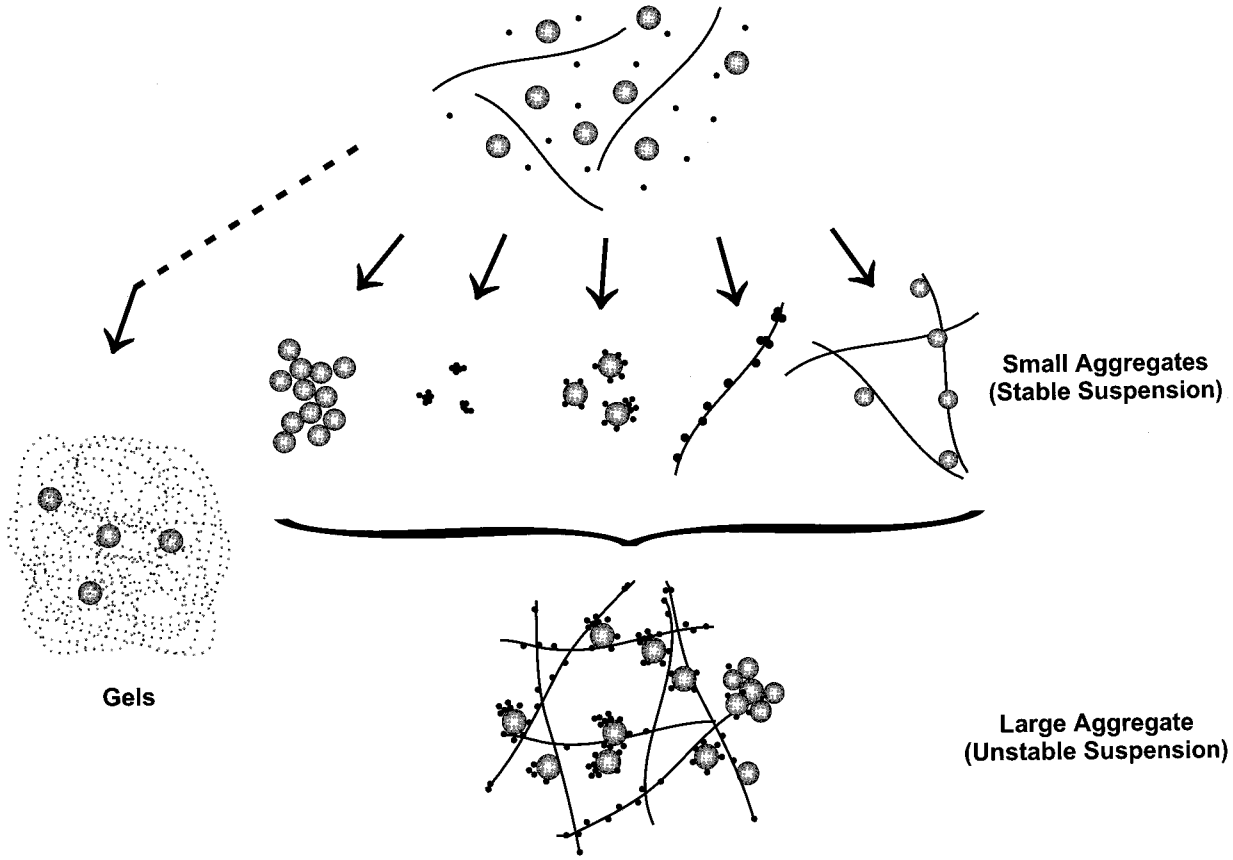

FIGURE 8. Major types of aggregates formed in the three-colloidal component system: FC (or AROM) = small points; IC = circles; RB = lines. Both FC and polysaccharides can also form gels, which are represented here as gray areas into which IC can be embedded.

(i) A linear representation of fulvic compounds (FC) is probably not realistic, as all models suggest that branching via covalent, hydrogen, or hydrophobic bonding is important. Traditionally, FC adsorption or complexation studies (*6*) have treated FC as a small, flexible, citric acid-type organic molecule (albeit with aromatic groups and a larger molar mass). On the other hand, most techniques used to characterize the morphology of FC conclude that they have a rather rigid, globular shape. The reality is likely somewhere between and is certainly dependent upon the physicochemical conditions of the medium. It is likely that FC can be treated both as a small but chemically heterogeneous molecule for the interpretation of complexation reactions and as a small, globular colloid for which the DLVO theory is applicable when interpreting aggregation processes.

(ii) The bridging of ICs by polymers would appear to describe well the interactions of IC with rigid polymers. Although this same conceptual model has also been employed to explain the role of long, flexible polymers in the field of water treatment (*91*), it does not appear to be well suited for understanding natural colloidal systems.

(iii) The concept of surface coverage has been very useful to the understanding of IC aggregation in the last 30 years. Most of this work, however, has been devoted to studying the aggregation of particles larger than 1 μm in the presence of small, adsorbable molecules such as phosphate, C_{12} or C_{16} fatty acids, citric acid, peptides, or FC. In such cases, surface coverage (and the related modifications in surface charge) can be unambiguously computed based on the chemical reaction of the adsorbant with the surface (*1, 2*), the corresponding equilibrium constant, and the maximum sorption capacity. In the context of the present paper, this concept is applicable to the adsorption of FC and even large polymers, provided they form a sufficiently thin layer (< a few nanometers), compared to the width of the interaction energy barrier for coagulation. On the other hand, for large semiflexible polymers forming thick layers or gels, the aggregation process cannot easily be related to the surface coverage. For understanding the interaction of RB with comparatively small IC, the surface coverage concept is also important; however, in this case, it is more related to the available sites on the RB or IC allowing the formation of networks rather than to charge neutralization. As demonstrated in ref *16*, intermediate surface coverage (related to the IC/RB ratio) is necessary for an optimal aggregation rate.

(5) An additional comment can be made on the analytical aspects related to the interactions of FC (or AROM), IC, and RB. The isolation of these components in order to study their individual properties is very difficult. In some cases, it is possible to extract them from specific ecosystems in which one of these components predominates; however, in most aquatic systems, all three components will be present, albeit in variable proportions. Due to the complexity of the aggregate structures (Figures 1−3), there is little hope to completely isolate each component by classical fractionation techniques such as chromatography or filtration. At the best, only enriched fractions of each component can be obtained if structural perturbations of the colloids or polymers are to be minimized. This greatly complicates the study of these colloidal components and their interactions with trace compounds. On the basis of the previous discussion, it is clear that the measurement of total organic carbon alone is a poor indicator of the role of natural organic matter in a given aquatic system. Although analytically more difficult, separate determinations of FC, RB, and AROM (*90*) are preferable if one is to draw unambiguous conclusions on the role of NOM in natural waters.

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Glossary

colloids	any organic or mineral entity with supramolecular structure and properties, but small enough so as not to quickly sediment without aggregation (typical size range = 1 nm−1 μm)
IC	inorganic colloids
FC	fulvic compounds (soil derived)
AROM	aquagenic refractory organic matter
FB	flexible biopolymers
RB	rigid biopolymers
NOM	natural organic matter

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