# EFFECT OF NATURAL ORGANIC COATINGS ON THE POLYMER-INDUCED COAGULATION OF COLLOIDAL PARTICLES

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# ABSTRACT

The coagulation of colloidal particles is important in a broad spectrum of industrial processes, including paper making, coal slurry processing, and pharmaceutical preparation, to name a few. Understanding the coagulation process is also important for predicting the fate and transport of particulate material and associated contaminants in natural aquatic systems as well. Although coagulation is an important process, little information is known regarding the primary mechanisms by which adsorbed polymers influence colloid stability in complex systems.

It has recently been suggested that a three-component model can be used to model coagulation in natural systems. In this model, the primary components include inorganic colloidal particles, large chain macromolecules and dissolved humic substances. In general this model predicts that the rate of coagulation will depend on the complex interactions between the three components. For example, when the concentration of macromolecular polymers is high, both dissolved humic substances and inorganic colloids may attach to large chain polymers. When the concentration of particles is high, on the other hand, the coagulation of inorganic colloids may be mediated by either dissolved humic substances through charge neutralization or by macromolecules through bridging. We currently lack a detailed understanding about how the specific interactions between these three different components influence aggregates in lakes, rivers and oceans.

In this study, we examined how the adsorption of dissolved humic substances influences the bridging coagulation of colloids by large-chain macromolecules. In particular, we investigated the effect of humic acid on the flocculation of well-characterized amidine polystyrene latex microspheres (mean diameter 0.12 microns) by a polymeric flocculant, (polyvinyl alcohol, or "PVA"). The coagulation of the particles was studied in the presence of varying concentrations of PVA and humic acid by examining the rate of change in hydrodynamic diameter using a photon correlation spectrometer, or PCS. Stability ratios (W) were calculated from this rate data and compared to adsorption isotherms, electrophoretic mobility, and hydrodynamic layer thickness measurements to develop a mechanistic understanding regarding the role of adsorbed organic coatings in controlling the polymer-induced flocculation of colloidal particles. All coagulation experiments were carried out at 0.01M NaCl, and therefore both electrostatic and polymeric forces may be important in controlling coagulation.

Our results demonstrate that in the absence of humic acid PVA is an effective flocculant over a wide range of polymer concentrations. Under these conditions, we suspect that coagulation is controlled by the bridging interactions between PVA and the latex microspheres. The primary evidence for this conclusion comes from the fact that PVA is an uncharged large-chain polymer

under the conditions of our experiments. Thus, the adsorption of PVA should have little effect on the electrostatic interactions between primary particles upon close particle-particle approach.

In natural systems, we suspect that most particles will be coated with humic materials at high surface coverage. When we tested a high concentration of humic acid, under which conditions the surface of the latex particles is saturated with adsorbed humic acid, the particles are stable at all dosages of PVA tested. Under these conditions, the high stability is presumably a result of repulsive electrostatic interactions between adsorbed humic acid layers on the latex particles. Adsorption experiments further indicate that the coating of the latex particles with humic acid at high dose also results in a decrease in the number of active sites available for bridging. In our experiments, multilayer adsorption doesn't appear to be an important process affecting coagulation.

Coating the particles with humic acid at relatively low dosages (<0.2mg/L), on the other hand, yields markedly better coagulation than when PVA is the sole flocculant. Here, both polymer bridging and charge neutralization appear to play a role in controlling the coagulation rate of these particles. It appears that low dosages of humic acid reduce the electrostatic potential between particles sufficiently to allow for more effective contacts between PVA molecules and particles.

The results presented here suggest that the predominance of polymer bridging in natural systems may depend on the preferential displacement of low molecular humic and fulvic acid and/or favorable interaction between large macromolecules and particle surfaces coated with humic materials. Further study is needed to more fully characterize the interactions between heterogeneous solutions of polymers in controlling coagulation in natural waters.

**Dedicated To My Parents**

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## FIELDS OF STUDY

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# CHAPTER 1

# INTRODUCTION

The polymer-induced coagulation of colloidal particles is a key step in many important industrial and environmental processes. For example, cationic polyelectrolyes are used as coagulants in paper manufacturing, mineral separation, and for the removal of particulate matter from the aqueous phase in water and wastewater treatment processes [1, 2]. In surface water and ground water, the stability and mobility of colloidal particles depend, to a large extent, on the presence of adsorbed, natural organic polymers [3, 4, 5, 6, 7].

A number of mechanisms have been proposed to describe how organic matter influences the stability of naturally occurring colloids. For example, there is extensive evidence that low molecular weight natural organic molecules (e.g., humic and fulvic acid) affect the surface charge of particles in fresh water and seawater and that this controls particle stability [8, 9, 10, 11, 12, 13, 14]. For example, Tiller and O'Melia [12] measured the coagulation kinetics of hematite particles in the presence of a number of anionic polyelectrolytes, including humic material, in well-controlled laboratory experiments. They found that at low solution ionic strength the adsorption of aquatic natural organic matter increases the stability of the hematite particles. Increasing the ionic strength, however, decreases the repulsive electrostatic interactions between adsorbed organic matter layers, and subsequently, results in a decrease in particle stability.

Recent evidence suggests that the high molecular weight fraction of organic matter may also play an important role in controlling particle coagulation in lakes and rivers [15, 16, 17, 18, 19]. Instead of decreasing the rate of coagulation, however, this fraction of organic matter may enhance the coagulation rate of particles in natural systems. For example, Buffle et al. [15, 16, 17, 18, 19] have collected surface water samples in a number of Swiss lakes and rivers and analyzed the three-dimensional configuration of aggregates using transmission electron microscopy (TEM). Their studies show that a significant fraction of particles are attached to large organic polymers through bridging interactions. Based on these results, recent studies have attempted to extend the original bridging model proposed by La Mer [20] to model polymeric bridging of colloids in natural systems [15, 21].

Despite the ubiquitous presence of both large and small chain organic molecules in most natural waters, little is known about how heterogeneous solutions of polymers influence the aggregation of colloidal particles. For example, it is not clear how the adsorption of low molecular weight humic materials may affect colloidal stability in the presence of large organic macromolecules. In this study, we examine how the adsorption of a well-characterized humic acid influences the polymeric bridging of colloidal particles by a nonionic polymer (polyvinyl alcohol or "PVA"). Our work provides important new insight into the effect of humic acid coatings on the polymer-induced coagulation of colloids in both natural and engineered systems.

# CHAPTER 2

# BACKGROUND

Particles play an important role in a wide range of processes occurring in both natural and engineered systems. For example, many toxic compounds in aquatic systems (surface water, soil, sediment, ocean and ground water) strongly partition to natural particles [22]. Thus, the circulation and fate of these compounds are strongly dependent on the fate of these particles. In addition, understanding the interactions between particles is important in many industrial processes such as coal-water slurry stabilization, production of dyes, and water and wastewater treatment [23].

## 2.1 COLLOIDS IN NATURAL WATERS

A large portion of particulate matter in natural system is colloidal in size. Colloids range in size from 1 nm to 1 μm. This size range is important in controlling many of the general properties of particulates in aquatic environments [24]. Colloidal constituents may be organic, inorganic compounds, as well as microorganisms [23, 25]. They include clays, metal oxides and substances such as calcium carbonate, silica, dissolved organic carbon (e.g., polysaccharides) and cellular debris [23, 24].

A number of processes influence the fate of colloids in natural systems. Colloids are generated by processes such as physical fragmentation, erosion and precipitation [25]. For example, Ryan et al. [26] have shown that changes in ionic strength may result in the detachment and mobilization of colloids in ground water. A review of important colloid generation processes is provided in Elimelech and Ryan [26]. Colloids are removed from water by processes such as coagulation, attachment to sediment and soil, and dissolution. Due to their large specific surface area, colloids may sorb significant quantities of contaminant; thus the removal of colloids in natural waters and wastewater treatment is extremely important.

One of the primary processes controlling particle fate in natural waters is coagulation. In natural aquatic systems, coagulation of colloidal particles is important since it results in the formation of large floes with high settling velocity, which in turn, affects the movement and transport of these particles.

O'Melia [27] was one of the first researchers to study the behavior of small particles in natural aquatic systems. His conclusion was that the transport and fate of particles are influenced significantly by the coagulation process.

## 2.2 MECHANISM OF PARTICLE COAGULATION

For the coagulation process to occur, two steps are necessary; transport and coalescence [26]. Three different mechanisms are involved in particle transport; the first is Brownian or molecular diffusion in which the motion of particles is mainly due to thermal effects [27]. Here, the motion of the particles is only a function of the product of the Boltzman constant ($k$) and absolute temperature ($T$) and independent of fluid flow and gravity forces. The continuous bombarding of these particles by the surrounding water molecules results in the transfer of kinetic energy from water molecules to these particles, thus causing the motion of the particles. The diffusion coefficient will decrease with increasing particle size. The second mechanism is fluid shear; either turbulent or laminar velocity gradients occur in all real flowing fluids, this causes the particles to travel at different velocities. The different velocities or gradients can produce interparticulate contacts. The rate of coagulation in this case depends on the mean velocity gradient. The third transport mechanism is differential sedimentation (gravity), which arises due to differences in the settling velocities of particles and depends upon the buoyant weight of these particles.

The second step necessary for coagulation to occur is coalescence; or the sticking of particles. The collision of particles as a result of different transport mechanisms may or may not result in sticking. Whether the particles stick depends on many factors such as the surface charge of the particles, size of particles, polymer adsorption onto the surface of particles, and van der Waal's attractive forces.

Two classes of colloidal systems are recognized; hydrophobic (negligible affinity for water) and hydrophilic (high affinity for water) colloids [28]. In simple systems, hydrophobic colloids owe their stability to an electrical double layer, which causes repulsion between particles. Hydrophilic colloids, on the other hand, are stable because the solvation of their polar groups (ionic or non-ionic) is strong enough to overcome the van der Waal's cohesive forces [29].

Most particles in the aquatic environment have some net surface charge. There are three principal ways the particles acquire surface charge; the first is the presence of surface functional groups (e.g., amino groups, carboxyl group). In this case, the degree of ionization of these groups controls the surface charge of particles. Surface charge of particles may also arise as a result of lattice imperfections at the solid surface and isomorphous replacement within the lattice. For example if a Si atom is replaced by an Al atom (Al has one electron less than Si) in a $SiO_2$ array, this will result in a negatively charged framework. Similarly, isomorphous replacement of the Al atom by Mg atoms in the network of aluminum oxide will yield a negatively charged lattice. The third cause for surface charge is the adsorption process, namely the adsorption of organic matter and/or ions which yields negatively charged particles in most cases.

Two electrostatic layers around any colloidal particle in water are known to exist [25]; a fixed layer that is a compact layer of counterions (ions with charge opposite to the particle charge) and a diffuse layer. Both layers combined (the so-called double layer) contain positive and negative charges and result in an electrostatic potential. , Another plane of importance around the particle is the shear plane, which encloses the water envelope that moves with the particle [26]. The electrostatic potential at the shear surface is termed the zeta potential. For highly charged colloids, the reduction of electrostatic repulsive forces is necessary to destabilize the colloidal suspension.

A number of mechanisms and/or processes can lead to a reduction of electrostatic repulsive interactions between colloidal particles. The presence of different salts in solution will influence the double layer around particles. At high ionic strength, the diffuse layer becomes compressed due to screening of charges by electrolyte. In such cases, the decrease in repulsive interactions allows particles to approach at smaller separation distances. As particles come closer, van der Waal's attractive forces will dominate, which in turn, will result in particle destabilization. Thus, particles tend to be less stable in estuarine and ocean waters where the ionic strength is high. J. Lick et al, [30] for example, investigated the rate of aggregation and disaggregation of fine grain sediment in different waters and concluded that particles flocculate faster in seawater than in fresh water. The effect of nonspecific electrolytes is limited to screening of particle charge through the compression of double layer interactions. These types of ions are not able to cause charge reversal or charge neutralization because they are not bound to the particle surface to any significant extent.

Adsorption of charged polymers (i.e., polyelectrolytes) may also influence the electrostatic interactions between particles. For example, polyelectrolytes like humic and fulvic acids when adsorbed to positively charged colloidal particles are able to neutralize the charge of the particles. At high concentration, adsorption of polyelectrolytes may cause charge reversal. Some ions, such as phosphate and copper also adsorb to colloidal surfaces and cause charge reversal. Once the electrostatic repulsion between particles is eliminated, van der Waal's attractive forces become dominant and coagulation is rapid.

Van der Waal's forces, also called London-van der Waal's forces, play an important role in controlling particle coagulation. They arise from the attraction between oscillating charges. At close separation (less than 20 nm) van der Waal's attraction energy is inversely proportional to the square of the distance between two particles and directly proportional to the Hamaker constant. The Hamaker constant depends on the density and polarizability of the particulate material. In aqueous systems, Hamaker constants are typically on the order of $10^{-19}$ or $10^{-20}$ J. When the separation distance between particles is larger than 20 nm, the attraction energy of van der Waal's forces is inversely proportional to the cube of the distance.

Recent studies have shown that surface roughness may significantly affect van der Waal's forces [31, 32]. Toikka et al. [33] used an atomic force microscope (AFM) to measure the interaction energy between zinc sulfide particles at varying ionic strengths. At high ionic strength, electrostatic repulsion is negligible and therefore van der Waal's forces should dominate. However, Toikka et al. found that at high ionic strength, van der Waal's forces are negligible when the particles posses surface roughness. They observed that van der Waal's forces were below the sensitivity of the AFM. Apparently the presence of surface roughness decreases the effective range of these forces between approaching particles. Y. Walz et al. [34] measured van der Waal's attraction energy of polysterene latex particles and a flat plate using internal reflection microscopy (IRM) and also demonstrated the importance of surface roughness on these forces.

## 2.3 ROLE OF POLYMER ADSORPTION IN CONTROLLING COAGULATION

Adsorbed layers of polymers play a significant role in controlling colloid stability, both in natural and engineered systems. At high concentration, polymers may stabilize colloids through steric forces. Upon close particle-particle approach, adsorbed layers will overlap within the gap between particles, which will result in dehydration of the hydrophilic (hydrated) polymer chains. This in turn will result in an increase in the free energy and thus repulsion between particles. [28]. The thickness of the adsorbed layer and the size of the particle are important factors in determining the degree of steric stabilization. Larger colloidal particles will need thicker adsorbed layers to achieve the same degree of stability since the attractive van der Waal's forces are directly proportional to particle size.

At intermediate polymer concentrations, an individual polymer chain can attach to two or more particles, bridge them together and thus destabilize a colloidal suspension. This can occur even if the polymer and particles have the same charge because chemical adsorption interactions may overcome electrostatic repulsion [35]. The molecular weight of the polymer has a significant effect since it is related to the formation of loops and tails which are necessary for bridging to occur.

Healy and La Mer [36] proposed that optimum bridging flocculation occurs when particle surfaces are covered at half the maximum polymer surface coverage. Hogg [37 ] has reviewed the La Mer model and developed a new model assuming that particles and adsorbed polymer molecules can reorient themselves into configurations favorable to bridging. According to his model, almost all the surface sites on particles are implicitly considered to be capable of adsorbing polymer molecules. Soto et al. [38] has argued that not all the available sites on the particle are "active sites". They specified only the sites that are capable of interacting with a given polymer as "active". According to their hypothesis, the relative number of active sites depends on the nature of colloid particles and polymeric species. The estimation of the relative number of active sites can be obtained from adsorption density measurements at saturation. Using these concepts, they developed a new model incorporating the active/non active fraction. Their model produced satisfactory results upon comparison with experimental data for a simple apatite-dolomite system.

In a landmark study, Yokoyama and coworkers [39] demonstrated the importance of polymer conformation in controlling colloid stability. In this study, they systematically investigated the stabilization effect of Gum Tragacanth (GT) (an acidic polyelectrolyte) on polysterene latex particles at varying pH. They carried out experiments to determine the amount of polymer adsorbed, electrostatic forces, and layer thickness values at different pH and ionic strengths. In their experiments, they showed that the layer thickness of adsorbed polymer varies significantly with pH. They attributed this variation in steric layer thickness to a difference in the solution conformation of polymer. At high pH, ionization of carboxylic acid groups associated with GT results in interchain repulsion and a rigid rod conformation. Under these conditions, GT adsorbs onto the surface of particles in a flat conformation with few loops or tails. The flat conformation of GT is insufficient to generate significant steric repulsive forces, and subsequently the particles coagulate. At low pH, ionization of surface charge on GT molecules is suppressed and the molecule adopts a random coil configuration in solution. Here, the extended conformation of GT on the latex surface results in repulsive steric interactions and enhanced colloid stability.

Yokoyama et al. also carried out deflocculation experiments [39]. From these experiments, they concluded that flocculated particles could spontaneously deflocculate by lowering pH. Lowering pH apparently changes the conformation of polymer molecules on the particle surface and subsequently increases the steric repulsive forces between particles, causing disaggregation.

## 2.4 INFLUENCE OF HUMIC SUBSTANCES ON COAGULATION IN NATURAL WATERS

A number of studies have shown that in natural aquatic systems, the stability of colloidal particles is significantly affected by the presence of humic substances [12, 25, 28]. These substances are made up of humic and fulvic acids, with the later being soluble over the complete pH range and the former being insoluble at pH below 2. These acids are polyanions with ill-defined structure. They have a carbon skeleton and oxygen-containing functional groups; carboxylic acid being the major oxygen-containing group and a minor amount of phenolic and methoxyl also present [40]. Fulvic acid in fresh water has a molecular weight on the order of 1000 Dalton and humic acids have sizes of 3000, generally. These compounds are composed of amiphilic molecules, that is molecules that have separate hydrophobic and hydrophilic groups [41].

Previous studies point out the important role of electrostatic interactions in controlling colloid stability in the presence of humic materials. Beckett et al. [42], for example, studied the role of humic substances and ionic composition in determining the surface charge of suspended particles in natural water. They also modeled the charge behavior of natural colloidal particles using geothite colloids coated with an adsorbed layer of humic substances. They concluded that the major factor determining the surface charge density of aquatic particles is the adsorbed layer of humic substances. This surface charge is then modified according to the concentration of divalent cations (Calcium, Magnesium) present, and to much lesser extent, to the pH.

Tipping and Higgins [43] studied the rate of aggregation and the electrophoretic mobility of a hematite suspension in the presence of humic substances and calcium. Their results showed that the stability of particles was enhanced by humic substances. Tipping and Ohnstad [44] looked at the stability of naturally occurring iron oxide particles at different calcium chloride concentrations and concluded that the calcium chloride concentration significantly affects the stability. They showed that at high calcium concentrations, divalent cations can form bridges between adjacent humic molecules and subsequently increase the rate of coagulation. J. Edzwald [45] also investigated the effect of fulvic acid on the stability of natural particles. He concluded that particles are unstable in lakes but that the stability of particles depends on water hardness and the abundance of dissolved organic carbon. Liang [46] also studied the effect of fulvic acid on hematite stability. She found that humic and fulvic acid significantly influence hematite particle stability, primary as a result of electrostatic interactions between particles.

R. Gibbs [6] carried out well-controlled laboratory experiments to study the effect of natural organic coatings on the coagulation rate of particles. His results showed that when natural organic coatings were removed, the coagulation rate was four times higher than the rate of natural samples (particles with organic coatings). Recently, Amal and co-workers [4] investigated the aggregation kinetics of fulvic acid-coated hematite particles in the presence of calcium chloride. Zeta potential measurements showed that the adsorption of fulvic acid is not due solely to electrostatic interactions, but a combination of electrostatic interactions, specific chemical affinity, and hydrophobic interactions. They also showed that coating the particles produced more compacted aggregates than for uncoated particles.

Tiller and O'Melia [12] carried out numerical calculations using a lattice adsorption model and compared these calculations with data from laboratory experiments for some anionic polymers (polyacrylic acid, polyaspartic acid and humic acid). They concluded that positively charged hematite particles are coagulated by charge neutralization at low ionic strength and intermediate polymer surface coverage. Furthermore, they found an absence of steric repulsion at low ionic strength even at high surface coverage. They hypothesize that the electric double layer under these conditions extends beyond the layer thickness of adsorbed polymer and therefore dominates the interactions. At higher ionic strength, polymer adsorption results in a layer thickness which can be of the same order of the Debye length (the effective length of electrostatic interactions), and hence influence colloid stability through steric repulsion forces. It is interesting to note that at intermediate ionic strength, a combination of steric and electrostatic forces (so-called electrosteric) may be important. However, little is known about these types of interactions.

## 2.5 LARGE-CHAIN NATURAL ORGANIC POLYMERS

Recent studies suggest that natural organic polymers, other than humic substances, may play an important role in controlling the coagulation rate of naturally occurring colloids. Buffle et al. [47], for example, has shown that natural organic matter in aquatic systems is heterogeneous in nature. They classified NOM in aquatic systems into three classes; rigid biopolymers, fulvic compounds and flexible biopolymers (see table 2.1). Rigid biopolymers include polysaccharides, which originate from plankton as exudates and cell wall components and usually are highly hydrated. They also include DNA, which is released from plankton upon death. Flexible biopolymers, on the other hand, include aquagenic refractory organic matter, rapidly degradable polysaccharides, and proteins. Aquatic refractory organic matter is composed of chemical heterogeneous compounds resulting from microbial cell degradation. Rapidly degradable polysaccharides and proteins are characterized by rapid degradation in the water column. Recent studies indicate that special consideration should also be given to nano-bacteria with a diameter less than 0.5 pm which constitute a significant portion of organic matter biomass in natural waters.[48 ]

The presence of large macromolecular chain compounds in natural waters may play a role in coagulation of colloidal suspensions through bridging flocculation. Generally most proteins and degradable polysaccharides have a negligible effect since they degrade rapidly. However, little information is known about the interactions of refractory flexible biopolymers on colloid surfaces in natural water. Rigid biopolymers like organic fibrils are known to enhance bridging flocculation. These fibrils are usually larger in size than the colloids, and are known to provide sites for attachment of particles. Although in this case particles may be described as being "coagulated", little or no particle-particle contacts occur.

Despite the heterogeneity of organic polymers in natural waters, little information is known regarding how the stability of a colloidal suspension is influenced by the presence of multiple polymeric species in solution. The few studies in this general area have focused on systems of industrial importance. Moore et al. [49] for example, combined a low molecular weight cationic polymer with a high molecular weight anionic polymer, and found that this mixture produced synergism in the flocculation of paper pulp. Recently, Somasundaran and Yu [50] investigated the flocculation of alumina in the presence of two polymers (polystyrene sulfonate and polyacrylamide). They compared the stability of alumina particles in the presence of each polymer individually with the stability in the presence of a mixture of both polymers. Their results showed that the mixture of two polymers adsorb completely onto the surface of the particles producing significantly higher flocculation rates than in the presence of each polymer alone. They attributed the high affinity of the polymer mixture for the positively charged alumina particles to the formation of "anchors". They explained that the anionic polyelectrolyte (polystyrene sulfonate molecules) acted as anionic anchors for the adsorption of long chain cationic polymers and this resulted in enhanced interparticulate bridging and superior floculation.

Somasundaran and Yu [50] also examined how the sequence of polymer addition influenced stability in the presence of multiple polymers. Their results showed that when the two polymers were added in a premixed form, the flocculation was not as good as when adding the polymers one after another. They attributed this to the fact that fewer molecules of the anionic polymer will be available to form anchors on the surface of the particles due to the interaction of these molecules with the cationic polymer in the bulk solution. Apparently, polymer-polymer interactions in solution resulted in a reduction in bridging. However, it should be noted that this flocculation rate was still significantly higher than for each polymer alone as mentioned above. They concluded that while in a single polymer system flocculation of positively charged alumina particles is mainly due to charge neutralization by anionic polymer, enhanced flocculation is obtained with double flocculants due to polymer-polymer interactions which result in excellent interparticle bridging.

Currently, little information is known about how the interactions between large macromolecular polymers and humic substances influence coagulation in natural systems. In one of the few studies with implications in this area, Narkis and Rebhun [51] investigated the flocculation of clay particles by a cationic polymer in the presence of humic and fulvic acid. Their results showed that the presence of organic matter resulted in a high demand for the cationic flocculant. In particular, The optimum dose to induce charge neutralization in the presence of organic matter was 11 mg/L as compared to 0.5 mg/L for organic matter-free clay particles. They argued that the cationic polymer reacts preferentially with the organic matter in solution. Thus, the flocculation of the suspension begins only after the polymer has completely reacted (i.e. neutralized) all the organic matter in solution. They concluded that the main interference caused by the presence of organic matter in solution is the inhibition of the reaction of flocculant with suspended solids. Lurie and Rebhun [52] also investigated the effect of humic substances on flocculation by high and low molecular weight polyelectrolytes and showed similar findings.

## 2.6 RESEARCH OBJECTIVES

In this study, we further examine the coagulation of colloidal particles in the presence of complex mixtures of polymer species. In particular, we investigate how the presence of humic acids influences the coagulation of colloidal particles by a large chain non-ionic polymer. Our results provide important new information about the interactions between polymeric species at surfaces and have implications for coagulation in both natural and engineered systems.

| Molecule | Size (Da) | Percentage |
|---|---|---|
| Humic/Fulvic Acid | 500 to 5000 | 20-80% |
| Rigid Polysaccharides | $10^4$ to $10^5$ | 10-30% |
| Flexible Polysaccharides | $10^3$ to $10^6$ | 10-30% |
| Proteic Compounds | $10^4$ | < 20% |
| Aquagenic Refractory Organic Matter (AROM) | 500 to 1000 | 10-90% |

Table 2.1: Organic matter compositions in natural waters

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 MATERIALS

Surfactant-free amidine polystyrene latex particles were purchased from Interfacial Dynamics Corporation (Portland, OR). At the neutral pH conditions used in this study, the particles are positively charged and have a surface charge density of 8.4μC/$cm^2$, as determined by the manufacturer. The mean diameter of these particles is 0.12 μm as determined by the manufacturer and confirmed in our laboratory using a photon correlation spectrophotometer, or "PCS" (90 Plus particle size analyzer, Brookhaven Instruments Corporation, NY). Amidine polystyrene latex particles with a mean diameter of 0.49 pm were used in select adsorption measurements. Prior to use, particles were diluted into carbonate buffer (pH 7) prepared with MilliQ-quality water. Sodium bicarbonate ($NaHCO_3$) was utilized to prepare the carbonate buffer solution. A stock solution of 0.1M sodium bicarbonate was prepared with MilliQ water. Approximately 0.5 ml of this stock solution was added to 1L of MilliQ water and allowed to equilibrate with the atmosphere for at least 8 hours. Generally, a buffer solution with a pH of 7 was obtained.

Humic acid and poly (vinyl alcohol) were supplied by the Aldrich Chemical Company (Milwaukee, WI). Aldrich humic acid was prepared by the base extraction of coal by the manufacturer, and is not isolated from natural waters. However, a number of studies utilize this material and therefore it represents a good model humic material. The humic acid used in this study has a molecular weight of 4100 g/mol [53] and is a negatively charged polyelectrolyte due to the dominance of carboxylic acid groups. However, significant variation in the size of Aldrich humic acid has been observed for different "batches". To prepare humic acid, the specific amount needed to produce the desired concentration was completely dissolved in buffer solution. After that, the solution was filtered using a 0.45 μm paper filter and stored at $4^{o}$ C. The poly (vinyl alcohol) used here has an average molecular weight of 115,000 g/mol, as provided by the manufacturer, and is uncharged at the solution conditions of our experiments. All solutions were prepared in MilliQ water using only analytical-grade reagents.

## 3.2 METHODS

### ADSORPTION MEASUREMENTS

The adsorption of humic acid to amidine latex particles was determined spectrophotometrically using an UV-VIS 240IPC double beam spectrophotometer (Shimadzu Corporation, MD). All adsorption measurements were carried out at a temperature of 25°C and a pH of 6.8. To carry out a humic acid adsorption experiment, 40 pL of the 0.49 pm amidine latex particles were added to 4 ml of humic acid and the mixture was incubated for 2 hours in a 10 ml polypropylene centrifuge tube. After which time, the latex particles were separated from the liquid phase by filtration through 0.22 pm pore size Millex-GV disposal filters (Millipore, Bedford, MA). Control tubes containing humic acid and no latex particles were treated in an identical manner to ensure that there was no adsorption of humic acid onto the filter surface. The amount of humic acid adsorbed at a wavelength of 350 nm was calculated by measuring the depletion in solution.

The adsorption of PVA to amidine latex particles was determined in a similar manner using a total organic carbon analyzer (TOC 5000A, Shimadzu Corporation MD). In these experiments, however, we used the 0.12 pm latex particles and 0.1 pm pore size Millex disposal filters (Millipore, MA). Control tubes containing PVA and no latex were utilized, again to verify that no adsorption onto the surface of the filters was occurring. To determine the adsorption of PVA to humic-acid-coated latex particles, humic acid was added to the particles and incubated for two hours prior to the addition of PVA. Following this initial incubation period, the suspension was centrifuged for at least one hour in order to separate the particles from any humic acid remaining in solution. The particles were then resuspended, exposed to a solution of PVA, and the depletion of PVA in solution monitored using the TOC analyzer. Control experiments (data not shown) carried out with humic-acid-coated particles, but in the absence of PVA, demonstrated that no measurable desorption of humic acid was occurring during the course of a PVA adsorption experiment.

## STABILITY MEASUREMENTS

Initial coagulation experiments focused on examining the stability of 0.12 pm latex particles in the presence of a single polymer; either humic acid or PVA. The stability of the latex particles in these experiments was determined by measuring the change in the average hydrodynamic diameter of the latex particles using the PCS. All measurements were conducted at a temperature of $25^{\circ}$C, at a scattering angle of $90^{\circ}$, and in the presence of 0.01M sodium chloride. The initial pH in all stability experiments was 6.8, and no measurable change in this value was observed over the course of a stability experiment. Special precautions were taken to ensure that samples were free of dust. In particular, all solutions were diligently covered immediately upon preparation.

The coagulation experiments were carried out as follows: 3ml of initially stable latex suspension were added to a well-cleaned cuvette. Then, 1ml of 0.04M sodium chloride, which had previously been equilibrated with a known amount of humic acid or PVA, was added and the change in hydrodynamic diameter immediately monitored by the PCS. Stability ratios were calculated by comparing the rate of change in hydrodynamic diameter for a given experiment ($k_{\exp}$) to the rate of change for rapid coagulation ($k_{rapid}$):

$$W = k_{rapid} / k_{\exp} \qquad [1]$$

The rate of change in the hydrodynamic diameter for rapid coagulation was determined at IM NaCl in the absence of humic acid and PVA.

To determine the stability of humic-acid-coated particles in the presence of PVA a similar procedure was followed. In these experiments, however, humic acid was added to the particles and incubated for two hours to allow for sufficient time for the adsorption of humic acid to the latex surface. Following this incubation period, the suspension was sonicated to disperse the particles prior to the addition of PVA. Upon addition of PVA, the change in hydrodynamic diameter was measured as a function of time using the PCS and stability ratios calculated as described above.

## ELECTROPHORETIC MOBILITY

The electrophrotic mobility of 0.12 pm latex particles was determined utilizing an electrophoretic light scattering instrument (ZetaPlus Brookhaven Instruments Corp., NY). All mobility measurements were carried out at 25°C and neutral pH. To measure the mobility of the latex particles, suspensions were prepared in identical manner to those used in stability measurements. Each calculated mobility value represents the average of at least 15 independent measurements.

## HYDRODYNAMIC LAYER THICKNESS (HLT) MEASUREMENTS

The PCS instrument was used to determine the hydrodynamic layer thickness of adsorbed polymers.To calculate the hydrodynamic layer thickness, the diameter of the bare particles was subtracted from the diameter of the particles determined in the presence of varying amount of polymers. HLT values were determined only at high stability (usually greater than 100) to minimize the effects of coagulation on the size of the particles. The diameters of the particles in the presence and absence of polymer were determined based on the average of 10 independent measurements.

# CHAPTER 4

# RESULTS AND DISCUSSION

In initial experiments, we examined the affinity of humic acid for the surface of amidine latex particles at different salt concentrations (0.01, 0.1 and 1.0 M NaCl) and these data are shown in Figure 4.1. As can be seen, humic acid has a high affinity for the surface of amidine latex particles and the amount adsorbed varies with salt concentration. The plateau point (maximum surfaces density of humic acid) increases from approximately 60mg/g at 0.01M NaCl (filled triangles) to close to 150mg/g at 1M NaCl (filled circles). The observed increase in adsorbed amount with increasing salt concentration is likely due to screening of the electrostatic repulsion between segments of adsorbed humic acid molecules. In addition, a decrease in the size of humic acid in bulk solution at high ionic

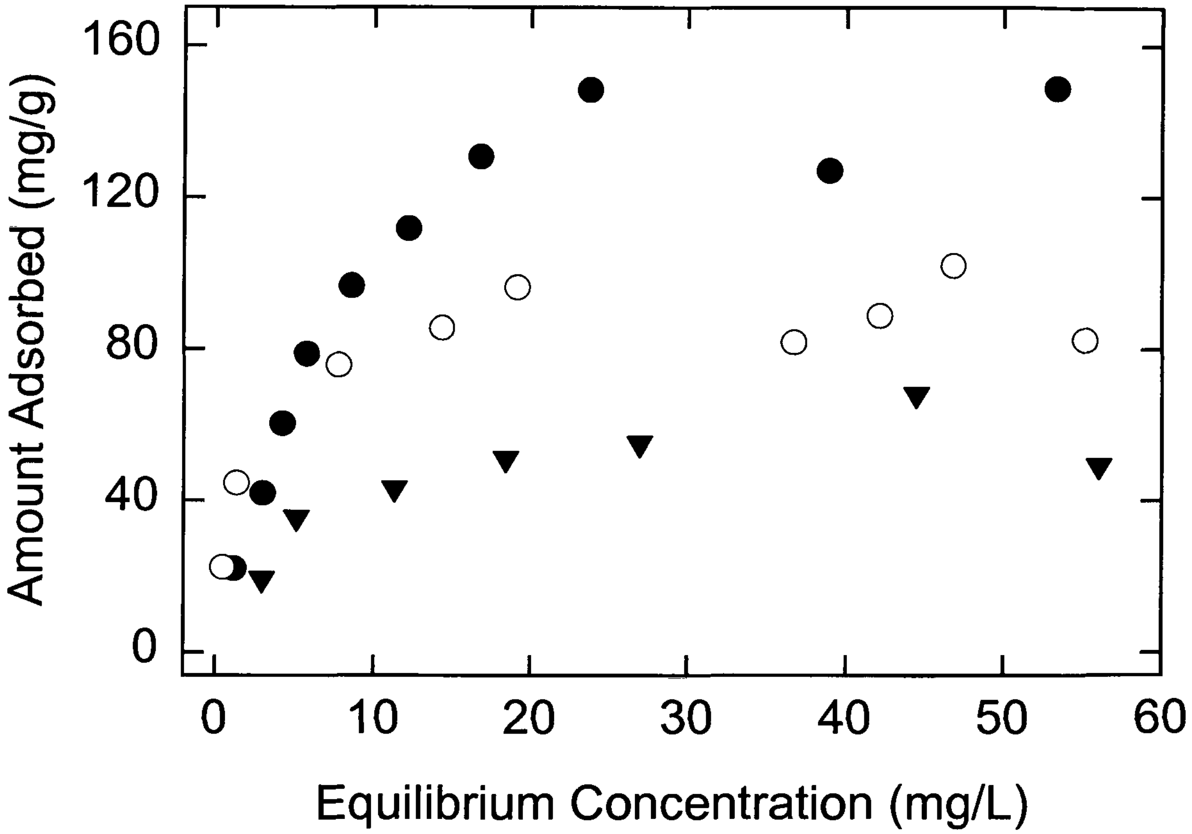

**Figure 4.1.** Adsorption of Humic Acid onto the Surface of Amidine Latex Particles at 0.01 M (▼), 0.1 M (○), and 1.0 M (●) NaCl.

strength may also contribute to the increase in adsorbed amount with increasing ionic strength. Several studies have shown that humic substances behave as flexible, linear polyelectrolytes in aqueous solution [12]. Increasing the ionic strength of solution will lead to a continuous change in humic acid conformation from an uncoiled macromolecule (i.e., expanded conformation) at low salt to a fully coiled state (i.e., compact conformations) at high salt. Thus, at the salt concentration (0.01 M NaCl) and pH (6.8) of all subsequent stability experiments, we expect humic acid to be fairly rigid in solution and adsorb in a flat conformation on the latex surface. Hydrodynamic layer thickness measurements (data not shown) carried out at low salt concentrations using the PCS demonstrate that the adsorbed thickness of humic acid is less than 10 nm.

Upon addition of polymer (either humic acid or PVA) to an initially stable particle suspension, the particle diameter may either remain stable or increase. Figure 4.2, shows the change in particle diameter with time as a function of humic acid concentration. At a humic acid dose of 2mg/L, the particle diameter is stable, thus indicating little aggregation is occurring. On the other hand, a humic acid dose of 0.2mg/L will cause a rapid increase in diameter with time, which is indicative of a high coagulation rate.

The importance of interparticle forces in controlling the coagulation rate of the particles can be determined by calculating the stability factor ($W$). The value of $W$ is calculated using equation (1) based on the kinetic data shown in Figure 4.2. The influence of humic acid on the stability of the latex particles at a

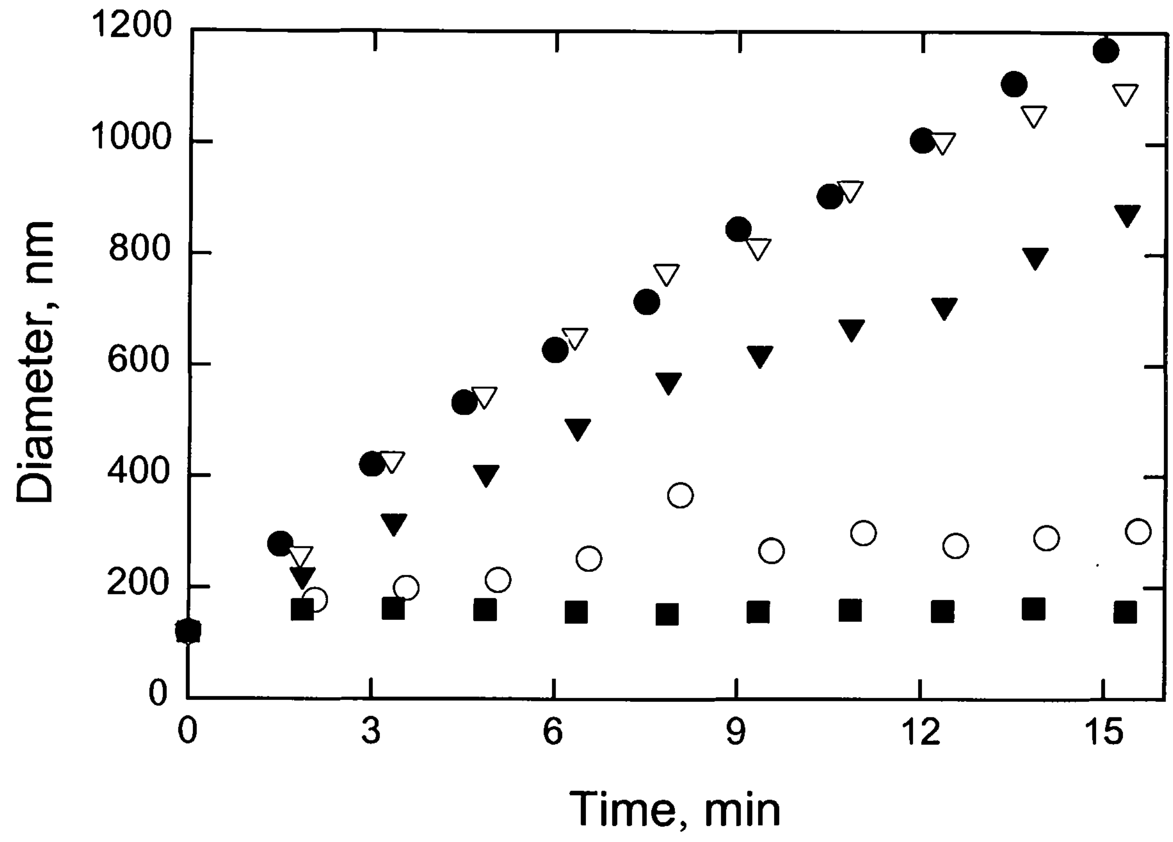

**Figure 4.2** Change in Particle Diameter As a Function of Time at Humic Acid Concentrations of 2.0 (■), 0.01 (O), 0.1 (▼) and 0.2 (∇) mg/L. All Experiments Were Carried Out at a Salt Concentrations of 0.01M NaCl. The Coagulation of the Bare Particles at 1M NaCl (●) is Shown for Comparison.

salt concentration of 0.01 M is shown in Figure 4.3. Physically, $1/W$ represents the fraction of particle-particle collisions that result in a sticking event. Thus, high values of $W$ indicate that particles are stable (i.e., coagulate at a slow rate), while low values of $W$ are indicative of unstable suspensions. The results in Figure 4.3 demonstrate that humic acid has a significant effect on the stability of the latex particles. Rapid coagulation ($W = 1$) is observed at humic acid dosages of 0.2mg/L, while the particles are relatively stable at dosages above and below 0.2mg/L humic acid. It should be noted that in the absence of humic acid little coagulation was observed at this salt concentration, and the stability factor was calculated to be greater than 100 (data not shown).

To better understand the mechanism of particle coagulation in the presence of humic acid we examined the electrophoretic mobility of the particles as a function of humic acid dose (see Figure 4.4). As can be seen, humic acid causes the particles to undergo charge reversal, with mobilities ranging from 3.48 (μm/s)/(V/cm) at the lowest humic acid concentration to –2.17 (μm/s)/(V/cm) at the highest concentration of humic acid tested. A net charge of zero was reached when the humic acid concentration was approximately equal to 0.2 mg/L, which is the concentration of humic acid corresponding to minimum stability as shown in Figure 4.3. The fact that minimum particle stability occurs at a humic acid concentration in which the net mobility is zero is strong evidence that humic acid coagulates the particles by charge neutralization. At high dosages of humic acid, the particles undergo charge reversal and therefore particle stability is largely controlled by repulsive electrostatic interactions between adsorbed humic acid

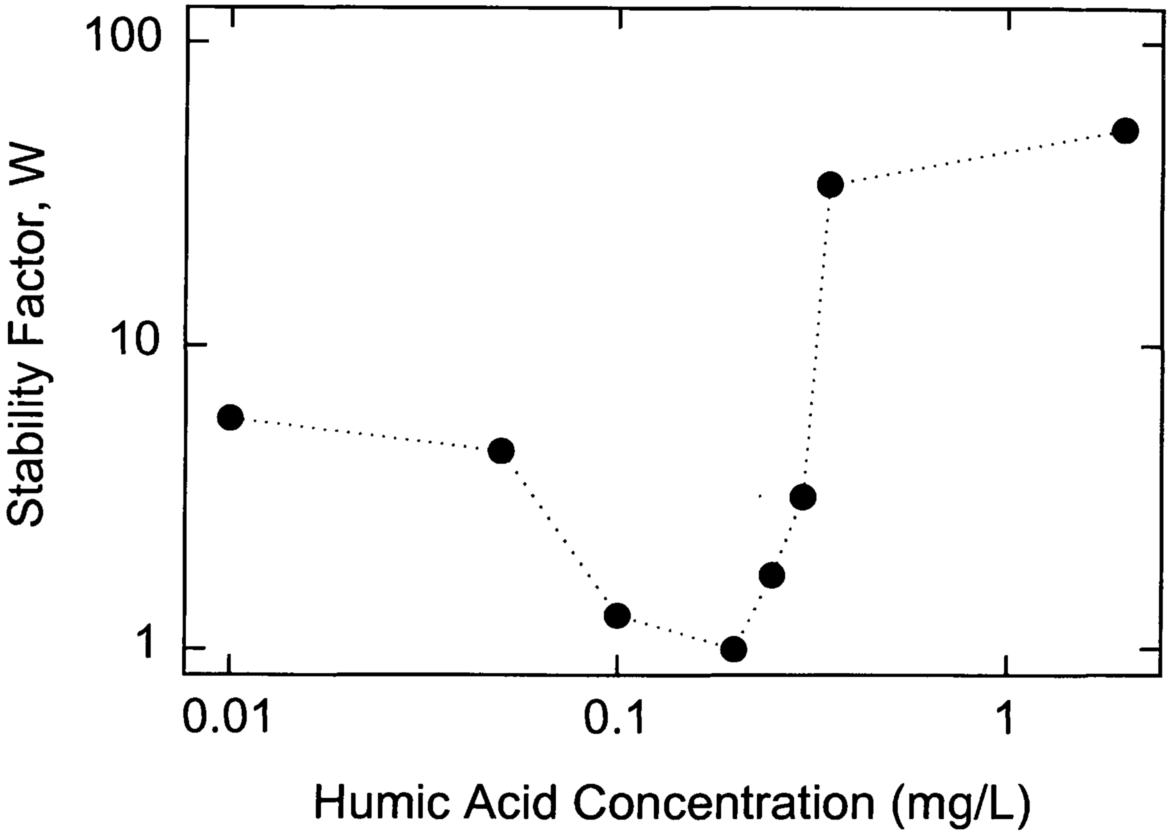

**Figure 4.3.** Stability of Amidine Latex Particle As a Function of Humic Acid Concentration at 0.01 M NaCl.

layers. Next, we examined how the presence of a nonionic polymer (PVA) influences the stability of the polystyrene latex microspheres. Figure 4.5 shows the stability of the bare latex particles as a function of PVA dosage at a salt concentration of 0.01 M NaCl. As shown in the figure, the particles remain relatively stable at low and high polymer concentrations, while coagulation is more rapid at intermediate concentrations of PVA (0.05 to 0.08mg/L). The non-ionic character of PVA suggests that the coagulation observed at intermediate polymer concentrations is most likely a result of polymer bridging interactions. Previous research has documented the importance of polymer bridging in controlling the flocculation of colloidal silica particles in the presence of PVA [54]. At high PVA surface coverage, the data in Figure 4.5 indicate particle stability increases, presumably due to the formation of steric repulsive forces between adsorbed polymer layers.

In natural waters, we suspect the presence of low molecular weight organic coatings may play a significant role in controlling the bridging coagulation of colloidal particles. To examine this hypothesis, we investigated how the adsorption of humic acid to the surface of the polystyrene latex particles affects polymer bridging in the presence of PVA. The stability of the latex particles as a function of PVA dose at a relatively high concentration of humic acid (2.5mg/L) is shown in Figure 4.6 (open circles). Under these conditions, the surface of the amidine latex particles is saturated with adsorbed humic acid. The stability of the latex particles as a function of PVA concentration, in the absence

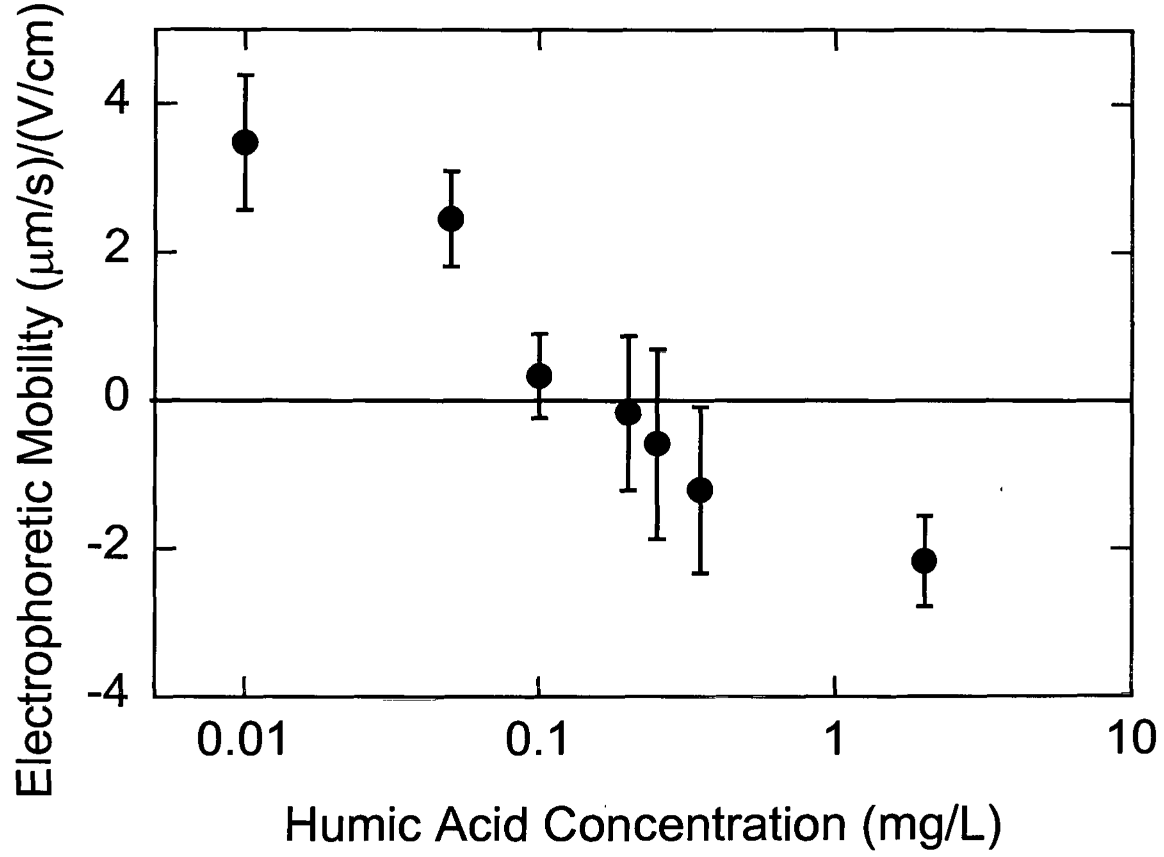

**Figure 4.4.** Electrophoretic Mobility of Amidine Latex Particles As a Function of Humic Acid Concentrations at 0.01 M NaCl.

of humic acid, is reproduced here from Figure 4.5 for comparison (filled circles). It is clear that coating the particles at this humic acid concentration stabilizes the suspension. The high particle stability in this case is most likely a result of a lack of available bridging sites for PVA, along with the repulsive electrostatic interactions between adsorbed humic acid layers. Given that most particles in natural waters are coated with a layer of organic material [55], preferential displacement of previously sorbed polymers and/or favorable interactions between adsorbed molecules and polymers in solution appear to be a necessary condition for the bridging coagulation of aquatic colloids.

Although the data presented above suggest that humic acid may inhibit bridging coagulation, it should be noted that the high stability of the latex particles observed in these experiments may also be due to the formation of steric repulsive forces arising from multilayer adsorption of PVA onto humic-acid-coated particles. To help clarify the relative importance of bridging interactions and multilayer adsorption in controlling colloidal stability, we carried out additional adsorption experiments. Figure 4.7 shows the adsorption of PVA onto bare and humic-acid-coated amidine latex particles. We find that when the particles are coated with humic acid at high concentration (2.5mg/L), the amount of PVA adsorbed is low (filled triangles). Perhaps the adsorption of humic acid reduces the potential for hydrophobic interactions and/or hydrogen bonding between PVA and the latex surface. Thus, particle stability in our experiments appears to be largely due to the electrostatic repulsion between humic-acid-coated surfaces and is not influenced to any significant extent by multilayer adsorption of

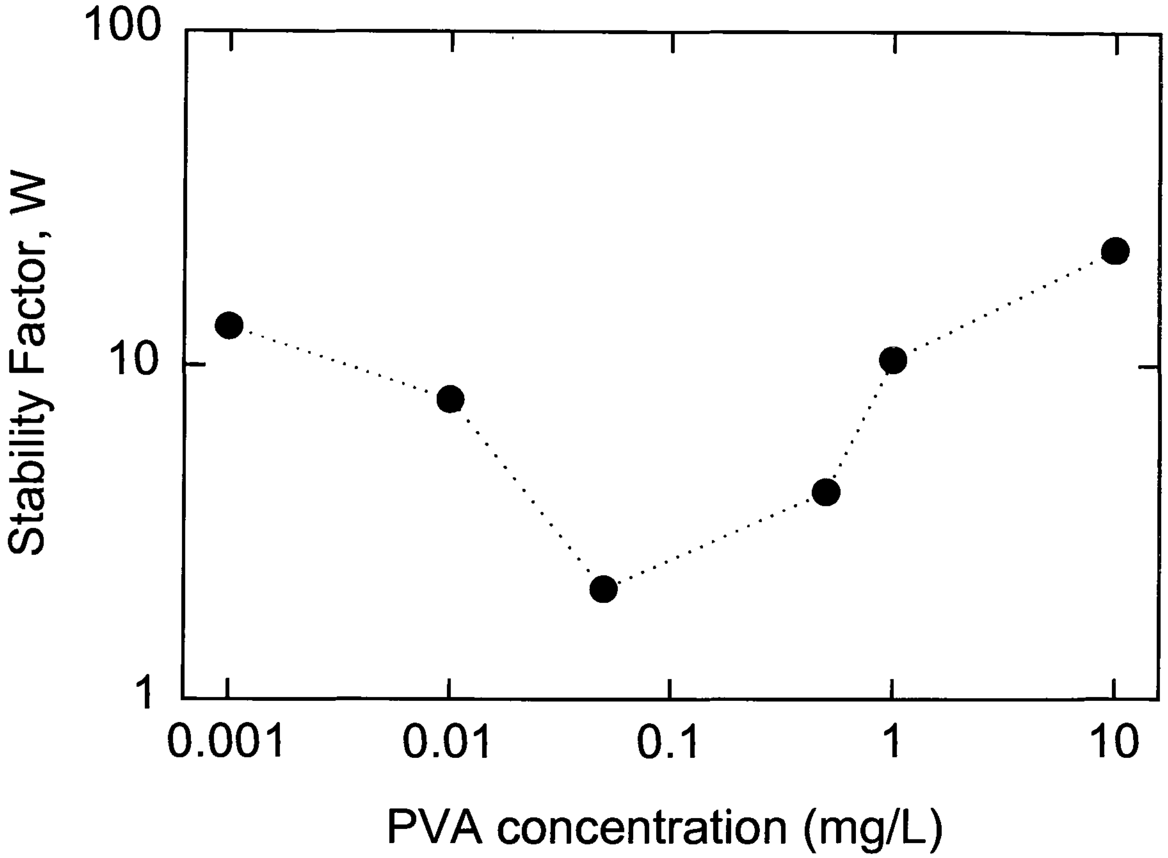

**Figure 4.5.** Stability of Amidine Latex particles As a **Function** of PVA Concentration at 0.01 M NaCl.

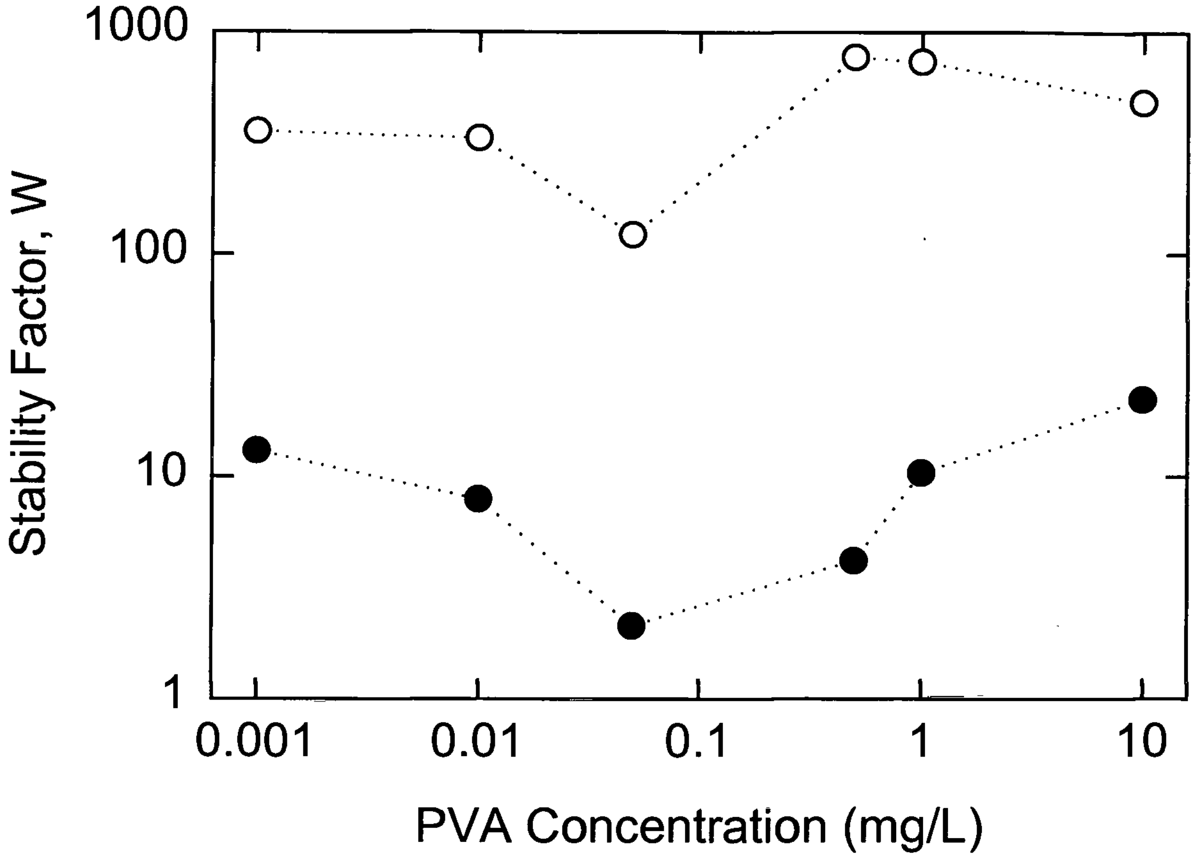

**Figure 4.6**. Stability of the Bare (●) and Humic-Acid-Coated (O) Latex Particles at a Humic Acid Concentration of 2.5 mg/L in the Presence of 0.01 M NaCl.

PVA. At low humic acid dosage (0.05mg/L), the amount of PVA adsorbed is similar (30 mg/g) in both the presence (open circles) and absence (filled circles) of humic acid.

In general, our results suggest that polymer bridging in natural waters will be influenced by the interactions between large chain polymers in solution and any previously adsorbed layers of organic material. The discussion above, however, assumes that organic coatings on naturally occurring particles are composed predominantly of humic and fulvic acids. A number of experimental studies provide evidence supporting the idea that humic acids may dominate the adsorbed fraction of organic matter in natural waters. For example, humic materials account for roughly 50% of the natural organic matter present in many aquatic systems [56, 57], have highly refractory structures, and are surface active [55, 58]. Furthermore, the small size of humic materials provides a kinetic advantage during the adsorption process over larger natural organic polymers such as polysaccharides.

Although research has shown that large molecular weight polymers may eventually displace smaller chains over long time scales [59, 60], the displacement process depends on the specific polymer-polymer and polymer-particle interactions in the system. Ramachandran and Somasundaran, for example, have shown that at low ionic strength the faster adsorption kinetics of low molecular weight polystyrene sulfonate (PSS) prevents the adsorption of larger PSS chains [61]. The fast adsorption of low molecular weight PSS results in the formation of electrostatic repulsive forces between these small PSS chains

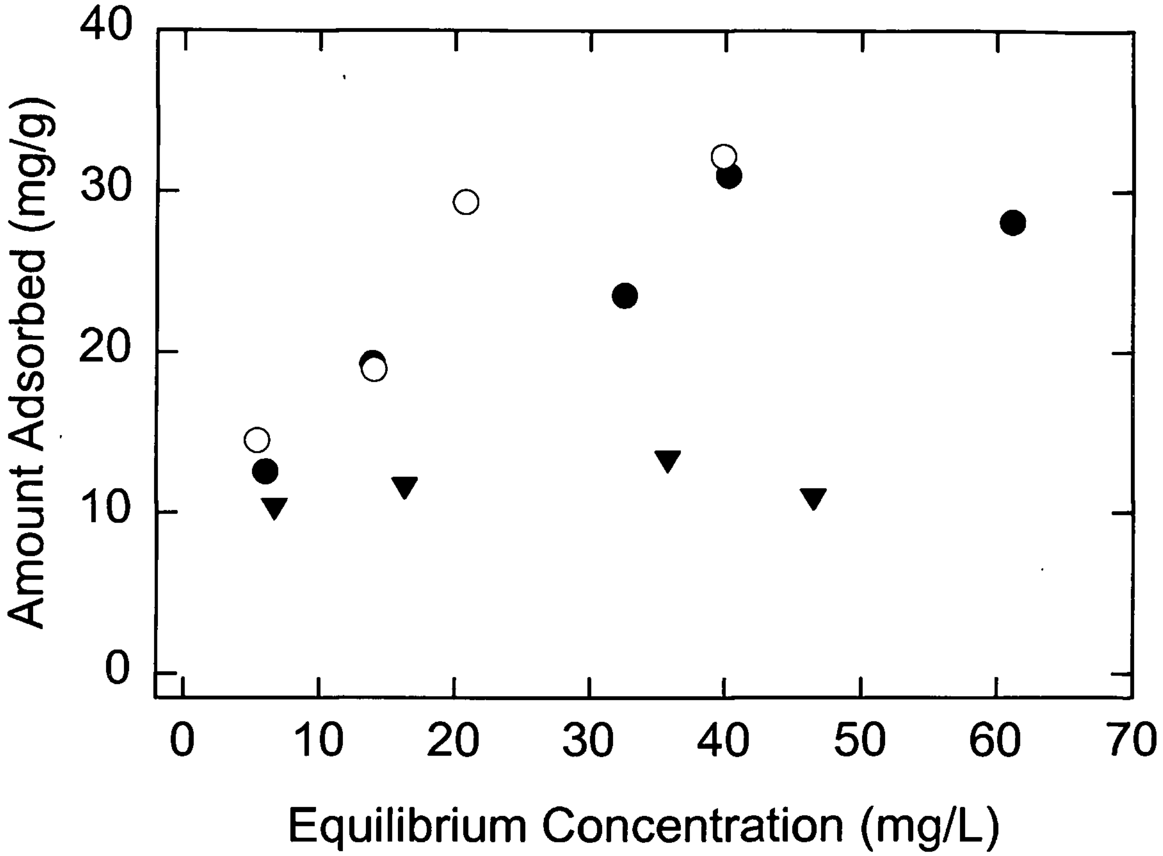

**Figure 4.7.** Adsorption of PVA onto the Surface of Bare (●), and Humic Acid-Coated Latex Particles at a Humic Acid Concentration of 2.5 mg/L (▼) and 0.05 mg/L (O) at 0.01M NaCl.

and large unadsorbed PSS molecules. In natural systems, the interactions between large and small organic polymers during adsorption and coagulation processes are largely unknown but will likely depend on the characteristics of the individual polymers, solution conditions, as well as particle surface properties. Further study is needed to elucidate competitive adsorption of heterogeneous solutions of organic polymers in natural systems.

We also examined how decreasing the surface coverage of humic acid influences the bridging process in the presence of PVA. At intermediate dosages of humic acid (0.2mg/L) we find that the particles are unstable at all PVA concentrations less than 1 mg/L (see Figure 4.8). Here, the neutralization of surface charge as a result of humic acid adsorption appears to control stability at most PVA concentrations, although polymer bridging may also be occurring at intermediate dosages of PVA. At high dosages of PVA (>1mg/L) colloid stability increases, most likely as a result of the formation of steric repulsive forces between adsorbed PVA layers. However, it should be noted that the concentration of humic acid in natural waters is generally between 1-10 mg/L and therefore these results may have less significance to environmental systems.

At low dosages of humic acid (0.05 mg/L) the particles remain unstable at all PVA concentrations less than 1mg/L (see Figure 4.9). It appears that this low dosage of humic acid enhances the coagulation of the latex particles, as compared to colloid stability in the presence of PVA and no humic acid (filled circles). The decrease in stability in this case is most likely due to the reduction in electrostatic

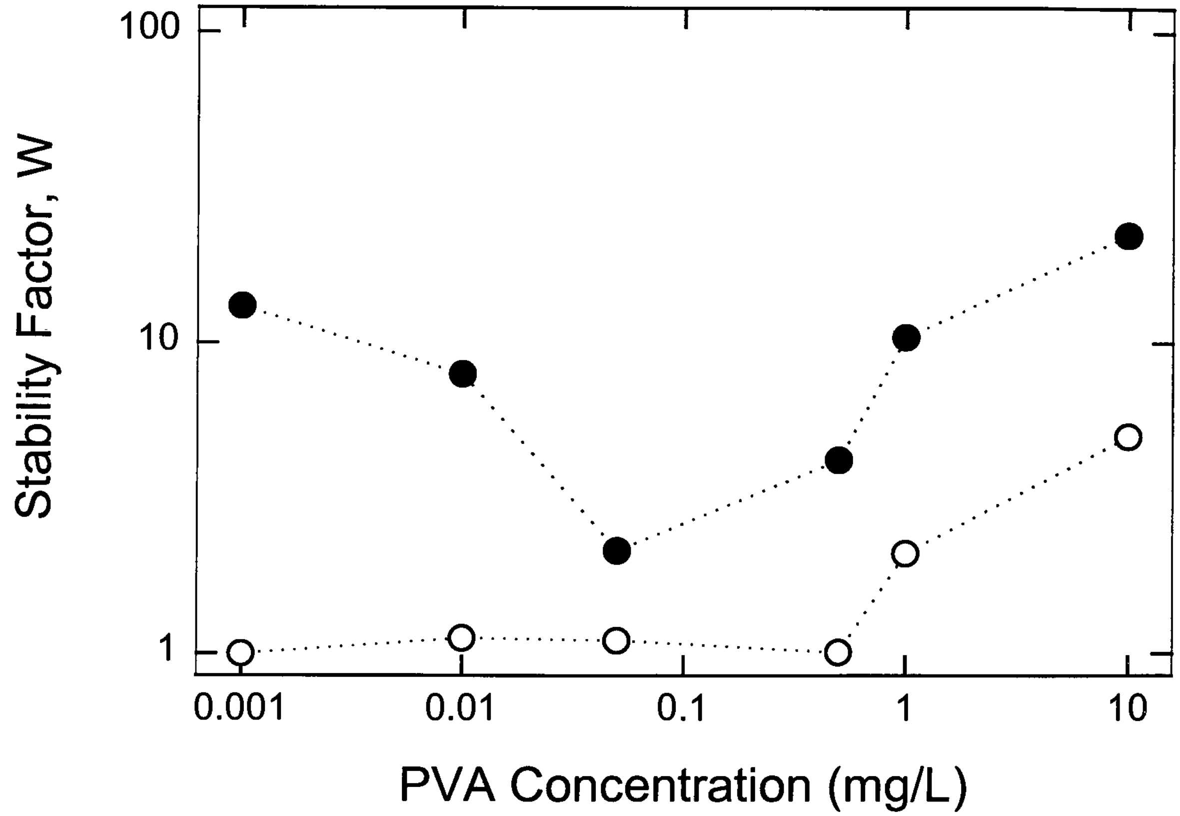

**Figure 4.8.** Stability of the Bare (●), and Humic-Acid-Coated (O) Latex Particles at a Humic Acid Concentration of 0.2 mg/L in the Presence of 0.01 M NaCl.

forces between particles at this humic acid concentration (see Figure 4.4). Perhaps in the absence of humic acid electrostatic forces extend beyond the thickness of the adsorbed PVA layer. Thus, under these conditions, some bridging coagulation is prevented as a result of strong electrostatic forces between particles and the subsequent lack of available contact points on approaching particles for PVA binding. When small amounts of humic acid are added to the suspension this leads to a reduction in electrostatic repulsion and may subsequently allow for more effective bridging by PVA. It should be pointed out, however, that the enhanced particle coagulation observed at low humic acid concentration could also be due to an increase in the affinity of PVA for the latex surface in the presence of humic acid. However, adsorption data (see Figure 4.2) indicate that the presence of low concentrations of humic acid have little measurable effect on the adsorption density of PVA.

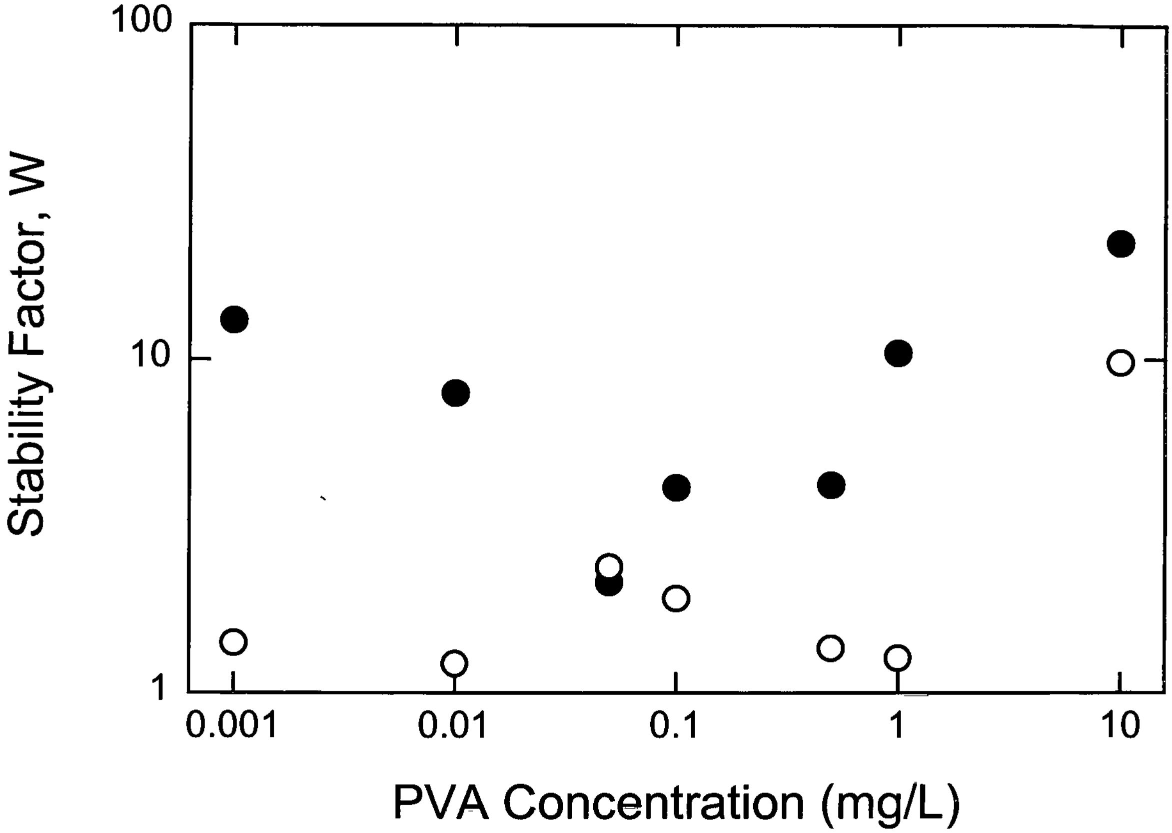

**Figure 4.9.** Stability of the Bare (●) and Humic-Acid-Coated (O) Late Particles at a Humic Acid Concentration of 0.05 mg/L in the Presence o 0.01 M NaCl.

# CHAPTER 5

# CONCLUSIONS AND FUTURE WORK

In this research, we investigate the effect of humic acid coatings on the bridging coagulation of polystyrene latex particles by PVA. We find that the presence of humic acid significantly affects the stability of the latex particles in the presence of this nonionic polymer. When the particles are coated with high dosages of humic acid, the particles are stable regardless of PVA dose, mainly as a result of electrostatic repulsion from the adsorbed humic acid layers and lack of available binding sites for polymer bridging. Coating the particles with humic acid at low dosages yields markedly better coagulation than when PVA is the sole flocculant. Here both the electrostatic forces and bridging appear to be important in controlling the flocculation rate of these particles. These data suggest that polymer bridging in natural systems may require the preferential displacement of low molecular humic and fulvic acids and/or favorable interactions between large macromolecules and particle surfaces coated with humic materials.

## FUTURE WORK

In this study, we used humic acid supplied by Aldrich Chemical Co. as a model for natural organic coatings to investigate its interactions with a nonionic polymer (PVA). Humic acids from different sources, however, will have different characteristics such as acidity, hydrophobicity and molecular weight. These characteristics can have a significant effect in our system. To better understand the effect of humic acid coatings on the flocculation of particles by polymers, a further investigation that examines the effect of humic acids from different sources (rivers, soils) is required. Furthermore, large-chain macromolecules with different electrostatic characteristics and molecular weights may also affect these interactions. Thus, carrying out these experiments with different polymers will help further elucidate these interactions.

It would also be interesting to carry out these experiments at high salt concentration where the electrostatic repulsion is minimal and humic acid adsorption is characterized by a compact polymer conformation. Maybe, under these conditions, humic acid will interact with the polymer in a different way, which, in turn, may significantly affect the coagulation rate. For example, raising the salt concentration is known to enhance hydrophobic interactions through a "salting out" effect. At high salt concentration multilayer adsorption and bridging may play a more important role in controlling coagulation, even at high humic acid surface coverage.

Lastly, there is a need for mathematical models to describe the bridging coagulation of colloids in the presence of multiple polymeric species in solution. Perhaps a starting point would be to modify existing bridging models developed by Hogg [37], Healy [36] and Soto [38] by including the effect of polymer adsorption on the fraction of available sites for bridging. Developing expressions describing how competitive adsorption processes influence the fraction of active sites would be a major component of this work.

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