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This comprehensive text is a **revision** of the popular ***Wet End Chemistry: An Introduction***, published by TAPPI PRESS in 1992. This text offers an introductory overview of wet end chemistry. Written by Dr. Bill Scott of Miami University, this text will be a valuable reference tool for everyone involved in wet end chemistry.

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***THERE IS NO SUBJECT INDEX FOR THIS PUBLICATION**

Chapter 5

Surface and Colloid Science Concepts Important to Papermaking Chemistry

The objective of this chapter is to introduce the basic surface and colloid science concepts that operate in papermaking chemistry in order to provide a foundation for future study. The discussion first presents a case for categorizing most papermaking chemistry phenomena as hydrophobic or hydrophilic colloid systems. Next, various mechanisms proposed for the aggregation behavior of hydrophobic colloids are defined and their relevance to papermaking introduced. This is followed by a brief discussion of the adsorption of polymers onto solid surfaces. The chapter next deals with the surface chemistry concepts related to sizing. The final section discusses surface activity and other phenomena related to association compounds. In all instances, the discussion will be introductory in nature, with the emphasis on general concepts and important terminology. The information presented in this chapter will be applied throughout the remainder of the book.

1. Definition of papermaking chemistry

Papermaking chemistry can be defined as the "surface and colloid chemistry of papermaking furnish components." To demonstrate the basis for this definition, we will consider some characteristics of a typical furnish.

Table 5-1. "Resident species" of a papermaking furnish

1. Dissolved electrolytes
2. Suspended fibers
3. Suspended fiber fines
4. Suspended filler particles
5. Water
6. Surface-active molecules (either alone or as aggregates). (Examples: detergents, dispersants, wood extractives, defoamers)
7. Dissolved polyelectrolytes (Examples: polyacrylamides, cationic starch, wet-strength agents, dry strength agents)
8. Aggregated sizing molecules.

2. Resident species of a typical papermaking furnish

Table 5-1 lists many of the "resident species" of a papermaking furnish. These species are present at various concentrations and combine to make up a headbox consistency of 0.3% to 4.0%, depending upon the grade of paper being manufactured. The environment can be relatively static (e.g. a high density stock chest) or quite dynamic (e.g. a high-turbulence headbox).

3. Important interactions among furnish components

Furnish components interact with one another in a variety of ways (**Table 5-2**). Interactions may be desirable or undesirable. For example, the deposition of an alum/rosin size precipitate onto fibers is desirable, but the formation of an alum scale precipitate is undesirable. In addition, the papermaker may or may not be able to control the interactions listed in the table.

4. Wet end intermolecular forces

Interactions between two particles involve both attractive and repulsive forces. Chemists usually refer to two categories of attractive interactions at the atomic and molecular level: namely *primary* and *secondary* bonding interactions. Primary bonding forces unite atoms into molecules or chemical compounds. In organic compounds these bonds have energies of 420-840 kJ/mol of bonds formed, operating at interatomic distances of 0.1-0.2 nm.

Secondary bonding forces involve energies of 840 kJ/mol operating over distances of 0.2-0.3 nm. Hydrogen bonding is a special case of secondary bonding. A hydrogen bond has an energy range of 12-21 kJ/mol and a bond distance of 0.28 nm. It is important in the water-fiber interactions and fiber-fiber interactions that

Table 5-2. Examples of important interactions among furnish components

1. Aggregation of fibers, fillers, and fines
2. Adsorption of dissolved polymers onto fibers, fines and fillers
3. Aggregation of pitch and sizing molecules
4. Adsorption of pitch and sizing molecules onto fibers, fines, and fillers
5. Neutralization of negative charges on suspended and dissolved anionic materials
6. Establishment of equilibria between dissolved inorganic salts and insoluble ionic products
7. Development of micelles composed of surface-active molecules
8. Sorption of water by fibers, fines, and starches

lead to bonding in paper. Secondary bonding forces are referred to collectively as Van der *Waals Forces.*

In **Table 5-2**, the equilibrium between dissolved ions and their insoluble precipitates involve primary, ionic bonds. Similarly, charged polyelectrolytes may also participate in ionic interactions, but to a lesser degree than salts. The remainder of the interactions in the table involve secondary bonding.

5. Dimensions of furnish components

All the furnish components listed in **Table 5-1** have at least one very small dimension (**Table 5-3**). Such particles have high specific surface areas (surface area per unit weight). For example, cubes of density 1.0 gm/cm^3 having edge lengths in the 10.0 μm to 0.1 μm range, which are typical dimensions for papermaking components, will have specific surface areas ranging from 0.6 m^2/g to 600 m^2/g. Further discussion of the relative dimensions of papermaking components can be found in Linhart.[1]

Table 5-3. Smallest dimension of furnish components

Component	Size	Dimension
Fiber	10-20 μm	Width
Fibril	<1 μm	Width
Nonfibril fiber fine	<1-2 μm	Diameter
Filler particle	0.1-10 μm	Diameter
Dispersed rosin size aggregate	<1 μm	Diameter
Dissolved polyacrylamide molecule	<1 μm	Length

Solvent-exchanged, water swollen fibers and fines have specific surface areas ranging from 10 m^2/g to 50 m^2/g. Other particulate papermaking materials, such as fillers, also have high specific surface areas. These will be described in greater detail in Chapter 10.

6. The "colloidal" state

When the surface area-to-mass ratio of a dispersed particle becomes large, then an appreciable fraction of its molecules lie in the interface between the particle and the dispersion medium. These "surface" molecules participate in secondary bonding interactions with other molecules identical to themselves located in the bulk of the particle and with the molecules of the surrounding medium. Whenever the two kinds of interactions are unbalanced, then excess energy exists at the particle surface. This excess energy, in turn, strongly influences the behavior of the entire system of dispersed particles.

When the surface chemical properties of a dispersed system are important to the overall chemical behavior of the system, the study of the system involves a branch of physical chemistry known as *colloid chemistry*. Thus, papermaking chemistry is really colloid chemistry because of the large specific surface areas involved and because most papermaking chemistry interactions occur at particle surfaces.

In summary, many papermaking furnish particles have colloidal dimensions and high specific surface areas. In addition, many of the interactions that occur among these particles involve secondary bonding forces. These are two primary traits of colloid systems and it is appropriate to define wet end chemistry in terms of surface and colloid science.

7. Classification systems in colloid chemistry

Having established that papermaking chemistry can be considered to be colloid chemistry, it is convenient to consider papermaking chemistry in terms of common colloid systems. For example, most colloid systems can be classified as either *lyophobic* or *lyophilic*. **Table 5-4** lists the principal characteristics of the two systems.

Table 5-4. Characteristics of lyophobic and lyophilic colloid systems

Lyophobic Systems

1. Suspensions of particles — not solutions
2. Little attraction or affinity between the solvent and particle
3. Unstable with respect to the formation of aggregates
4. Interface exists between the particle and suspending medium that strongly affects system behavior

Lyophilic Systems

1. True solutions of very large molecules or aggregates of small molecules
2. Strong attraction between solvent and particle
3. No true interface between particle and medium

The prefix "lyo-" means "solvent" and since papermaking is carried out in water, the relevant colloid systems are designated *hydrophobic* and *hydrophilic*. **Table 5-5** lists some typical examples of hydrophobic and hydrophilic papermaking systems.

Table 5-5. Examples of hydrophobic and hydrophilic papermaking systems

Hydrophobic

1. All pigments dispersed in water
2. Fines dispersed in water
3. Rosin size in water
4. Dispersed rosin size emulsion

Hydrophilic

1. Starch dissolved in water
2. Gums dissolved in water
3. Hemicelluloses dissolved in water
4. Surfactants, dispersants, wetting agents dissolved in water
5. Retention, drainage, and formation aids dissolved in water

Two types of hydrophilic colloids are important in papermaking. The first type includes materials like retention and drainage aids that affect the behavior of hydrophobic substances. Dry strength and wet strength additives also fall into this category of hydrophilic materials. The second type of hydrophilic colloids are the *association compounds*, such as wetting agents, surfactants, defoamers, and dispersants. These will be discussed in greater detail later in the chapter.

a. Further comments about the use of the term "hydrophobic"

Further comments are in order about the application of the term "hydrophobic" to the common papermaking systems listed in **Table 5-5**. Pigments and fiber fines are known to be wettable and to interact with water. Indeed, the surface of a fiber fine is covered with a gel formed by solvated hemicellulose and cellulose molecules. Even rosin size dispersion must interact with water to a certain degree or it would be impossible to form a stable suspension. Nevertheless, dispersions of these materials do exhibit the characteristics of lyophobic colloids listed in **Table 5-4** and do not have any of the properties listed for lyophilic systems in **Table 5-4**.

Another way to look at the matter is to realize that individual particles may have wettable, water-attracting (hydrophilic) surfaces, yet produce dispersed systems having hydrophobic characteristics.

b. Stability of hydrophobic dispersions

The study of hydrophobic dispersions is concerned principally with the *rate* at which they revert to their equilibrium, aggregated state. Indeed, all of the hydrophobic systems listed in **Table 5-5** become aggregated during papermaking. In practice, the papermaker wishes to control the aggregation process in order to achieve a uniform distribution of materials throughout the sheet, while at the same time retaining the maximum percentage of incoming materials in the sheet. Uncontrolled aggregation leads to poor paper quality and deposit problems.

The stability of a hydrophobic colloid dispersion is indicated by its ability to remain dispersed and is measured by the time it takes for the particles to settle out of the liquid phase. This phase separation may be due to gravity sedimentation of the primary dispersed particles or the aggregation of primary particles into larger aggregates that sediment. The main types of aggregation mechanisms are listed in **Table 5-6**.

Table 5-6. Hydrophobic colloid aggregation mechanisms

1. Coagulation: The destabilization of a colloidal suspension with salts or very low molecular weight, high charge density polyelectrolytes.
2. Flocculation: The destabilization of a colloidal suspension by bonding the particles together with a long chain polymer.

The terms coagulation and flocculation are often used interchangeably. However, since they represent two distinct aggregation mechanisms, it seems logical to apply different terms to them. That practice will be followed in this book.

8. Surface charge on hydrophobic particles

An electrostatic charge develops at the solid/water interface when solids are dispersed in water. In papermaking systems, this charge may arise from dissociated surface carboxyls and sulfonic acid groups and the adsorption of substances, such as hemicelluloses, dissolved lignin, retention aids, and cationic starches onto surfaces. Mineral fillers, such as clay and titanium dioxide, also develop surface charge by ionization of the particle/water interface and by adsorption of other charged substances.

The description of charges at solid/liquid interfaces was first outlined by Helmholtz[2] in 1879 and was elucidated in subsequent years by Gouy[3], Chapman[4], and Stern[5]. **Fig. 5-1** depicts a currently accepted representation of the phenomenon.[6–8] The surface potential is determined by the type and surface density of charged groups. Papermaking particles are generally anionic in nature. Therefore, **Fig. 5-1** is drawn with a negative charge at the surface.

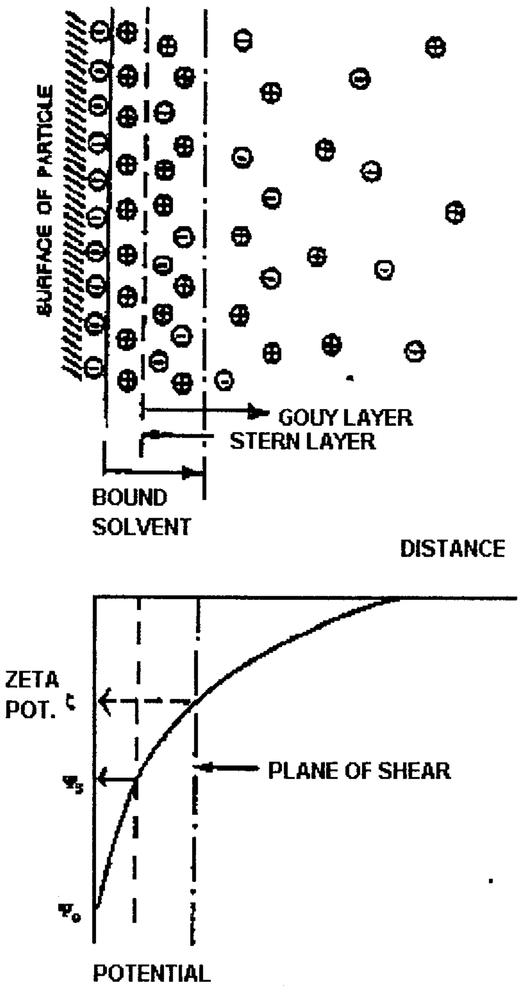


Figure 5-1. Representation of the electrical double layer existing at the surface of a hydrophobic particle suspended in water. The zeta potential, ξ, is taken to be the potential at the slip plane, within which counterions bound to the particle travel with the particle and outside of which counterions are free to move independently of the particle.

Ions of opposite charge to that of the particle surface (counterions) are held closely adjacent to the surface by electrostatic and Van der Waals forces. The potential energy drops off rapidly in this region. A hydrodynamic slip plane exists between the tightly bound counterions and solvent molecules adjacent to the surface (Stern Layer) and the rest of the solution. The less ordered, diffuse portion of the system is called the Gouy-Chapman Region. The potential falls off at a slower rate in this region than in the Stern Layer until zero potential is realized in the bulk of the solution.

The potential at the interface plane between the Stern Layer and Gouy-Chapman region is called the *zeta potential,* ξ. The common methods of measuring surface charge actually give values for zeta potential rather than surface charge. (Charge measurement is discussed in Chapter six.) The common name applied to the entire system is the *electrical double layer.*

There is no overall net charge in the suspension due to the requirement of electro-neutrality. However, local areas of positive and negative potential exist close to the surface of the particles being observed. The strength of these potentials and the distances involved determine the resistance of hydrophobic suspensions to aggregation.

9. Importance of the electrical double layer

The stability of a hydrophobic suspension is measured by its ability to remain dispersed over a period of time. This stability depends upon the relative magnitudes of the repulsive and attractive forces that exist between the suspended particles and how likely the particles are to collide with one another.

Attractive and repulsive forces arise from a number of sources. Van der Waals forces are always attractive for particles of the same chemical composition. Electrostatic forces arising from the interaction of particle electrical double layers are always repulsive if the particles have the same charge. They are attractive for particles of opposite charge. Stabilizing and destabilizing forces can also be developed by adsorbed polyelectrolytes.

The Van der Waals attractive forces and double layer repulsive forces were combined by Derjaguin, Landau, Verwey, and Overbeek into what is now referred to as the *DLVO Theory*.[8] This theory considers the attractive and repulsive forces that exist between two particles and describes the potential energy as a function of distance between them.[8] **Fig. 5-2** illustrates this treatment.

In the figure, the electrostatic repulsion energy, V_R, is represented by the upper dashed curve. The Van der Waals attraction energy, V_A, is the lower dashed curve. And the Total Potential Energy, V_T, is the solid curve. The depth of the minimum in the Total Potential Energy Curve is an indication of the stability of a particle-particle aggregate. A shallow minimum suggests that the aggregate can be disrupted more readily than when a deeper minimum exists.

10. Aggregation and stabilization of hydrophobic dispersions

We will now discuss how aggregation can be caused to occur. We will also describe how a system can be stabilized if a dispersed condition is desired.

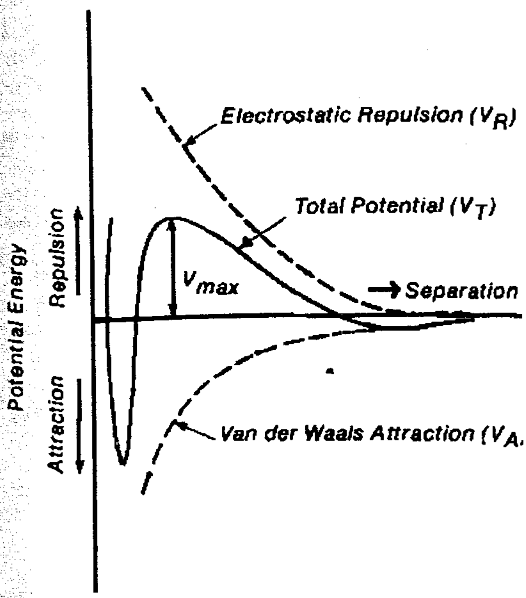


Figure 5-2. Representation of interparticle interaction energy as a function of the distance of separation between two particles. The figure illustrates the combining of attractive and repulsive potential energies. The electrostatic repulsion energy (V_R) is represented by the upper dashed curve. The Van der Waals attraction energy (V_A) is the lower dashed curve. The Total Potential Energy (V_T) is the solid curve. The depth of the minimum in the Total Potential Energy Curve is an indication of the stability of the particle-particle aggregate. A shallow minimum suggests that the aggregate can be disrupted more readily than when a deeper minimum exists.

a. Coagulation by charge neutralization

As discussed above, a layer of strongly adsorbed counterions and a diffuse region of counter- and co-ions make up the electrical double layer of particles suspended in water. This layer has a certain thickness for a given set of conditions. The thickness of the double layer decreases when electrolytes are added to the suspension due to an increase in the availability and number of counterions. Increased counterion concentration reduces the zeta potential and, thereby, the repulsion component of the total potential. Particles can then approach one another more easily and aggregation becomes more likely. Aggregations by this mechanism is referred to as *charge neutralization* because the addition of excess counterions moves the net potential towards a state of zero charge. Charge neutralization is a coagulation phenomenon. (See **Table 5-6**.)

There are two further points to be made regarding this mechanism. First, there exists a critical concentration of salt where the double layer is sufficiently suppressed for coagulation to proceed. This is normally referred to as the *critical coagulation concentration*, or C.C.C.

The second point deals with the relative effectiveness of different cations in reducing the double layer thickness of anionic surfaces. Shultz and Hardy found that the valence magnitude of the ion charged oppositely to the surface had the principal effect on colloid stability.[9] They found that the higher the valence, the more effective was the ion in reducing surface charge — with the ratios of ionic valence +1, +2, and +3 required to achieve the C.C.C. being 4000:100:15.[9] Thus, Al^{+3} salts (e.g. alum $Al_2(SO_4)_3$) are more effective than Ca^{+2} salts (e.g. $CaCl_2$), which, in turn, are more effective than Na^{+1} salts (e.g. NaCl).

Of importance to the papermaker is that coagulation produces tight aggregates where the particles come into close contact. Such aggregates tend to drain well and produce a well-formed sheet.

b. Patch model

When low molecular weight (100,000-1 million) cationic polyelectrolytes with high charge density (>4 meq charge/g) are mixed with anionic particles, the polymer molecules are believed to adsorb completely onto the particle surfaces and form a "patch" of positive charge (**Fig. 5-3**).[10] This patch effectively reverses the anionic charge at that site on the particle surface while the rest of the particle remains anionic. (The overall potential may also remain anionic.)

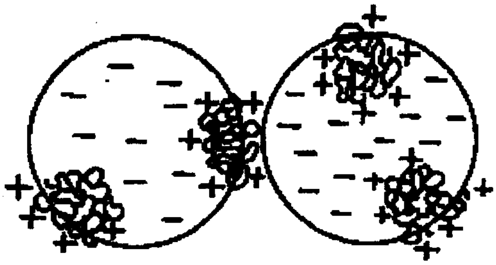


Figure 5-3. Schematic representation of the model for patch flocculation behavior. The positively charged patches on one particle are attracted to negative regions on the surface of another particle and electrostatic attraction draws them together so that Van der Waals forces can cause them to aggregate.

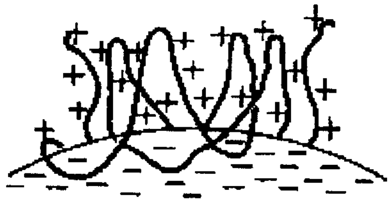
After the polyelectrolyte is adsorbed, collision of the positively charged patch with an uncovered negative area on another particle leads to coagulation. The aggregation rate is greater than that produced by coagulation with a simple electrolyte.

Patching, being a charge neutralization phenomenon, produces closely packed aggregates that promote good formation and good drainage.

c. Flocculation by bridging polymers

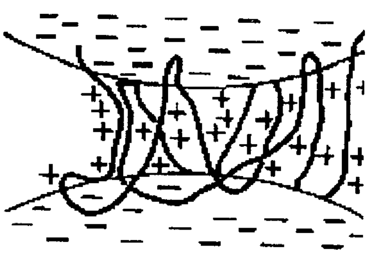
The flocculation of colloidal materials by polyelectrolytes of high molecular weight (>1 million) is presumed to take place by a bridging mechanism.[11,12] In this mechanism, the polymer adsorbs onto the particle surface with a series of loops and tails extending into the liquid phase (**Fig. 5-4.a**). These loops and tails extend well beyond the double layer. Flocculation then occurs by adsorption of the extended loops and tails onto the negative surface of a second particle (**Fig. 5-4.b**). Bridging flocculation is dependent on the collision frequency of the two particles and repulsion between their double layers does not come into play. Flocculation is the primary mechanism for high molecular weight retention aids. It is a very important phenomenon in paper making.

Figure 5-4.a



Initial Adsorption

Figure 5-4.b



Initial Flocculation

Figure 5-4. Schematic representation of the model for bridging flocculation behavior. (a) The positively charged high molecular weight polyelectrolyte partially adsorbs onto the surface of the negative particle. Loops and trains of the polymer extend out into the surrounding medium. (b) The extended loops and trains of the adsorbed polyelectrolyte adsorb onto a second particle forming a "bridge" between the two.

The charge density and molecular weight of a bridging polymer are very important. Higher molecular weights promote increased bridging because longer polymer chains extend farther into the surrounding water and away from the particle surface. Polymer charge density influences the attraction of the polymer to the particle surface and the strength with which the macromolecule bonds to the surface.

Combining a low molecular weight, high charge density cationic polymer with a high molecular weight, low charge density anionic polymer is often done to produce the strongest aggregates. Such systems are referred to as *dual polymer* systems. In this instance, the cationic polymer forms cationic patches that serve as anchor points for the bridging anionic polymer.

d. Steric stabilization

In addition to stabilizing a hydrophobic colloid suspension by the development of a high surface charge, a system may also be stabilized when long chain polymers are adsorbed onto particle surfaces in a manner that the solvated polymer loops and tails extending away from one particle interfere with the solvated loops and tails from another particle, preventing the particles from approaching closely enough to aggregate(**Fig. 5-5**).[13] Such polymers are normally nonionic in nature and are of high molecular weight. This phenomenon is often called *protective colloid* action.

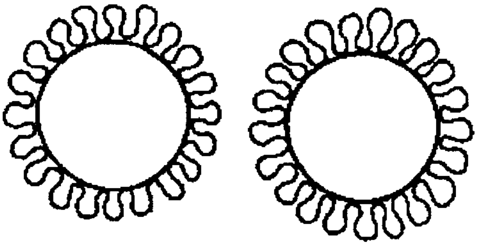


Figure 5-5. Schematic representation of the model for steric stabilization. In this instance the surfaces of particles are covered by adsorbed high molecular weight polymer material that extends out past the electrical double layer. When two particles approach one another, the extended polymer and its associated solvation water provides a steric barrier that holds the particles apart far enough that Van der Waals attractive forces cannot operate.

11. Adsorption of polymers from solution by solid surfaces

In the preceding section we discussed the patch and bridging aggregation mechanisms. Both require dissolved polymers to attach themselves to the surface of the particles that are to be aggregated. This process is called *polymer adsorption.*

Most adsorbing polymers of interest to papermakers are positively charged (cationic). Examples include cationic retention aids, cationic starch, and cationic wet strength resins. These materials all have a natural attraction for negatively charged fibers and fines. For the most part, nonionic and anionic polymers are not attracted to these particle surfaces and any adsorption that occurs must be promoted by the use of a cationic substance such as alum or a low molecular weight, high charge density cationic polymer. Consequently, our treatment of this subject will be focused primarily on cationic polymers.

a. General mechanism

In a system containing dispersed papermaking particles (fibers, fines, fillers, size particles) and dissolved cationic polymers (cationic starch, retention aids, wet strength resins) there is always movement of the particles and molecules caused by mixing forces and diffusion. These motions lead to particle-particle and particle-polymer collisions. Since cationic polymers and anionic fibers are oppositely charged, an attractive force develops that promotes polymer diffusion to fiber surfaces. Once the polymer contacts the surface, other forces come into play that bond the molecule to the surface (hydrogen bonding, Van der Waals forces).

Some important factors that affect polymer adsorption are listed in **Table 5-7**. Notice that the list includes not only polymer attributes, but also variables associated with water and the papermaking system. Subsequent chapters will delve more deeply into these subjects with respect to specific additives, retention systems, and wet end chemistry process control.

Table 5-7. Factors that affect polyelectrolyte adsorption

- **Polymer Characteristics**
  (Backbone conformation and flexibility, charge density, molecular weight, chain length)
- **Fiber Characteristics**
  (Number of available adsorption sites, surface charge, surface area, fines content)
- **Chemical Environment**
  (pH, conductivity, interfering substances, anionic polymers)
- **Physical Environment**
  (Shear and turbulence, furnish consistency, order of addition)

b. Polymer adsorption isotherms

Polymer adsorption occurs very rapidly when fibers and cationic polymers are mixed together — on the order of a few seconds or less for the major portion of the reaction. A plot of adsorption versus time produces the type of curve illustrated in **Fig. 5-6**. Such a curve is called a Langmuir adsorption isotherm. The specific isotherm obtained for a given system depends upon the factors listed in **Table 5-7**.

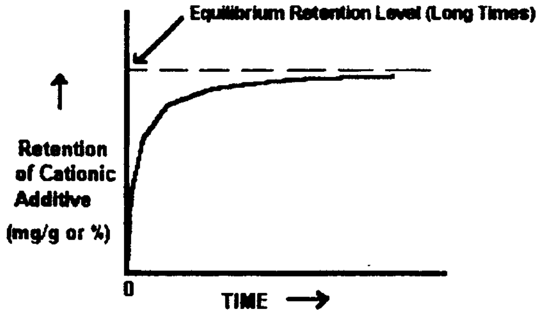


Figure 5-6. Typical cationic polymer adsorption isotherm for cationic polymeric additives on papermaking fibers. Such a curve is called called a Langmuir adsorption isotherm.

The "equilibrium retention level" in the above figure varies greatly from system to system, depending upon the conditions listed in **Table 5-7**. Experience has shown that for most cationic additives, very high equilibrium retention levels can be achieved at addition levels below 1%. For example, Marton and Marton found the behavior illustrated in **Fig. 5-7** in a lab experiment with a single cationic starch.[14]

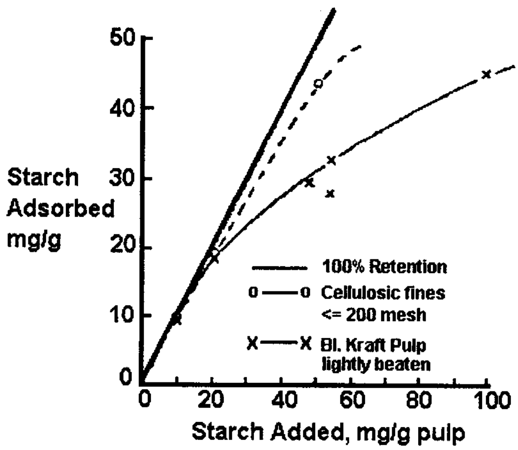


Figure 5-7. Effect of starch addition level on adsorption. (One minute contact time.)[14]

c. The effect of fines level on cationic starch adsorption by pulp [15]

Cationic starch and other cationic polymers tend to adsorb more on the fines in a furnish due to their high specific surface area. **Table 5-8** illustrates this point.

Table 5-8. Effect of fiber and fines surface area on polymer adsorption[15]

Ratio, fiber:fines	Total surface area, m^2/100 g	Relative cationic starch adsorption (fiber:fines)
75:25	290	38:62
65:35	358	27:73

An excellent discussion of all of the factors that influence polymer adsorption on papermaking particles can be found in Reference [16].

12. Surface science and papermaking

We now turn to another aspect of the surface and colloid science of papermaking — namely, surface chemistry. In Chapter 2, we mentioned that water has a high surface tension. We now return to that subject.

a. Source of surface tension

Liquid surfaces are in a state of tension which causes them to contract to their minimum surface area. For example, liquid droplets adopt spherically shaped forms. This phenomenon expresses itself in other ways as well. For example:

- Water can be added to a glass until it appears to "pile up" on top without spilling over.
- Water bugs "walk" on the surface of a pond without breaking through.
- A water surface will support a steel pin, even though the density of steel is much greater than the density of water.

What is the origin of this behavior? **Fig. 5-8** schematically depicts the situation that exists in a container of water. Bulk water molecules are, on average, surrounded in all directions by a uniform molecular environment. This means that they undergo balanced attraction and repulsion interactions with surrounding water molecules. On the other hand, surface molecules are not uniformly surrounded by water molecules because the concentration of water in the vapor phase above the surface is much lower than in the bulk phase. Therefore, surface molecules do not experience balanced intermolecular interactions on all sides. In particular, there are far fewer interactions above the surface than below it.

Conceptually, one can imagine that the greater degree of interaction with bulk molecules leads to the exertion of a downward force on surface molecules, with a resultant surface "contraction". This contraction produces an apparent "surface tension".

b. Papermaking phenomena and surface tension

Table 5-9 lists several important papermaking phenomena that are influenced by surface tension. The list contains phenomena related both to paper quality and process efficiency.

Table 5-9. Papermaking phenomena affected by surface tension

- Sizing
- Foaming
- Air entrainment
- Detergency
- Fiber-fiber bonding
- Wetting and absorbency
- Wet web strength
- Corrugating medium gluability

c. Surface energy

The following scenario represents another way to consider surface tension. The unbalanced forces on surface molecules cause them to migrate from the surface to the bulk. A reverse diffusion of molecules from the bulk to the surface also occurs. Equilibrium exists when the two rates are equal. In fact, there is a net migra-

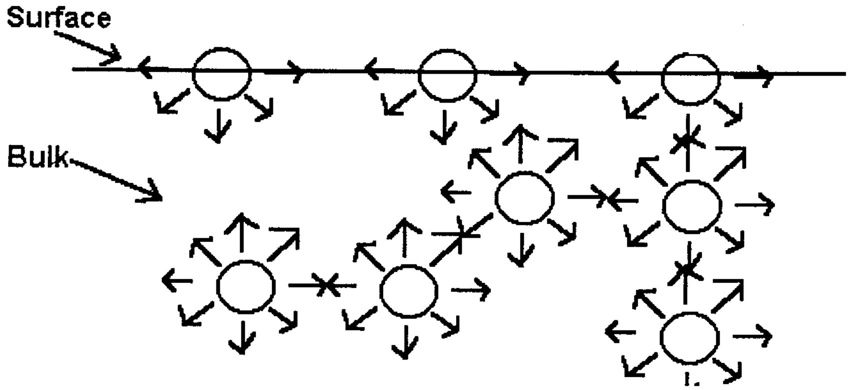


Figure 5-8. Forces acting on surface and bulk molecules

tion of molecules from the surface. Thus, the surface density is lower than the bulk density and the surface molecules are farther apart than the bulk molecules. This gives rise to an excess interaction energy in the surface - a surface energy arises. This surface energy means that it takes work to create new liquid surface. The following relationship exists between the work energy, W, required to produce a new surface and the created surface area, A.

$$W = \gamma A$$

The proportionality constant, γ, is referred to as the surface tension of the liquid. It has units of mN/m when referred to as a force. It can also be referred to as surface free energy, which has units of mJ/m^2. Surface tension values for several common liquids are listed in **Table 5-10**.

Table 5-10. Surface tension of common liquids

Liquid	Surface Tension, γ (20°C, mN/m)
Perfluoropentane	9.9
Diethyl ether	17.0
Ethanol	22.3
Methanol	22.5
Acetone, Methyl ethyl ketone	24.0
Carbon tetrachloride	26.4
Benzene	28.9
Ethylene glycol	46.5
Glycerol	63.3
Water	72.9
Mercury	484

c. Interactions between liquids and solid surfaces

Many papermakers are interested in how water and other fluids interact with paper surfaces. Internal sizing, surface sizing, and coating all are related to this topic. If a liquid drop is placed on a solid surface, the equilibrium condition is expressed by a thermodynamic relationship called the Young Equation (**Fig. 5-9**).

The Young Equation defines the contact angle at the liquid-solid-vapor point in terms of three surface tensions. In papermaking, we believe that sizing influences the surface energy of the solid paper surface and, hence, affects γ_{SV} and γ_{SL}. If the liquid (usually water) surface tension is taken to be constant, then it follows that the contact angle, θ , gives an indication of sizing degree. In fact, a contact angle test is used to measure sizing for certain papers. We will return to this important topic in Chapter 12 when we discuss internal sizing. For more thorough treatments of the subject, you are referred to the general colloid chemistry reference books listed at the end of this chapter.

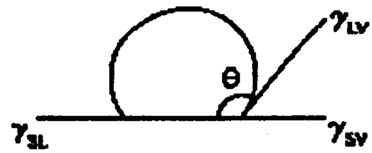


Figure 5-9. The equilibrium condition for a stationary drop on a solid surface — the Young Equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

where:

γ_{SV} = surface tension at the solid—liquid vapor interface

γ_{SL} = surface tension at the solid—liquid interface

γ_{LV} = surface tension at the liquid—vapor interface

13. Association colloids

One way to produce a colloidal system is to have a large number of small solute molecules associate together to form an aggregate which is very much larger than the individual solvent molecules and falls into the colloidal size range. If the solute molecules associate by Van der Waals forces, then the aggregate has special properties and is referred to as an *association colloid.* Solutions formed by soaps and detergents fall into this category. Most surface active substances used as wetting agents, detergents, and emulsifying agents also behave like association colloids. Since true molecular solutions are involved, association colloids fall into the hydrophilic class of colloids. **Table 5-11** lists some typical applications of these materials in the paper industry.

Table 5-11. Applications of association colloids in the paper industry.

1. Pulp washing improvement
2. Pulp fluffing improvement
3. Paper softening
4. Defoaming and antifoaming
5. Absorbency improvement in papers
6. Deposits control
7. Felt washing and conditioning
8. Corrosion inhibition
9. Yankee dryer adhesion control.

The molecules of association colloids are *amphipathic.* In other words, they have a "dual" character and exhibit both hydrophilic and hydrophobic traits. The hydrophilic portion of the molecules normally dissolves in water to form molecularly dispersed solutions. The hydrophobic part is chemically similar to materials normally insoluble in water. The compounds in **Table 5-12** are good examples of this. In all cases the hydrocarbon portion of the molecule resembles liquid hydrocarbons or benzene derivatives which are sparingly soluble in water. The salt-like parts resemble sodium sulfate, sodium formate, or ammonium bromides, all of which are water soluble.

Many association colloid materials utilized by the papermaker are called *chemical processing aids*. These materials are utilized primarily to enhance the cleanliness of a paper machine system and to improve machine runnability. These substances are extremely important and their application programs are often complex. A good review of chemical processing aids can be found in the notes from the 1986 TAPPI Chemical Processing Aids Seminar and a recent TAPPI publication "Chemical Processing Aids: A Practical Guide".[17]

Table 5-12. Association colloids compounds.

Anionic
- Sodium alkyl aryl sulfonates
- Sodium cetyl sulfate
- Sodium oleate
- Sodium dodecyl sulfate

Nonionic
- Nonylphenoxypoly(ethyleneoxy)
- Ethanol

Cationic
- Cetyltrimethylammonium bromide

Amphoteric
- Dodecyl-beta-alanine

a. Surface activity

Amphipathic association molecules often cause a dramatic, spontaneous lowering of the surface or interfacial tension, even when present in very small concentrations. This occurs because the system tends to decrease its surface energy whenever possible, which can occur if the amphipathic molecule orients itself on the surface with its polar group oriented into the water and its hydrocarbon group extending into the air or oil interface. Materials that exhibit this behavior are called *surfactants*.

b. Micelle formation

As was mentioned above, association compounds form micelles of colloidal dimensions. It is thought that micelles have structures similar to that shown in **Fig. 5-10**. Micelle formation involves a delicate balance between the hydrophobic and hydrophilic portions of the molecule and depends as well on the solvent properties and concentration of the substance. The concentration at which micelle formation occurs spontaneously is called the "critical micelle concentration".

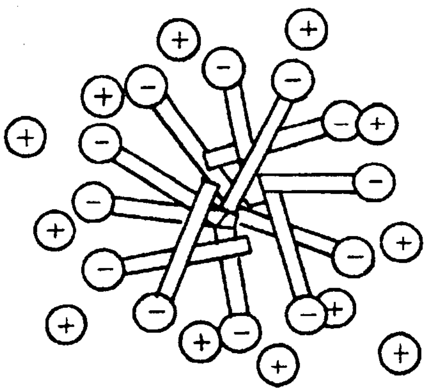


Figure 5-10. Schematic representation of micelle formation from surfactant molecules in water.

c. Detergency

Detergents are used for the removal of dirt from solid surfaces by surface chemical means. Good examples of detergents in the paper industry are the many different felt and fabric cleaning systems available today. A satisfactory detergent must possess the following properties:[18]

- Good wetting characteristics in order that the detergent intimately contacts the surface to be cleaned.
- Ability to remove or to help remove dirt into the bulk of the liquid.
- Ability to solubilize or disperse removed dirt and prevent it from being redeposited onto the cleaned surface or from forming a scum.

The removal of dirt or deposits from solid surfaces involves a combination of mechanical action and surface chemistry. In the absence of a detergent, water is often unable to remove a deposit due to its high surface tension and poor wetting action. When a detergent is added, the hydrophobic part of detergent molecules adsorb onto the deposit and onto the solid surface and reduce the adhesion of the deposit to the surface. It is then possible to dislodge the deposit by mechanical action. The dislodged deposit particles remain in suspension because detergent molecules form adsorbed layers on both the particles and cleaned surface.[19]

The most successful detergents form micelles, and this originally led to the opinion that micelles were directly involved in detergent action, their role probably being that of solubilizing oily material. However, detergent action is dependent upon the concentration of unassociated surfactant and practically unaffected by the presence of micelles (other than as a reservoir for replenishing the unassociated surfactant adsorbed from solution). It appears, therefore, that the molecular properties of surfactants associated with detergency also lead to micelle formation as a competitive, rather than as a contributing, process.[20]

d. Emulsions

An emulsion is a suspension of droplets of one liquid in another. If a vessel containing two immiscible liquids is shaken vigorously, both liquids are broken up into droplets whose size depends upon the viscosity of the liquids, the interfacial tensions, and the vigor of the shaking. The coalescence of the droplets is retarded in the presence of small amounts of additional components, called emulsifiers, and a stable emulsion is formed. Depending upon which liquid is affected most by the emulsifier, either an oil-in-water (O/W) or a water-in-oil (W/O) emulsion is produced. Many retention aids are delivered as water-in-oil emulsions. Synthetic and rosin sizes are O/W emulsions.

The most important physical property of an emulsion is its stability. Emulsion stability refers to three phenomena: creaming, coagulation, and emulsion breaking by droplet coalescence. In all three instances the emulsion separates into two phases. It is the function of the emulsifying agent to facilitate emulsification and promote emulsion stability. The emulsifying agent forms an adsorbed film around the dispersed droplets which helps to prevent coagulation and coalescence. The stabilizing mechanisms are usually complex and may vary from system to system. Factors which favor emulsion stability are low interfacial tension between the dispersed droplets and dispersing medium, a mechanically strong and elastic interfacial film between the droplets and medium, electrical double layer repulsion between dispersed droplets, narrow droplet size distribution, and a high viscosity in the dispersing medium. The detailed mechanisms involved in emulsification are quite complex. Refer to References [22 and 23] for further treatment of the subject.

e. Foams

Air gets mixed with paper stock at many points in a paper mill and can be a source of significant problems. Among the many troubles related to air are decreased washer efficiency, decreased pumping capacity, excessive foaming, decreasing drainage rate, sizing reduction, increased pitch and deposit problems, and pinholes in the sheet.

An excellent discussion of current theoretical ideas about the action of defoamers can be found in Reference [17]. For a surfactant-type defoamer to work, it must spread rapidly and thoroughly on the film surface — thereby displacing the liquid in the film and thinning the film to the point of mechanical instability. It is predicted that, as the defoamer becomes saturated with foam stabilizer, the driving force for spreading decreases and the defoamer becomes less effective. This is indeed observed in cases involving tightly closed white water systems. There has not been widespread application of the theory to date. Instead, the formulation of defoamers and antifoams relies heavily on the considerable body of existing empirical knowledge.

14. Summary

This concludes our brief review of relevant colloid and surface science concepts. We began by defining papermaking chemistry as the surface and colloid chemistry of the components of a papermaking furnish. We then explained that this definition applies because the dimensions of papermaking furnish components fall into the range of colloidal particles and the types of chemical interactions occurring among particles in the wet end involve secondary bonding forces characteristic of colloidal systems.

Next, papermaking furnish systems were classified as being either hydrophobic or hydrophilic in nature, with the single most important characteristic of hydrophobic systems being their tendency to aggregate. It was pointed out that the papermaker wishes to control such aggregation during furnish preparation and sheet formation. The basic mechanisms of aggregation were described.

Adsorption of cationic polymers is a critical step in the function of many additives. Consequently, the fundamentals of this process were next reviewed. This was followed by a discussion of association colloids and surface science. These subjects were then combined in the subject of surface active materials.

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