

4.10 Polymers

Natural products are generally produced by the dehydration condensation of hexose (C_6) sugars or amino acids. In contrast, man-made polymers are often produced by the free-radical polymerization of monomers that contain a double bond. *Homopolymers* are made from repeating units (links, monomers) that are all the same. The polymers most useful as surfactants use two different monomers - anchor (A) units that adsorb on the solid and backbone (B) units that are soluble in the liquid. In *random copolymers* the A units are spaced at random along a backbone of mostly B units. In *block copolymers* there are long sequences of A units followed by long sequences of B units.

4.10a Polyelectrolytes

Polyelectrolytes are composed of ionizable repeating units. The degree of ionization depends on the pH, temperature, concentration of the polyelectrolyte, and the concentration and charge on other salts in the mix. The ionizable units are highly hydrated, so polyelectrolytes are water-soluble. See Corner [ref list] for further discussion of synthesis and applications.

A polyelectrolyte whose charge is due to hydrolysis of acid or base groups will be ionized only within a limited range of pH. Moderate concentrations of multiply charged ions with a charge opposite to that on the polyelectrolyte will cause precipitation of the polyelectrolyte by forming ionic bonds linking two polyelectrolyte molecules or two sections of the same molecule. Because polyelectrolytes provide both charge and steric stabilization, they are effective at lower doses and over a broader range of conditions than other surfactants are.

Many inorganic sols such as sulfur or gold are not hydrated by water and thus agglomerate instead of dispersing in water. Such hydrophobic sols can be stabilized against agglomeration by coating them with a hydrophilic polyelectrolyte that serves as a *protective colloid*.

Several factors can reduce the effectiveness of polyelectrolytes as dispersants. High shear processing may tear the polyelectrolyte anchor groups from the particle surface or, particularly for particles with $d_p > 1 \mu\text{m}$, may push the particles close enough to get past the electrostatic repulsion barrier and into the primary (coagulation) well. Freeze-thaw cycling can destroy dispersion stability by eliminating the solvation sheath which makes the polyelectrolyte hydrophilic. Exposure to heat may cause desorption from the particle surfaces as the solubility of the polyelectrolyte increases with temperature.

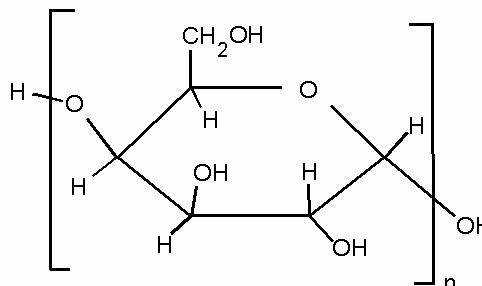
Some ions have specific interactions with particular polyelectrolytes that induce coagulation at very low concentrations. This occurs when the ion is just the right size to fit into a chelation site on the polyelectrolyte or when the ion has d or f orbitals that can interact with π or unshared electron pairs on the polyelectrolyte.

4.10b Natural Products

Starches and proteins have been used since earliest recorded history to stabilize dispersions. India ink is an aqueous suspension of chimney soot stabilized with gum arabic.

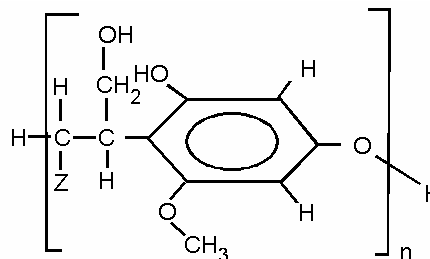
POLYSACCHARIDES

These are polymers of monogalactose and are used as protective colloids. Agar, alginate, and carrageen are extracts from seaweed. The cold water extract consists of sulfonated linear galactose polymers, while the hot water extract contains branched structures. Other polysaccharides are gums from trees, pectins from fruits, starches from vegetables, and celluloses from woody fibers. The properties and edibility vary depending on the source. Polysaccharides are frequently used as binders and water-wicking (tablet disintegration) agents in commercial granules and as thickening or gelling agents to reduce or prevent settling in commercial slurries. In these applications they are NOT dispersants.



LIGNIN DERIVATIVES

These sulfonated products are derived from the paper-pulping process. A typical surfactant would be a mix of polymers with 5 to 250 substituted phenylpropane units. Adsorption on a particle produces both a negative charge and a steric coating that together prevent particle-particle contact. The polyanionic character and polymeric flexibility permit lignins to surround and neutralize multiply charged metal ions, thus reducing the ionic strength of the solution.



Strong adsorption of polyelectrolytes inhibits crystal growth, so lignins can be used as scale (wall fouling) inhibitors or for crystal size control. Highly sulfonated lignins are hygroscopic and can serve as wetting or redispersing agents. The sodium, calcium, and ammonium salts are used to reduce the viscosity of Portland cement and can disperse organics in water without reducing the surface tension or causing foam. They add considerable color to any formulation and are insoluble in organic liquids.

Example: Westvaco's Polyfon™ series, Lignotech USA's Marasperse™ series

PROTEIN-BASED SURFACTANTS

Proteins are condensation polymers of amino acids. Commercial surfactants are based on natural products from animals, vegetables, and fish.

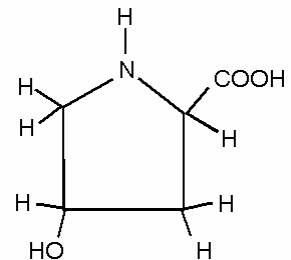
Example: Inolex's Maypon™ series

Albumins are simple proteins found in most animal tissues and in many plants. Hen egg whites are about 6 percent ovalbumin, and dried egg white is called albumen (spelled with an "e").

Albumins are soluble in cold water and are useful as protective colloids. They are coagulated by heat, acids, multiply charged ions, and alcohols.

GELATIN

Gelatins (collagens) are natural protein polymers extracted from animal skins, tendons, bones, and hooves. They contain high percentages of glycine [$\text{NH}_2\text{CH}_2(\text{CO})\text{OH}$], proline, and hydroxyproline links which provide polar and hydrogen-bonding groups that allow strong interactions with polar and hydrogen-bonding surfaces. Gelatins are readily available in food stores and have been used as protective colloids for gold and silver sols ever since Newton's time (about 1700). They swell (but do NOT dissolve) in cold water and are soluble in hot water. They are coagulated by multiply charged cations.



4.10c Homopolymers

WATER-SOLUBLE NONIONICS

These adsorb to form a dense coating that prevents close approach and shields particle polarizability attraction. Typical coating agents are polyethylene oxide $-\text{[CH}_2\text{CH}_2\text{O]}_n-$, polyvinyl alcohol $-\text{[CH}_2\text{CHOH]}_n-$, and polyvinyl 2-pyrrolidinone, $-\text{[CH}_2\text{CH}(\text{NC}_4\text{H}_6\text{O})]_n-$.



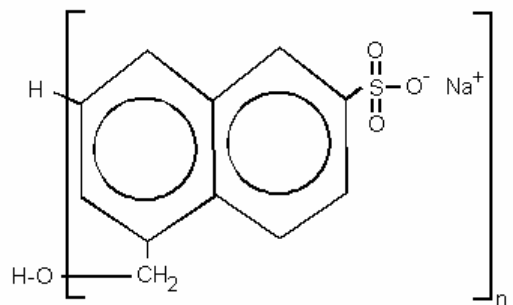
These derivatives of polymerized 2-propenoic acid may be acrylates (R is H) or methacrylates (R is CH_3). The chain may be anionic (Z is $\text{O}^- \text{H}^+$ or $\text{O}^- \text{Na}^+$) or cationic (Z is $\text{NR}_3^+ \text{X}^-$).

Example: Vanderbilt's DarvanTM C (R is CH_3 , Z is $\text{O}^- \text{NH}_4^+$)

CONDENSED NAPHTHALENE SULFONATES

These condensation product with formaldehyde has properties similar to lignin sulfonates, but have less color and produce less foam. Butyl or isopropyl naphthalene sulfonates act as wetting agents for organic powders. There are usually 2 - 6 units of β -sulfonated naphthalene, connected by $-\text{CH}_2-$ groups on the ring.

Example: W. R. Grace's DaxadTM 11 to 19 series, Rohm & Haas's TamolTM N Micro



4.10d Random Copolymers

Surfactants with multiple anchors adsorb more strongly than surfactants having a single anchor group. The nonadsorbed, solvated backbone links between the anchor groups are held as loops and tails, forming a steric barrier to agglomeration.

ETHYLENE / ACRYLIC ACID

Because the acid groups can ionize, these polymers are called *ionomers*. Products to suit different applications can be made by varying the proportions of ethylene (lipophilic) and acrylic acid (hydrophilic) links. A typical polymeric mixture would have a number-average of about 40 units (total for both monomers). Ionic repulsion forces these ionomers to have extended structures in low ionic strength solutions at high pH. The presence of multiply charged counterions causes partial charge neutralization and cross-linking, leading to more compact structures which, when adsorbed, provide stronger steric repulsion.

Example: Allied Signal's AClyn™ series

VINYLBENZYL / METHACRYLATE

Vinylbenzyl quaternary amine chloride / methyl methacrylate is most effective as a dispersant if the charge density is high. A typical polymer would contain 150 vinyl benzyl units and 30 methacrylate units. The charge is not dependent on pH and is not much affected by ionic strength. The trimethylamine form of the polymer is water soluble and does not reduce surface tension, but if a few percent of the methyl groups are replaced by dodecyl groups, the polymer becomes more hydrophobic and does reduce surface tension. (see Wessling and Pickelman [ref list]).

4.10e Block Copolymers

The long sequences of anchor units in these dispersants can keep them strongly adsorbed even if there is extensive dilution after the initial treatment.

POLYETHOXY/POLYPROPOXY ALCOHOLS RO-PEO-PPO-H

The numbers and locations of alkane, ethylene oxide and propylene oxide units along the polymeric chain can be adjusted to make surfactants whose hydrophilicity and lipophilicity match any specified solid-liquid combination. Materials with 60 - 180 total carbons and a high ethylene oxide content make good dispersants for organic pigments or iron oxides in aqueous systems.

Example: BASF's Pluronic™ series

Derivatives of ethylenediamine (NH₂CH₂CH₂NH₂) provide branched chain alternatives to the linear alcohol derivatives.

Example: BASF's Tetronic™ series

"AB" DISPERSANTS

Oil-soluble AB dispersants have an alkane backbone formed by opening the double bonds of 2-propenoic acid (acrylic acid) units. One or both ends of the backbone are terminated with a section containing several isocyanate ($-N=C=O$) groups. The isocyanate groups are converted to acids or amides which can form strong attachments to the particles to be dispersed.

Water-soluble AB dispersants have a polyester backbone formed by opening the cyclic ester caprolactone, $-O(CH_2)_5(CO)-$, at the ether group. The anchor groups are the same as for the acrylics.

Jakubauskas [see refs] describes the wide variety of AB dispersant configurations and applications that are now available.

Example: DuPont's ElvaciteTM AB series

4.11 Other Ways to Change the Surface

4.11a Covalently Bonded Surface Coating

The following methods may be too complex to consider for making up laboratory dispersions, but they are often used to control the surface chemistry of commercial products.

OXIDATION -- Exposure of metals (or carbon) to oxygen, heat, moisture, and acid will often produce a thin oxide layer that can prevent sintering, provide a surface charge, or aid in bonding organic surfactants to the surface.

SILYLATION -- Organic silanes will react with active hydrogens on a surface to make it lipophilic rather than hydrophilic. Example: Union Carbide's UcarsilTM, Petrarch's series

HYDROUS ALUMINA -- Sodium aluminate reacts with acid (and aluminum oxychloride reacts with base) to produce aluminum hydroxide, which adsorbs strongly on many surfaces. Several different types of hydrous alumina may be formed by varying the reaction conditions. The coating can make an inorganic surface compatible with organic liquids.

HYDROUS SILICA -- Sodium silicate reacts with acid to form hydrous silica, which adsorbs strongly on many inorganic materials. Coatings of different porosities may be formed by varying the reaction conditions. The silica surface is negatively charged above pH 2 unless the solution contains a high concentration of multiply charged cations.

ORGANIC TITANATE -- One or more of the ester groups of tetra-alkyl titanate, $Ti[OR]_4$, an organic alcohol ester of titanate, will react with active hydrogens on a surface to anchor the organic titanate to the surface. This converts the exterior of the particle from a hydrophilic array of active hydrogens to a layer of lipophilic alkane tails. Example: DuPont's TyzorTM series

4.11b Physical Encapsulation

If an organic solute is more soluble in hot water than in cold water, we can coat an inorganic powder with the solute by adding the solute to a hot dispersion of the powder, then cooling the dispersion. The filtered and dried powder can then be dispersed in organic liquids that are compatible with the solute.

A powder will become electrically charged when it is shaken in a metal container if there is a difference in electronic work functions of the metal and powder surfaces. When a large (core) powder is shaken together with a smaller (shield) powder which takes an opposite charge, the shields will form a rather strongly bonded powder coating on the cores. If the shields are made of a thermoplastic polymer, they may be more securely attached to the cores by impact sintering (near their melting point) to form a continuous film. If the shield film has properties different from the core's original surface, it can make the core compatible with and dispersible in a different range of liquids.

4.12 Complications for Industrial Materials

Many industrial products become ingredients for mixtures made by another manufacturer. The final consumer product is often a very complex mixture of materials from several sources. Thus, a dispersant which was added by a pigment manufacturer to produce a stable aqueous dispersion may cause a house-paint manufacturer great trouble if it permits the pigment to be washed off houses during the first rainfall.

Something that is an advantage in one setting may be a problem in another setting. A dispersant that is added to prevent settling in one part of the process will be a nuisance when we want to form flocs to aid in filtering the product. Customers may insist that we remove a colored or bad-smelling surfactant prior to shipping the product.

Most manufacturers are secretive about the ingredients and processes used to make their products, so the raw material suppliers, the intermediate producers, and the final mixing and consumer sales company typically have little exchange of information about what surfactants and impurities will be present in the final product.

4.12a Order of Addition of Ingredients

To minimize lump formation, wetting agents should be added to the liquid before the powder is added. Salt and pH adjustments to optimize surfactant effect should also be done before adding the powder, and pH must be monitored and adjusted as powder adsorbs surfactant from solution. It is useful to hold a part of the liquid out of the initial dispersion mix so that a high solids concentration can be used during deagglomeration. When that step is complete, the dispersion may be diluted to the final concentration by mixing in the remaining liquid.

4.12b Mixing Cationic and Anionic Surfactants

If a solution of anionic surfactant is mixed with a solution of cationic surfactant, the two oppositely charged surfactants will precipitate or unite to form zwitterion complexes. If anionic

surfactant is added to a dispersion stabilized by a cationic surfactant, the precipitation of cationic surfactant will deplete the solution of cationic surfactant, causing cationic surfactant to desorb and precipitate until a balance between the various adsorption, precipitation, and ion pairing equilibria is attained. At the final equilibrium there may not be enough cationic surfactant remaining on the powder to maintain a stable dispersion.

4.12c Mixing Dispersions of Oppositely Charged Particles

If a dispersion stabilized by positive surface charge is mixed with a dispersion stabilized by negative surface charge, the oppositely charged particles will be strongly attracted to form a mixed agglomerate. This process is called heterocoagulation to contrast it with coagulation induced by high salt concentrations.

4.12d Acids, Bases, Extremes in pH

If the pH of the final mix is outside the region required to provide a good surface charge (or surfactant charge or surfactant adsorption or surfactant chemical stability), the dispersion may agglomerate. The best pH range for causing a negatively charged organic acid surfactant to adsorb on a positively charged metal hydroxide surface extends from one pH unit below the pK_a for the surfactant to one pH unit below the pH_{isoe1} for the powder surface (see Figure 7--1).

The pK_a is the pH above which the surfactant loses a proton and becomes an anion. The order of pK_a values is sulfate < phosphate < carboxylate. If a dispersion is acidified, the sulfates retain their anionic character and remain strongly adsorbed (on positively charged surfaces) to the lowest pH values. Tetra-alkyl quaternary amines ($R_4N^+ X^-$) are salts that dissociate to cationic surfactants at both high and low pH. Primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) amines may adsorb an extra proton to become cationic surfactants at low pH, but they lose the proton and the charge to become nonionic at high pH.

Organic sulfates and esters decompose by hydrolysis when exposed to hot dilute acids (pH below about 4). Esters also hydrolyze in hot dilute base (pH above about 10). Amides are more resistant to hydrolysis than the corresponding sulfates or esters. Polyethoxy chains (ether links) are stable to either hot dilute acid or hot dilute base.

4.12e Multiply Charged Ions

Plant process water, other raw materials, or a customer's end-use formulation may contain multiply charged ions such as Ca^{++} or SO_4^{--} . These can coagulate a stabilized dispersion unless we increase the amount of surfactant used in the formulation. There are three different mechanisms:

-- Ions can precipitate or form solution complexes with oppositely charged (or neutral) surfactants, causing desorption of the surfactant from the particles.

-- Ions adsorb on oppositely charged particles, causing particles to lose their charge. In rare cases, adsorption of a high surface density of multiply charged ions can provide a high charge on the particle and may help stabilize the dispersion.

-- Ions contribute to the ionic strength according to their charge squared, so multiply charged ions cause a large increase in ionic strength, reducing the thickness of the counterion atmosphere as well as the height of the electrostatic barrier to coagulation.

Because sulfates and quaternary amines hydrolyze at extreme pH values, they retain their charges better at high ionic strengths than do phosphates, carboxylates, or amines.

4.12f Oxidizing, Reducing, Biodegrading Agents

Branched chains and aromatic groups are more resistant to these agents than straight chain hydrocarbons are. Polyethoxy chains are stable to oxidizing and reducing agents.

Perfluorocarbons are very resistant to degradation by any means.

4.12g Heterogeneity and Variability

Every industrial product has its own special characteristics due to chemical or physical heterogeneity. Chemical heterogeneity arises from intentional additives, impurities, outer layer precipitates, adsorbed coatings, or hydration and hydrolysis due to humidity. Physical heterogeneity includes size, shape, and variations in surface smoothness due to nonuniform conditions of crystallization or grinding. Different batches of a single product may contain different crystal phases or crystals with different length-to-width ratios. Since each crystal face adsorbs surfactant in a different way, variations in aspect ratio cause variations in specific surface area and also in the adsorption constant.

Sequential lots of powder will vary due to impurities in the raw materials, reaction byproduct distribution, separation efficiency, and other processing conditions, so the quality of powder dispersion may vary unless process monitoring detects and process control compensates for these influences.

Non-surfactant compounds can affect the dispersion by adsorbing on the surface of a solid, changing its charge or competing with the adsorption of surfactant. The non-surfactant may also alter the association patterns of the liquid by trapping liquid molecules in solvation bonds and thus changing local polarizability.