

-- 4: Surface Chemistry --

The task of selecting surfactants to disperse a specific solid in a specific liquid is easier if you understand the chemistry of the solid surface, the liquid, and the available surfactants. This chapter discusses the most common categories of these chemicals and comments on the characteristics that are of special interest when preparing a dispersion.

4.1 Chemical Classes of Solid Surfaces

The interaction of a particle with the liquid surrounding it depends more on the particle's surface than on its bulk composition. Once we know the surface composition, we can predict how pH will modify it, what surfactants might adsorb on it, and how ions in solution will affect its behavior.

4.1a Metals and Carbon Black

Bare metal surfaces have high values of the following properties:

- density
- reactivity
- surface energy (also called surface tension)
- polarizability (a measure of the ability of charges in the material to rearrange in an electric field)
- adsorptivity (readily forming coatings of surfactants or particles)
- electrical conductivity

Many metals oxidize in air or water to form surface oxides and hydroxides. The high surface energy makes bare metal surfaces susceptible to sintering, which reduces surface area and hence net surface energy by forming "necks" of metallic bonds between the particles. The high polarizability causes metal particles to attract one another to form strong agglomerates. However this same factor causes them to attract surfactants strongly, so metal powders are easily coated with protective films which help prevent agglomeration. If the surface is coated with an oxide film or strongly adsorbed material, sintering and strong agglomeration cannot occur.

Carbon black is porous, has low density, has a rigid framework, and does not sinter, but it is similar to metals in being electrically conductive and having a high polarizability and surface energy. The pores provide higher energy adsorption sites than the surface, so surfactant tends to adsorb there first or to migrate there, so that the addition of surfactant often does not start to coat the outer surface or promote dispersion until the pores have been filled.

4.1b Oxides and Hydroxides

Oxides often hydrolyze in the presence of water to form hydroxide layers at the surface, so the two classes of material behave similarly. There are three ways to stabilize particles that have a hydroxide surface -- charging through proton gain or loss, charging by an adsorbed charge, and steric stabilization.

At low pH, hydroxide surfaces adsorb protons to produce a positively charged surface. At high pH they lose protons to produce a negatively charged surface. The useful pH range may be limited because the solubility of oxides and hydroxides is strongly pH dependent, especially when the cation can form hydroxyl complexes. Thus, the aluminum hydroxide coating on a silica particle may dissolve if the dispersion experiences either high or low pH during processing.

Surface protons or metal ions may exchange places for cations in solution, especially if the solution species are multiply charged. Surface hydroxyls can exchange with anions in solution in a parallel manner. If the charge on the adsorbed species is larger than the original site's charge, the original surface charge can be reversed.

Since the hydroxide group is fairly reactive, coupling agents such as organosilanes and organic titanates can be used to bond an organic group to the surface. The organic tails of these chemically bonded coatings prevent the hydroxide surfaces from coming close enough to form strong agglomerates. See the discussion of flocculation in Chapter 1.

Oxides or hydroxides which are dispersed in nonaqueous liquids often form flocs if a small amount of water is added to the system. The water adsorbs on the hydroxide surface and enhances the attraction between particles.

4.1c Salts

Salt particles are composed of *cations* (positively charged metal ions) and *anions* (negatively charged nonmetals or oxygenated nonmetal ions). Salts have high surface energies and may have an excess of either anions or cations in the lattice. The excess produces a surface charge which can stabilize the dispersion against agglomeration.

The solubility of a salt in water may be enhanced by the presence of a solute that will form strong complexes with the cation or anion. Salts dispersed in nonaqueous liquids will floc in a manner similar to hydroxides if a small amount of water is added to the system.

4.1d Nonoxide Refractories

Nonoxide refractories consist of nonmetallic atoms held together by covalent bonds. Refractories have low values of density, polarizability, surface energy, reactivity, and adsorptivity. Because of their low polarizability, the particles are more easily dispersed in organic liquids than in water. They do not form strong flocs.

4.1e Nonpolar Polymers

Nonpolar polymers have no strongly polar groups on their repeating units. They have low surface energies, so they do not readily wet into water unless a surfactant is used to provide a water-compatible coating. Good surfactants for dispersing nonpolar polymers in water have long, nonpolar tails and strongly *hydrophilic* (Greek for "water-liking") heads. Since nonfunctional polymers have low polarizabilities, they do not form strong flocs.

4.1f Polar Polymers

Polar polymers have strongly dipolar, hydrogen-bonding, or reactive groups along the chain, so their surface energies and polarizabilities are high. The particles are often incompatible with water and strongly attracted to one another, so flocculation can be a serious problem. A dispersion of polar polymer powder may be stabilized by hydrophilic polar polymeric surfactants which adsorb on a surface at random points along the chain. This creates around the particle a cushion of polymer loops sticking out into the liquid. Long before the particles are close enough for their surfaces to collide, these loops hinder the particles from coming close enough to form strong attractions.

4.1g Biological Materials

Biological materials are generally more complex and thus more likely to decompose due to heat or to a harsh chemical environment than are the simpler synthetic organic chemicals. They often have structures suitable for extensive hydrogen bonding. Biological materials usually have densities close to that of water and are negatively charged in aqueous suspension at normal pH's, so they may need no added surfactant to form a stable dispersion.

4.2 Chemical Classes of Liquids

At the molecular level a liquid may be viewed as a dynamic network of moving, rotating, and twisting molecules, whose shapes and interactions with neighbors fluctuate as they tumble and wiggle through the system. This dynamic structure becomes more orderly near surfaces which have strong electrostatic fields (charged particles), strong alternating charge patterns (salts), strong hydrogen bonds (metal hydroxides) or large polarizabilities (metals).

4.2a Nonpolar

Nonpolar liquids show little association structure, whether or not an interface is nearby. Intermolecular forces are small --principally superposition and resonance forces -- and the attraction to a surface is both small and nonspecific, so no particular orientation is preferred. Ionization is slight because the ions cannot be protected by a solvation sphere from combining with ions of opposite charge. What few ions and polar groups are present will have a large influence, however, since the low polarizability of nonpolar liquids does little to hasten the decay of an electric field with distance.

4.2b Polar

Polar molecules have strong electric fields about any bond involving atoms that are far apart on the periodic chart. Ethers, ketones, halides, sulfides, and esters are the most common polar organic groups. Polar molecules tend to orient themselves with respect to each other so as to form association groups. These are the lowest energy configurations consistent with their geometry and thermal jostling.

Polar groups interact more strongly with a polar surface than nonpolar portions of the molecule do. The surface's adsorption of the polar groups produces a coated particle with a nonpolar exterior which may then adsorb another layer with the nonpolar parts adsorbed and the polar parts on the surface. This ordering process extends outward until thermal jostling overwhelms the decreasingly effective orientation forces.

The strength with which the initial layer is adsorbed depends on both the energy of interactions of the surface with a single liquid molecule and also on the degree to which the liquid molecular configurations fit into the spacing of the array of surface atoms. The polarizability and solvating power of polar liquids are higher than for nonpolar liquids, so more ionization occurs, but electrostatic field strengths drop off more rapidly.

4.2c Hydrogen Bonding

Hydrogen bonding involves quantum forces that arise when a hydrogen atom in a polar bond comes near an atom with an unshared pair of electrons. A liquid's viscosity may decrease when its hydrogen-bonded molecules are reorganized into solvation spheres about added ions or charged particles. Since the rotation of hydrogen-bonding groups near a polar particle's surface is hindered, the liquid's polarizability decreases near a charged surface, and the interaction of two nearly touching particles will be larger than would be predicted from the polarizability of the bulk liquid.

The water molecule has two unshared pairs of electrons and two active hydrogens in a tetrahedral structure. A good electrostatic model used two charges of $z = +0.24$ located 0.1 nm from the oxygen atom toward the H atoms and two charges of $z = -0.24$ located 0.08 nm toward the lone pair electrons. Each water molecule can participate in four hydrogen bonds, so liquid water has a strong three-dimensional hydrogen-bonded network.

Water forms labile "hydrophobic" clathrate structures around nonpolar solute segments such as hydrocarbon or fluorocarbon chains. Here the repulsion between solute and solvent leads to structural order in the liquid. The ordering caused by attraction depends on the magnitude of the enthalpic part of the interaction, but the ordering caused by repulsion depends on the entropic part of the interaction. The entropy for the clathrate structure of water surrounding a hydrocarbon depends on the surface area exposed to the hydrocarbon; at 298K it is some 48 J/m². This phenomenon explains the high interfacial tensions for water-hydrocarbon or water-fluorocarbon systems. Since the clathrate changes the translational and rotational freedom of the water molecules, it also affects the dielectric permittivity and viscosity of water.

4.2d Molten Salts and Metals

Because we rarely encounter these liquids in industrial slurry operations, they are not covered in this book. Most surfactants would be either destroyed or rendered ineffective by the high temperatures, the ionic strengths, and polarizabilities in such liquids.

4.2e Classification by Solubility Parameters

The solubility parameter δ [J/m^3 , N/m^2 , or Pa] is a measure of the cohesive energy density (or attractive forces) in liquids. It was originally formulated as a single parameter to characterize a liquid, but it is now generally subdivided into three contributions -- dispersion (related to polarizability), dipolar (related to electric dipole moment), and hydrogen-bonding (related to other interactions) -- whose SQUARES are combined to form the net value as

$$\delta_{\text{net}}^2 = \delta_{\text{disp}}^2 + \delta_{\text{polar}}^2 + \delta_{\text{H}}^2$$

Solubility parameters may be used to match a solvent blend to achieve maximum solubility for a prospective polymer or to determine the lipophilic tail group best suited to a particular organic liquid. If the three components of the solvent match the three components for the polymer, solubility should be high. The solubility parameter contribution (where $w = \text{disp, polar, or H}$) for a mix of N components is related to the volume fractions ϕ_j and solubility parameter contributions for the components of the mix as

$$\delta_{w,\text{mix}} = \sum_{j=1}^N \phi_j \delta_{w,j}$$

Simple graphical methods have been replaced by computer methods for determining optimum mixtures of solvents. For commercial formulations this task is complicated by the need to consider viscosity, evaporation rates, flammability, and toxicity of the resulting mixture. Some typical solubility parameters are listed in Appendices B and C. For more extensive listings and discussions of applications, see Hansen and Beerbower [ref list] and also Barton [ref list].

4.3 Chemical Classes of Non-Surfactant Solutes

Solutes may be added in carefully controlled quantities as intentional parts of the slurry or they may be present in varying and poorly characterized amounts as incidental impurities from either the raw materials or the manufacturing process. The interactions of solutes with the powder, liquid and surfactant may improve or ruin a dispersion.

4.3a Nonpolar

Nonpolar solutes such as alkanes, aromatics, and perfluorocarbons are generally quite soluble in nonpolar liquids. The unsaturated (π) bonds in aromatics may form complexes with atoms or

groups having a deficiency of electrons. Thus the presence of small quantities of nonpolar aromatics may significantly enhance the solubility of metal atoms or hydrogen bonds, in a nonpolar alkane liquid.

Nonpolar solutes are generally not very soluble in water (or other hydrogen-bonding liquids). See Section 4.2.3 for a discussion of hydrophobic clathrates.

4.3b Polar

Polar solutes may form pair or multi-molecular complexes with a polar liquid or with other polar solutes. The complexing ability of the more soluble polar molecules can have an important influence on the activity of metal ions (less often on nonmetal ions) or on the hydrogen-bonding ability of the liquid.

In many organic molecules, one portion is polar and hydrophilic and another portion is nonpolar and hydrophobic. The nonpolar part can disrupt the structure of water in the same way as a nonpolar molecule would. Members of a series of related compounds become increasingly surface-active as the difference in hydrophilicity of the two portions increases.

4.3c Hydrogen-Bonding

Hydrogen-bonding solutes are often good surfactants. They tend to have stronger and more specific bonds with ions and hydrogen-bonding liquids and surfaces than polar solutes do. This can be a problem if a strongly adsorbed hydrogen-bonding impurity prevents the adsorption of a surfactant that we have added to produce a good dispersion.

4.3d Polymers

Polymers contain long chains of repeating units. In some cases the chains are cross-linked to form a more rigid structure. If the structure is flexible, the dissolved polymer molecule can twist into many shapes. This conformational freedom produces a large entropic contribution to the free energy of interaction with the liquid. If the polymer is very compatible with the liquid, all conformations will be equally likely and the statistical distribution of configurations is called a *random coil* structure. If there are specific attractions within the polymer that lead to special conformations, the structure may have a special name, such as the alpha-helix for proteins.

If the repeat unit of the polymer has an ionizable group, then strong intramolecular repulsions will occur when those groups become ionized. Charge repulsion will push the ionized groups as far apart as possible, leading to a highly extended structure. If the ionized groups are on side-chains off the main chain, the charge repulsion will lead to a bristle structure.

If a long portion (tail) of the polymer is incompatible with the liquid, it may condense with the tails of other solute molecules to form an ordered structure known as a micelle. These are discussed further in Chapter 6.

4.3e Salts

This classification includes all ionizing solutes -- organic and inorganic, acids, bases, and salts. The degree of ionization will depend on the temperature, pH, complexation with the liquid and other solutes, adsorption on solid surfaces, and the concentrations of other salts. Ionizing solutes disrupt liquid structures by attracting and orienting liquid molecules into solvation sheaths about the ions. They form complexes with other solutes and competitively adsorb on particle surfaces to deactivate them toward surfactant adsorption. Ions are not distributed uniformly in the solution, but tend to form counterion atmospheres about charged particles. (See Chapter 3.)

It is a mistake to conclude from the simple formula for AlCl_3 that the principal ions in aqueous solution are the fully dissociated ions Al^{+++} and Cl^- . Multiply charged ions almost always form complexes with ions of the opposite charge, so in addition to Al^{+++} , such species as $\text{AlCl}_x(\text{OH})_y^{+3-x-y}$ may be present, where the subscripts x and y are integers whose sum cannot exceed 4. Neither the theoretical nor the experimental determination of the concentrations of these various species is easy, but you must do one or the other if you want to see how changes in the chemical composition of a solution affects liquid-particle-surfactant interactions.

4.4 Chemical Classes of Surfactants

4.4a Surfactant Molecular Structure

Surfactants are composed of molecules that distribute themselves so as to have a higher concentration in the interfacial region (between the liquid and a gas, solid, or second liquid phase) than in the bulk of either phase. This interfacial excess concentration arises because the surfactant molecular structure consists of one portion that is relatively soluble in (compatible with) the liquid and a second portion that is relatively insoluble in the liquid.

Many solutes have some slight increase in concentration near an interface, but the use of the term *surface-active agent* (or *surfactant*) is properly applied only to those compounds that have a strong tendency to concentrate near the interface. The surfactant molecules preferentially orient themselves with the liquid-soluble portion sticking into the liquid and the liquid-insoluble portion floating on the liquid-gas surface, adsorbed at the solid surface, or sticking into the second liquid. The presence of a surfactant at the interface increases the compatibility (reduces the interfacial energy density) between the liquid with the gas, solid, or second liquid.

In general we can refer to something compatible with a liquid (such as a soluble surfactant) as *lyophilic* (from the Greek for "solvent-liking") and something incompatible with a liquid (such as an agglomerating colloid) as *lyophobic*. These terms are useful for materials which are NOT surfactants, but since surfactant molecules have both lyophilic and lyophobic regions, we use other terms to characterize the interaction of surfactants with liquids.

Most commercial dispersions use either water or a relatively nonpolar organic liquid (an oil) as the liquid, and we frequently want to disperse an organic (oil-like) material in water, so surfactants are often characterized as having a *hydrophilic* (Greek for "water-liking") head and a *lipophilic* ("oil-liking") tail. The water-soluble head is often a small ionic (or polar or hydrogen-bonding) group. The oil-soluble tail is often a hydrocarbon chain. While most industrial

surfactants have a single head and tail, other configurations are possible. Some biological surfactants have two tails. Associative thickeners (used to produce a weak gel network in paints so that the particles cannot settle out) have a lipophilic group at each end of a very long hydrophilic chain. Block copolymers have numerous hydrophilic and lipophilic regions.

Many terms have been used to describe surfactants. Some are general -- soap, detergent, amphiphilic or amphipathic compounds (from the Greek for "both-liking" or "both-natures"). Some are used only in specific applications -- wetting agent, emulsifier, flocculant, foaming agent, anti-foam agent, prefoamer, collector (for modifying mineral surfaces in froth floatation separations), and depressant (to reduce the attraction of gangue to the foam in froth floatation).

4.4b Surfactants as Dispersants

Any surfactant which aids in keeping particles from agglomerating may be called a dispersing agent or *dispersant*. Since a surfactant that causes particle repulsion (and is therefore a dispersing agent) under one set of conditions may cause attraction (and thus be an agglomerating agent) under another set of conditions, I have used the more general term surfactant in most of the discussions here.

4.4c Classification by Charge on the Interfacial Ion

The primary classification of surfactants is through the charge on the portion of the surfactant that concentrates at the interface. Sodium dodecyl benzene sulfonate is an *anionic* surfactant because it dissociates to a water-soluble sodium ion and a negatively charged (anionic) dodecyl benzene sulfonate ion which concentrates at the interface. Dodecyltrimethyl ammonium chloride is a *cationic* surfactant because it dissociates to a water-soluble chloride ion and a positively charged (cationic) dodecyltrimethyl ammonium ion concentrates at the interface.

A *nonionic* surfactant is one which has no ionizing groups, such as an alcohol. Commercial, nonionic surfactants often contain small quantities of anionic surfactants to aid in dispersing the concentrate in water.

Surfactants whose charge is positive at low pH, zero at moderate pH, and negative at high pH are called *amphoteric* surfactants. The *isoelectric pH* for an amphoteric surfactant is the pH at which the charge is zero. This concept is similar to that of the isoelectric point for a metal hydroxide surface.

If a neutral molecule has both a positively charged group (such as a quaternary ammonium ion) and a negatively charged group (such as a carboxylate ion), it is called *zwitterionic*. These may be amphoteric as well, becoming cationic at low pH and anionic at high pH. The two separated charges give the molecule a very large dipole moment, so it is strongly attracted to polarizable surfaces. These surfactants can also adsorb on surfaces of any charge -- the positive group on a negatively charged surface, the negative group on a positively charged surface.

Cationic surfactants adsorb best on anionic surfaces, for which the opposite charge leads to stronger adsorption forces. Similarly, anionic surfactants adsorb best on cationic surfaces.

In the absence of ionic forces, polarizability, dipole, and hydrogen bonding cause nonionic surfactants to adsorb on solids with positive, negative, or no charge. Amphoteric surfactants are best used when solution conditions will produce opposite charges on the surfactant and the particles. Zwitterionics work with particles of either charge.

4.4d Classification by Chemistry of the Tail Group

The secondary classification of surfactants is through the functional groups attached to the hydrocarbon backbone. Since good dispersions rely on having a head that is chemically compatible with (adsorbed on) the particle's surface and a tail that is chemically compatible with (soluble in) the liquid. If the head is not adsorbed on the particle, the surfactant can have no effect on dispersion. If the tail is relatively insoluble, the surfactant-coated particles will flocculate so as to minimize tail-liquid interactions for the surfactant.

4.4e Classification by Hydrophile-Lipophile Balance (HLB)

The *hydrophile-lipophile balance (HLB)* is a measure of compatible a surfactant is with the aqueous phase compared to an oil phase. The scale was set with oil-soluble 9-octadecanoic acid (oleic acid) at an HLB of 1 and water-soluble sodium 9-octadecanoate (sodium oleate) at an HLB of 20. Becher [see ref list] reviews the HLB concept and its many applications.

How does the HLB change with structure? While octadecane, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$, is a very good lipophile, it is NOT a surfactant, since no part of the molecule is hydrophilic. If one end group ($-\text{CH}_3$) is converted to an acid ($-\text{COOH}$), the water-solubility improves a bit, so octadecanoic acid is a surfactant. Shortening the carbon chain from 18 to 12 carbons lowers the lipophilicity and raises the HLB further. Soluble compounds such as sucrose are very good hydrophiles and are completely soluble in water, but are NOT surfactants because they have no lipophilic regions.

Commercial surfactants are complex mixtures, and their reported HLB's are usually based on comparisons of their solubility with pure compounds of known HLB. The HLB can be estimated from the sum of functional group contributions (see Appendix C). Becher [see ref list] notes that HLB is related to the critical micelle concentration C_{CMC} [mol/m^3] and thus to the free energy of micellization ΔG_{mic} [J/mol] by

$$\text{HLB} = K_1 + K_2 \ln C_{\text{CMC}} = K_1 + K_2 \Delta G_{\text{mic}} / RT$$

where K_1 and K_2 are constants that are different for each specific series of related surfactants.

Sometimes a binary mixture of surfactants (A plus B) works much better than a single surfactant. In such cases, one surfactant should adsorb well on the solid, the other should solvate well in the liquid, and both should have a mutually compatible portion to provide a bridge between solid-A and B-liquid phases. Several manufacturers sell paired series of mutually compatible surfactants to provide a wide variety of adsorbing and solvating combinations.

Example: ICI America's SpanTM and TweenTM series; DuPont's MerpolTM and DuPonolTM series