

Colloidal Dispersions in General

The Difference Between Metallic Colloids and Plant Derived Colloidal Minerals

Chemical species present in water may be considered to physically occur in a variety of modes. These modes define an essentially continuous series that can be referred to as the **solute/colloid/suspended particle continuum**. While the pure end member modes are easily conceptualized as: a) dissolved ions or molecules; and b) macroscopic particles, the intermediate modes require further explanation. The word 'colloid' as used here collectively identifies **the intermediate continuum of modes**. Chemical species which may be referred to as 'colloidal' include: a) discreet chemical species with sufficient size or mass to behave as colloids (large macromolecules); b) amorphous or crystalline chemical compounds which exist in the solid phase as colloids; c) collections of a few to hundreds of smaller molecules which form species of colloidal dimension (aggregates); and d) chemical species who are associated with colloids (usually by adsorption) and whose behavior is controlled by the colloids.

A **colloidal system** is more easily described than a colloid itself, and is described as a **two-phase system** in which one phase is uniformly and permanently distributed or **dispersed** in the second phase. This is in contrast with both a true solute/solvent system, which comprises a single phase, and a suspended-particle/solvent system which is a two phase system but is typically not uniform and never permanent. Although natural colloidal systems exist for every binary combination (except gas-in-gas) of solid, liquid and gas phases (e.g., fog is a liquid-in-gas colloidal system, emulsions are liquid-liquid systems), the most geochemically relevant systems are those with an aqueous dispersing media and dispersed solid particles, known as **sols**. Chemically, colloids behave like solids requiring consideration of surface area and charge and other aspects of heterogeneous reaction theory. Physically or hydrodynamically however, colloids behave somewhat like solutes principally because of their small size.

Long-term kinetic stability as a dispersion fundamentally defines a colloid and a colloidal system. An exceedingly wide variety of natural colloidal material has been identified and are listed in Table 1. The list may be subdivided into the two main groups of colloids.

Table 1. Aquatic colloidal materials

Hydrophobic Colloids – (Metallic)

Phyllosilicates, clays *

Iron, manganese, and aluminum oxides and hydroxides

Framework silicates

Carbonates, sulfides, and phosphates

Biocolloids (bacteria, virus)

Hydrophilic Colloids-(Plant Derived)

- Macromolecular organic matter
- Polymeric precipitates

The first four listing represent sparingly soluble minerals and this lack of solubility suggests an inherent resistance to interaction with water. They are called lyophobic, solvophobic or hydrophobic. On the other hand, macromolecular organics (humic and fulvic acids, polysaccharides, proteins, peptides, amino acids, man-made polymers, etc.) and polymeric precipitates (silica gel, etc.) tend to be polar and form direct hydrogen bonds with water. These materials are lyophilic, solvophilic or hydrophilic.

For **hydrophobic colloids**, permanent dispersion or suspension is maintained by the random thermal activity of water molecules (**Brownian movement**) and/or convection (arising from small thermal differences in the fluid). In order for Brownian movement to be effective, the particle must be sufficiently small to allow spatially uneven bombardment by water molecules. Evenly distributed bombardment of the surface of a large particle result in no net displacement and consequently gravity and density differences ultimately cause the particle to settle (Halliday and Resnick, 1967) or float on the aqueous medium. If not for ions of like charge present on the colloid surface, the hydrophobic nature of these particles would tend to force them together during mutual particle collisions and promote aggregation which would lead to larger and larger particle sizes and eventual destruction of the colloidal system. These ions promote coulombic repulsion between particles and allow interactions with water molecules thus making the particles effectively more hydrophilic.

Naturally **hydrophilic colloids** (e.g., macromolecules), which more closely approach true solute behavior, maintain their colloidal stability via interactions between **polar or charged functional** groups and water molecular dipoles. Large molecules which are inherently hydrophobic (e.g., oils and greases) may form stable colloidal systems (an emulsion or liquid-in-liquid colloidal system) through interaction with surfactants,, which are large molecules with both hydrophobic and hydrophilic portions. The hydrophobic molecule interacts with the hydrophobic portion of the surfactant while the hydrophilic end interacts with water. A micelle is formed and the hydrophobic molecule is stabilized.

The other fundamental property of colloidal systems, in addition to their physical stability, is their ability to scatter light, known as the Tyndall effect. Interactions between a beam of incident light and colloidal particles include refraction, polarization, reflection and adsorption. The collective effect is that some of the incident light is scattered in all directions and the colloidal suspension appears turbid. The light scattering characteristics of a given suspension are related to concentration, size, shapes and molecular weight of the colloidal particles, albeit in very complex ways (Moore, 1972). These relationships have led to the development of important tools for the investigation of colloids (Rees, 1987).

Although **particle size** is not part of the technical definition of a colloid, in order for particles to be dispersed by Brownian motion, they must be very small but yet not so small that they are actually ions or individual simple molecules (i.e., not part of the aqueous

phase). In order to produce the Tyndall effect they must have sufficient size to interact with light. Generally, a **“colloid” is operationally defined**, typically in terms of its ability to pass a certain filter or molecular sieve size or its rate of settling through a certain length of water column. Similarly, it is conceptually convenient to describe the differences between solutes, colloids and suspended solids in terms of particle diameters or molecular weights. However, there are numerous operational factors such as filter efficiency, density and surface charge which influence and generally complicate separations based on size. Colloids clearly **lie between solutes and suspended solids** in the size continuum of water-dispersed particulate matter as shown in Figure 1, but the size cutoffs are a matter of debate (see Table 2). Generally the size of colloids is quoted as simply being sub-micron or, more specifically, ranging **from 0.001 to 1.0 μm** . A slightly larger lower size limit is used by some while others extend the upper range to 2-5 μm to coincide with the classical clay-silt boundary, while still other further extend this range to 10 μm s (Stumm and Morgan, 1981). As is generally the case when describing a continuum, intermediate limits and bounds are necessarily arbitrary.

Table 2. Generally Accepted size limits for colloids.

Lower size diameter (μm)	Upper diameter (μm)	Source
0.001	1	Domenico and Schwartz (1990)
0.0005	5	Driscoll (1986)
0.001	1	Freeze and Cherry(1979)
0.001	1	Metcalf and Eddy, Inc. (1991)
0.003	1	Pankow (1991)
0.005	10	Stumm & Morgan (1981)

It should be pointed out that particle “sizes” are referenced either to their linear dimensions of length, width or diameter (units of microns or nanometers) or their mass (usually in terms of molecular weights or daltons). The choice depends largely on the method used to study the particles. Obviously there can be no universal conversion between the actual size and mass due to shapes and densities but a few thousand daltons may be taken to be about 0.001 μm .

The colloid-suspended particle boundary can be based on the wide-spread use of 0.45 μm filtration, but larger particles do in fact behave like colloids. An upper size limit of approximately 2 to 5 μm s better describes the hydrodynamic behavior of larger colloids that make them kinetically stable in water. The difficulty in using size as a descriptor of colloids is illustrated by extremely elongated particles such as asbestos fibers which often behave as colloids, despite their long dimension often exceeding several microns, due to their sub-micron diameters.

The significance of colloids mainly arises from their **very large specific surface areas** which facilitate reactions between truly dissolved solutes and the particulate surface. These heterogeneous reactions include: adsorption; catalysis of complexation, redox and hydrolysis reactions among solute species; and dissolution, precipitation and leaching. Increased surface area is a factor in increasing either the equilibrium capacity and/or the chemical kinetic rates of these reactions. The significance of small particles like colloids in influencing the available surface area can be illustrated in several ways.

As particle size decreases the total surface area per unit mass of suspended material increases dramatically. Gregg and Sing (1982) and Parks (1900) provide formulae for computation of specific surface areas for different shapes and non-uniform size distributions. According to the above formulas, 1 μm spheres of quartz would have a specific surface area of 2.26 m^2/g . Simple estimates such as these tend to underestimate surface areas of natural materials due to complex shapes, porosity, and surface defects (White and Person, 1990; Davis and Kent, 1990 and others). For example, Parks (op. cit.) shows a plot of measured specific surface area as a function of grain size for natural quartz sand and crushed quartz which indicates approximately 10 m^2/g is reasonable for 1 μm diameter particles.

Figure 2 illustrates the effect of dividing a 1 cm cube of hematite into smaller and smaller cubes. Not only does the number of cubes increase tremendously, the total surface area approaches 1000 m^2/g at the lower size limit for colloids. Taking this one step further, consider the reactivity of the hematite itself. Obviously, any reaction must take place with the surficial atoms of iron and oxygen, for example those within 2 angstroms of the surface. As the particle size decreases below 1 micron, the percentage of atoms near the surface rises dramatically and approaches 100% at 0.001 μm . Thus almost the entire mass of hematite is immediately available for reaction.

Experimental adsorption data is typically reported in the form of isotherms which compare the dissolved concentration of some solute (mass/vol.) with the sorbed concentration (mass/mass). The same experimental data may be normalized to the measured surface area of sorbent and reported as adsorption density (G , sites/ μm^2). Davis and Kent (1900) report site density data derived from numerous sources for various materials, including $\alpha\text{-FeOOH}$, other iron oxides, titanium oxide polymorphs, aluminum oxides and hydroxides, amorphous silica and kaolinite.

A colloid, like any other particle in an aqueous media, is bounded by an interface which separates the two phases. Such an interface is a region of tremendous complexity, lateral inhomogeneity, extreme microtopography and is rarely if ever static (Hochella, 1990). Electrical charges are an integral and ubiquitous characteristic of solid-aqueous phase interfaces and strongly influence the thickness and nature of the transition zone between the two phases. The total amount of **electrical charge at the interface** is a surface area-intensive function. In the case of colloidal particles, or any suspended particle for that matter, this electrified nature of the interface has three very important consequences:

- 1) first, electrical forces of attraction and repulsion control how closely two particles may approach one another and whether or not there will be sufficient tendency for them to remain together if the approach is close enough or forceful enough – this is the basis for coagulation or agglomeration of suspended matter. This controls the stability and transportability of the particles in the aqueous media.

- 2) secondly, the electrical charges associated with particle interfaces influences the processes of adsorption which allow metal ions, anions and organic molecules to become associated with the particles. So electrical forces influence the identity and abundance of sorbed ions and molecules associated with colloids.

All surface electrical charges have their ultimate origin in unsatisfied chemical bonds associated with the solid phase but the physical location of the unsatisfied bonds determines the characteristics of the electrified interface (Sposito, 1992). "Permanent" (i.e., not affected by the aqueous environment) surface charges have their origin within the bulk solid phase where substitutions of similar-sized but different-charged atoms lead to a net lattice charge imbalance. These charges are typically negative in sign (e.g., substitution of Al^{3+} for Si^{4+} in the tetrahedral layer or Mg^{2+} for Al^{3+} in the octahedral layer of smectite clays). The result of the lattice charge deficiencies is a non point-source electrostatic surface charge which gives rise to such phenomena as cation exchange. Non-stoichiometric substitutions in other minerals such as carbonates can generate similar charges.

Another source of surface charge is found on developing or broken surfaces which abound in yet unsatisfied or now 'dangling' bonds respectively. These bonds are exposed to the mobile aqueous phase and tend to react strongly with water. Lasaga (1990) presents detailed theory and evidence for the nature of the water-surface reactions but, in general, positive surface charges (e.g., due to an incompletely bonded Si atom) attract the negative charge of an OH^- ion or the negative dipole of a water molecule. Water bound in this way may dissociate to form a surface OH (X-OH) or the X-OH may protonate to form X-OH_2^+ or deprotonate to form X-O^- . In short, surface bound water behaves amphotericly (as an acid or base) and therefore the character of the surface and its charge is interactive with the $[\text{H}^+]$, as well as other characteristics of the surrounding aqueous environment. Any ions which function like H^+ and OH^- in this case are referred to as potential-determining ion (PDIs). When water (OH^- and H_2O^+) is involved, the surface charge is a function of the pH of the aqueous medium (positively charged at lower pHs and negatively charged at higher pHs). The pH where the surface is neutral is the ZPC or zero point of charge.

The interactions of colloids with one another and with macroscopic solid phases are governed by hydrodynamic and chemical forces (O'Melia, 1989). **Stability of colloids** (not to be confused with chemical stability with respect to dissolution) refers to their ability to remain suspended by avoiding aggregation due to particle interactions. Similarly, permanent physical interactions between colloids and a porous matrix will remove colloids from suspension. Hydrodynamic forces tend to bring suspended particles into contact with other particles and with bounding surfaces. Gravitational aggregation is caused by differential rates of settling due to size differences, while random collisions of small particles due to Brownian motion results in perikinetic flocculation. Collisions also occur when particles are being transported in zones of steep fluid, and consequently particle, velocity profiles (orthokinetic flocculation). Aggregated particles are then subject to rapid sedimentation. The bulk chemical properties between settling colloidal aggregates and not-settling particles can be very different (Ranville et al., 1991).

Collision of two particles can have two outcomes, either the particles adhere to each other or they do not. Interfacial electrostatic forces, as previously described, govern how stable the particle associations will be (O'Melia, 1987). As two similar, like-charged hydrophobic particles approach each other they begin to experience electrostatic repulsion as the gap between them closes. As the separation (d) decreases, the repulsive forces increase and

more energy is required to continue the approach. If the separation can be made sufficiently small, van der Waals' attractive forces begin to come into play and ultimately overwhelm the repulsive forces and aggregation can take place. The maximum net repulsive force must be overcome to achieve aggregation. The thickness of the diffuse charge layer surrounding the particle controls the magnitude of the repulsive force and this thickness is decreased by the presence of ions in the aqueous media (i.e., ionic strength). As ionic strength increases, the diffuse charge cloud shrinks and the repulsive force that is required to be overcome decreases, therefore aggregation is more likely. Similarly, increases in temperature increase aggregation.

Colloids are in general too small to be observed by optical microscopy. Techniques which can provide information about colloids are: transmission and scanning electron microscopy, laser light-scattering, field-flow fractionation, ultrafiltration/chemical analysis, and ultracentrifugation/chemical analysis.

REFERENCES

- Davis, J.A., and Kent, D.B., 1990, Surface complexation modeling in aqueous geochemistry, in Hochella, M.E., Jr., and White, A.F., ed., *Reviews in Mineralogy, Vol 23, Mineral-Water Interface Geochemistry*: Washington, D.C., Mineralogical Society of America, pp. 177-248.
- Domenico, P.A. and Schwartz, F.W., 1990, *Physical and Chemical Hydrology*, John Wiley & Sons, NY, NY. 824 p.
- Driscoll, F.G., 1986, *Groundwater and Wells*. 2nd Ed., Johnson Division, St. Paul, MN. 1108 p.
- Freeze, R.A. and Cherry, J.A., 1979, *Groundwater*, Prentice-Hall, NJ. 604 p.
- Gregg, S.J. and Sing, K.S.W., 1982, *Adsorption, Surface Area and Porosity*, 2nd ed.: London, Academic Press. 303pp.
- Halliday, D., and Rsnick, R., 1967, *Physics*, 2nd: New York, NY, John Wiley, Inc. 1324 pp.
- Hochella, M.F., Jr., 1990, Atomic structure, microtopography, composition and reactivity of mineral surfaces, in Hochella, M.E., Jr. and White, A.F., ed., *Mineral-Water Interface Geochemistry, Reviews in Mineralogy*: Washington, D.C., Mineralogical Society of America, pp. 87-132.
- Lasaga, A.C., 1990, Atomic treatment of mineral-water surface reactions, in Hochella, M.E., Jr., and White, A.F., ed., *Mineral-Water Interface Geochemistry, Reviews in Mineralogy*: Washington, D.C., Mineralogical Society of America, pp. 17-86.
- Metcalf and Eddy, Inc., 1972, *Wastewater Engineering*, McGraw-Hill, NY, NY. 824 p.
- Moore, W.J., 1972, *Physical Chemistry*, 4th ed.: Englewood Cliffs, NJ, Prentice-Hall, Inc. 977

pp.

O'Melia, C.R., 1987,, Particle-particle interactions: in Stumm, Aquatic Surface Chemistry, John Wiley and Sons, New York.

Pankow, J.F., 1991, Aquatic Chemistry Concepts, Lewis Pubs., Chelsea, MI., 673 p.

Parks, G.A., 1990, Surface energy and adsorption at mineral/water interfaces: an introduction, in Hochella, M.E., Jr., and White, A.F., ed., Mineral-Water Interface Geochemistry, Reviews in Mineralogy: Washington, D.C., Mineralogical Society of America, pp. 133-175.

Ranville, J.F., Harnish, R.A., and McKnight, D.M., 1991, Particulate and colloidal organic material in Pueblo Reservoir, Colorado: Influence of autochthonous source on chemical composition, in Baker, R., ed., Organic Substances and Sediments in Water, Vol. 1: Chelsea, MI, Lewis Publishers, pp. 47-74.

Rees, T.F., 1987, A review of light-scattering techniques for the study of colloids in natural water: J. Contam. Hydrology, v.1, pp. 425-439.

Sposito, G., 1992, Characterization of particle surface charge, in Environmental Particles, Vol. 1: Boca Raton, FL, Lewis Publishers, pp. 291-314.

Stumm, W., and Morgan, J.J., 1981, Aquatic Chemistry: New York, NY, John Wiley & Sons. 780 pp.

White, A.F., and Peterson, M.L., 1990, Role of reactive-surface-area characterization in geochemical kinetic models, in Melchior, D.C., and Bassett, R.L., eds., Chemical Modeling of Aqueous Systems II, 416, ACS Symposium Series: Washington, D.C., American Chemical Society, pp. 461-477.