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Advanced Colloidal Chemistry for PhD Students.

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In this meeting or lecture the focusing will be on the following points:

1-The most important type of soil mineral colloids or which of the soil mineral colloids regards as a most important or popular one? Why? Explain your idea about your selection?

2-Why the focusing is more on iron oxides in comparing with other oxides?

3-Which of mineral colloids and organic collides is playing an important role in soil chemistry and sustainable agriculture ? Explain it depending on your information about soil colloidal chemistry.

4-Explain your idea about types humus or organic colloids.

5-Enumerate factors affecting on type or properties of humus colloids.
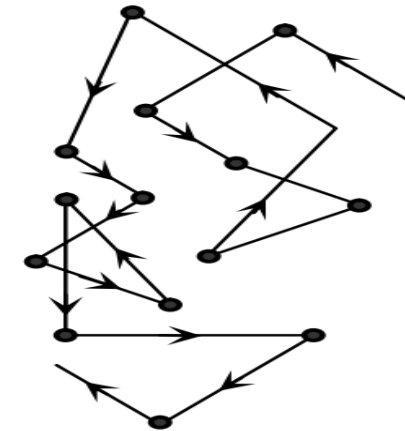
Colloids:

Thomas Graham is the first one whom used the term of colloids on 1861 .It is a Greek word derivative from Kolla means Glue and Eidos means like ((Kalloeidos = Colloids)).

These particles are not just extra-small fragments of rock and organic matter. They are highly reactive materials with electrically charged surfaces. Because of their size and shape, they give the soil an enormous amount of reactive **surface area**. It is the colloids, then, that allow the soil to serve as nature's great electrostatic chemical reactor.

Each tiny colloid particle carries a swarm of positively and negatively charged ions (cations and anions) that is attracted to electrostatic charges on its surface. The ions are held tightly enough by the **soil colloids** to greatly reduce their loss in drainage waters, but loosely enough to allow plant roots access to the nutrients among them. Other modes of adsorption bind ions more tightly so that they are no longer available for plant uptake, reaction with the soil solution, or leaching loss to the environment. In addition to plant nutrient ions, soil colloids also bind with water molecules, biomolecules (e.g., DNA, hormones, or antibiotics), viruses, toxic metals, pesticides, and a host of other mineral and organic substances in the environment. Hence, soil colloids greatly impact nearly all ecosystem functions.

• General Properties of Soil Colloids

- Size
- surface area
- Surface charges
- Adsorption of cations:
- Adsorption of water:
- Cohesion
- Adhesion
- Swelling and shrinkage:
- Dispersion and flocculation:
- Brownian movement:

Brownian movement of

Short notes about soil colloids properties , then we discuss some of them in detail :

1- Patrice Size:

The clay and humus particles in soils are referred to collectively as the **colloidal fraction** because of their very small size and colloid-like behavior. They are visible or can be seen only with an electron microscope. Particles behave as colloids if their diameter less than about 1 μm (0.000001 m) although some soil scientists consider 2 μm to mark the upper boundary of the colloidal fraction to coincide with the definition of the clay particle size fraction.

2- Surface area :Due to their small size, all soil colloids expose a large **external surface** area per unit mass, more than 1000 times the surface area of the same mass of sand particles. Some silicate clays also possess extensive **internal surface** area between the layers of their plate like crystal units. To grasp the relative magnitude of the internal surface area, remember that these clays are structured much like this book. If you were to paint the external surfaces of a book (the covers and edges), a single brush of paint would do. However, to cover the internal surfaces (both sides of each page in the book) you would need a very large amount of paint.

The total surface area of soil colloids ranges from 10 m square/g for clays with only external surfaces, to more than 800 m square/g for clays with extensive internal surfaces. To put this in perspective, we can calculate that the surface area exposed within 1 ha (about the size of a football field) of a 1.5-m-deep fine-textured soil (45% clay) might be as great as 8,700,000 km square (the land area of the entire United States).

How clay particle size and soil bulk density affects on soil surface area?

Increase in particle size causes decrease in soil surface area and vice versa.

Bulk density = (Mass(g) /volume (cm^3)

Example about surface area for 1.3 g soil for a cubic 8mm length as shown in figure in the next slide:

Surface area and particle size. Consider a 1.3 g cube 8 mm on a side (a). The cube has six faces with a total of 8*8*6 =384 mm^2 surface area (6 faces • 64 mm^2 per face) or a specific surface for one gram soil = (384 /1.3 =295 mm^2/g). If this cube were cut into smaller cubes of only 2 mm on each side (b), the same mass would now be present as 64 (4 • 4 • 4) cubes, each with 24 mm^2 of surface area (6 faces • 4 mm^2 per face) for a total surface area of 1536 mm2 (24 mm2 per cube • 64 cubes), or a specific surface of 1182 mm^2/g (1536/1.3). This is four times as much surface area as the single large cube. The curve (c) explains why nearly all of the adsorbing power, swelling, plasticity, heat of wetting, and other surface area–related properties are associated with the clay fraction in mineral soils.

Note: the surface area will be explain in special lecture.

3-Surface Charges

The total surface charge (internal and external surfaces) of soil colloids carry positive and/or negative electrostatic charges. For most soil colloids, electronegative charges predominate, although some mineral colloids in very acid soils have a net electropositive charge. As we shall see in Sections 8.3 to 8.7, the amount and origin of surface charge differs greatly among the different types of soil colloids and, in some cases, is influenced by changes in chemical conditions, such as soil pH .

The charges on the colloid surfaces attract or repulse substances in the soil solution as well as neighboring colloid particles. These reactions, in turn, greatly influence soil chemical and physical behavior this called cation exchange.

4-Adsorption of Water

In addition to adsorbing cations and anions, soil colloids attract and hold a large number of water molecules. Generally, the greater the external surface area of the soil colloids, the greater the amount of water held when the soil is air-dry (Figure 8.2). While this water may not be available for plant uptake (see figure in the next slide)on the colloid surfaces attract the oppositely charged end of the polar water molecule. Some water molecules are attracted to the exchangeable cations, each of which is hydrated with a shell of water molecules. Water adsorbed between the clay layers can cause the layers to move apart, making the clay more plastic and swelling its volume . As a soil colloid dries, water adsorbed on the external and internal surfaces is removed, so the particles and their constituent layers are brought closer together, shrinking the soil volume.

Cohesion Versus Adhesion

Hydrogen bonding accounts for two basic forces responsible for water retention and movement in soils: the attraction of water molecules for each other (**cohesion**) and the attraction of water molecules for solid surfaces (**adhesion**). By adhesion (also called *adsorption*), some water molecules are held rigidly at the surfaces of soil solids. In turn, these tightly bound water molecules hold, by cohesion, other water molecules farther removed from the solid surfaces. Together, the forces of adhesion and cohesion make it possible for the soil solids to retain water and control its movement and use. Adhesion and cohesion also make possible the property of plasticity possessed by clays.

Hydrogen Bonding

Through a phenomenon called **hydrogen bonding**, a hydrogen atom of one water molecule is attracted to the oxygen end of a neighboring water molecule, thereby forming a low-energy bond between the two molecules. This type of bonding accounts for the polymerization of water. Hydrogen bonding also accounts for the relatively high boiling point, specific heat, and viscosity of water compared to the same properties of other hydrogen-containing compounds, such as H_2S, which has a higher molecular weight but no hydrogen bonding.

Hydration

Polarity also explains why water molecules are attracted to electrostatically charged ions and to colloidal surfaces. Cations such as H^+, Na^+, K^+, and Ca^{2+} become hydrated through their attraction to the oxygen (negative) end of water molecules. Likewise, negatively charged clay surfaces attract water, this time through the hydrogen (positive) end of the molecule. Polarity of water molecules also encourages the dissolution of salts in water since the ionic components have greater attraction for water molecules than for each other. When water molecules become attracted to electrostatically charged ions or clay surfaces, they are more closely packed than in pure water. In this packed state, their freedom of movement is restricted and their energy status is lower than in pure water. Thus, when ions or clay particles become hydrated, energy is released. That released energy is evidenced as *heat of solution* when ions hydrate or as *heat of wetting* when clay particles become wet. The latter phenomenon can be demonstrated by adding a few drops of water to dry,

Allophane and Imogolite. Relatively little is known of factors influencing the formation of allophane and imogolite. While they are commonly associated with materials of volcanic origin, they are also formed from igneous rocks and are found in some Spodosols. Apparently, volcanic ashes release significant quantities of $Si(OH)x$ and $Al(OH)x$ materials that precipitate as gels in a relatively short period of time. These minerals are generally poorly crystalline in nature, imogolite being the product of a more advanced state of weathering than that which produces allophane. Both types of minerals have a pronounced capacity to strongly retain anions as well as to bind with humus, protecting it from decomposition.

Q: What are the most important properties of soil colloids? Why?

Specific surface area (Sm) :

Specific surface area is a total surface area per mass of dry soil or total surface area per volume of soil solids or per unit volume of soil:

1-Sm =SA/Ms (m^2 g^{-1}).

2-Svs =SA/Vs (m^2 m^{-3}).

3-Svt =SA/Vst (m^2 m^{-3}).

SA= Total surface area.

Ms =Mass of soil solids.

Vs =Volume of soil solids.

Vt =Total volume of soil.

Most of chemical and physical reactions occur at the surface.