COLLOIDS
and
COLLOIDAL DISPERSIONS
2nd week

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Kinetic Properties of Colloids

Grouped under this heading are several properties of colloidal systems that relate to the motion of particles with respect to the dispersion medium.

The motion may be,

- thermally induced → Brownian movement
  → Diffusion
  → Osmosis
- gravitationally induced → Sedimentation
- applied externally → Viscosity

Electrically induced motion is considered in the section on electrical properties of colloids.

◆ Brownian Motion

- It describes the random movement of colloidal particles and may be observed with particles at about 5 μm.
- It was explained as resulting from the bombardment of the particles by the molecules of the dispersion medium.
- The velocity of the particles increases with decreasing particle size.
- Increasing the viscosity of the medium decreases and finally stops the Brownian movement.

Diffusion

- Particles diffuse spontaneously from a region of higher concentration to one of lower concentration until the concentration of the system is uniform throughout.
- **Diffusion is a direct result of Brownian movement.**

- According to Fick's first law;

the amount of substance (dq) diffusing in time (dt) across a plane of area (S) is directly proportional to the change of concentration (dc) with distance traveled (dx).

$$dq = -DS\frac{dc}{dx}dt$$

Stokes-Einstein equation

- If the colloidal particles can be assumed to be approximately spherical, the following equation can be used to obtain the radius of the particle and the particle weight or molecular weight:

$$D = \frac{RT}{6\pi \eta r N}$$

D: diffusion coefficient (obtained from Fick's law)
R: molar gas constant,
T: absolute temperature,
η: viscosity of the solvent,
r: radius of the spherical particle,
N: Avogadro's number.

The measured diffusion coefficient can be used to obtain the molecular weight of approximately spherical molecules, such as egg albumin and hemoglobin, by use of the below equation:

$$D = \frac{RT}{6\pi \eta N} \sqrt[3]{\frac{4\pi N}{3M\bar{v}}}$$

M: molecular weight

$\bar{v}$: the the partial specific volume

(approximately equal to the volume in cm^3 of 1 g of the solute, as obtained from density measurements)

Analysis of these equations allows us to formulate the following three main rules of diffusion:

a) the velocity of the molecules increases with decreasing particle size,

b) the velocity of the molecules increases with increasing temperature, and

c) the velocity of the molecules decreases with increasing viscosity of the medium.

◆ Osmotic Pressure

The osmotic pressure of a dilute colloidal solution is described by the **Van't Hoff Equation:**

$$\pi = cRT$$

Π: osmotic pressure
c: molar concentration of solute.

This equation can be used to **calculate the molecular weight of a colloid in a dilute solution.**

For very diluted solutions the equation can be converted as:

$$\pi = \frac{c_g}{M} RT$$

Here, c_g is the grams of solute per liter of solution and M is the molecular weight,

◆ Sedimentation

The velocity, v, of sedimentation of spherical particles having a density, ρ, in a medium of density ρ_0 and a viscosity η_0 is given by **Stoke's Law:**

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta_0}$$

where g is the acceleration due to gravity. If the particles are subjected only to the force of gravity, than the lower size limit of particles obeying Stokes's equation is about 0.5 μm.

- This is because Brownian movement becomes significant and tends to offset sedimentation due to gravity and promotes mixing instead.

- Consequently, a stronger force must be applied to bring about the sedimentation of colloidal particles in a quantitative and measurable manner.

- This is accomplished by use of the **ultracentrifuge** which can produce a force one million times that of gravity.

Viscosity

- Viscosity is an expression of the resistance to flow of a system under an applied stress.
- The more viscous a liquid is, the greater is the applied force required to make it flow at a particular rate.

- Viscosity studies also provide information regarding the shape of the particles in solution.

- Einstein developed an equation of flow applicable to dilute colloidal dispersions of spherical particles, namely,

$$\eta = \eta_0(1 + 2.5\phi)$$

In this equation, which is based on hydrodynamic theory, η_0 is the viscosity of the dispersion medium and η is the viscosity of the dispersion when the volume fraction of colloidal particles present is Φ.

The volume fraction is defined as the volume of the particles divided by the total volume of the dispersion; it is therefore equivalent to a concentration term. Both η_0 and η can be determined using a capillary viscometer.

Several viscosity coefficients can be defined with respect to this equation.

These include

- Relative viscosity (η_{rel})
- Specific viscosity (η_{sp})
- Intrinsic viscosity (η)

Electrical Properties of Colloids

Particles dispersed in liquid media may become charged mainly in 3 ways:

1. selective adsorption of a particular ionic species present in solution. Examples:
- an ion added to the solution
- the hydronium or hydroxyl ion of pure water

2. charges on particles arise from ionization of groups (such as COOH) that may be situated at the surface of the particle. In this case, the charge is a function of pK and pH.

3. difference in dielectric constant between the particle and its dispersion medium could cause a the charge on a particle surface

◆ The Electric Double Layer

- Consider a solid surface in contact with a polar solution containing ions, (for example, electrolyte solution).
- Let us suppose that some of the cations are adsorbed onto the surface, giving it a positive charge (aa' layer).

- Anions in the solution will attract to the positively charged surface by electric forces (bb' layer) that also serve to repel the approach of any further cations once the initial adsorption is complete.

As a result, an equilibrium situation is set up in which some of the excess anions approach the surface, whereas the remainder are distributed in decreasing amounts as one proceeds away from the charged surface.

- ✓ aa’ is the surface of the solid. The adsorbed ions give the surface positive charge. **potential-determining ions**.

- ✓ *bb’* layer is a region of tightly bound solvent molecules, together with some negative ions.**counterions**/**gegenions.**

- ✓ In the region cc’, there is an excess of negative ions.
- ✓ Beyond cc’, the distribution of ions is uniform and electric neutrality is obtained (*dd’ layer*)

- ✓ Thus, the electric distribution at the interface is equivalent to a double layer of charge, the first layer (**aa’ to bb’)** tightly bound and a second layer **(from bb’ to cc’)** that is more diffuse.
- ✓ The so-called diffuse double layer therefore extends from **aa’ to cc’.**

Electrothermodynamic (Nernst) Potential, E,

- The potential at the solid surface aa’ due to the potential-determining ions is defined as the difference in potential between the actual surface and the electroneutral region of the solution.

Electrokinetic, or Zeta, Potential, ζ.

- The potential located at the shear plane ***bb’*** is defined as the difference in potential between the surface of the tightly bound layer (shear plane) and the electroneutral region of the solution.

Stability of Colloid Systems

- The presence and magnitude, or absence, of a charge on a colloidal particle is an important factor in the stability of colloidal systems.
- Stabilization is accomplished essentially by two means:

1. providing the dispersed particles with an electric charge
2. surrounding each particle with a protective solvent sheath that prevents mutual adherence when the particles collide as a result of Brownian movement. (This second effect is significant only in the case of **lyophilic sols.**)

- **A lyophobic sol is thermodynamically unstable.** The particles in such sols are stabilized only by the <u>presence of electric charges on their surfaces</u>. The like charges produce a repulsion that prevents coagulation of the particles.

- **Addition of a small amount of electrolyte** to a lyophobic sol tends to stabilize the system by imparting a charge to the particles.

- Addition of electrolyte beyond that necessary for maximum adsorption on the particles, however, sometimes results in the accumulation of opposite ions and reduces the zeta potential below its critical value.

- The critical potential for finely dispersed oil droplets in water (oil hydrosol) is about **40 millivolts,** this high value signifying relatively great instability.

- The **critical zeta potential of a gold sol is nearly zero**, which suggests that the particles require only a minute charge for stabilization; hence, they exhibit marked stability against added electrolytes.

DLVO Theory

According to this approach, the forces on colloidal particles in a dispersion are due to

- **electrostatic repulsion** and
- **London-type Van der Walls** attraction.

These forces result in potential energies of repulsion, V_R, and attraction, V_A, between particles; together with the curve for the composite potential energy, V_T.

- There is a **attraction near the origin** and a **high potential barrier of repulsion at moderate distances.** A secondary trough of attraction (or minimum) is sometimes observed at **longer distances of separation between particles.**
- The presence of a secondary minimum is significant in the controlled flocculation of coarse dispersions.

Lyophilic and amphiphilic colloids are thermodynamically stable and exist in true solution so that the system constitutes a single phase.

The addition of an electrolyte to a lyophilic colloid in moderate amounts does not result in coagulation, as was evident with lyophobic colloids.

If sufficient salt is added, however, agglomeration and sedimentation of the particles may result. This phenomenon, referred as **"salting out".**

Sensitization and Protective Colloidal Action

- ✓ **The addition of a small amount of hydrophilic or hydrophobic colloid to a hydrophobic colloid of opposite charge** tends to sensitize or even coagulate the particles due to a **reduction of the zeta potential below the critical value** (usually ± 20-50 mV are optimal).

- ✓ A reduction in the thickness of the ionic layer surrounding the particles and a decrease in the coulombic repulsion between the particles can also resulted with the instability of the hydrophobic particles.

- The addition of large amounts of the **hydrophilic colloid** however, stabilizes the system, the hydrophile being adsorbed on the hydrophobic particles.
- This phenomenon is known as **Protection,** and the added hydrophilic sol is known as a **Protective Colloid**.
- The protective property is expressed most frequently in terms of the **Gold Number**.
- The **Gold Number** is the minimum weight in milligrams of the protective colloid (dry weight of dispersed phase) required to prevent a color change from red to violet in 10 mL of a gold sol on the addition of 1 mL of a 10% solution of sodium chloride.

Pharmaceutical Applications of Colloids

- Colloids are extensively used for modifying the properties of pharmaceutical agents. The most common property that is affected is the solubility of a drug.
- However, colloidal forms of many drugs exhibit substantially different properties when compared with traditional forms of these drugs.
- An other important pharmaceutical application of colloids is their use as drug delivery systems. The most often-used colloid-type drug delivery systems include hydrogels, microspheres, microemulsions, liposomes, micelles, nanoparticles,nanocrystals

- Certain medicinals have been found to possess unusual or increased therapeutic properties when formulated in the colloidal state.
- **Colloidal silver chloride, silver iodide**, and **silver protein** are effective germicides and do not cause the irritation that is characteristic of ionic silver salts.
- Coarsely, powdered sulfur is poorly absorbed when administered orally, yet the same dose of **colloidal sulfur** may be absorbed so completely as to cause a toxic reaction and even death.
- **Colloidal copper** has been used in the treatment of cancer, **colloidal gold** as a diagnostic agent for paresis, and **colloidal mercury** for syphilis.