Colloid solutions

Derjaguin, Landau, Verwey and Overbeek theory (DLVO theory)

DLVO theory suggests that the stability of a particle in solution is dependent upon its total potential energy function V_T. This theory recognizes that V_T is the balance of several competing contributions:

$$V_T = V_A + V_R + V_S$$

where V S is the potential energy due to the solvent, it usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. Much more important is the balance between V_A and V_R, these are the attractive and repulsive contributions. They potentially are much larger and operate over a much larger distance

$$V_A = -A/(12 \pi D^2)$$

where A is the Hamaker constant and D is the particle separation. The repulsive potential V_R is a far more complex function.

$$V_R = 2 \pi \varepsilon a \xi^2 \exp(-\kappa D)$$

where a is the particle radius, π is the solvent permeability, κ is a function of the ionic composition and ξ is the zeta potential.

DLVO theory suggests that the stability of a colloidal system is determined by the sum of these van der Waals attractive (V_A) and electrical double layer repulsive (V_R) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together (figure 1). But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together. Therefore if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place.

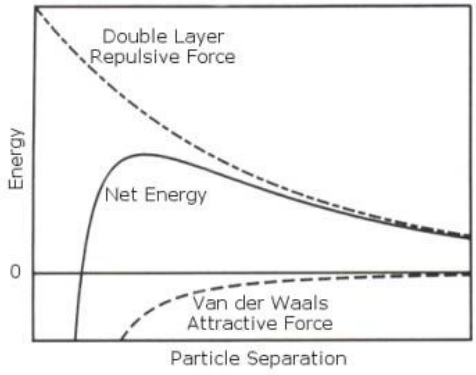

Figure 1: Schematic diagram of the variation of free energy with particle separation according to DLVO theory. The net energy is given by the sum of the double layer repulsion and the van der Waals attractive forces that the particles experience as they approach one another

In certain situations (e.g. in high salt concentrations), there is a possibility of a "secondary minimum" where a much weaker and potentially reversible adhesion between particles exists together (figure 2). These weak flocs are sufficiently stable not to be broken up by Brownian motion, but may dissociate under an externally applied force such as vigorous agitation.

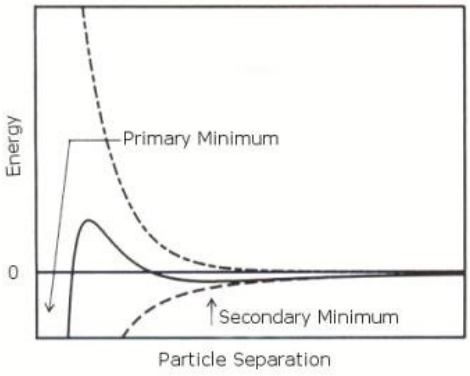

Figure 2: Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum.

Therefore to maintain the stability of the colloidal system, the repulsive forces must be dominant. How can colloidal stability be achieved? There are two fundamental mechanisms that affect dispersion stability (figure 3):

- Steric repulsion - this involves polymers added to the system adsorbing onto the particle surface and preventing the particle surfaces coming into close contact. If enough polymer adsorbs, the thickness of the coating is sufficient to keep particles separated by steric repulsions between the polymer layers, and at those separations the van der Waals forces are too weak to cause the particles to adhere.

More information:

- What are colloids?
- Colloid stability
- Malvern's analyzers for measuring colloid stability

Online presentations and application notes :

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- Electrostatic or charge stabilization - this is the effect on particle interaction due to the distribution of charged species in the system.

Each mechanism has its benefits for particular systems. Steric stabilization is simple, requiring just the addition of a suitable polymer. However it can be difficult to subsequently flocculate the system if this is required, the polymer can be expensive and in some cases the used polymer is undesirable e.g. when a ceramic slip is cast and sintered, the polymer has to be 'burnt out'. This causes shrinkage and can lead to defects.

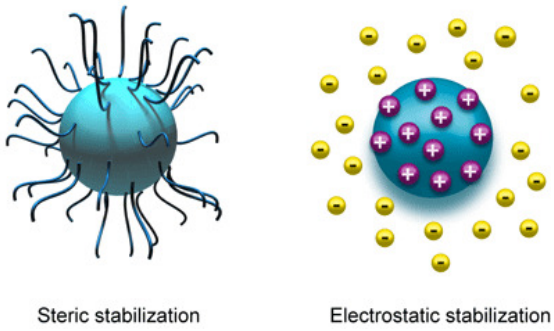

Figure 3: Types of colloidal stabilization.