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Nano Zetasizer ZS

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Brand

Malvern Instruments

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Organisation

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Applications

Zeta
Potential

An
Introduction in 30 Minutes

Introduction

Zeta potential is a physical property which is exhibited by any particle in suspension. It can be used to optimize the formulations of suspensions and emulsions. Knowledge of the zeta potential can reduce the time needed to produce trial formulations. It is also an aid in predicting long-term stability.

Colloid Science

Three of the fundamental states of matter are solids, liquids and gases. If one of these states is finely dispersed in another then we have a 'colloidal system'. These materials have special properties that are of great practical importance. There are various examples of colloidal systems that include aerosols, emulsions, colloidal suspensions and association colloids. In certain circumstances, the particles in a dispersion may adhere to one another and form aggregates of successively increasing size, which may settle out under the influence of gravity. An initially formed aggregate is called a floc and the process of its formation flocculation. The floc may or may not sediment or phase separate. If the aggregate changes to a much denser form, it is said to undergo coagulation. An aggregate usually separates out either by sedimentation (if it is more dense than the medium) or by creaming (if it is less dense than the medium). The terms flocculation and coagulation have often been used interchangeably. Usually coagulation is irreversible whereas flocculation can be reversed by the process of deflocculation. Figure 1 schematically represents some of these processes.

Figure 1: Schematic diagram showing various mechanisms where stability may be lost in a colloidal dispersion

Colloidal Stability and DVLO Theory

The scientists Derjaguin, Verwey, Landau and Overbeek developed a theory in the 1940s which dealt with the stability of colloidal systems. DVLO 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:

$$V_T = V_A + V_R + V_S$$

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

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

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

$$V_R = 2 a^2 \exp(-D)$$

where a is the particle radius, ϵ is the solvent permeability, ψ_0 is a function of the ionic composition and ζ is the zeta potential.

Figure 2(a): Schematic diagram of the variation of free energy with particle separation according to DVLO theory.

DVLO 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 2 (a)). But if the particles collide with sufficient energy to overcome that barrier, the

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

If the zeta potential is reduced (e.g. in high salt concentrations), there is a possibility of a "secondary minimum" being created, where a much weaker and potentially reversible adhesion between particles exists (figure 2 (b)). These weak flocs are sufficiently stable not to be broken up by Brownian motion, but may disperse under an externally applied force such as vigorous agitation.

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.

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

Figure 3: Steric and electrostatic stabilization mechanisms of colloidal dispersions

a ceramic slip is cast and sintered, the polymer has to be 'burnt out'. This causes shrinkage and can lead to defects.

Electrostatic or charge stabilization has the benefits of stabilizing or flocculating a system by simply altering the concentration of ions in the system. This is a reversible process and is potentially inexpensive.

It has long been recognised that the zeta potential is a very good index of the magnitude of the interaction between colloidal particles and measurements of zeta potential are commonly used to assess the stability of

colloidal systems.

Origins of Surface

Charge

Most colloidal dispersions in aqueous media carry an electric charge. There are many origins of this surface charge depending upon the nature of the particle and its surrounding medium but we will consider the more important mechanisms.

Ionisation of Surface

Groups

Dissociation of acidic groups on the surface of a particle will give rise to a negatively charged surface.

Conversely, a basic surface will take on a positive charge (figure 4). In both cases, the magnitude of the surface charge depends on the acidic or basic strengths of the surface groups and on the pH of the solution. The surface charge can be reduced to zero by suppressing the surface ionisation by decreasing the pH in case of negatively charged particles (figure 4(a)) or by increasing the pH in the case of

positively charged particles (figure 4(b)).

Figure 4(a): Origin of surface charge by ionisation of acidic groups to give a negatively charged surface

Figure 4(b): Origin of surface charge by ionisation of basic groups to give a positively charged surface