

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.

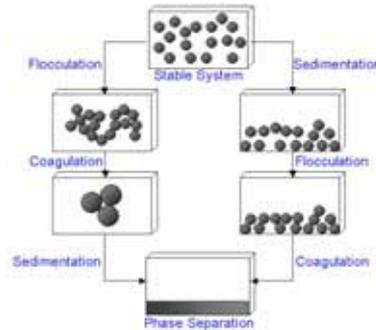


Figure 1: Schematic diagram showing various mechanisms where stability may be lost in a colloidal dispersion

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

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

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

$$V_R = 2 \pi \epsilon a \zeta^2 \exp(-\kappa D)$$

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

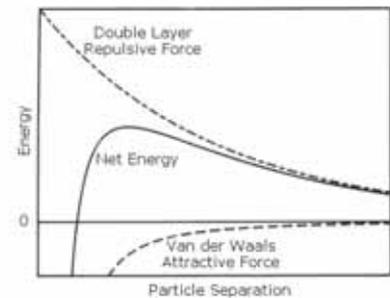
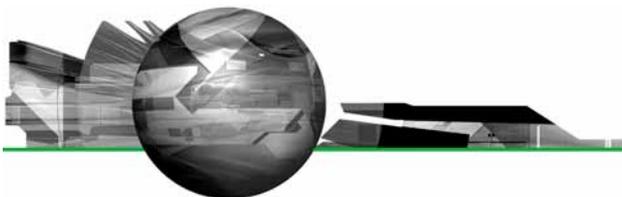


Figure 2(a): Schematic diagram of the variation of free energy with particle separation according to DVLO theory.

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



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.

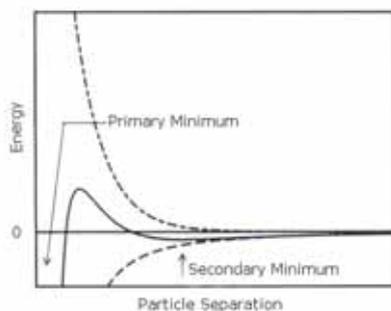


Figure 2(b): Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum.

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 the polymer is undesirable e.g. when

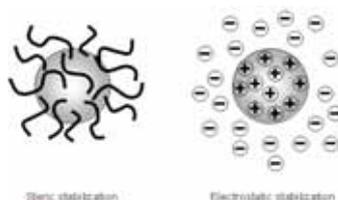


Figure 3: Steric and electrostatic stabilization mechanisms of colloidal dispersions

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 it’s 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)).

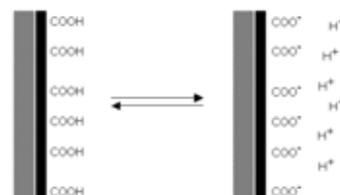


Figure 4(a): Origin of surface charge by ionisation of acidic groups to give a negatively charged surface

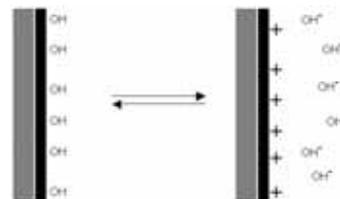
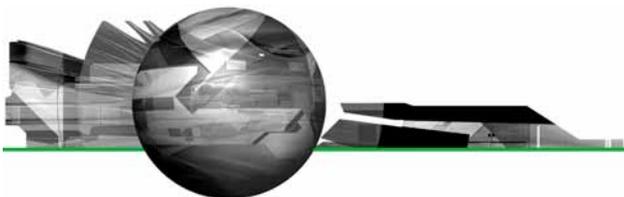


Figure 4(b): Origin of surface charge by ionisation of basic groups to give a positively charged surface



Differential loss of ions from the crystal lattice

As an example, consider a crystal of silver iodide placed in water. Solution of ions occurs. If equal amounts of Ag^+ and I^- ions were to dissolve, the surface would be uncharged. In fact silver ions dissolve preferentially, leaving a negatively charged surface (figure 5). If Ag^+ ions are now added the charge falls to zero. Further addition leads to a positively charged surface.

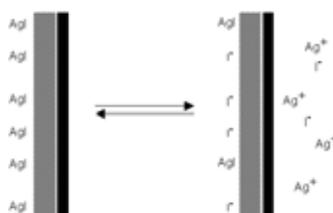


Figure 5: Origin of surface charge by differential solution of silver ions from a AgI surface

Adsorption of charged species (ions and ionic surfactants)

Surfactant ions may be specifically adsorbed on the surface of a particle, leading, in the case of cationic surfactants, to a positively charged surface (figure 6(a)) and, in the case of anionic surfactants, to a negatively charged surface (figure 6(b)).

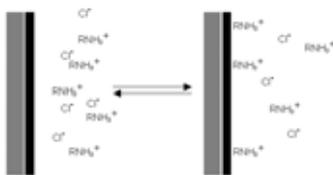


Figure 6(a): Origin of surface charge by specific adsorption of a cationic surfactant. $R =$ hydrocarbon chain

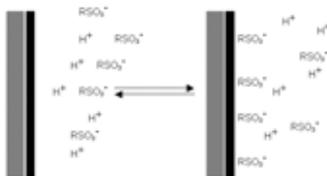


Figure 6(b): Origin of surface charge by specific adsorption of an anionic surfactant. $R =$ hydrocarbon chain

The Electrical Double Layer

The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions, ions of opposite charge to that of the particle, close to the surface. Thus an electrical double layer exists round each particle.

Zeta Potential

The liquid layer surrounding the particle exists as two parts; an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move it. Those ions beyond the boundary move with the bulk dispersant. The potential at this boundary (surface of hydrodynamic shear) is the zeta potential (figure 7).

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. However, if the particles have low zeta potential values then there will be no force to prevent the

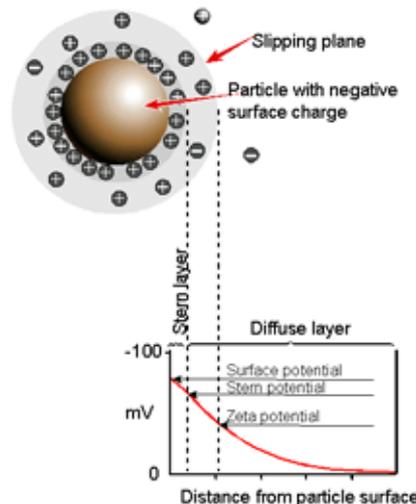


Figure 7: Schematic representation of zeta potential

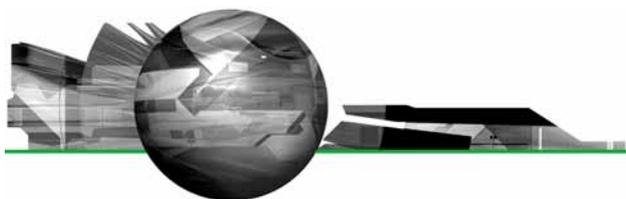
particles coming together and flocculating.

The general dividing line between stable and unstable suspensions is generally taken at either $+30$ or -30 mV. Particles with zeta potentials more positive than $+30$ mV or more negative than -30 mV are normally considered stable. However, if the particles have a density different from the dispersant, they will eventually sediment forming a close packed bed (i.e. a hard cake).

Factors Affecting Zeta Potential

(1) pH

In aqueous media, the pH of the sample is one of the most important factors that affects its zeta potential. A zeta potential value on its own without defining the solution conditions is a virtually meaningless number. Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles tend to acquire more negative charge. If acid is added to this suspension then a point will be reached where the charge will be



neutralised. Further addition of acid will cause a build up of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. There may be a point where the plot passes through zero zeta potential. This point is called the isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is least stable.

A typical plot of zeta potential versus pH is shown in figure 8. In this example, the isoelectric point of the sample is at approximately pH 5.5. In addition, the plot can be used to predict that the sample should be stable at pH values less than 4 (sufficient positive charge is present) and greater than pH 7.5 (sufficient negative charge is present). Problems with dispersion stability would be expected at pH values between 4 and 7.5 as the zeta potential values are between +30 and -30mV.

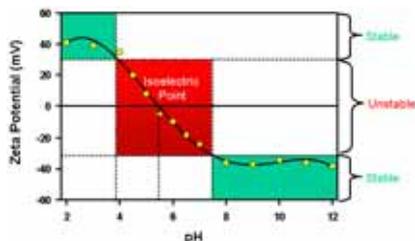


Figure 8: Typical plot of zeta potential versus pH showing the position of the isoelectric point and the pH values where the dispersion would be expected to be stable

2. Conductivity

The thickness of the double layer (κ^{-1}) depends upon the concentration of ions in solution and can be calculated from the ionic strength of the medium. The higher the ionic strength, the more compressed the double layer becomes. The valency of the ions will also influence double layer thickness.

A trivalent ion such as Al^{3+} will compress the double layer to a greater extent in comparison with a monovalent ion such as Na^+ .

Inorganic ions can interact with charged surfaces in one of two distinct ways (i) non-specific ion adsorption where they have no effect on the isoelectric point. (ii) specific ion adsorption, which will lead to a change in the value of the isoelectric point. The specific adsorption of ions onto a particle surface, even at low concentrations, can have a dramatic effect on the zeta potential of the particle dispersion. In some cases, specific ion adsorption can lead to charge reversal of the surface.

3. Concentration of a formulation component

The effect of the concentration of a formulation component on the zeta potential can give information to assist in formulating a product to give maximum stability. The influence of known contaminants on the zeta potential of a sample can be a powerful tool in formulating the product to resist flocculation for example.

Electrokinetic Effects

An important consequence of the existence of electrical charges on the surface of particles is that they interact with an applied electric field. These effects are collectively defined as electrokinetic effects. There are four distinct effects depending on the way in which the motion is induced. These are:

Electrophoresis: the movement of a charged particle relative to the liquid it is suspended in under the influence of an applied electric field

Electroosmosis: the movement of a liquid relative to a stationary charged surface under the influence of an electric field

Streaming potential: the electric field generated when a liquid is forced to flow past a stationary charged surface

Sedimentation potential: the electric field generated when charged particles sediment

Electrophoresis

When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. Viscous forces acting on the particles tend to oppose this movement. When equilibrium is reached between these two opposing forces, the particles move with constant velocity.

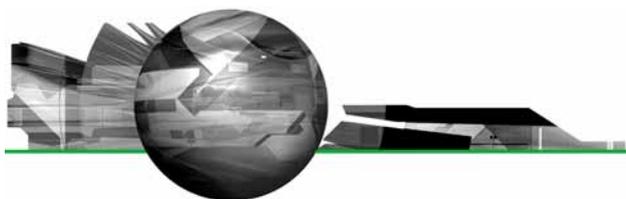
The velocity is dependent on the strength of electric field or voltage gradient, the dielectric constant of the medium, the viscosity of the medium and the zeta potential.

The velocity of a particle in a unit electric field is referred to as its electrophoretic mobility. Zeta potential is related to the electrophoretic mobility by the Henry equation:-

$$U_E = \frac{2 \epsilon z f(\kappa a)}{3 \eta}$$

where U_E = electrophoretic mobility, z = zeta potential, ϵ = dielectric constant, η = viscosity and $f(\kappa a)$ = Henry's function.

The units of κ , termed the Debye length, are reciprocal length and κ^{-1} is often taken as a measure of the "thickness" of the electrical double layer. The parameter 'a' refers to the radius of the particle and therefore κa measures the ratio of the particle radius to electrical double layer thickness (figure 9). Electrophoretic determinations of zeta potential are most commonly made in aqueous media and moderate electrolyte concentration. $F(\kappa a)$ in this case is 1.5, and this is referred to as the Smoluchowski approximation. Therefore calculation of zeta potential



from the mobility is straightforward for systems that fit the Smoluchowski model, i.e. particles larger than about 0.2 microns dispersed in electrolytes containing more than 10^{-3} molar salt.

For small particles in low dielectric constant media (eg non-aqueous media), $f(\kappa a)$ becomes 1.0 and allows an equally simple calculation. This is referred to as the Huckel approximation.

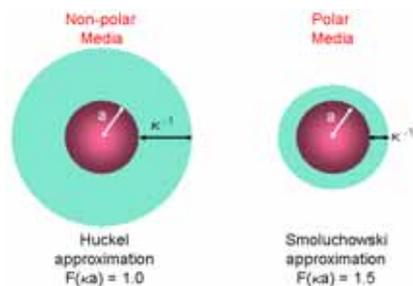


Figure 9: Schematic illustrating Huckel and Smoluchowski's approximations used for the conversion of electrophoretic mobility into zeta potential

Measuring Electrophoretic Mobility

The essence of a classical micro-electrophoresis system is a capillary cell with electrodes at either end to which a potential is applied. Particles move towards the electrode, their velocity is measured and expressed in unit field strength as their mobility.

Early methods involved the process of directly observing individual particles using ultra-microscope techniques and manually tracking their progress over a measured distance. This procedure, although still being used by many groups world wide, suffers from several disadvantages, not least that of the strenuous effort required to make a measurement, particularly with small or poorly scattering particles. The technique used in Malvern's Zetasizer Nano range of instruments is laser Doppler

electrophoresis in combination with M3-PALS.

The M3-PALS Technique

The Zetasizer Nano Series uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a patented technique called M3-PALS to measure particle electrophoretic mobility. Implementation of M3-PALS enables even samples of very low mobility to be analysed and their mobility distributions calculated.

PALS can give an increase in performance of greater than 100 times that associated with standard measurement techniques. This allows the measurement of high conductivity samples, plus the ability to accurately measure samples that have low particle mobilities, such as samples dispersed in non-aqueous solvents. Low applied voltages can now be used to avoid any risk of sample effects due to Joule heating.

Further information discussing the techniques of laser Doppler electrophoresis and M3-PALS can be found in various articles available on the Malvern Instruments web-site

Optical Configuration of a Zeta Potential Instrument

A zeta potential measurement system comprises of six main components (figure 10). Firstly, a laser ① is used to provide a light source to illuminate the particles within the sample. For zeta potential measurements, this light source is split to provide an incident and reference beam. The incident laser beam passes through the centre of the sample cell ②, and the scattered light at an angle of about 13° is detected ③. When an electric field is applied to the cell, any particles moving through the measurement volume will cause the intensity of light detected to fluctuate with a frequency proportional to the particle speed and this information is

passed to a digital signal processor ④ and then to a computer ⑤. The Zetasizer Nano software produces a frequency spectrum from which the electrophoretic mobility and hence zeta potential is calculated. The intensity of the detected, scattered light must be within a specific range for the detector to successfully measure it. This is achieved using an attenuator ⑥, which adjusts the intensity of the light reaching the sample and hence the intensity of the scattering. To correct for any differences in the cell wall thickness and dispersant refraction, compensation optics ⑦ are installed to maintain optimum alignment.

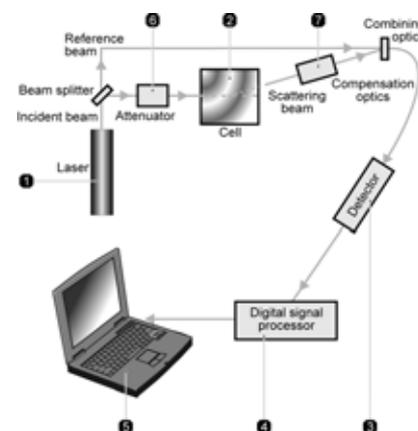
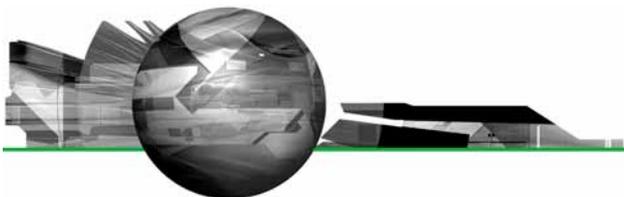


Figure 10: Optical configuration of the Zetasizer Nano series for zeta potential measurements

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Measuring Zeta Potential: A New Technique, Technical Note available from www.malvern.co.uk

Simplifying the Measurement of Zeta Potential Using M3-PALS, Technical Note available from www.malvern.co.uk

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