Basics of Zeta Potential

Application Note

Abstract

This Application Note describes the nature of the electrostatic potential near the surface of a particle, called the zeta potential. It explains how the zeta potential is determined by measuring the velocity of the particles in an electric field. It also explains how the charge on the particle surface affects properties of suspensions and emulsions.

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Introduction

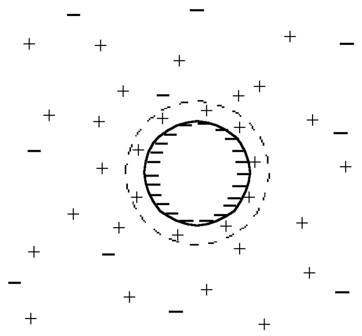

Figure 1. Distribution of charge around a negatively charged particle

The particles in a colloidal suspension or emulsion usually carry an electrical charge. The charge is more often negative than positive and it may arise in a number of ways.

Sometimes the surface of the particles contains chemical groups that can ionize to produce a charged surface. Sometimes the surface adsorbs ions of one sign in preference to ions of the opposite sign. In other cases, chemical compounds are added deliberately to adsorb on the particle surface and generate charge.

However it may happen, the amount of charge on the particle surface is an important particle characteristic because it determines many of the properties of the suspension or emulsion.

Charge distribution

Although the particles are electrically charged, the colloid as a whole is electrically neutral, because the charge on the surface of each particle is counterbalanced by charges (ions) of opposite sign in the surrounding solution.

The charges on the particle surface are normally considered to be attached rather firmly to it and to remain there (though they may exchange with charges of similar type in the solution). The surrounding (balancing) charge, by contrast, is much more loosely associated with the particle.

Because of the thermal motions of the solvent molecules and ions, this countercharge is spread in a *diffuse layer* that stretches out for some distance (on the order of nanometers) from the particle surface (Figure 1).

The oppositely charged ions (called *counter-ions*) tend to congregate around the particle and very few negatively charged ions (*co-ions*) can get close to the surface because of the repulsion from the charges on the particle. Farther away from the particle, the co-ions suffer less repulsion and eventually, at distances of at most a few tens of nanometers, the numbers of cationic and anionic charges are evenly balanced.

Measuring the charge

There are various ways to measure the particle charge, and the different methods do not always measure the same quantity. Most of the commercial devices for determining zeta apply an electric field to the suspension and measure how fast the particles move as a result. This process is called *electrophoresis*. The bigger the charge they carry, the faster the particles will move. This is how the Agilent 7020 ZetaProbe works too, but it measures particle motion in MHz electric fields, while the standard products use DC or slowly varying electric fields. And the ZetaProbe determines the particle motion by measuring the sound waves that the particles emit as they shake back and forth, while the other zeta devices use optical techniques which are limited to very dilute suspensions.

In electrophoresis measurements, one does not usually observe all of the particle charge. The electric field pulls the particle in one direction, but it also pulls the counterions in the opposite direction. Some of the counterions will move with the particle (those within the dotted circle in Figure 1, for example) so the measured charge will be a *net* charge.

The electrostatic potential near the particle surface is shown in Figure 2. It changes very quickly (and linearly) from its value at the surface through the first layer of counterions and then changes more or less exponentially through the diffuse layer. The junction between the bound charges and the diffuse layer is again marked by the broken line. That surface, which separates the bound charge from the diffuse charge around the particle, marks where the solution and the particle move in opposite directions when an external field is applied. It is called the *surface of shear* or the *slip surface*.

The voltage difference between that surface and the liquid beyond the double layer is called the *zeta potential*. It is this potential that determines how fast the particles move in an applied electric field.

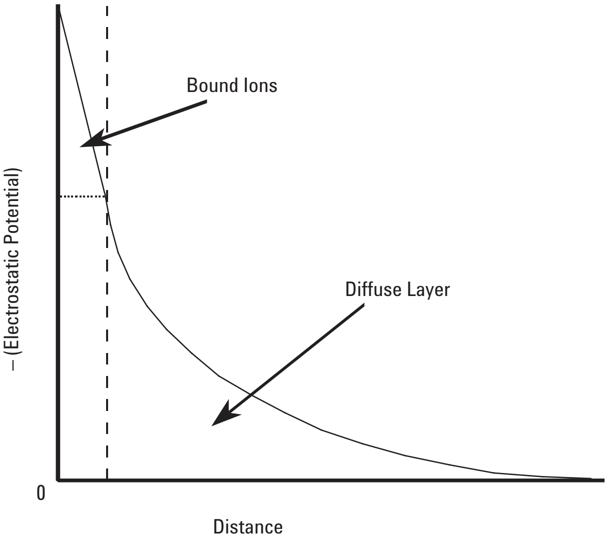

Figure 2. Electrostatic potential near a negatively charged spherical particle

The particle velocity is proportional to the strength of the applied field. By dividing the velocity by the field strength, we obtain a quantity that is a particle property, independent of field strength. This ratio of velocity to field strength is called the electrophoretic mobility in the case of a DC field, and the dynamic mobility in the AC field case. Zeta is calculated from the measured mobility using an appropriate theoretical formula.

Charge affects properties

At first it would seem to be a distinct disadvantage of this method that it only measures a part of the potential on the particle. But in fact that turns out to be an advantage.

When the charge is measured in this way, it reflects more realistically what one particle “sees” as it approaches another particle, and that is what determines the properties of the suspension. If the repulsion between approaching particles is large enough, they will bounce away from one another, and that will keep the particles in a state of *dispersion*.

If the repulsive force is not strong enough, the particles will come together and may stick in a permanent doublet. Then other particles may come along and be caught in the growing aggregate. The suspension is then unstable and the aggregates will quickly settle out from the surrounding medium.

If one is relying on the electric charge alone to keep the system in a disperse state, then the zeta potential will usually need to be kept above 25 mV in magnitude.

Generally speaking, the higher the absolute value of the zeta potential, the more stable the system will be. That means it will be better able to withstand additions of salt (which might otherwise destabilize it). It will also usually show a lower viscosity.

On the other hand, if one wants to separate the particles and remove them from the surrounding fluid, it will be advantageous to reduce the magnitude of the zeta potential.

Aside from its application to suspension stability, the zeta potential is also widely used as a monitor of surface chemistry. Since zeta is a surface property, it is very sensitive to any coating or adsorbed material on the surface. Thus, it is used to detect the presence of any surface contamination, to check coating consistency, and to monitor adsorption of polymeric dispersants.

Conclusion: importance of zeta potential

Particles in a colloidal suspension or emulsion usually carry an electrical charge, which affects the degree of dispersion or aggregation. The zeta potential is the electrostatic potential near the surface of a particle, and is determined by measuring the velocity of the particles in an applied electric field. When the absolute value of the zeta potential is greater, the system is more stable and the particles are more likely to remain dispersed and less likely to aggregate. The value of zeta is also very sensitive to surface chemistry, so it is an ideal indicator for detecting contamination or monitoring adsorption on the particle surface.

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