

# The Zeta Potential

#### Abstract

Describes the nature of the electrostatic potential near the surface of a particle, called the *zeta potential*. Explains how the zeta potential is determined by measuring the velocity of the particles in a d.c. electric field.

#### **Table of Contents**

| 1 | Introduction         | .2 |
|---|----------------------|----|
| 2 | Charge Distribution  | .2 |
| 3 | Measuring the Charge | .3 |

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### 1 Introduction

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 itself preferentially adsorbs ions of one sign of charge in preference to charges of the opposite sign. In other cases there may be deliberately added chemical compounds that preferentially adsorb on the particle surface to generate the 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.

## 2 Charge Distribution

Although we speak of the particles as being electrically charged it is important to realize that the charge on the surface of each particle is counterbalanced by charges (ions) of opposite sign in the surrounding solution. The suspension is neutral overall and also on a scale somewhat larger than the particles themselves.

The charges on the particle surface are normally considered to be attached rather firmly to it and to remain there more or less indefinitely (though they may be exchanging 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* which stretches out for some distance (of order nanometres) from the particle surface (Figure 1).

The oppositely charged ions (called *counter-ions*) tend to congregate around the particle and very few negatively charged (*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 nanometres, the numbers of cationic and anionic charges are evenly balanced.



FIGURE 1 DISTRIBUTION OF CHARGE AROUND A NEGATIVELY CHARGED PARTICLE.

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### 3 Measuring the Charge

There are various ways to measure the particle charge but it must be recognized that the different methods do not always measure the same quantity. One of the most effective methods is to apply an electric field to the suspension and to measure how fast the particles move as a result. That process is called *electro-phoresis*. The bigger the charge they carry, the faster the particles will move.

It turns out, however, that in such an experiment one does not usually observe all of the particle charge. The electric field pulls the particle in one direction but it will also be pulling the counterions in the opposite direction. Some of the counterions will move with the particle (those within the dotted circle, say) so the measured charge will be a *nett* charge taking that effect into account.

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 electrostatic potential on that surface is called the *zeta potential* and it is that potential which is measured, when one measures the velocity of the particles in a d.c. electric field.

The velocity (in metre/second) for a unit field strength (1 Volt per metre) is called the electrophoretic mobility, and is given the symbol  $\mu_E$ . It is related to the zeta potential ( $\zeta$ ), and is usually assumed to measure the potential at the point marked by the broken line in Figure 2. (See Electroacoustic Applications No 4.)



FIGURE 2 ELECTROSTATIC POTENTIAL NEAR A NEGATIVELY CHARGED SPHERICAL PARTICLE

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At first sight 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 also 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 (positive or negative).

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 pay to reduce the magnitude of the zeta potential.

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