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Zeta potential measurements in colloidal suspensions

S. Prabhu¹, K. Murugan²

^{1,2} Assistant Professor, Karpagam Institute of Technology, Coimbatore

Abstract: A parameter determining the stability of colloidal suspensions is the amount of surface charge on the particle. Higher the repulsion between like charged particles, better is the stability of the suspension. A method to quantify the suspension stability is its zeta potential which is a measure of the charges on the surface of the particle. This articles describes the measurement of zeta potential and the various factors affecting the zeta potential of suspensions.

Keywords: Zeta Potential, electro-phoresis, iso-electricpoint

1. Introduction

Particles in colloidal suspensions have positive or negative charges on their surface. This is mainly due to the ionization of chemical groups on the particle surface that produce a charged surface or the preferential adsorption of ions. Deliberately added chemical compounds can also absorb onto the particle surface thus rendering them charged. The amount of charge on the particles is an important characteristic of the particle which determines the properties of the colloidal suspension.

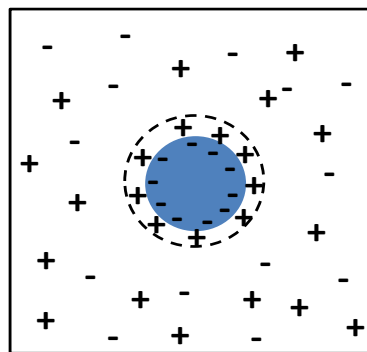


Figure 1: Distribution of charge around a negatively charged particle.

Though particles are electrically neutral the charge on the surface of each particle is counter balanced 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

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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 counter charge 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 accumulate 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.

2. Measuring the Charge on the surface of the particle

Though there are various ways to measure the particle charge the most effective method is to apply an electric field to the suspension and to measure how fast the particles move as a result. This process is called **electro-phoresis**.

Particles carrying bigger charge move faster. The electrostatic potential near the particle surface is shown in **Figure 2**. The electric field pulls the particle in one direction but it will also be pulling the counter ions in the opposite direction. Some of the counter ions will move with the particle (those within the dotted circle) so the measured charge will be a net charge taking that effect into account. It changes very quickly (and linearly) from its value at the surface through the first layer of counter ions 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 U_E . It is related to the zeta potential (ξ), and is usually assumed to measure the potential at the point marked by the broken line in **Figure 2**.

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**

$$U_E = 2 \varepsilon \xi f(\kappa a) / 3 \eta$$

where U_E = electrophoretic mobility, ξ = 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.

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 electric charge alone is relied upon to keep the system in a disperse state then the zeta potential will usually need to be kept above 25 mV (positive or negative).

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.

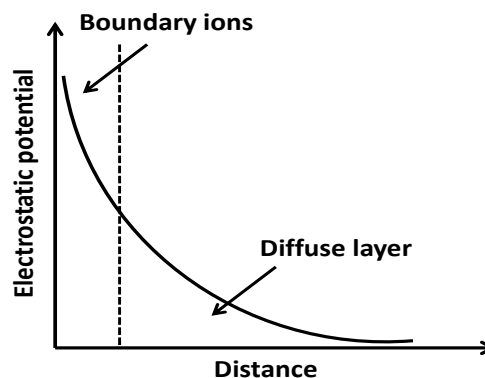


Figure 2: Electrostatic potential around a negatively charged spherical particle.

3. Factors Affecting Zeta Potential

3.1. 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 **iso-electric point** and is very important from a practical consideration. It is normally the point where the colloidal system is least stable.

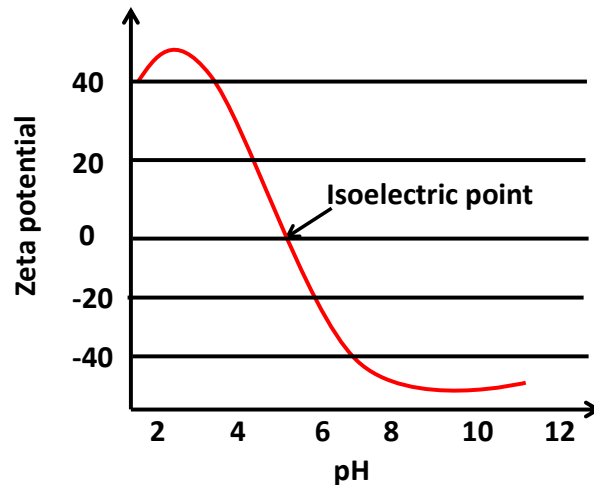


Figure 3: Typical plot of zeta potential versus pH showing the position of the isoelectric point

A typical plot of zeta potential versus pH is shown in figure 3. 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 -30 mV.

3.2. 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 iso-electric point. The specific adsorption of ions on to 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.

3.3 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.

4. Conclusion

This article discusses the method to measure the zeta potential in colloidal suspensions. Zeta potential is an important parameter that determines the stability of colloidal suspensions. It is important to measure the zeta potential of suspensions to get an idea about the properties of the suspensions and to devise methods to enhance their stability.

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