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WALLIS ζ – ZETA POTENTIAL ANALYZER

Zeta potential - Back to basic!

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Introduction

Charged particles in liquid medium are complex systems being studied for quite a long time. The understanding and control of charge properties of colloids is subject for novel discovery as much as industrial process management. Unfortunately, complexity of models and real world of colloids make that charge of colloids often misinterpreted. Here we propose, under *CORDOUAN lighthouse lighting*, a back to basic note to clarify Zeta potential understanding by sailing up the stream of original development of laser Doppler electrophoresis. After recalling how and what is really measured in Zeta potential measurement system, we then explain how these measurements relate to particle interactions and to colloids stability.

Electrophoresis physical principles

Electrophoresis phenomenon exists because particles in liquid are charged. The principle of measurement consists in applying a constant amplitude electric field ($\vec{E}$) to the colloidal solution. The resulting electrostatic force ($\overrightarrow{F_e}$) induces a motion of the particles with a charge q along the field direction. In addition, in a liquid media, the moving particles will undergo a friction force ($\overrightarrow{F_f}$) opposite and proportional (α) to their speed ($\vec{v}$) direction as illustrated on Figure 1. After an initial acceleration phase, the two forces canceled each other when the particles reach a stable, constant speed limit ($\vec{v}_{lim}$) given by:

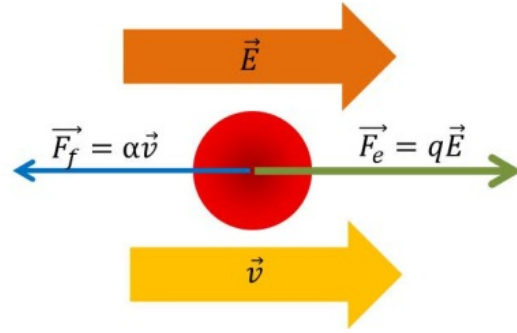$$\vec{v}_{lim} = \frac{q}{\alpha}\vec{E} \qquad (1)$$

Figure 1: Forces on positively charged particle in a liquid, moving under electric field.

The factor q/α, called the electrophoretic mobility μ_e, is the capacity for a charged particle to move in a fluid under the action of an electric field. The electrophoresis measurement principle is, by optical means, to measure the Doppler frequency shift generated by the speed of the particle to get $\vec{v}_{lim}$ and thus, knowing the electric field $\vec{E}$, determine the electrophoretic mobility. This μ_e parameter is deeply meaningful to characterize particles because it doesn't need any particular assumption about the charge repartition of the particle nor specific knowledge of particle size or shape indebted in the α parameter.

Electrophoretic mobility μ_e to Zeta potential relationship

One question raises at this point: how does electrophoretic mobility relates to zeta potential and to particle-particle interaction. The simplest way to explain that is first to consider the electrostatic potential of a charged particle in space which fully determines the interaction with other particles. The electrostatic potential $V(r)$ associated to a charge q in space is defined by:

$$V(r) = \delta\frac{q}{\varepsilon r} \qquad (2)$$

Where r is the distance to the center of charge, δ is a constant and ε is the dielectric constant of the medium. In vacuum $\delta = 1/4\pi$ and $\varepsilon = \varepsilon_0$. This potential is represented in Figure 2. The shorter the distance to the charge the strongest the interaction (the potential) is. Keeping in mind this basic model let's continue with the measured quantity: the electrophoretic mobility μ_e.
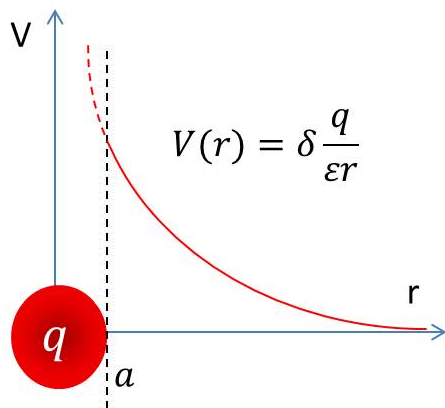

$$V(r) = \delta\frac{q}{\varepsilon r}$$

Figure 2: potential for one particle of radius a

If we assume that the particles are spheres immersed in a liquid of viscosity η and have a hydrodynamic radius R, the friction factor α (see **Figure 1**) is given from the Stokes[1] relation:

$$\alpha = 6\pi\eta R \qquad (3)$$

From (1), the electrophoretic mobility is then given by:

$$\mu_e = \frac{q}{6\pi\eta R} \qquad (4)$$

According to relation (2) one can define a new potential ζ , given by the following relation:

$$\zeta = b\mu_e\frac{\eta}{\varepsilon} = B\frac{q}{\varepsilon R} \qquad (5)$$

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[1] The α factor for spheres appears also in the particle size measurement by dynamic light scattering (DLS).

where B and b are constant factors, η is solvent viscosity and ε is solvent dielectric constant. ζ has the dimension of an electrostatic potential like V for an equivalent charge Bq (see (2) and **Figure 3**); it is called the Zeta potential. In fact, ζ represents the electrostatic potential measured at a distance R from the center of the particle. According to the Stokes model, the hydrodynamic radius R of the particles is the physical radius of the particles plus the surrounding ions/molecules environment "stuck" to the particle (see **Figure 3**). Therefore, the potential of the particle at this *new* radius, determining the amplitude of interaction with the other particles, is a fundamental characteristic of the stability of solution. Indeed, the lower the zeta potential, the easier it is for two particles to approach each other and eventually to aggregate together, so the less stable is the colloidal suspension.
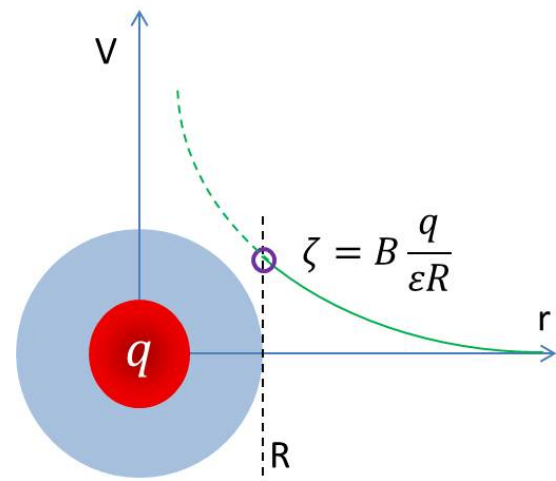

$$\zeta = B\frac{q}{\varepsilon R}$$

Figure 3: Zeta potential

The last point to understand in the definition of ζ is the signification of the parameter b. As one can see from (5), the determination of the Zeta potential requires to know the solvent viscosity and dielectric

constant. This reflects that Zeta potential is a global property of the particle associated to its surrounding solvent counter ions layer thus representing the global free net charge of particles.

Net charge models

The global net charge of particle is defined by the Henry function $f(\kappa a)$ that is corresponding to the b factor. Thus, the full Zeta potential equation from Wallis measurement is:

$$\zeta = \mu_e \frac{\eta}{\varepsilon} f(\kappa a) \qquad (6)$$

κ^{-1} is the Debye length corresponding to the size of the charge layer that surrounds the particle and a is the physical radius (ie hard sphere radius) of the particle (**Figure 4**). Note that $\kappa^{-1} + a = R$. By limiting the Henry function to these two parameters, shape effects are neglected which is a realistic assumption for hard surfaces. The Debye length κ^{-1} is solvent dependent consequently is the Henry function.
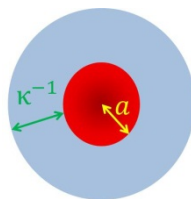

Figure 4: Debye length

In fact, the Henry function varies between 1 and 1.5 depending on the κa factor value. In practice, there are two opposite situations that correspond to most of the real experimental case, See **Figure 5**. First case: Smoluchowski approximation. Henry function equals 1, corresponding to a Debye length small compared to the particle physical radius. This case accurately described the aqueous type solution. Be-

cause of high polarizability of aqueous type solvent molecules, few will be enough to screen the particle potential thus, the surrounding layer of counter ions attracted and stuck to particles will be small. Second case: Hückel approximation. Henry function equals 1.5 corresponding to a Debye length large compared to particle size. This case accurately described organic like solvent. Because of low polarizability of organic like solvent molecules, a lot will be needed to screen the particle potential thus, the surrounding layer of counter ions attracted and stuck will be large.
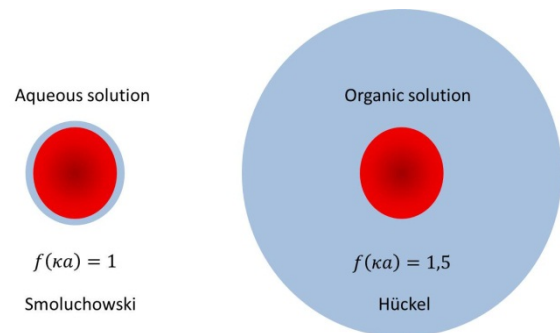

Figure 5: Henry function approximation

The hard step

The fine understanding of this complex world, opened by the measurement of Zeta potential, needs deeper explanation and further readings. In few words, the interaction of liquid's ions with solid surface like particle surface induces surface molecules dissociation or charge adsorption. It results an organization of charge near the solid surface depending of several properties of the surface and solvent (see **Figure 6**). This structure has been named the Electrical Double Layer (EDL) and is generally described by the Gouy-Chapman-Stern model [1-2]. It characterizes particle-particle interaction thus de-

termines the solution properties like stability, chemical activity, optical activity…etc. Such interactions are fully described by the DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek whom developed it [3]. It modeled the electrostatic potential created around the particles so that the particle-particle interaction can be analyzed. Even though this theory is complex, the knowledge of the Zeta potential is a global key to understand stability of colloids solution.
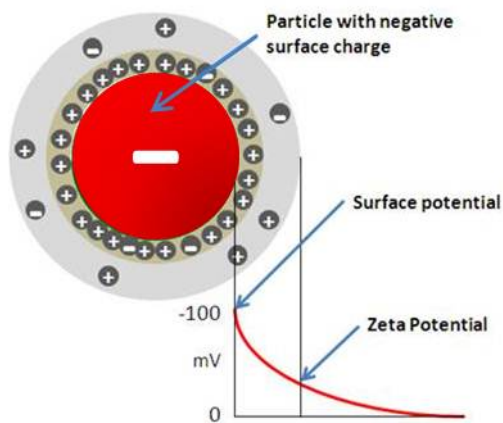
Conclusion

This document ought to introduce a basic understanding of Zeta potential with a simplified description of what happen at particle interface in liquid. It shows that Zeta potential reflects a particle-solvent interaction. It results that the knowledge of Zeta potential is a key factor for understanding stability of colloidal dispersion.

Figure 6: Electrical double layer

[1] ISO 13099-1, Colloidal systems — Methods for zetapotential determination — Part 1: Electroacoustic and electrokinetic phenomena

[2] V. DELGADO *et al.,* MEASUREMENT AND INTERPRETATION OF ELECTROKINETIC PHENOMENA (IUPAC Technical Report), *Pure Appl. Chem.*, Vol. 77, No. 10, pp. 1753–1805, 2005.

[3] J. Lyklema, Fundamentals of Interface and Colloid Science, Academic Press, 1995

WALLIS
Zeta potential analyzer

Measurement

Zeta potential range	-200 mV to 200 mV
Mobility range	10^{-10} to 10^{-7} m²/V.s
Sample concentration	0.0001% to 10% w/% (sample dependent)
Cell options	Cuvette cell with optical quality windows for aqueous and organic solvents
Sample volume	Typically 750 μL (Hellma cell – 10 mm light path)
Maximum sample conductivity	300 mS/cm
Sample Type	Aqueous & organic solvents – pH: 1-14 (depending on cuvette cell material)

Signal processing

Measurement technology	Laser Doppler Electrophoresis (LDE)
Laser source	20 mW diode @635 nm coupled to automated attenuation system. Other wavelengths available upon request.
Measurement angle	One angle for zeta potential at 17°
Fast Fourier transform Algorithm	Resolution: Mobility = 10^{-10} m²/V.s or Zeta = 0,1 mV (in water)
Detector	Avalanche Photodiode – APD

General

Temperature control range inside the cell	10°C to 90°C +/-0,1°C (depending on cuvette cell material)
Computer interface	USB 2.0 – Windows XP, Seven
Dimensions	45 cm x 45 cm x 40 cm (HWD)
Weight	17 kg
Power	100/115/220/240 VAC, 50/60 Hz, 100 W max

System Compliance

CE certification	CE marked product - Class I laser product, EN 60825-1:2001, CDRH
ISO norm	ISO 13099-2 : 2012 – Colloidal system – methods for zeta-potential determination – Part 2 : Optical methods

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