



Zeta Potential Determination of Colloidal Particles

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April 28, 2010

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Colloidal Systems

- Two (or more) separate phases: a dispersed phase and a continuous liquid phase
- The dispersed particles are small, typically micron or smaller, called colloidal particles, many are nanoparticles
- Slurry, paste, paint, toothpaste milk, mayonnaise, emulsions, suspensions, etc.

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Colloidal Particles

- Because their small sizes, colloidal particles have high specific surface area; consequently their surface characteristics, charge and morphology, and interfacial properties, play important roles in the stability and performances of colloidal systems
- Zeta potential determination probes surface charge as well as surface morphology

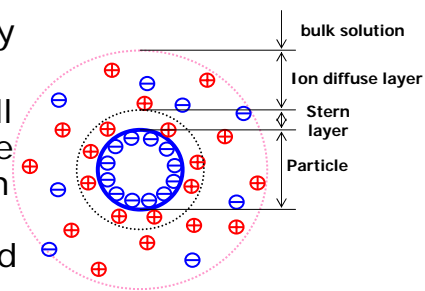
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Particles in Liquid

- When particles are dispersed in liquid, most of them will carry surface charge
- The surface charge will attract ions of opposite charge to form a Stern layer where the ions are strongly bound and a diffuse region where they are less firmly associated

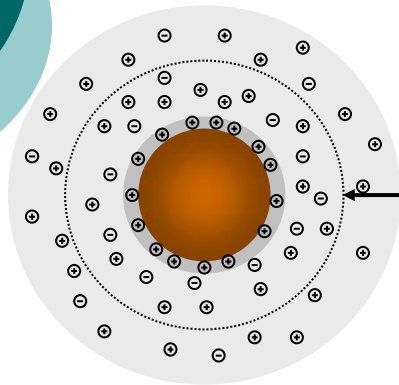


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the Slipping Plane (Shear Plane)



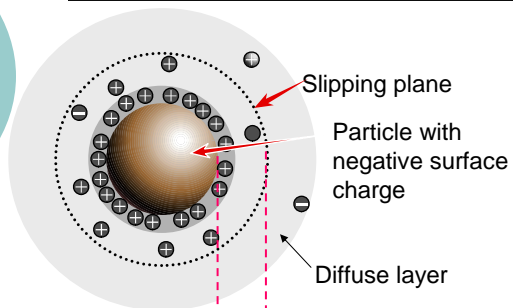
- Imaginary, non-existent
- Location unknown, somewhere in the diffuse layer
- Location varies with surface morphology
- Purely for the purpose of zeta potential determination

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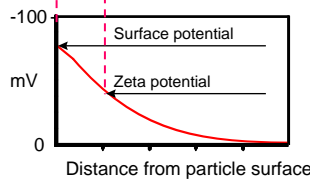
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Zeta Potential (ζ)



- Zeta potential is the potential at the slipping plane
- It is not the surface potential, may or may not be related



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Zeta Potential

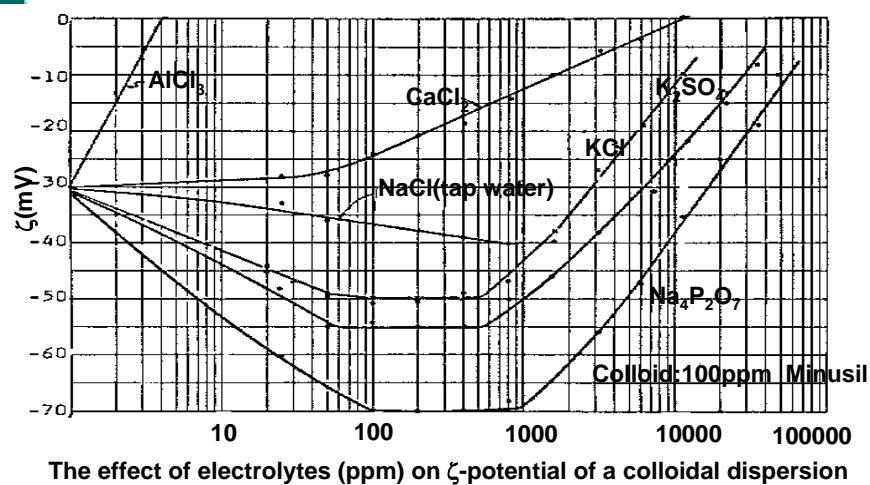
- It depends not only upon the particle surface but also on its environment
- It can be affected by small changes in the pH or ionic strength of the medium
- It also depends on surface morphology for "hairy" or even non-smooth particles

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The Effect of Electrolytes on Particle Zeta Potential



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Main Applications of Zeta Potential Determination

- Relative comparison of various systems with regard to their surface properties to predict or monitor stability of colloidal systems
- Identification of the isoelectric point (or point of zero zeta potential) of colloids
- Particle surface adsorption and morphology identification

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Stability Characteristics of Colloids

Stability Characteristics	$ \zeta\text{-Potential} $
– Maximum Agglomeration & Precipitation	0 to 3 mV
– Strong Agglomeration & Precipitation	5 mV
– Threshold of Agglomeration	10 to 15mV
– Threshold of Delicate Dispersion	15 to 30mV
– Moderate Stability	30 to 40 mV
– Fairly Good Stability	40 to 60 mV
– Very Good Stability	60 to 80 mV
– Extremely Good Stability	80 to 100 mV

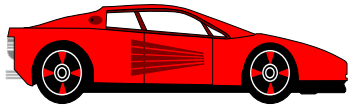
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ζ -Potential Applications: Paints

- Pigments in paint must be well dispersed in order to form smooth painting that has a right color
- Pigment agglomeration due to incorrect ζ -potential will cause changes in gloss, texture and color of the paint



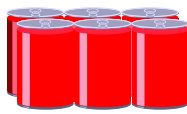
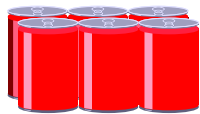
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ζ -Potential Applications: Beverage Emulsions

- Beverage emulsions consist of
 - Oil Phase: oils, weighting agent
 - Water Phase: water, hydrocolloids, acids
- If particle size, surface charge and density match are incorrect:
 - Creaming (phase separation)
 - Flocculation (oil droplets aggregation)
 - Coalescence (form big droplets)

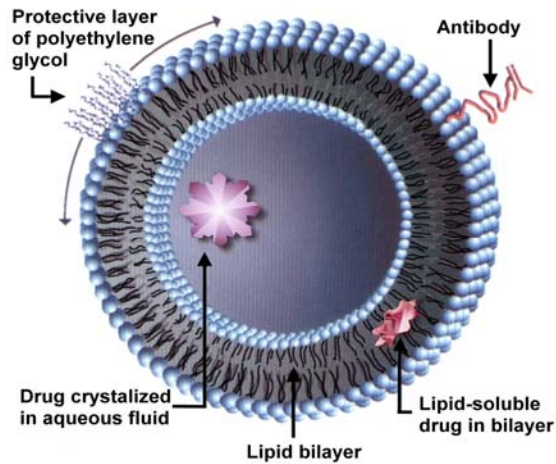


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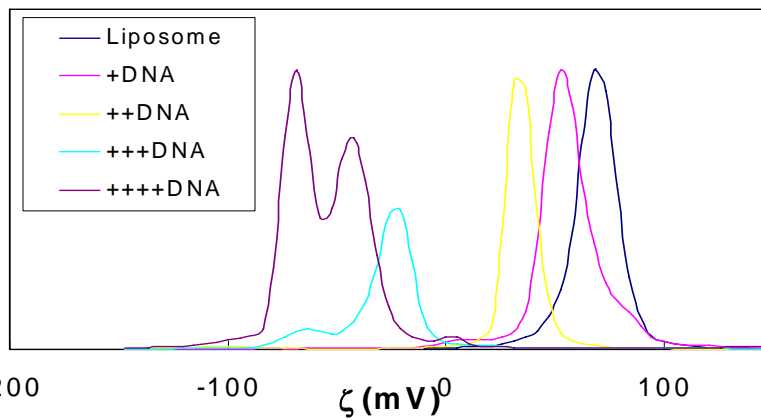
Drug-Liposome Associations



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Zeta Potential of Liposome/DNA Mixtures



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How to Determine Zeta Potential

- Optical Methods
 - Electrophoretic mobility (μ , velocity per field strength) of particles under an applied parallel electric field is measured
- Acoustic Methods
 - Dynamic electrophoretic mobility (μ_d) of particles is measured
- Streaming Potential Method
- In optical and acoustic methods zeta potential is *calculated* from mobility measurement based on a certain theoretical model

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Optical Methods

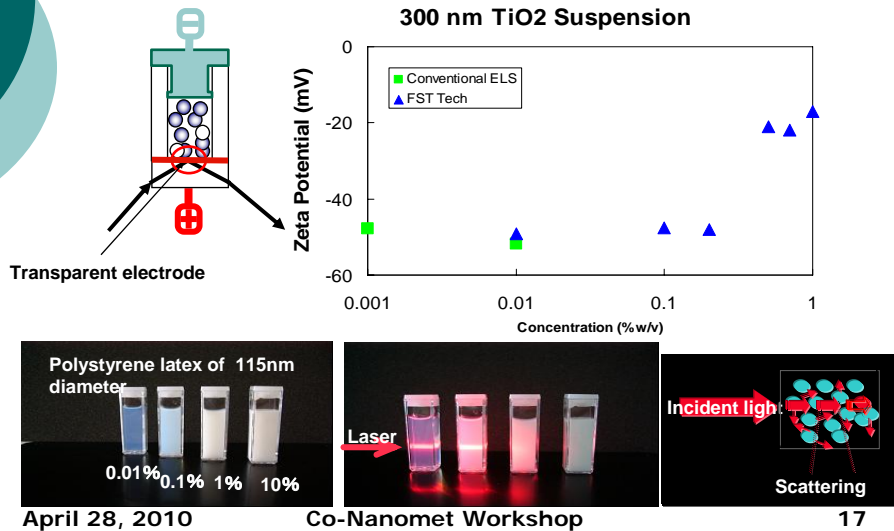
- Electrophoretic Light Scattering
 - Particle mobility distribution is obtained through detecting Doppler frequency shift distribution of scattered light, no calibration
 - Most widely used method: fast, statistically accurate, produce distributions
 - Mature technology for particles (nm- μ m) in dilute suspensions
 - Typical measurement range: ± 200 mV
 - Typical precision: 2-5 mV
 - Recent advancement enabling measurement of particles in high concentration

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Forward Scattering Through A Transparent Electrode (FST)



Optical Methods

- Microscopic Method
 - Originated from Microelectrophoretic measurement
 - Video microscope and image analysis software are used to track individual moving particles and compute their velocities
 - Particle size and concentration range are limited
 - Limited number of particles measured

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From Electrophoretic Mobility to Zeta Potential

- For non-conducting particles in dilute suspension

$$\zeta(mV) = \frac{3\mu\eta_o}{2f_1\varepsilon}$$

- f_1 varies smoothly from 1 (Hückel limit) to 1.5 (Smoluchowski limit) depending on particle size and ionic strength
- η_o = medium viscosity; ε = medium permittivity
- At 25°C, $\zeta = 12.85\mu$ mV
- Various models available for other situations

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Acoustic Methods

- Colloidal Vibration Current (CVI) Method
 - Particle dynamic electrophoretic mobility (μ_d) is measured from the ac current generated by particles in an acoustic field
- Electrokinetic Sonic Amplitude (ESA) Method
 - Particle dynamic electrophoretic mobility (μ_d) is measured from the acoustic signal generated by particles in an ac field

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Acoustic Methods

- Can be used in a broad particle concentration range
- Suitable for online measurement
- Knowledge of particle concentration and density is required
- For CVI measurement, additional properties of particles are required
- Only produce an average zeta potential
- Need a standard for calibration

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From Dynamic Electrophoretic Mobility to Zeta Potential

- For particles in dilute suspension

$$\mu_d = \frac{2\varepsilon\zeta}{3\eta} G(1+F)$$

- G: the frequency dependence related with the inertia effects; F: influence from the medium
- For CVI measurement at low frequencies

$$\mu_d = \frac{\varepsilon\zeta}{\eta} \frac{K_s}{K_m} \frac{(\rho_p - \rho_s)\rho_m}{(\rho_p - \rho_m)\rho_s}$$

- K and ρ are conductivity and density and the subscript m, p, and s are for medium, particle and suspension, respectively

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Streaming Potential Method

- Measurement of potential (U_{st}) generated from liquid flow through surfaces of charged particles
- More suitable for fibre, porous materials, and solid surfaces
- Produce an average zeta potential

$$\frac{U_{st}}{\Delta P} = \frac{\varepsilon\zeta}{\eta K_m}$$

- ΔP : flow pressure difference

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Reference Materials

- Because of the nature of zeta potential that changes with environment, currently there is no zeta potential standard (certified) reference material
- NIST has a mobility standard reference material that is not well received
- ELS does not need a calibrator since it is based on the first principle
- Reference (control) materials are used for instrument verification purpose
- Reference materials should be stable, monodisperse in size and in surface charge, preferably spherical

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ISO Standard for Zeta Potential Determination

- ISO/CD 13099-1 Methods for zeta potential determination — part 1: General Principle
- ISO/CD 13099-2 Methods for zeta potential determination — part 2: Optical Methods
- ISO/NWI 13099-3 Methods for zeta potential determination — part 3: Acoustic Methods



References

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