Introduction to Zeta Potential Analysis

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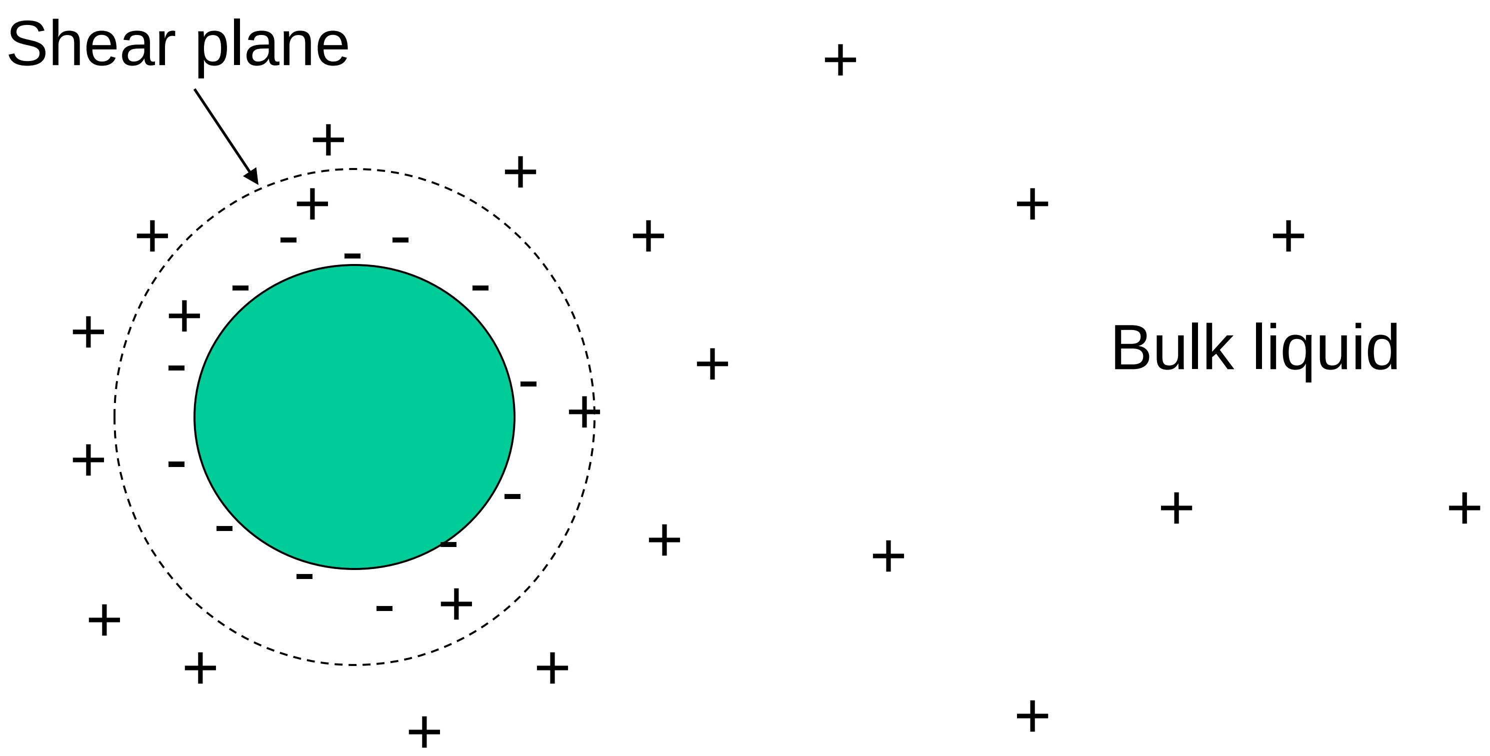
Controlling Particulate Suspensions

Suspension behavior is significantly affected by surface interactions. And that is controlled by size and chemistry of the interface.

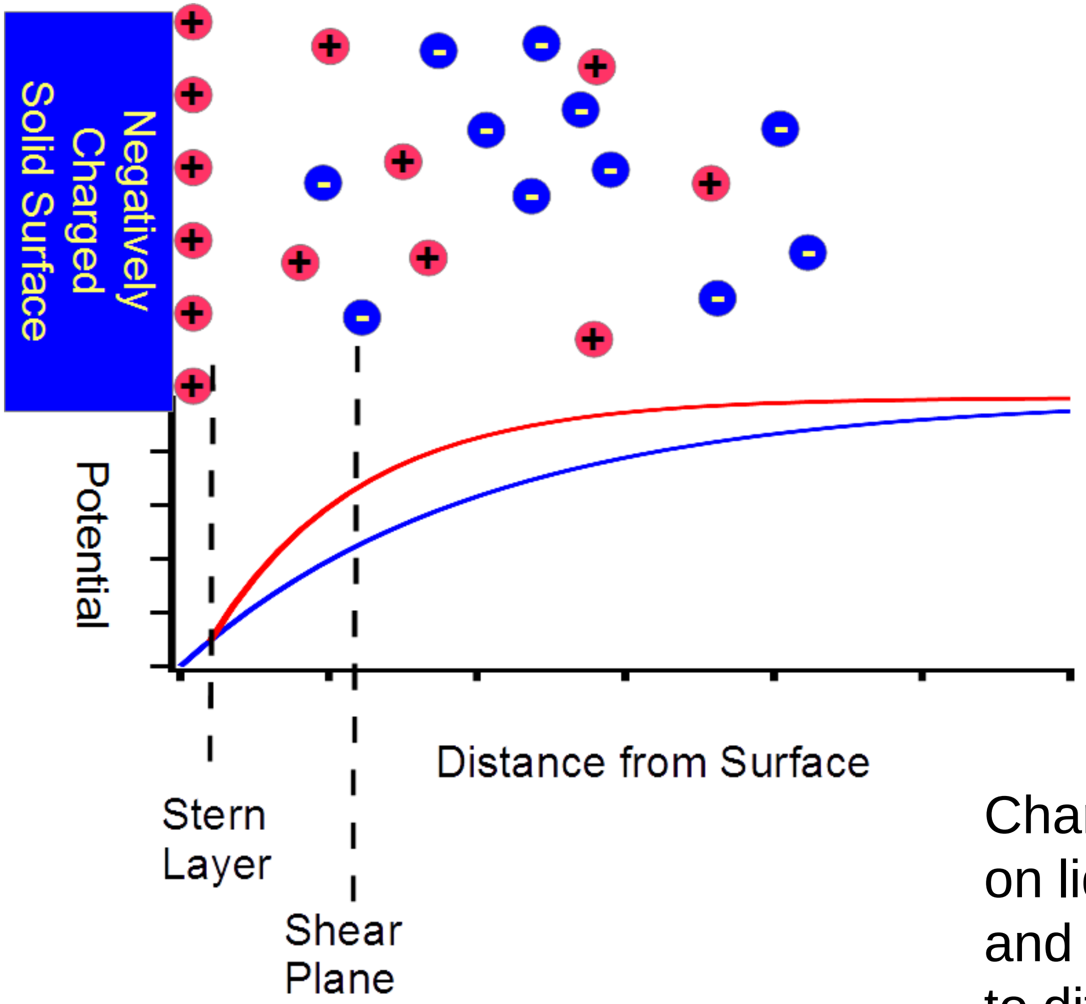
Size of interface	⇄	Chemistry of interface
↓		↓
Particle size distribution Particle shape Porosity		Surface charge Surface tension Contact angle

What is Zeta Potential?

- Zeta potential is the charge on a particle at the shear plane.



Effect of Liquid

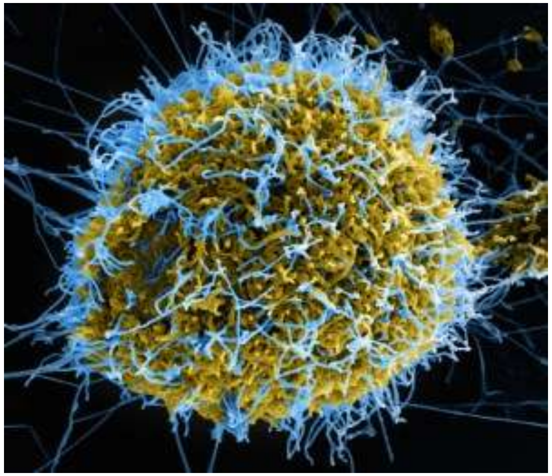


Charge at shear plane depends on liquid environment. The red and blue lines here corresponds to different salt concentration.

Quiz Time

Your colleague hands you a bucket of dry particles and says:
What is the zeta potential of these particles?

Before determining zeta potential of a particle, what do you need to know?



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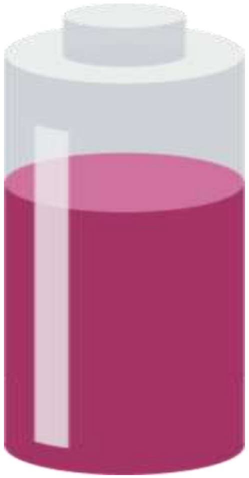
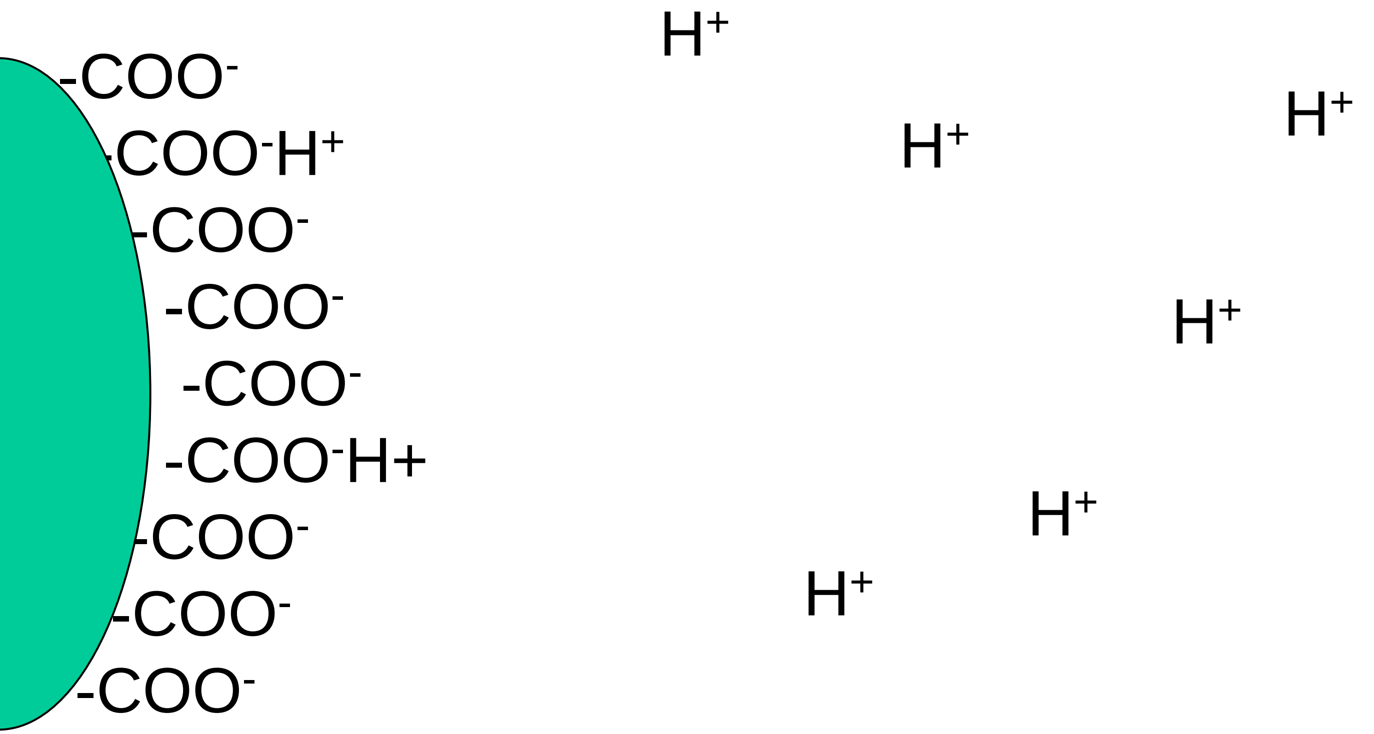


A. Liquid environment (ionic strength, pH, nature of ions)

How do Surfaces Acquire Charge?

Ionization of surface groups



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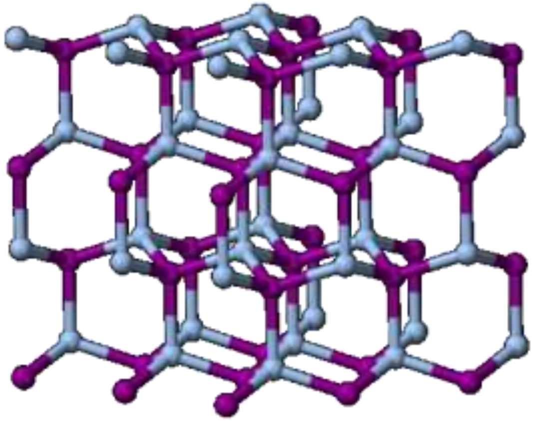
How do Surfaces Acquire Charge?

Differential loss of ions from surface

e.g., AgI,

Ag+ dissolves preferentially



Ag+ I- Ag+ I-

Ag+ surface Ag+

Holes from dissociated ion

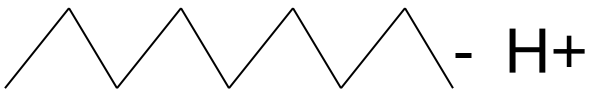
-1 -1 1 -1 1 -1

I I Ag I Ag I I Ag I Ag Ag I Ag I I Ag Ag I Ag I Ag I I Ag

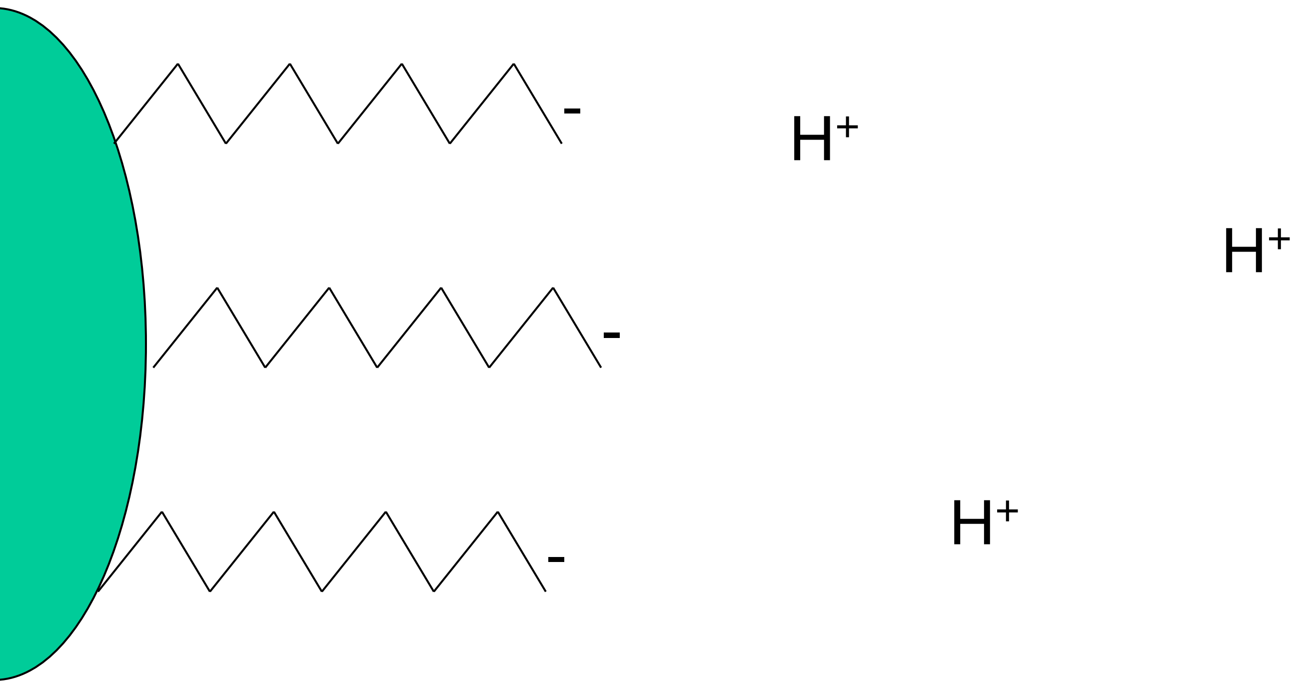
Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I

How do Surfaces Acquire Charge?

Specific adsorption of ions, e.g. ionic surfactants

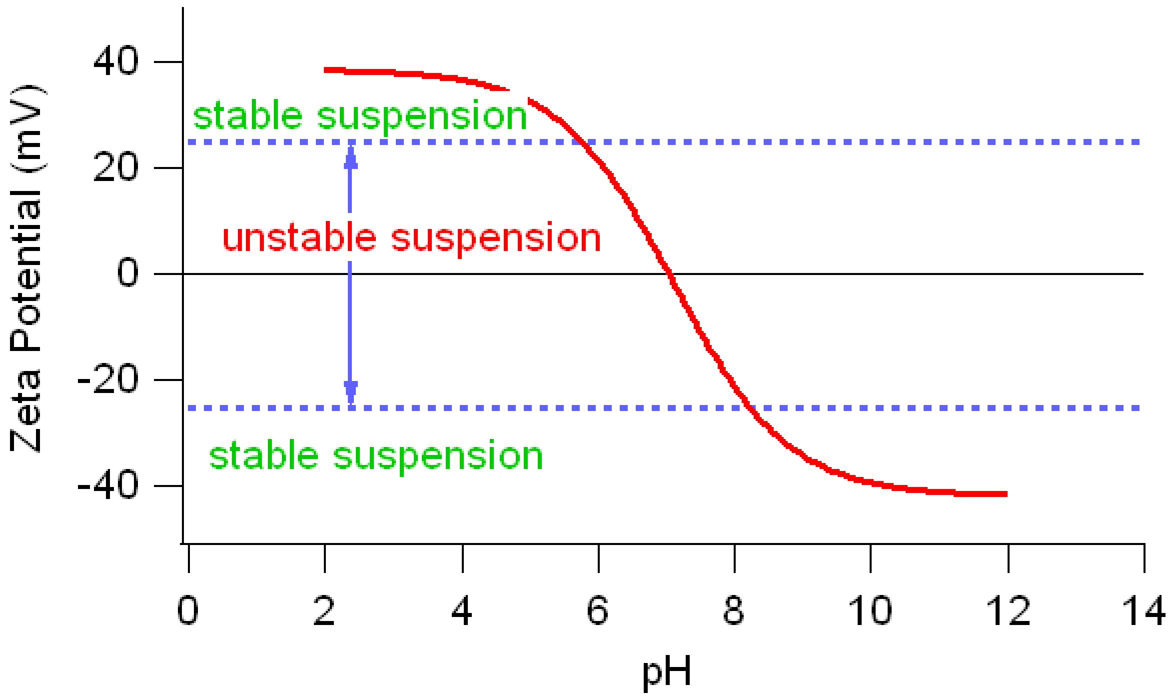


Anionic surfactant



Why Zeta Potential?

- Good way of evaluating electrostatic stabilization of suspensions
- Can use to predict interactions



How to Measure Zeta Potential:

- Acoustic techniques (use sound to probe particle response)
- It is much more popular to use light scattering to probe motion of particles due to an applied electric field. This technique is known as electrophoretic light scattering.
- Used for determining electrophoretic mobility, zeta potential.

Other Light Scattering Techniques

- Static Light Scattering: over a duration of ~1 second. Used for determining particle size (diameters greater than 10 nm), polymer molecular weight, 2nd virial coefficient, R_g.

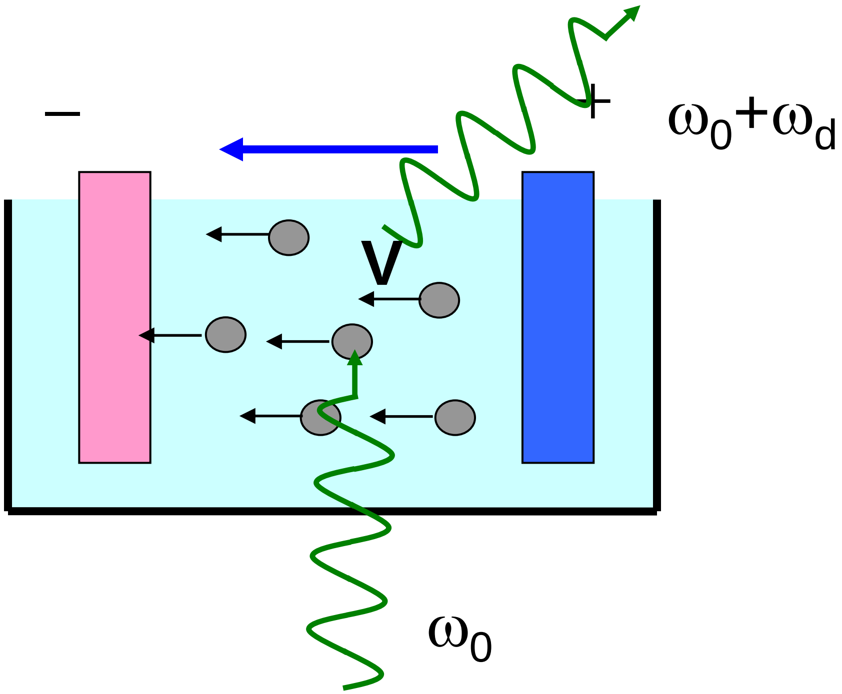
- Dynamic Light Scattering: use scattered light to probe random motion of particles. If this motion is due to Brownian motion the technique can be used to determine particle size.

How to Measure? With the SZ-100

- Single compact unit that performs size, zeta potential, and molecular weight measurements: the SZ-100

How to determine zeta potential

- Apply an electric field and probe response of particles to applied field.
- You need to see Doppler shift in scattered light due to particle motion with respect to fixed electrodes.



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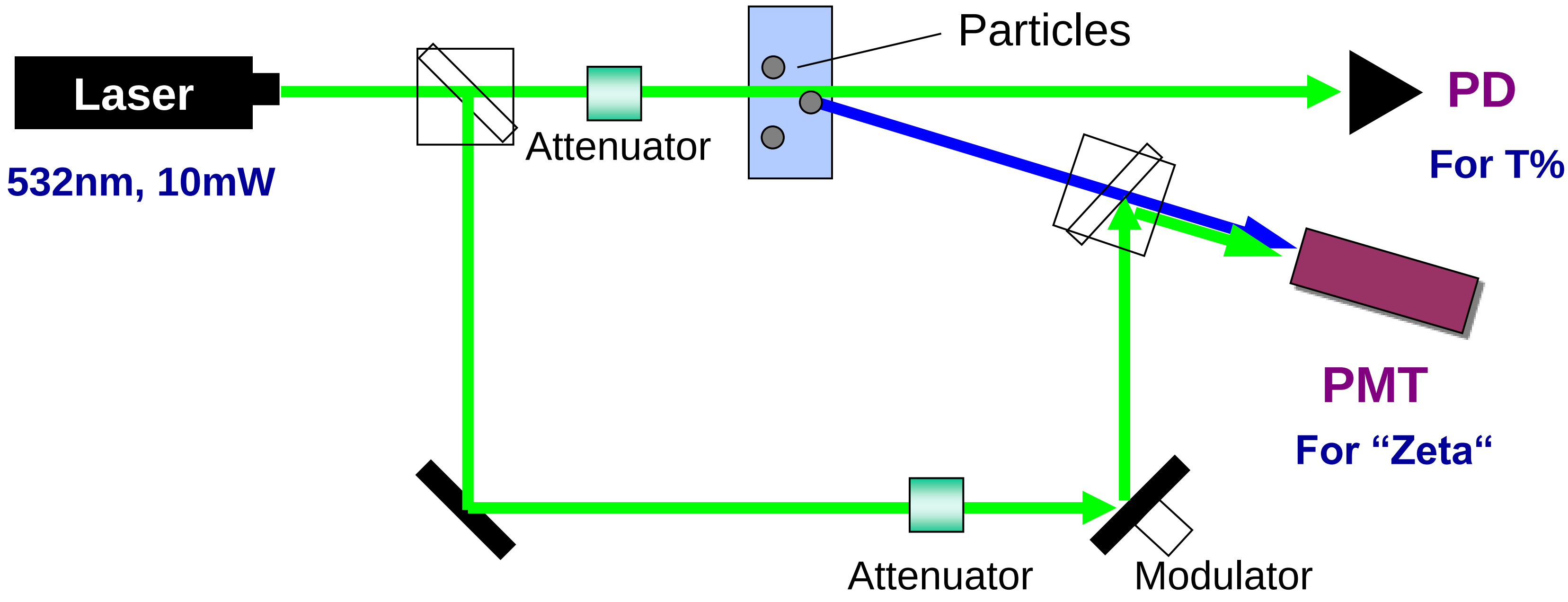
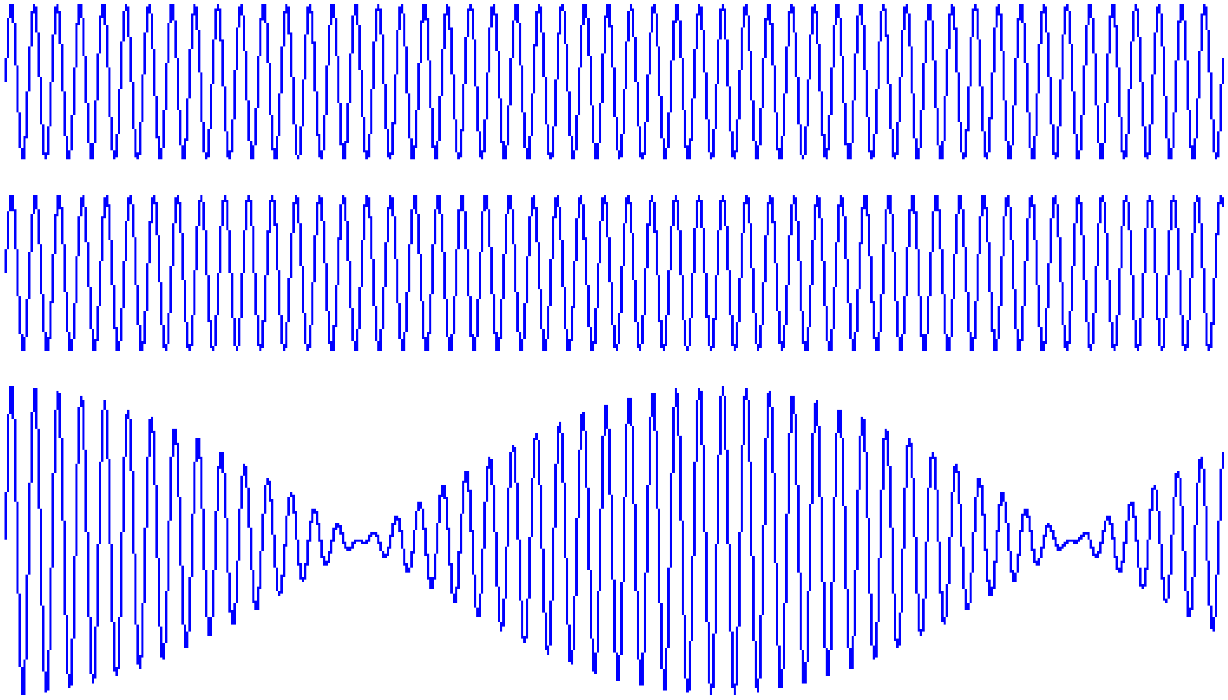
Optical System

Use optical mixing to extract motion of particles relative to electrodes.



Optical Mixing

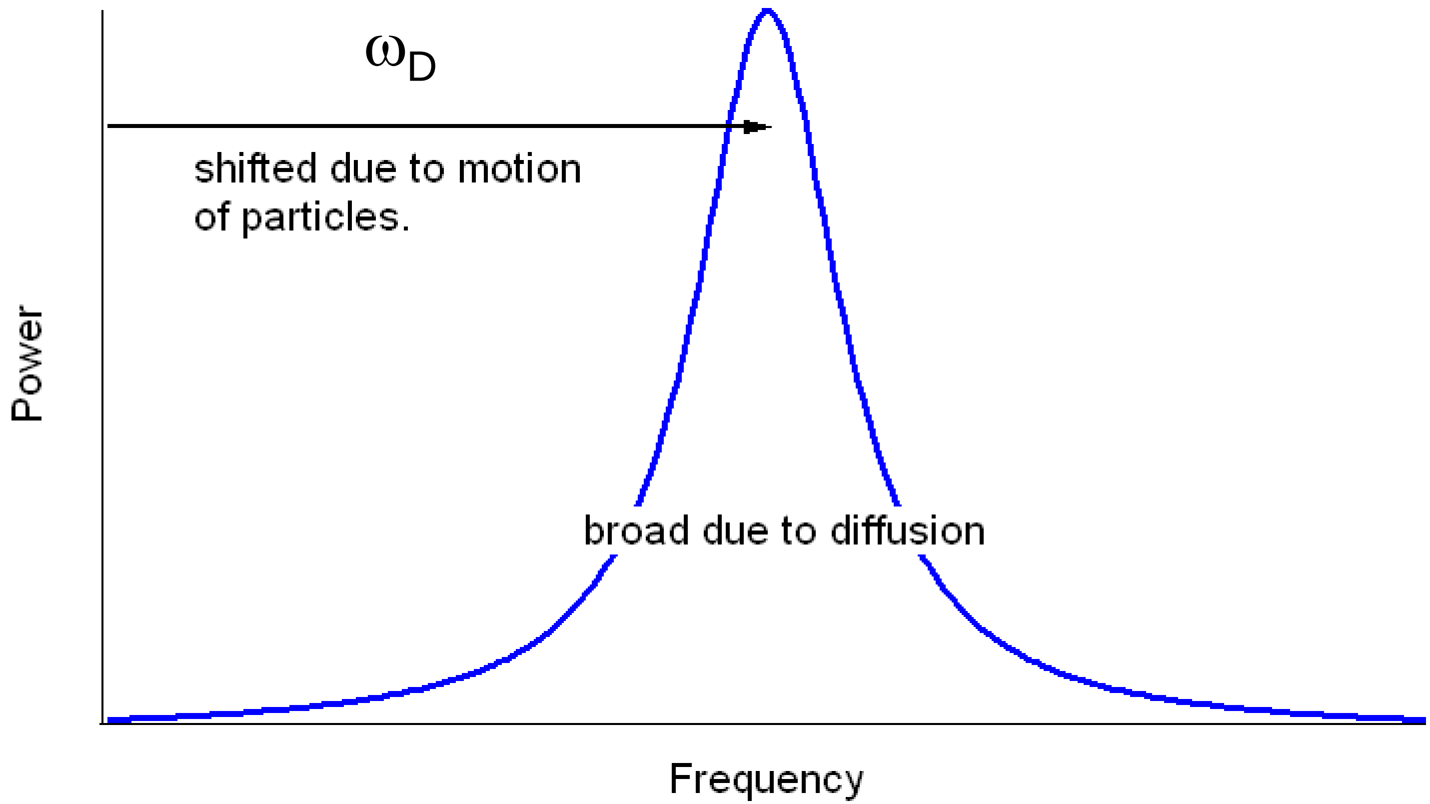
Frequencies differ by 3%



Sum of waves has easy to see oscillation

Data Analysis

- Analyze observed spectrum.



Doppler Shift Calculations

$$\omega_D = \vec{q} \bullet \vec{V}$$

$$\mu_e = \frac{V}{E}$$

ω_D = frequency (Doppler) shift, measured

q = scattering vector

(4πn/λ)sin(θ/2), known

V = particle velocity

E = electric field strength , known

μ_e= electrophoretic mobility (desired result)

Zeta Potential Calculation

- Need to use a model to obtain zeta potential (desired quantity) from mobility (measured quantity.
- Most common is Smoluchovski (shown here)

$$\mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta(T)}$$

ε_r = relative permittivity (dielectric constant)
ε_0 = permittivity of vacuum
ζ = zeta potential
η = viscosity (function of temperature)

Application (Zeta Potential)

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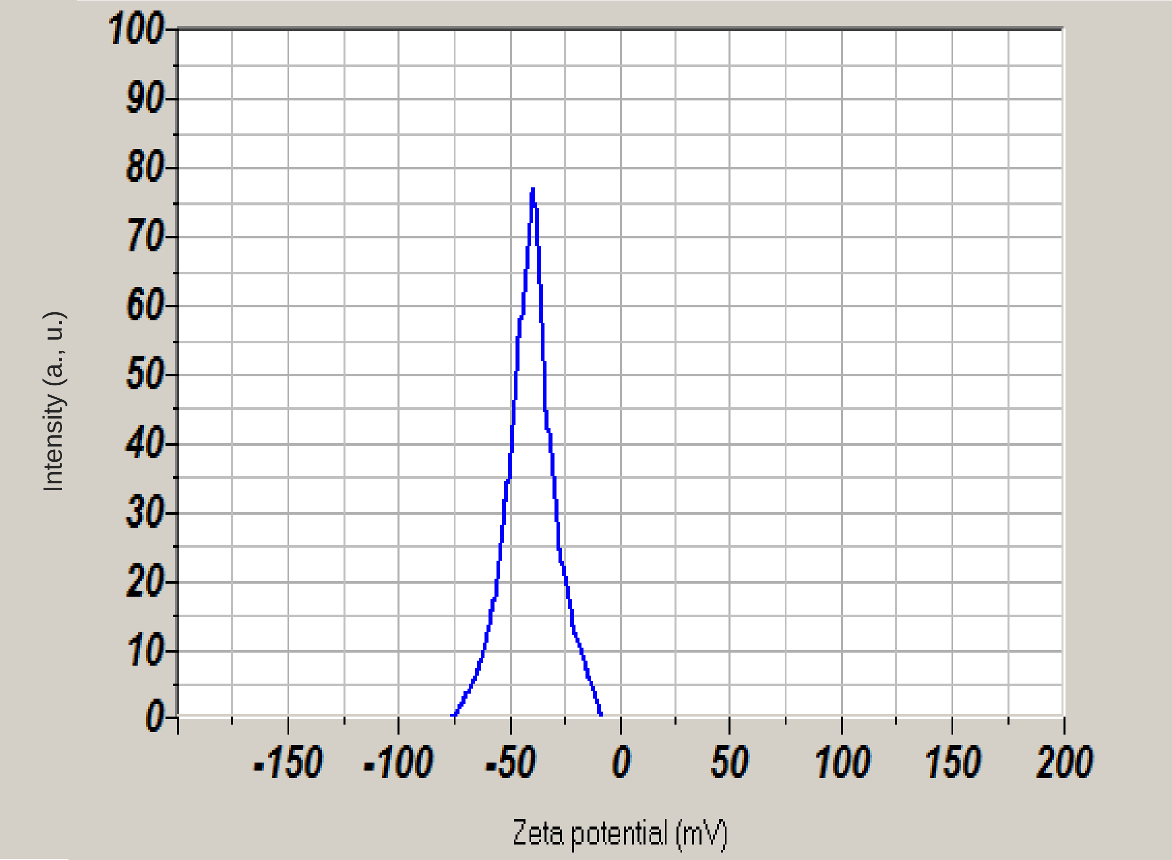
●Ceramics; Ludox^{R} Silica

Silica	Ludox Silica^{R} TM−50 with 0.01M_KCl
Sample Preparation	100 ppm

Conditions
Temperature; 25 C degree
Solvent; Water
Refractive Index; 1.333
Distribution base; Scattering light

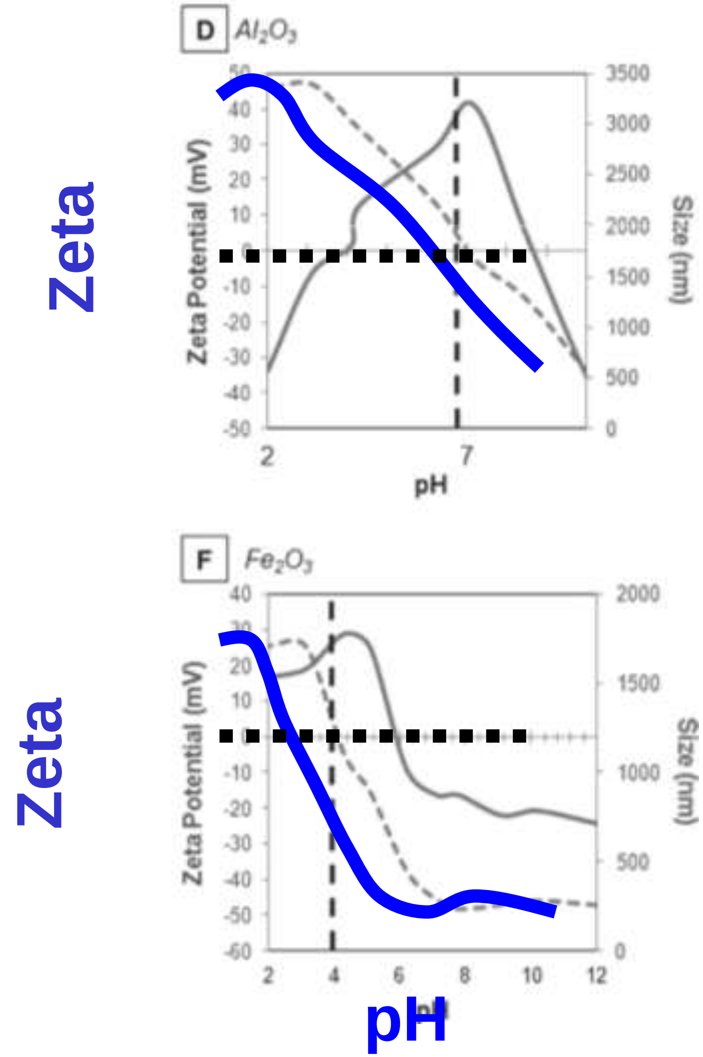
	Results
Mobility (μm･cm/V･s)	−3.02
Zeta Potential (mV)	−31.8



From GRACE's catalogue

Using Zeta Potential to Predict/Control Particle Interactions

- Note size maximum at IEP due to flocculation.
- If you mix Al_2O_3 with Fe_2O_3, what happens?
  - At pH 2, both are positive: no interaction
  - At pH 6, Al_2O_3 his positive and Fe_2O_3 is negative: particles stick together.
  - At pH 9, both are negatively charged, no interaction.

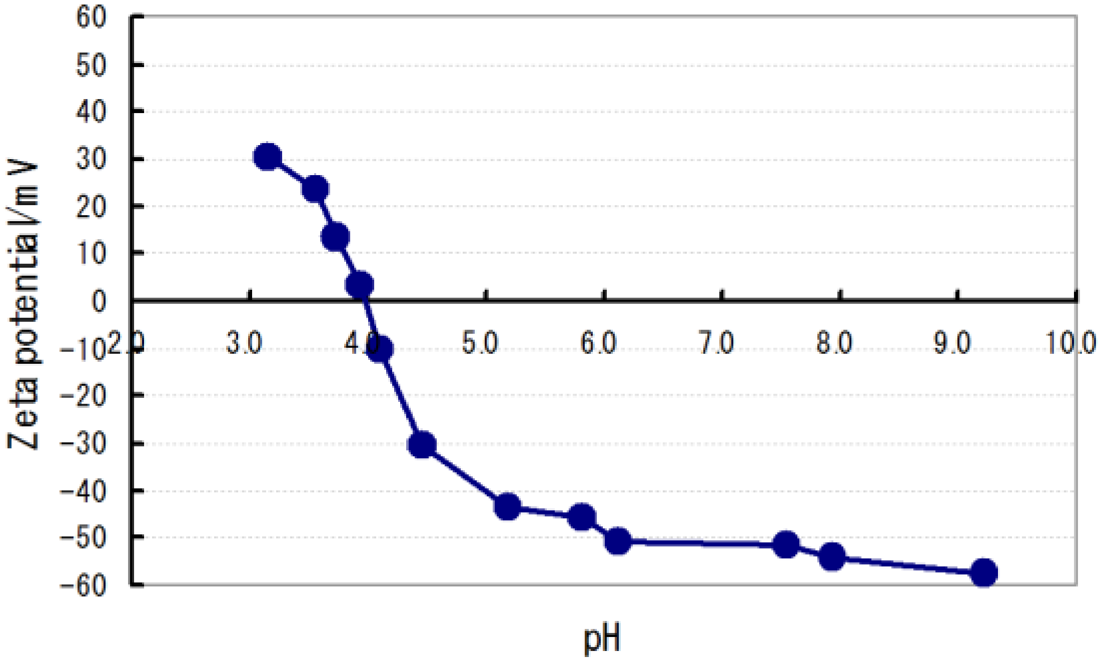


Data from Berg et al., *Nanotoxicology*, Dec. 2009; 3(4): 276-283

Application (Zeta Potential)

●Iso Electric Point of Coffee Mate

	Results
Iso-electric point	pH 4.0



If you want to bind Ludox HS (negatively charged at all “allowed*” pH values) to Coffee Mate, which pH (between 2 and 12) should you choose?

pH 2, pH 4, pH 6

Coffee mate has a positive charge at pH 2. Since it is positively charged, it will be attracted to the negatively charged Ludox.

*allowed for this example

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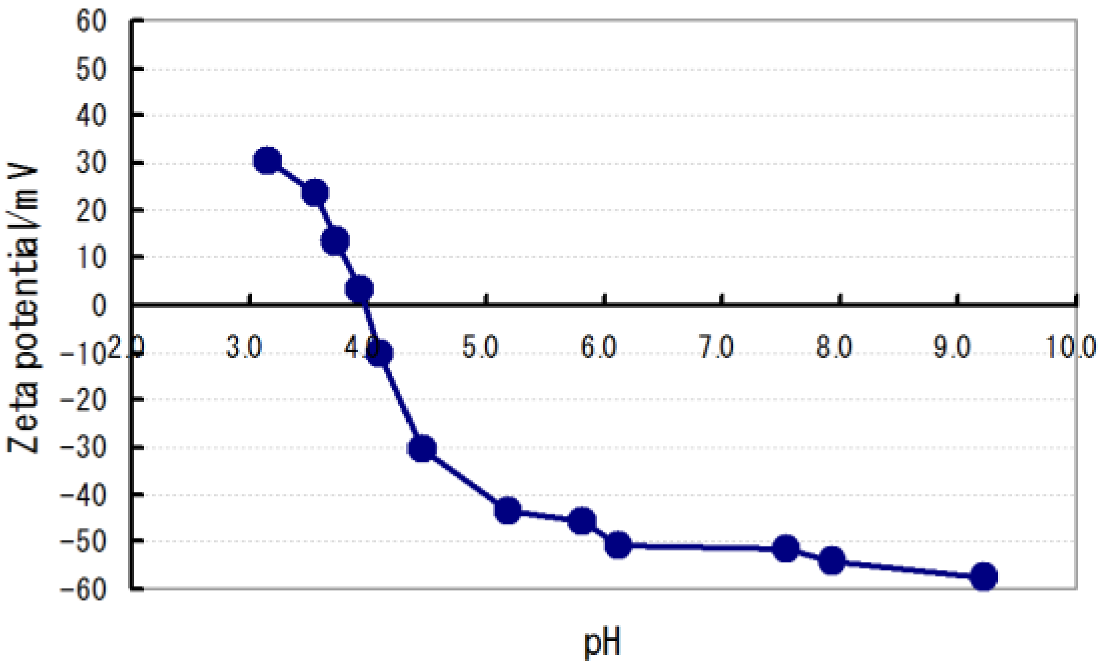

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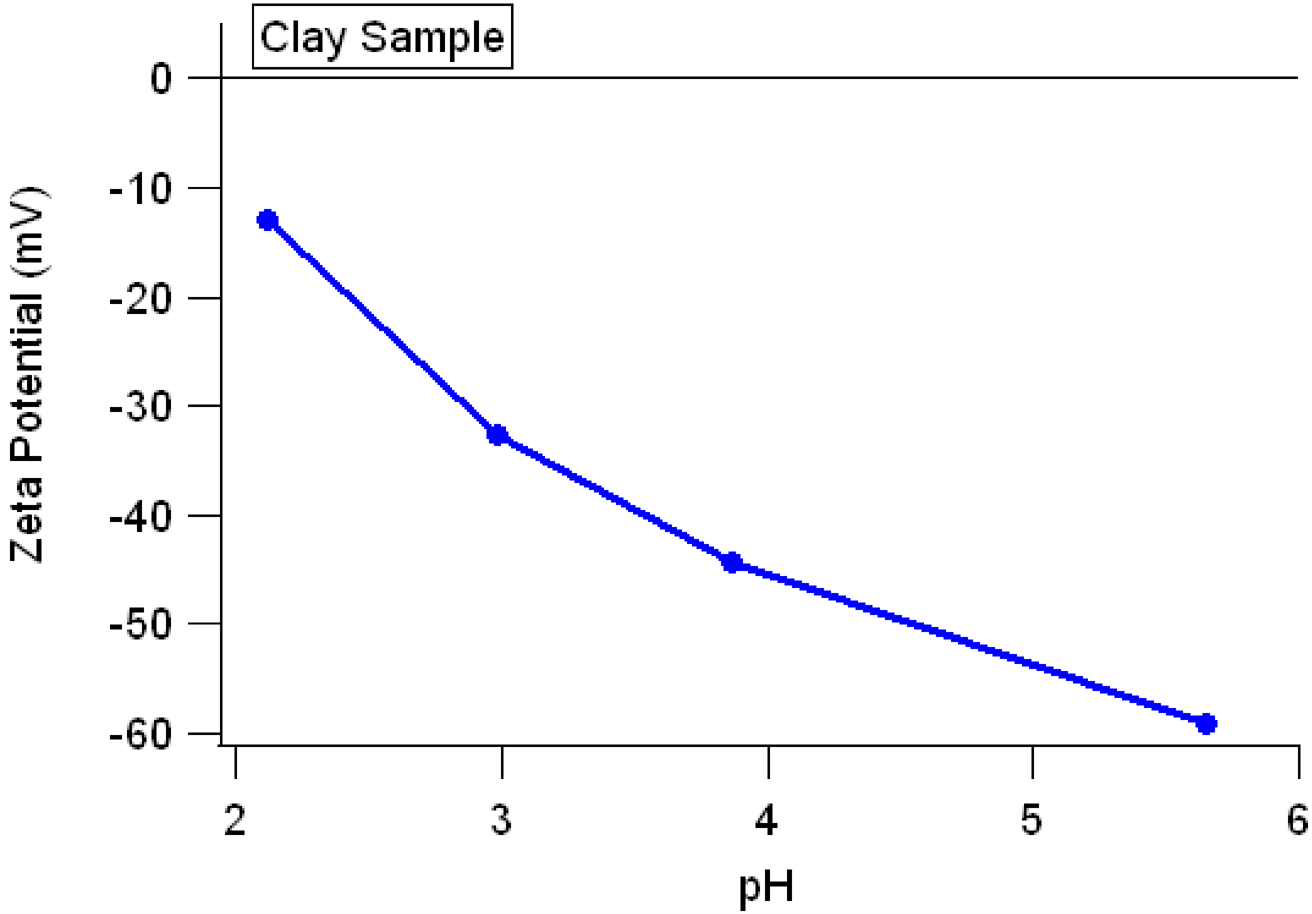
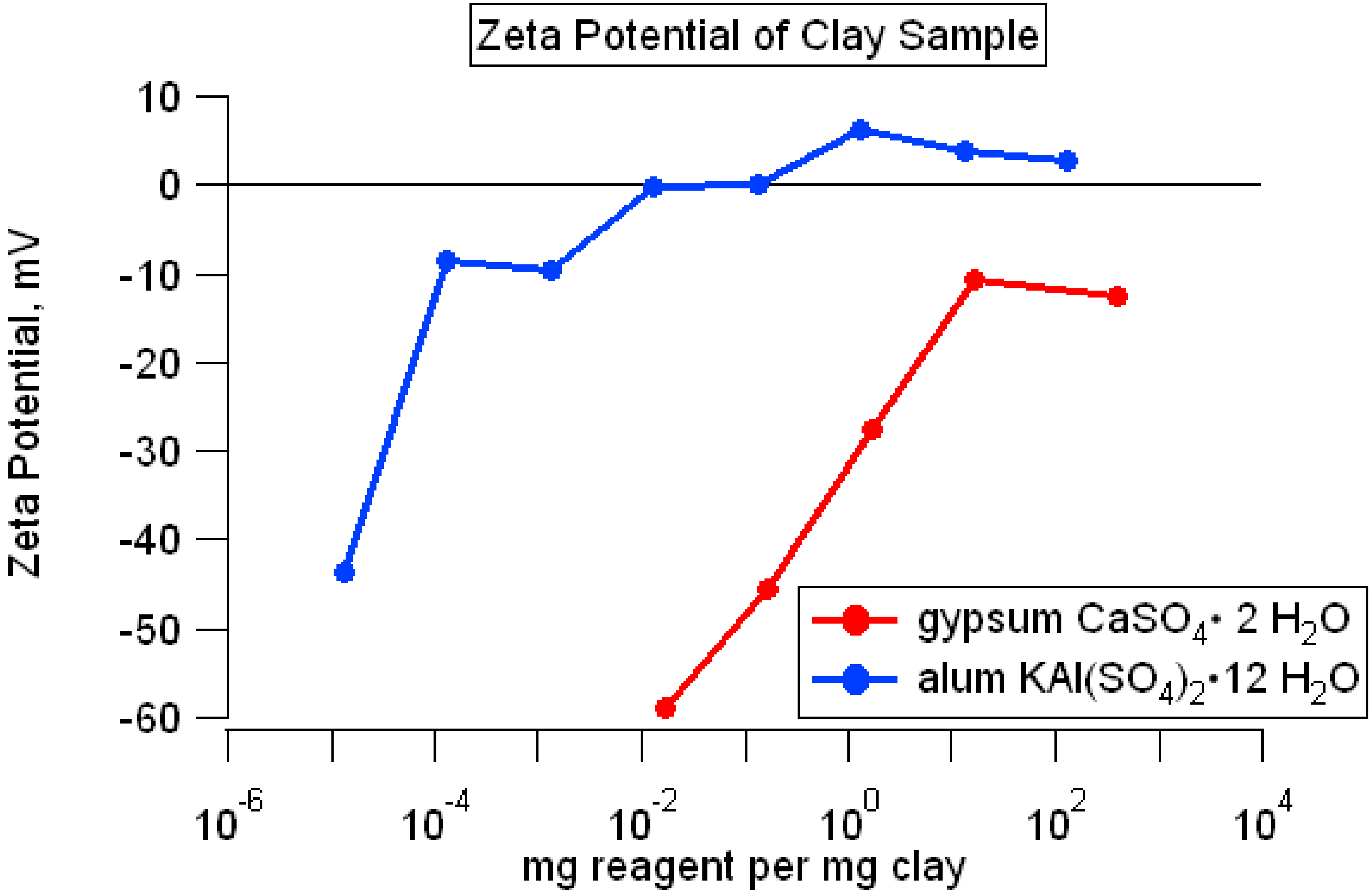
Clay IEP



To flocculate clay so it settles, pH must be quite low. You will need a lot of acid.

Clay IEP with other ions



To flocculate clay so it settles, choose alum at 0.01 g alum/g clay. Too much or too little and floculation is not ideal.

Zeta Practical Tips

Impurities

- Zeta is a surface property.
- Result is sensitive to surface active impurities.
  - Soaps/detergents
  - Specific ions (e.g., Cl^-, TSPP)
  - Grease/oil/fingerprints (hydrophobic materials will go to surfaces of aqueous suspension)
- Keep everything extremely clean
- Keep surfactant additives in mind when interpreting data.

Electrolyte

- Recall that potential is a function of ionic strength.
- Pure water has an ionic strength of ~10^{-7} M.
- A little bit of CO_2 from the air can raise ionic strength by a factor of 10 or 100 to 10^{-5} M.
- Use 1 mM electrolyte instead of no electrolyte to keep electrolyte levels (and therefore results) consistent from sample to sample.
- This doesn't apply for samples that already have substantial electrolyte.

Electrolyte Continued

- Titration is popular.
- Remember that acid and base will add to system ionic strength. pH 3 corresponds to 10^{-3} M electrolyte.
- Adding acid or base will increase ion concentration.
- Start with a 10 mM (10^{-2} M) salt (KNO_3) concentration to keep acid/base concentration from affecting results.

Why Zeta Potential?

- Use measured surface charge to predict colloidal stability
- Use measured surface charge to predict particle-particle interactions

Q&A

Ask a question at labinfo@horiba.com

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Thank-you