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Particle Analysis

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Getting a Charge Out of Nanoparticles: Zeta Potential

May 3, 2018

Controlling Suspensions

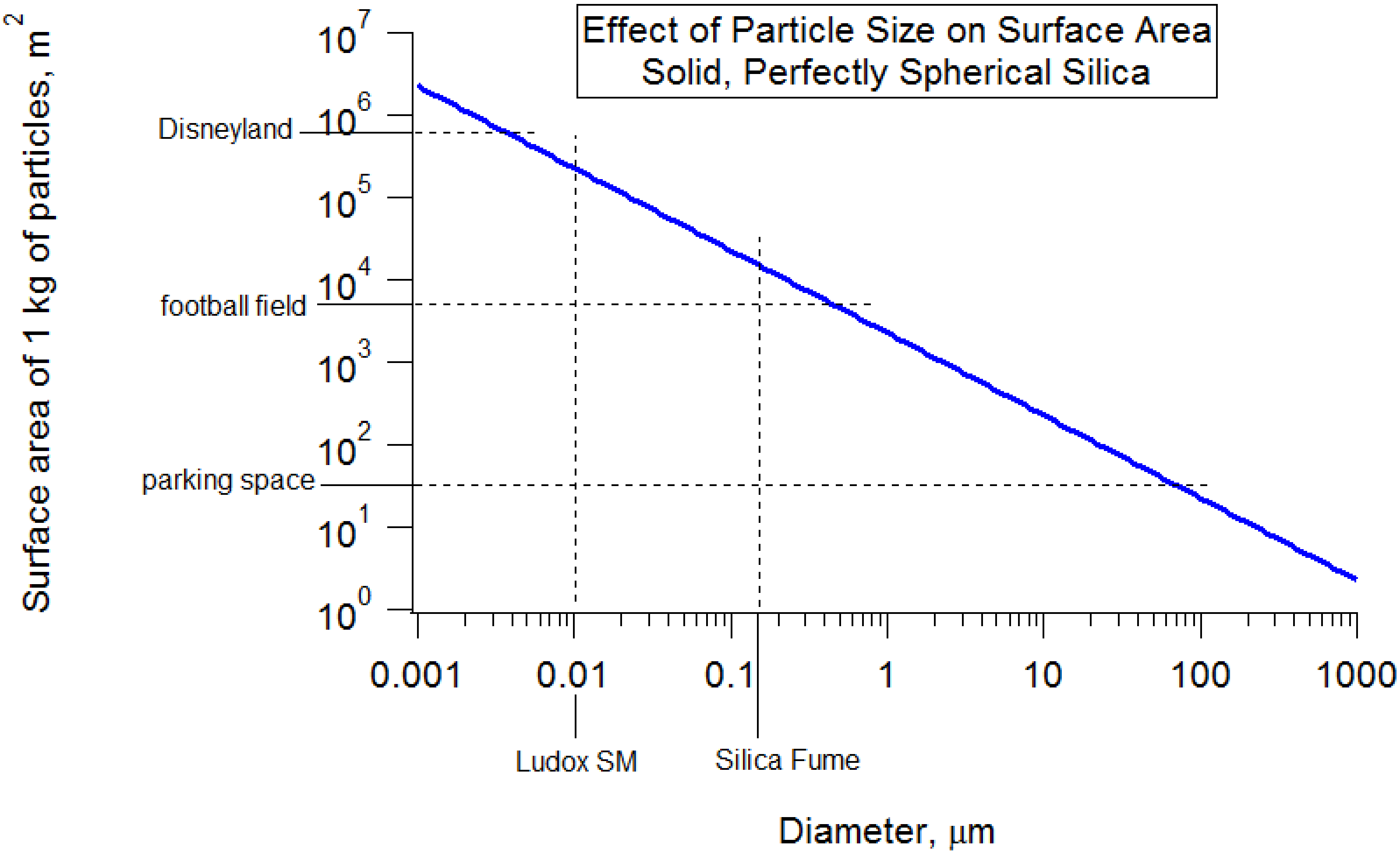
Suspension behavior is significantly affected by surface interactions. And that is controlled by size and chemistry of the interface.

Size of interface ⇄ **Chemistry of interface**

Size of interface
- Particle size distribution
- Particle shape
- Porosity

Chemistry of interface
- Surface charge
- Surface tension
- Contact angle

Small size -> Large surface area



Controlling Suspensions

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

Size of interface

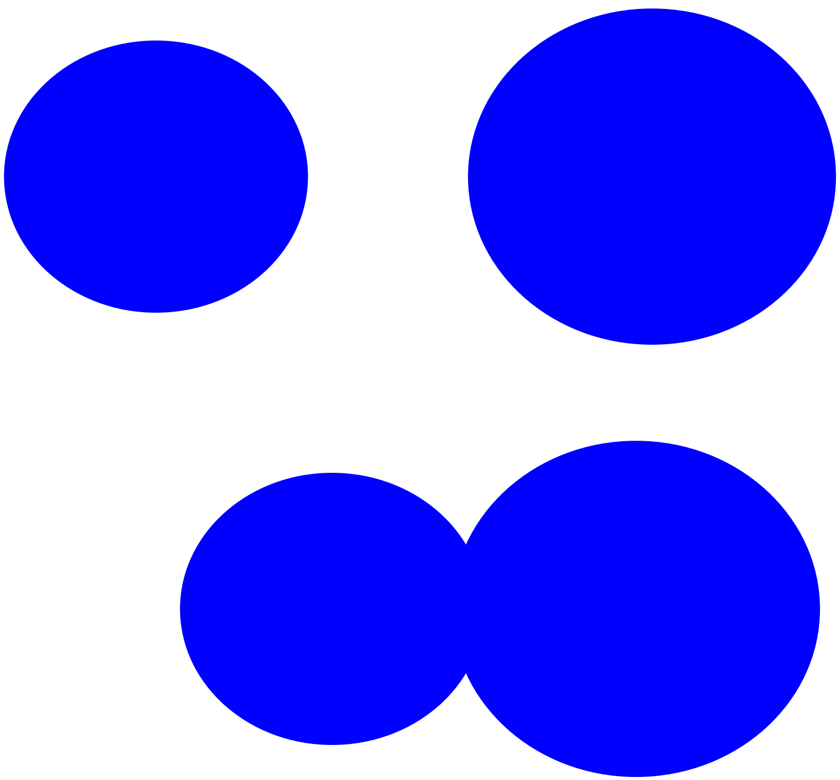
Chemistry of interface

Particle size distribution
Particle shape
Porosity

Surface charge
Surface tension
Contact angle

Fine Suspended Particles

Fine particles will tend to flocculate to reduce surface energy.



Less surface, lower free energy.

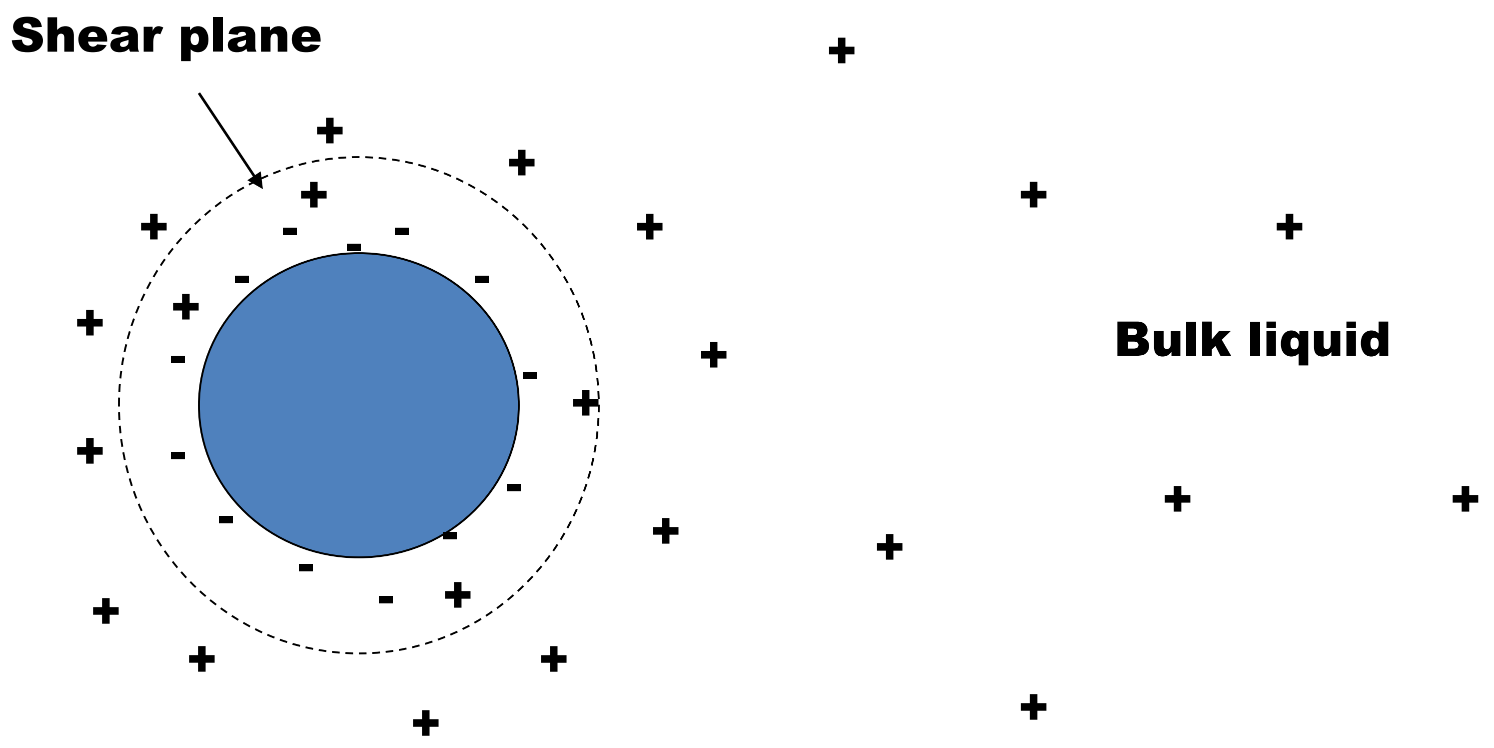
Why don't particles flocculate?

Most particles in aqueous suspension have a surface charge and therefore repel each other; they never touch.

Charge often determines suspension behavior!

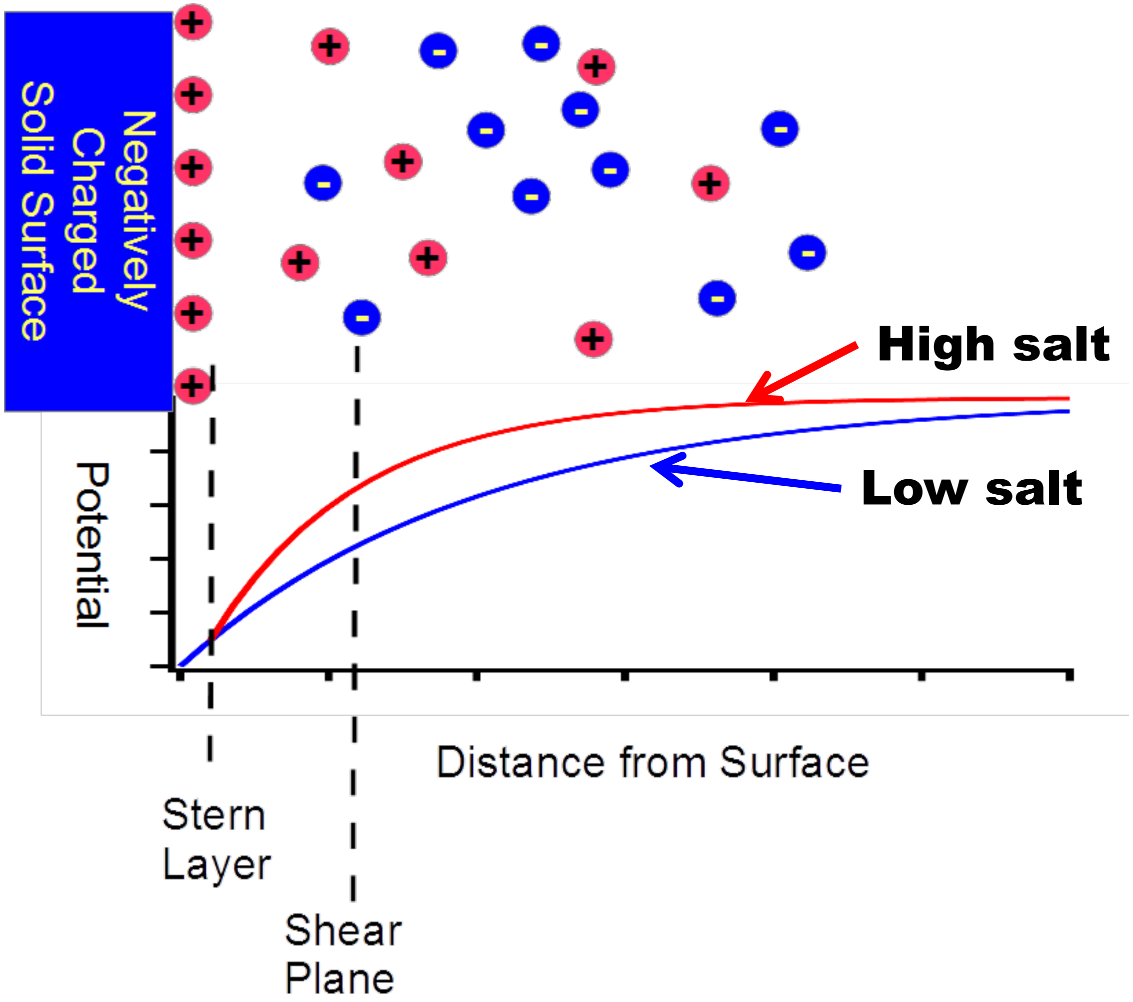
What is Zeta Potential?

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



Effect of Liquid

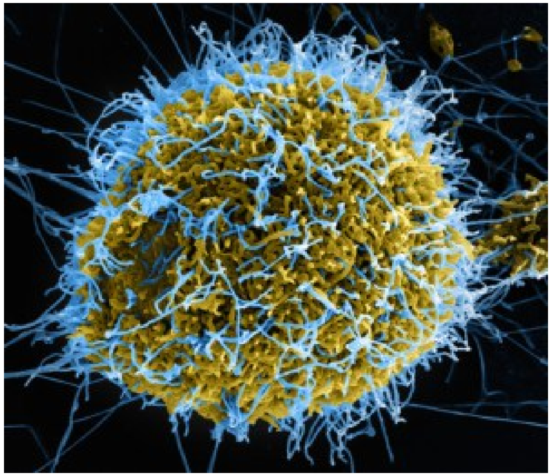
Charge at shear plane depends on liquid environment. The red and blue lines here corresponds to different salt concentration.



Quiz Time

Your colleague hands you a bucket of dry particles and asks “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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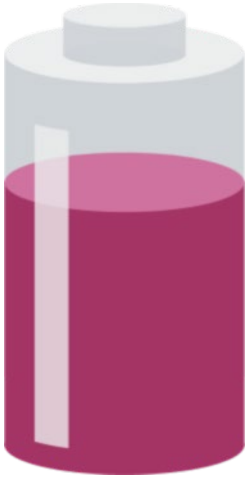
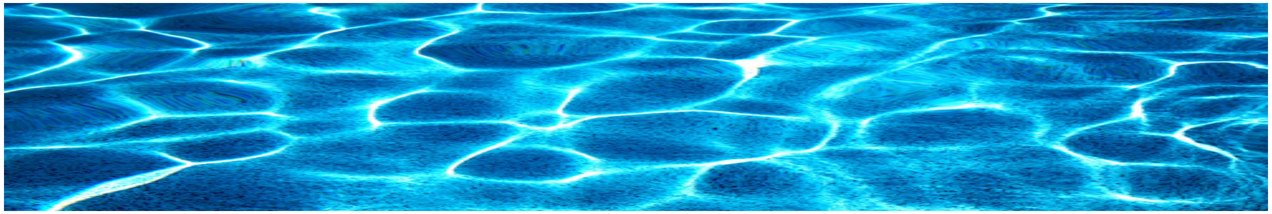
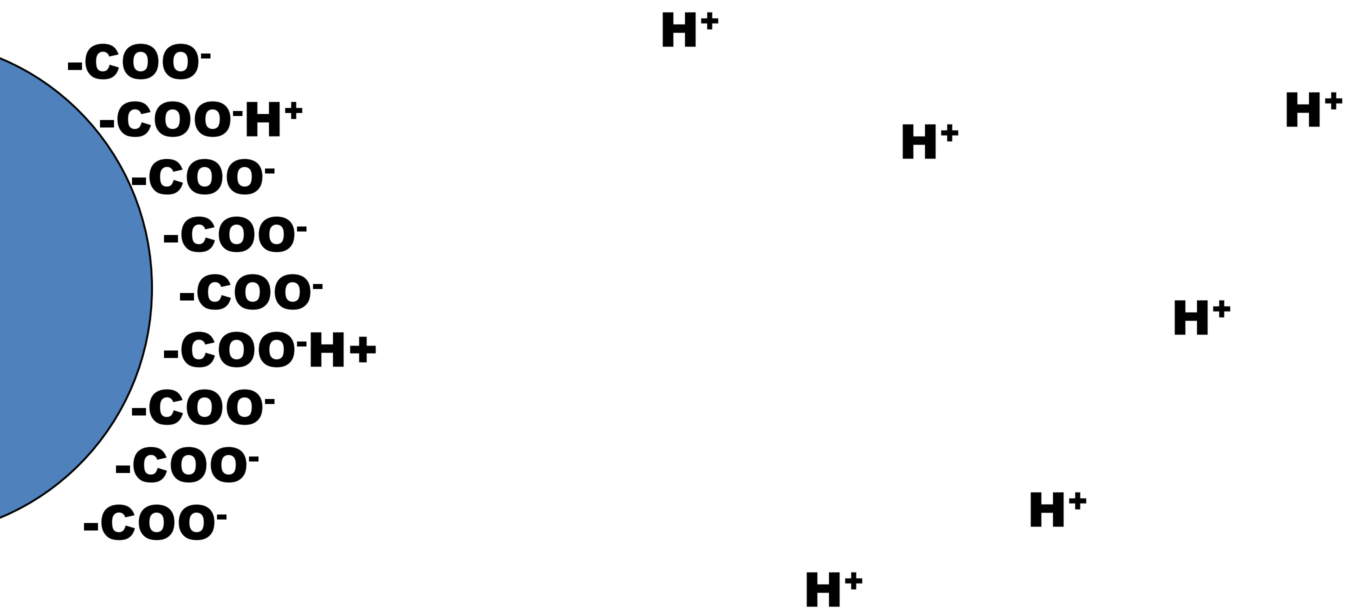


A. Liquid environment (ionic strength, pH, nature of ions)



How do Surfaces Acquire Charge?

Ionization of surface groups

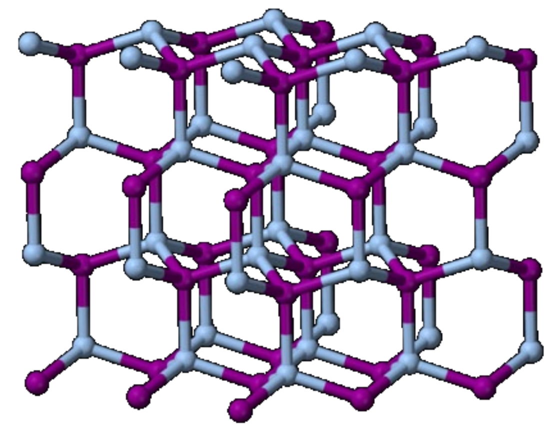


How do Surfaces Acquire Charge?

Differential loss of ions from surface

e.g., AgI,

Ag+ dissolves preferentially



Ag+ I- Ag+ I-

Ag+ surface Ag+

Holes from dissociated ion

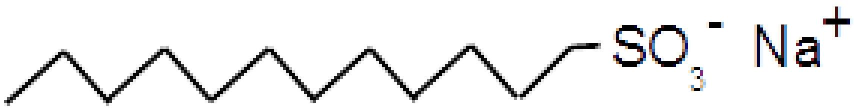
-1 -1 1 -1 1 -1

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

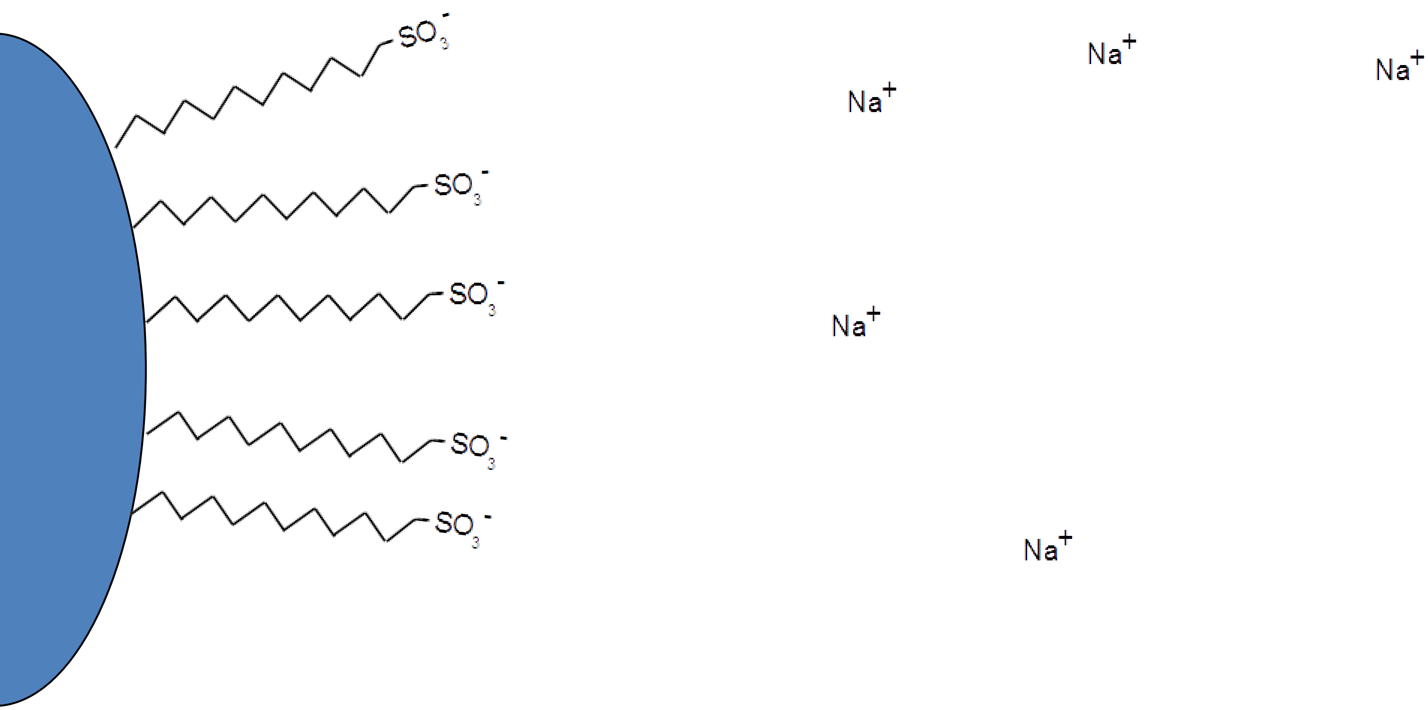
Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I Ag I

How do Surfaces Acquire Charge?

Specific adsorption of ions, e.g. ionic surfactants

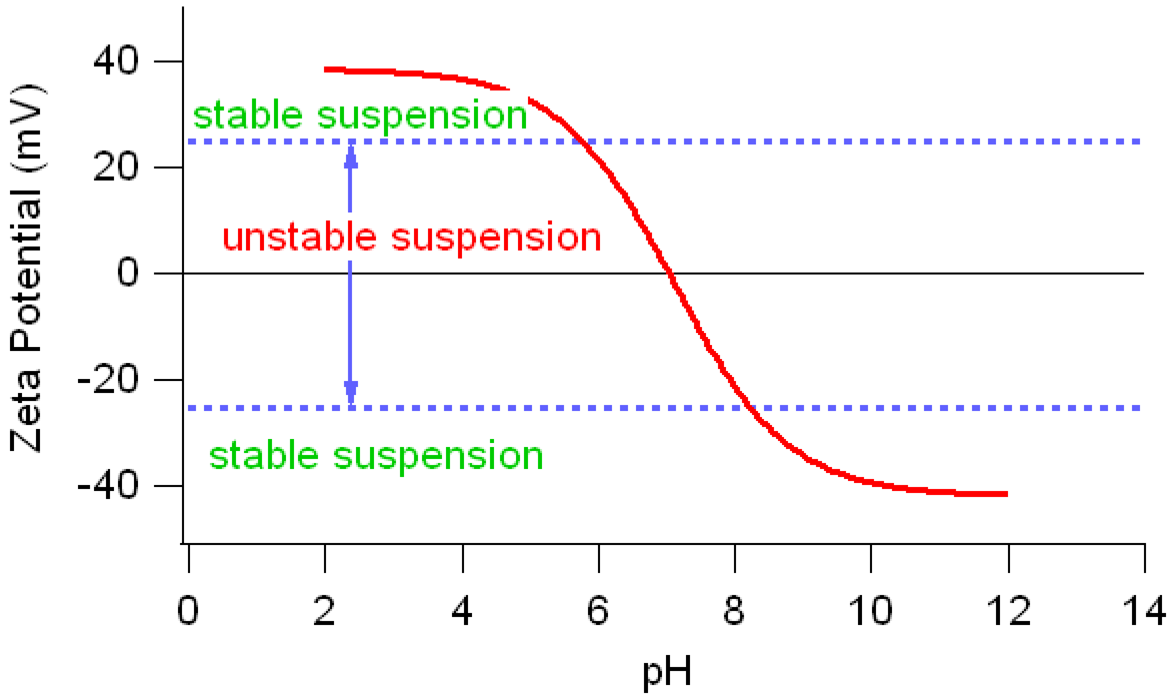


Anionic surfactant (SDS)



Why Zeta Potential?

- **Good way of evaluating <u>electrostatic</u> 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.**

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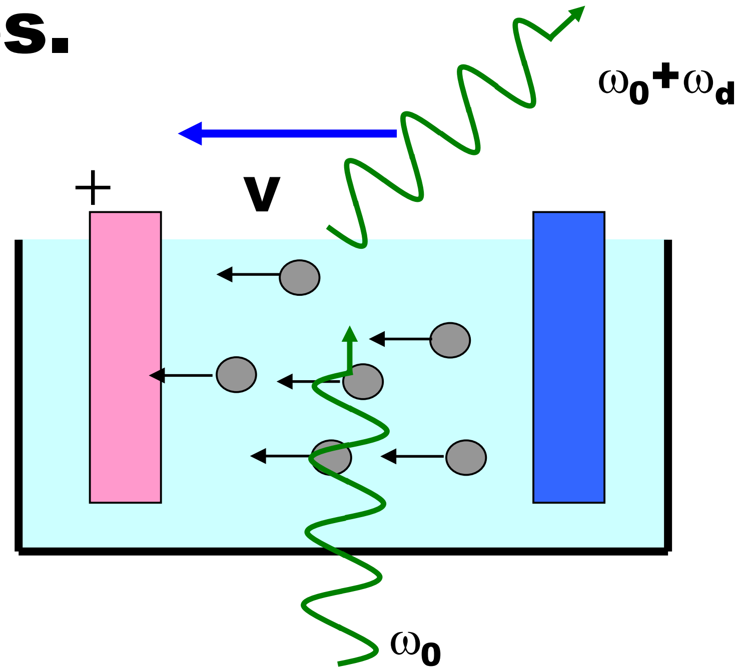
How to Measure? With the SZ-100

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

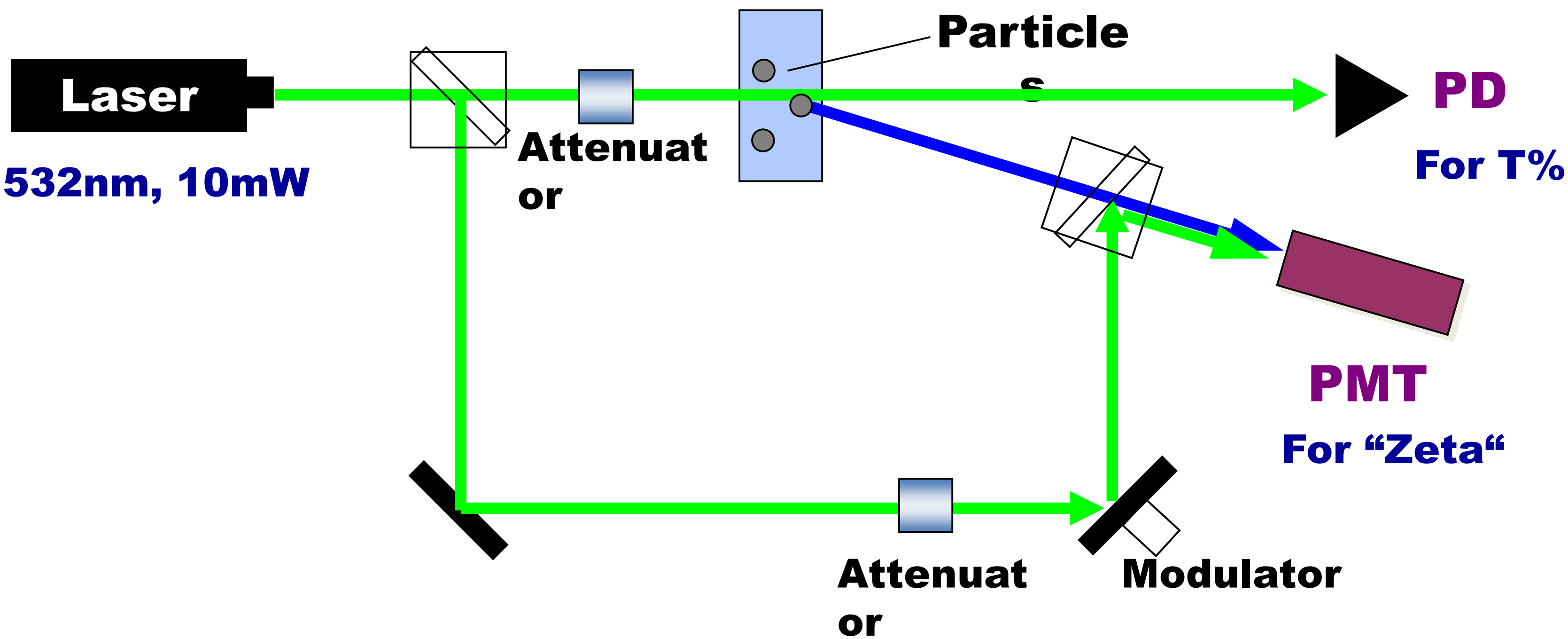
How to determine zeta potential

- **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.**



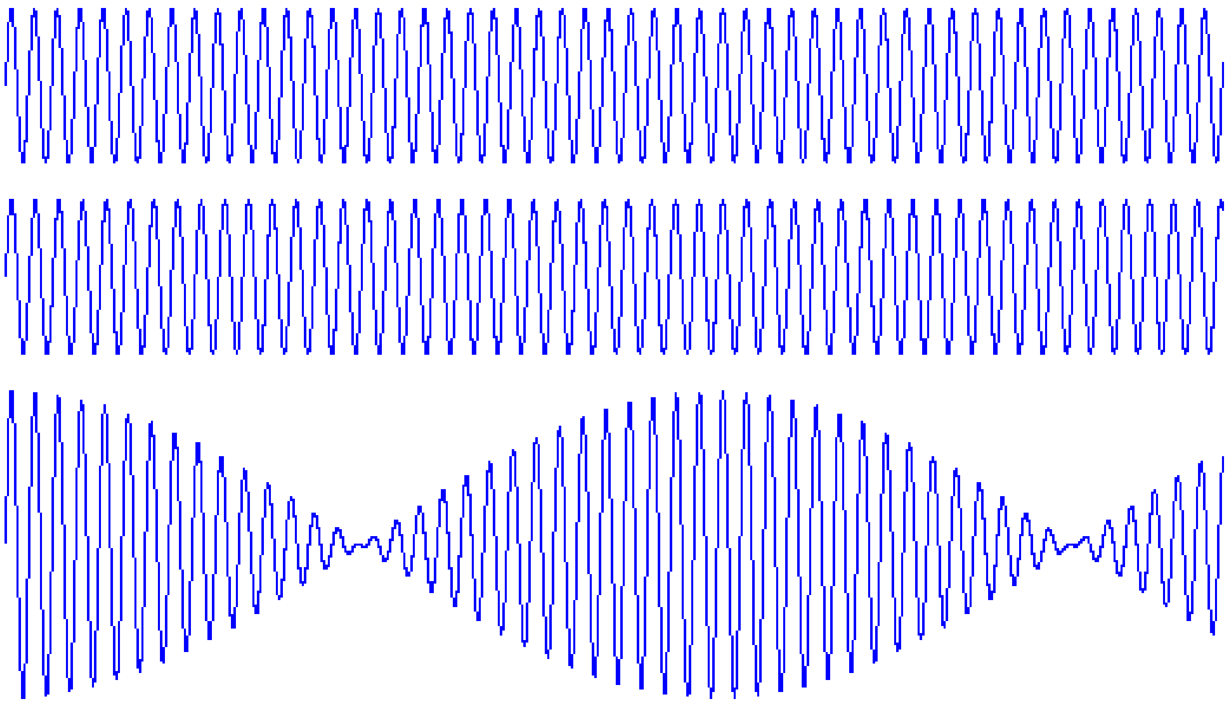
Optical System

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



Optical Mixing

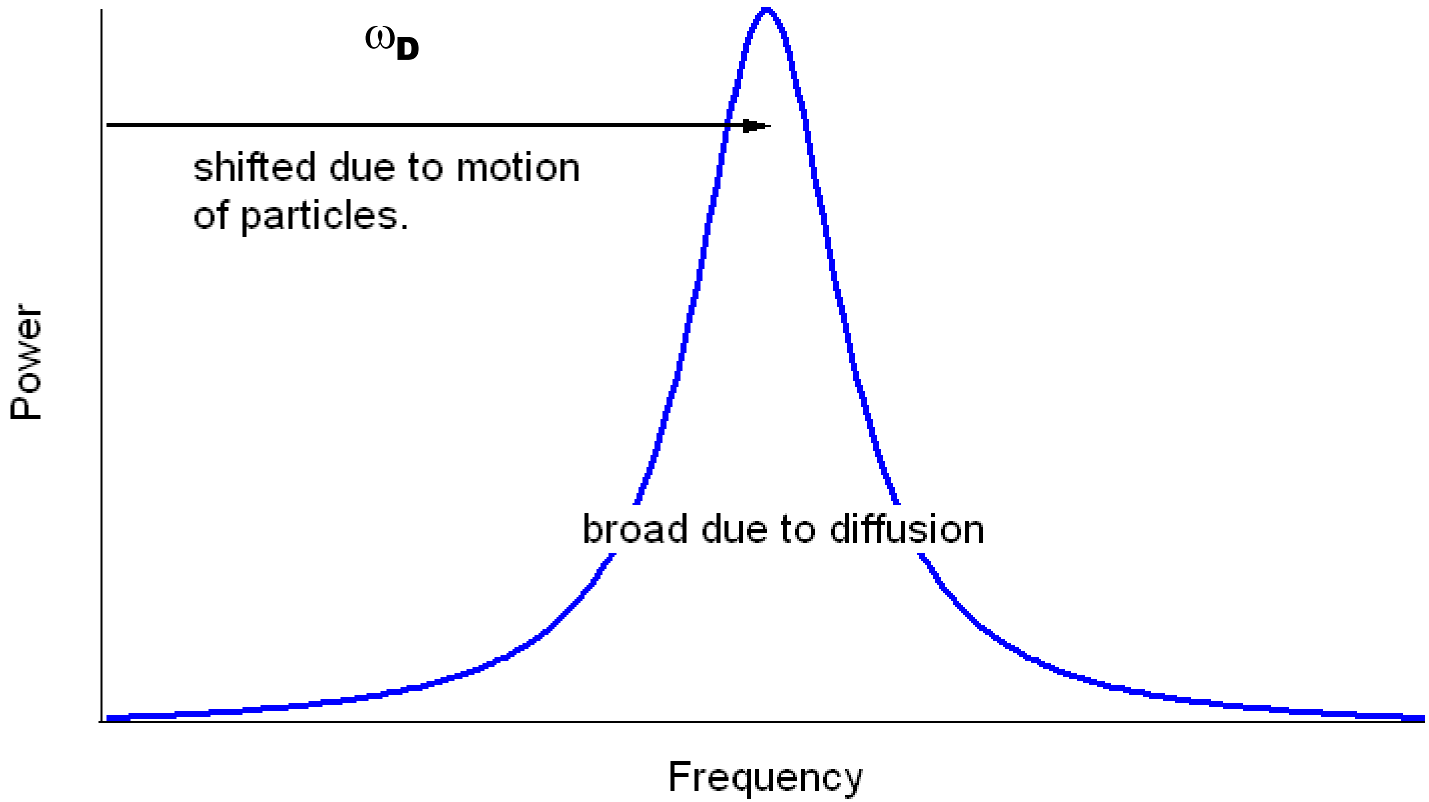
Frequencies differ by 3%



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

$(4\pi n/\lambda)\sin(\theta/2)$, 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)**

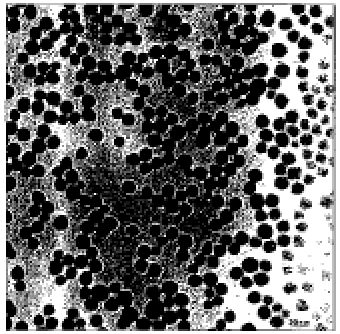
Application (Zeta Potential)

●Ceramics; Ludox[R] Silica

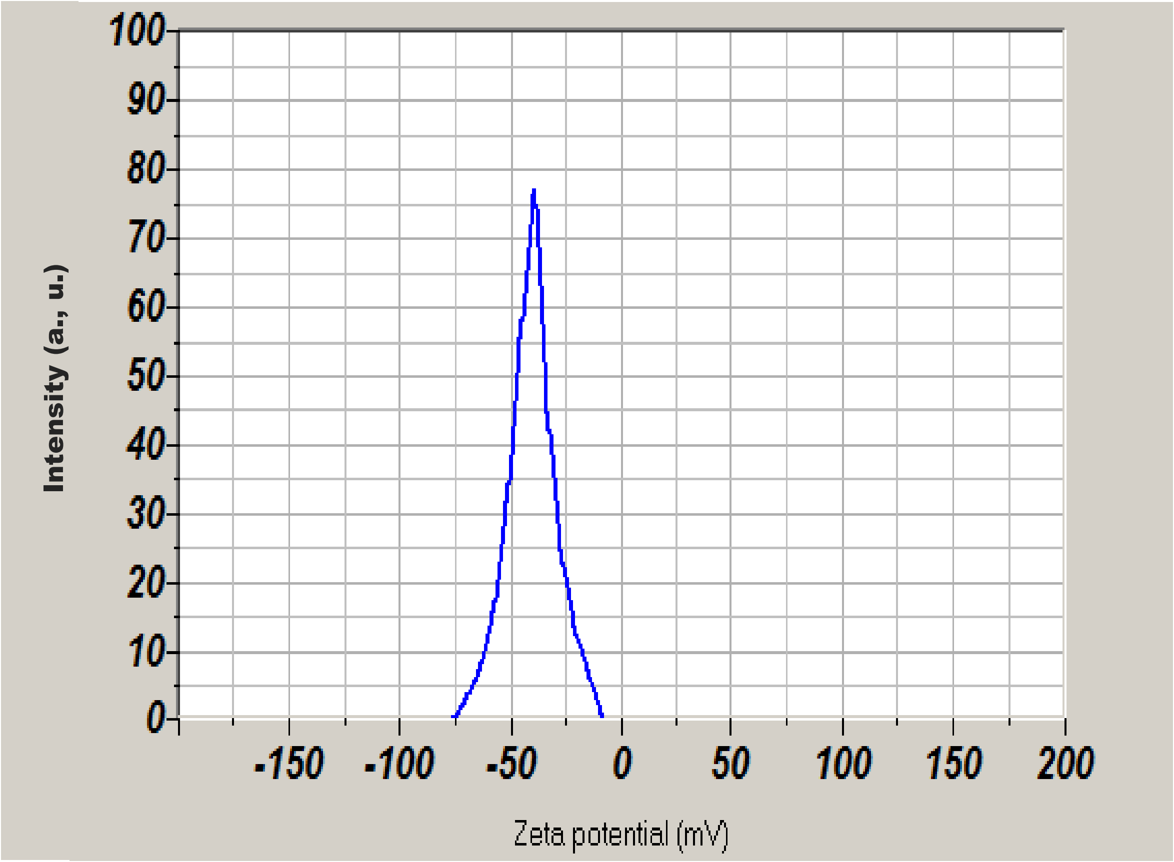
Silica	**Ludox Silica[R] TM-50 with 0.01M_KCl**
Sample Preparation	**100 ppm**

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

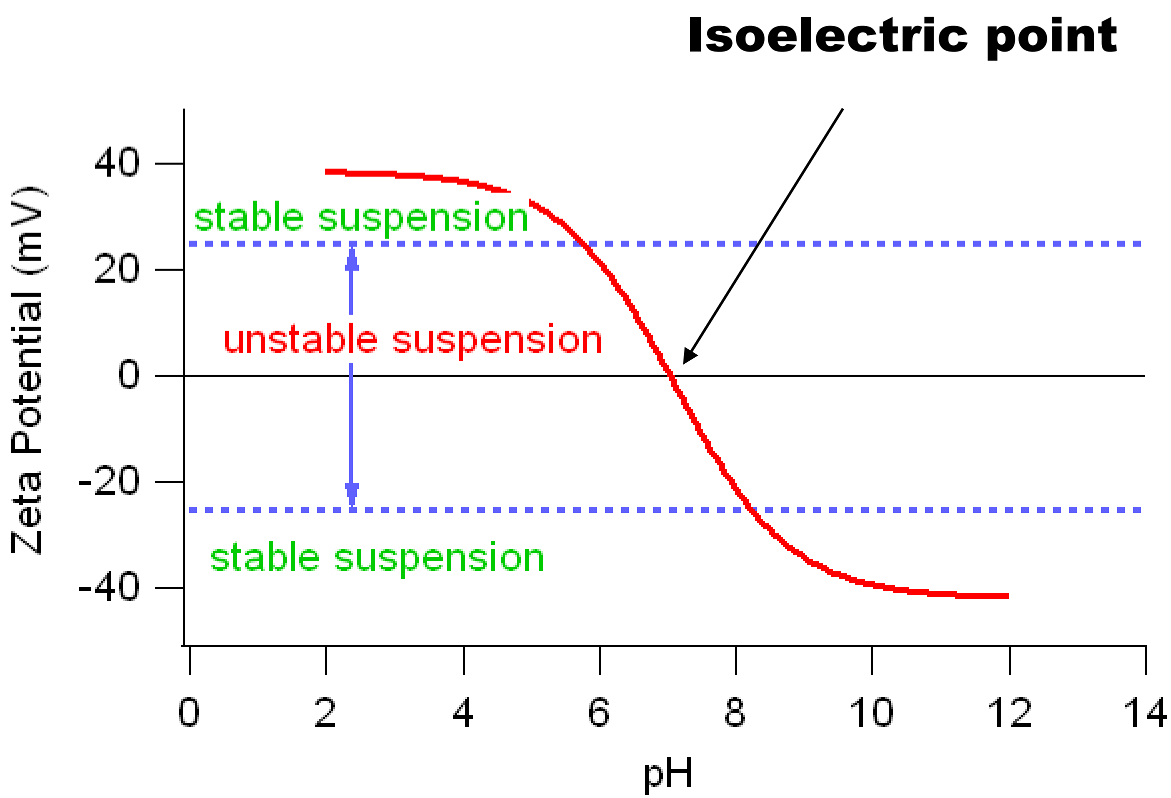
	Results
Mobility (μm·cm/V·s)	**-3.02**
Zeta Potential (mV)	**-31.8**



From GRACE's catalogue



Isoelectric point



X-axis can also be Ca++ or other ion concentration. But, pH is most common.

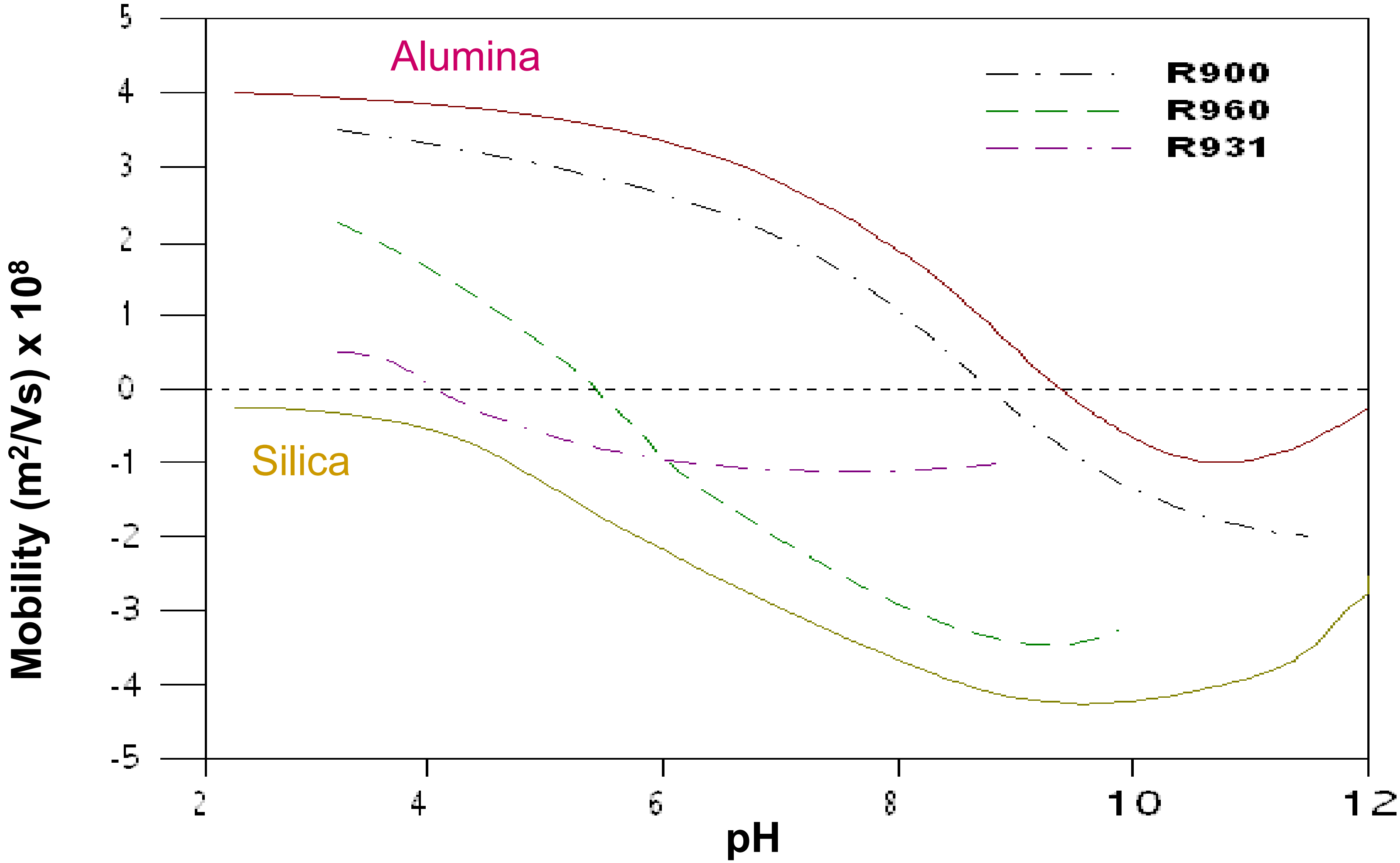
Why is IEP important?

- **When particle charge is important for stability (which is often), the IEP is a quick way of describing the region at which particle charge is low. And those are conditions under which flocculation will occur.**
- **Will depend on <u>surface (and liquid)</u>, not bulk material composition.**

Why Measure IEP?

- It serves as a method of characterizing sample.
- It tells you amount of reagent to add (or regimes to avoid) when processing the sample.

Grades of TiO_2



Care needed when dispersing!

Effect of Surface on IEP of TiO_2

Bulk % coating		IEP (pH units)
SiO_2	Al_2O_3	
- -	- -	6.8
- -	4.5	8.4 (R900)
6.5	3.5	5.8 (R960)
8.0	8.0	4.6 (R931)

Bulk percentages (elemental analysis) of each chemical coating not reliable indicator of how the surface will behave in solution

IEP of Al_2O_3 at pH 9, IEP of SiO_2 at pH 2~3

Imperative to check ZP vs pH profile for any material prior to use

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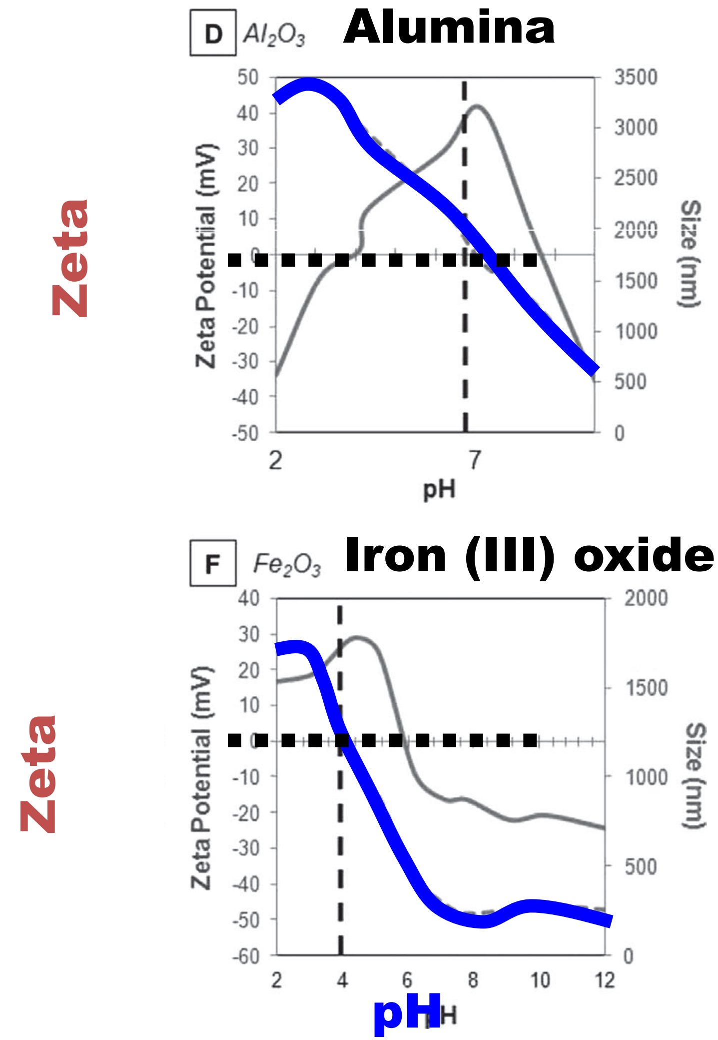
Using Zeta Potential to Predict/Control Particle Interactions

- **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.**

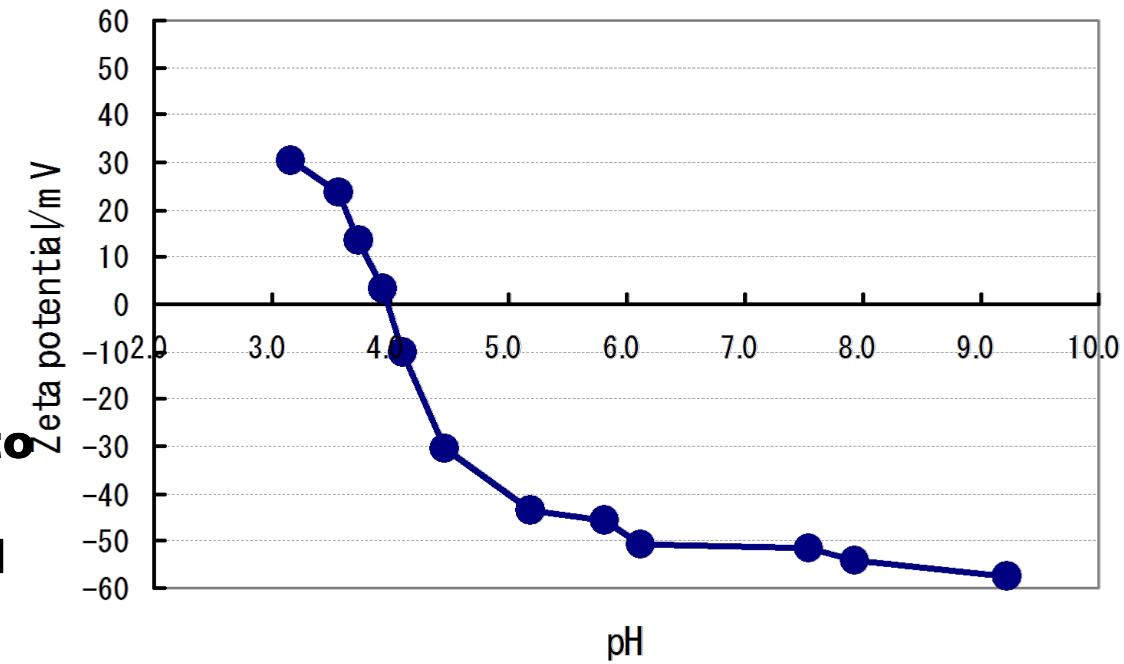


Data from Berg et al., *Nanotoxicology*, Dec. 2009; 3(4): 276-283

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?

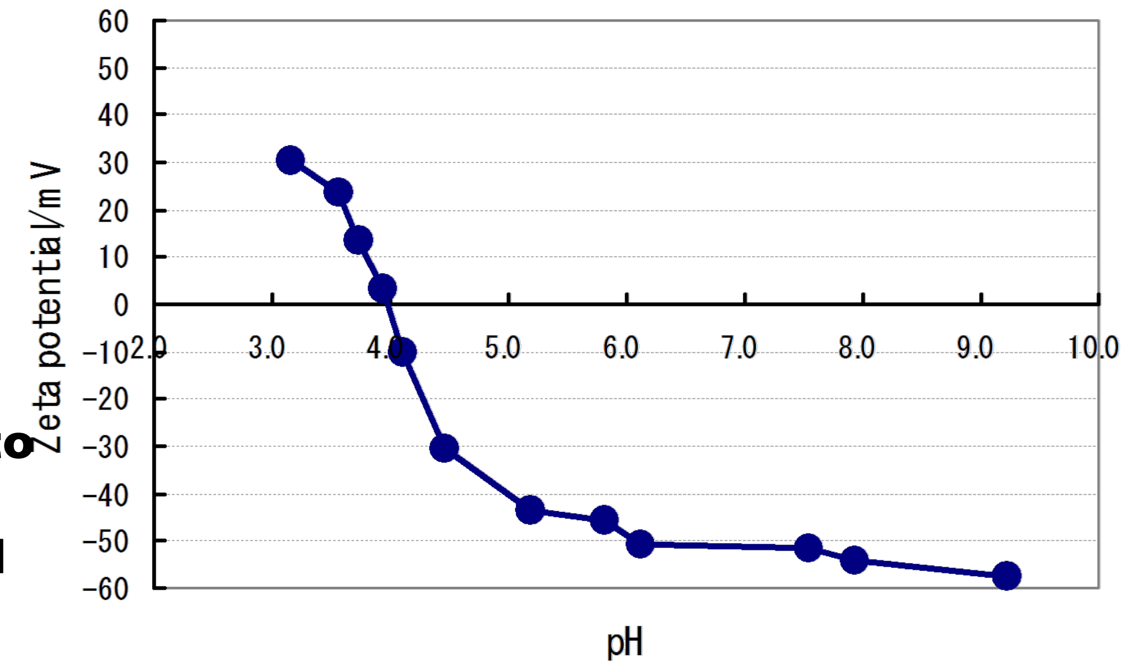
pH 2, pH 4, pH 6

***allowed for this example**

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**

Can compress all of this information

- Coffee Mate IEP: pH 4
- Al_2O_3 IEP: pH 7
- Fe_2O_3 IEP: pH 4

Practical Charge: Béarnase Sauce

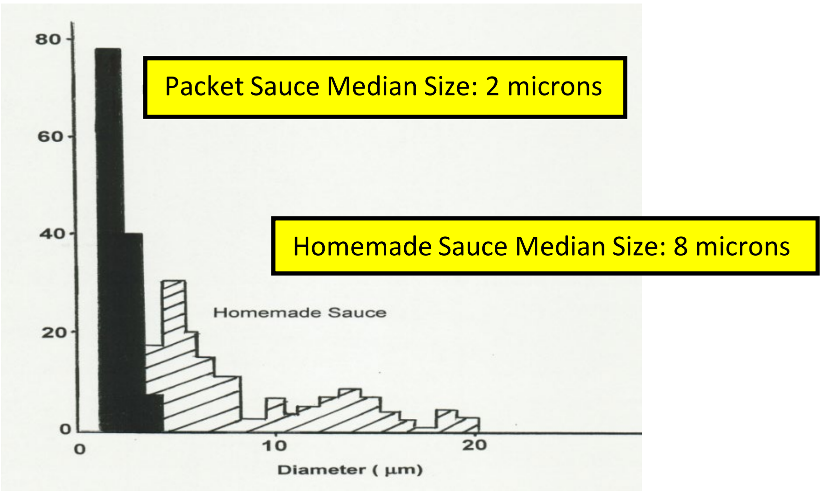
Monique's* Recipe for Béarnase Sauce
Mix vinegar, shallots, tarragon and ground pepper. Add ½ glass of white wine.
Boil until practically all the liquid has evaporated. Cool until nearly cold. Add egg-yolks, one-by-one while stirring vigorously. Add ½ glass of white wine and mix well.
Heat the mixture on a "bain-marie" while stirring all the time. When the sauce becomes creamy, cool slowly again continuously stirring. When the pot temperature is such that you can touch it with your hands, add clarified butter, a small amount at a time. The temperature of the clarified butter should be about the same as the temperature of the pot mixture. Continue stirring. When all the butter is incorporated, sieve the mixture and add one spoonful of cut chervill. Keep the sauce tepid on the bain-marie. Never heat it up again. The consistency of the sauce should be similar to that of mayonnaise .

This tastes great, but sometimes it fails

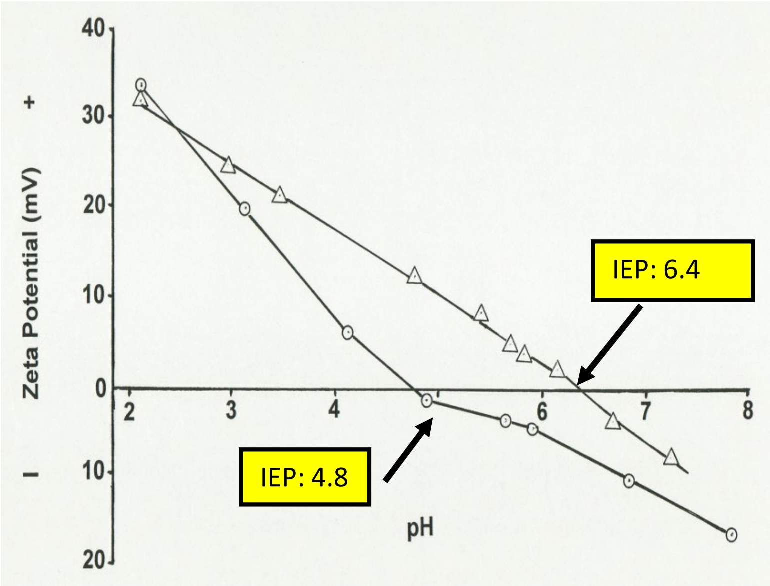
Packet Sauce Instructions
Add butter and milk to pan. Heat to boiling, add mix with stirring.
Simmer and stir until sauce has creamy consistency.

Q: Why does a homemade sauce taste better?
Q: Why does a packet sauce mixture always work?

Particle Science has answers!



Emulsion Particle Size determines sauce mouth feel/texture – large particles taste better.

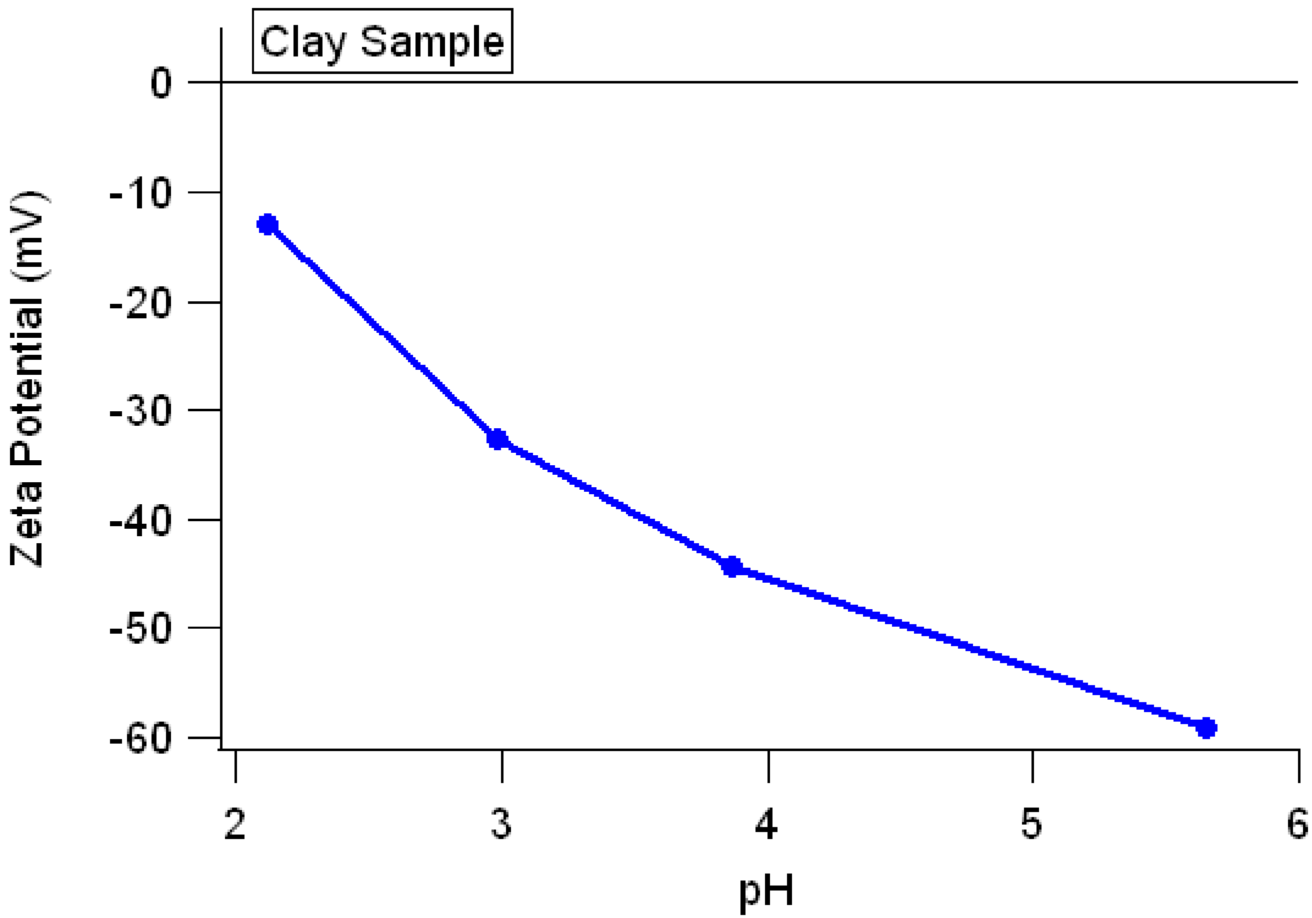


Egg Yolk Zeta Potential determines sauce stability

Vinegar will adjust pH of sauce. If you get the wrong egg, the IEP is at pH 4.8 and the emulsion droplets coalesce. You need to adjust the vinegar on a case by case basis.

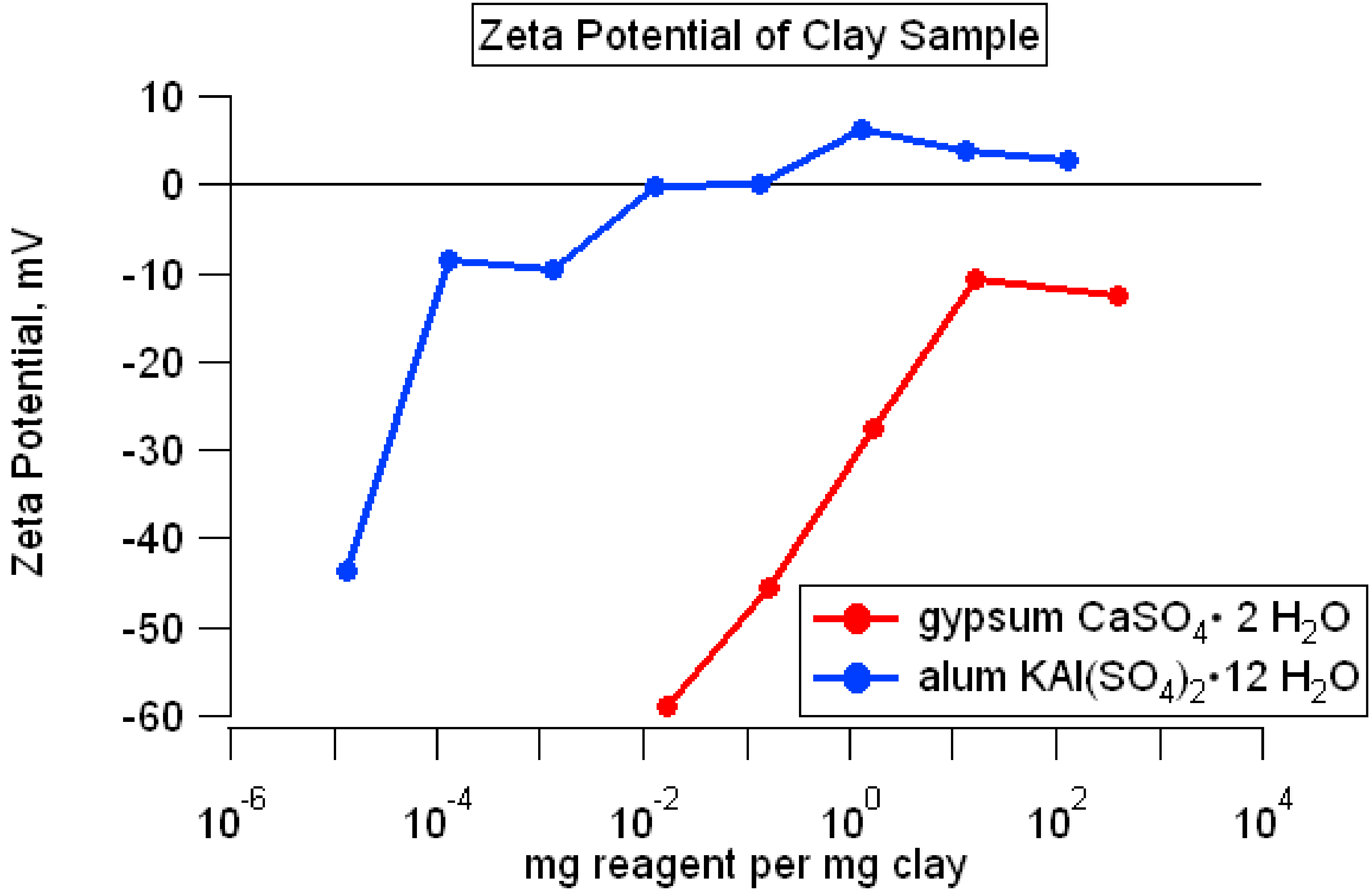
Environmental

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 <u>surface property</u>.**
- **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.**

Concluding Comments

- **Use measured surface charge (zeta potential) to predict colloidal stability**

- **Use measured surface charge to control particle-particle interactions**

Q&A

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Thank-you

Thank you

Thank you

Omoshiro-okashiku
Joy and Fun

감사합니다

Cảm ơn

ありがとうございました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

நன்றி

ขอบคุณครับ

Obrigado

Σας ευχαριστούμε

شُكْرا

Tack ska ni ha

Большое спасибо

Danke

Gracias