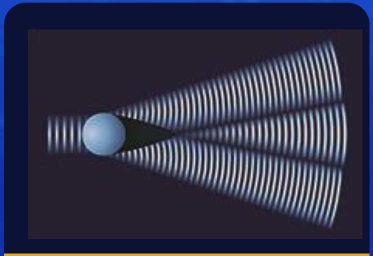
Modern Particle Characterization Techniques Series

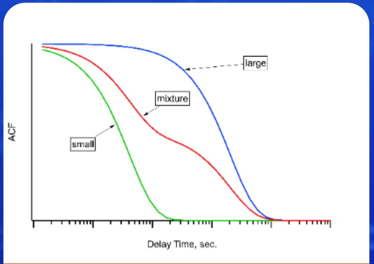
Dr. Mike Pohl

I: Introduction



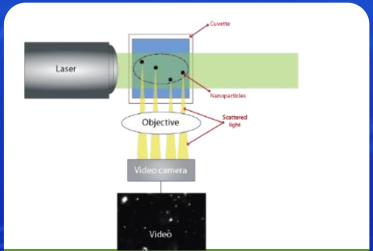
Julie Chen Nguyen

II: Laser Diffraction



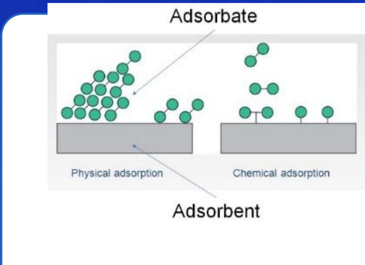
Dr. Jeff Bodycomb

III: DLS



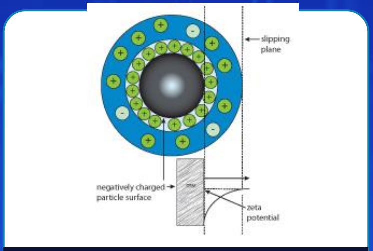
Dr. Sean Travers

IV: Multi-laser NTA



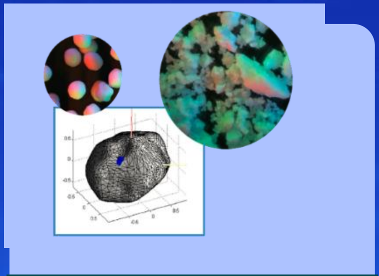
Carl Lundstedt

Series V: BET



Dr. David Fairhurst

VI: Zeta Potential



Darren McHugh

VII: Image Analysis

Webinar

Zeta Potential

A Necessary Parameter in Formulation and Applications of Suspensions

David Fairhurst, PhD.
Colloid Consultants, Ltd.

Fundamental Parameters that control the Nature and Behavior of all Particulate Suspensions

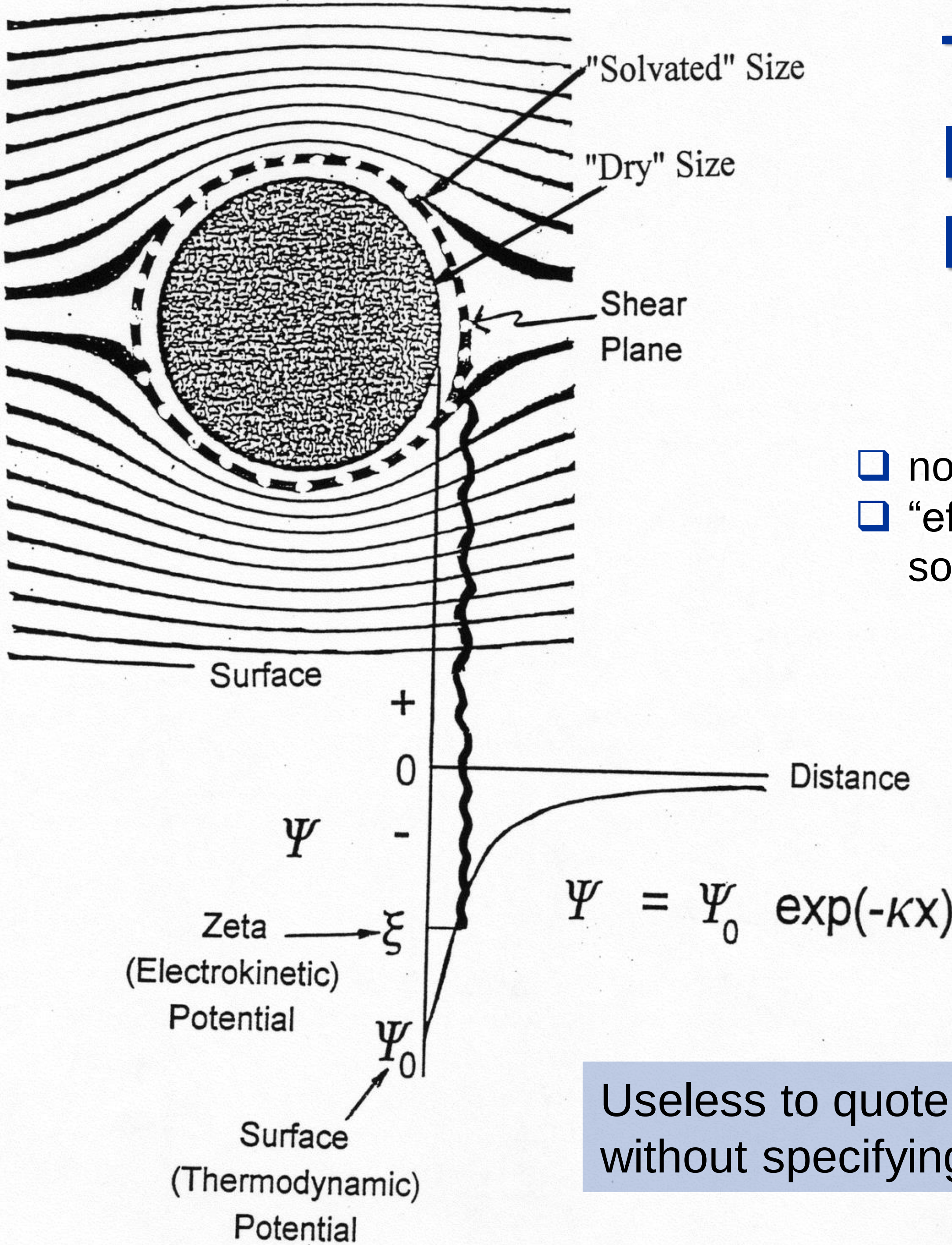
INTERFACIAL EXTENT ⇄ INTERFACIAL CHEMISTRY

Particle Size and Distribution*
Particle Shape and Morphology*
Surface Area* (external/internal)
Porosity

Surface Charge*
Nature/type of group(s)
Number and distribution
Dissociation/ionization
Preferential adsorption
Hydrophobic/hydrophilic balance
Surface(interfacial)**Tension**
Contact Angle

* HORIBA Scientific

Zeta Potential is related to surface charge



The Electric Double Layer and the Zeta Potential

The Zeta Potential (ζ) is a mathematical concept

- non-linear relation to surface charge
- "effectiveness" of the surface charge in solution

Magnitude of ZP depends upon

- Fundamental "surface" sites
  - how many, what type
- Solution conditions
  - electrolyte concentration, pH, temperature

Useless to quote a single zeta potential value without specifying suspension solution conditions!

Electrokinetic Phenomena

Arises when two phases move with respect to each other with an electric double layer at the interface

Four Related Phenomena
All involve relative movement

Charged surface →
← Ions and fluid

(Micro) Electrophoresis

Movement of charged surface - Stationary liquid - Applied electric field
Most widely adopted technique for suspensions → commercial instrumentation
Measure an electrophoretic mobility → calculate a zeta potential

Electro-osmosis

Movement of liquid -Stationary charged surface - Applied electric field
(i.e., the complement of electrophoresis)

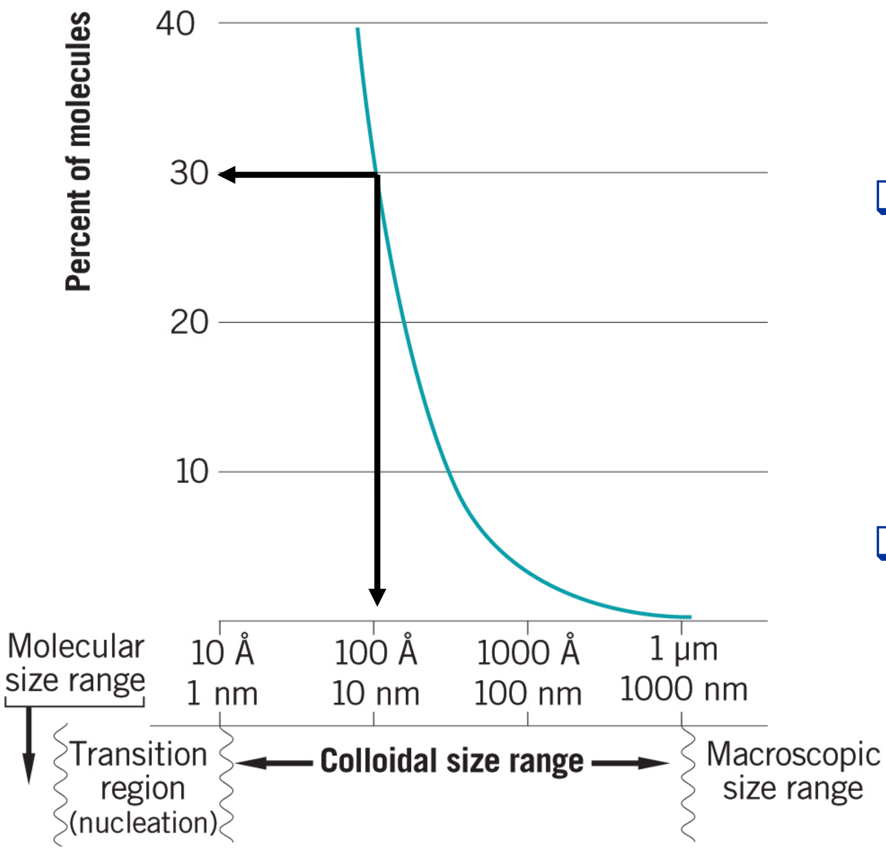
Streaming Potential

Measured electric field - Movement of liquid – Stationary charged surface
(i.e., the opposite of electro-osmosis)

Sedimentation Potential

Measured electric field - Movement of charged particles - Stationary liquid
(i.e., the opposite of electrophoresis)

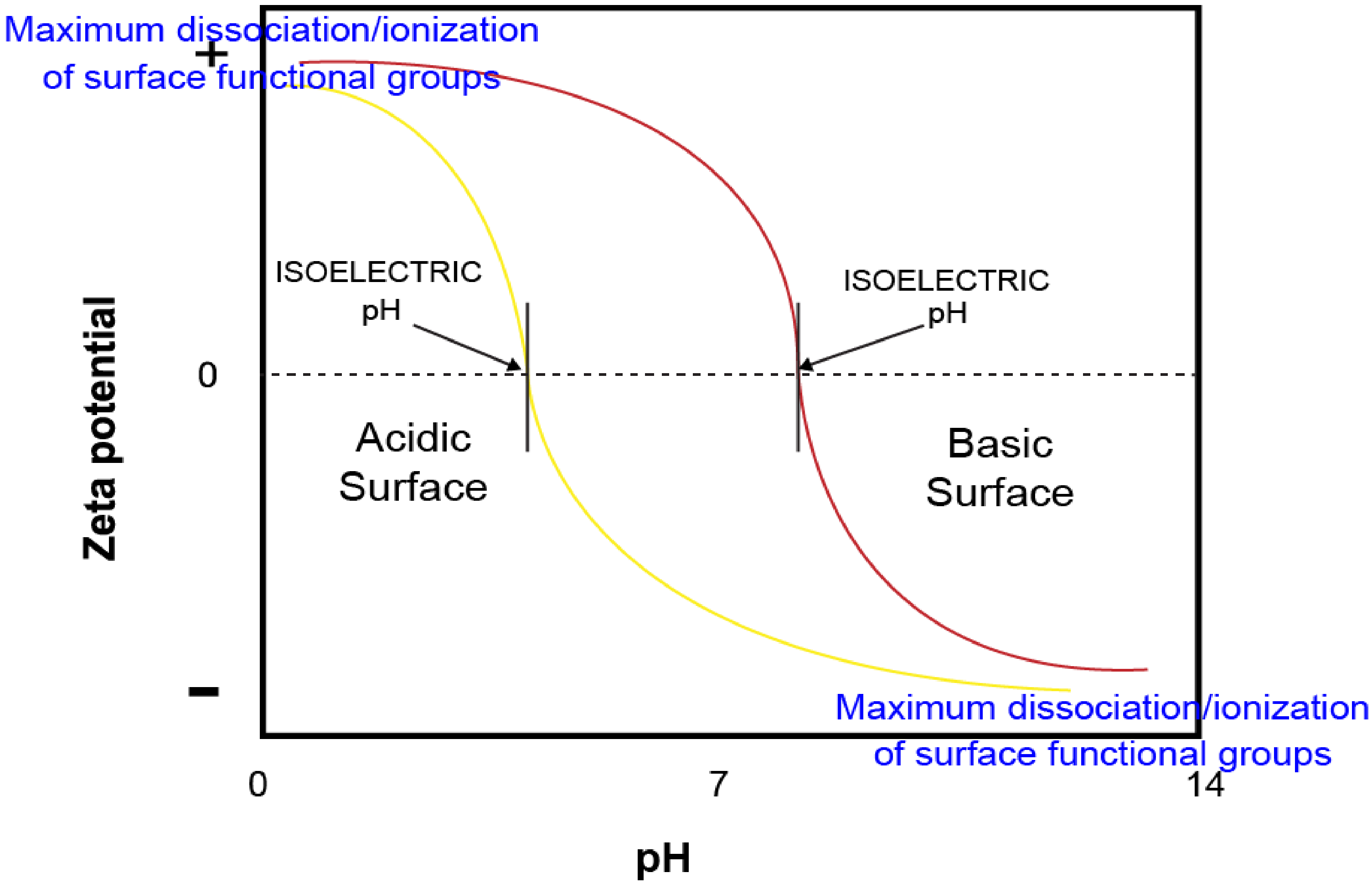
Nanoparticle Surface Chemistry



- ❑ At 10nm particle size *ca* 30% of molecules/atoms that comprise the molecular structure become "surface moieties"
- ❑ Crystal lattice defects (anisotropy) and impurities become critical attributes

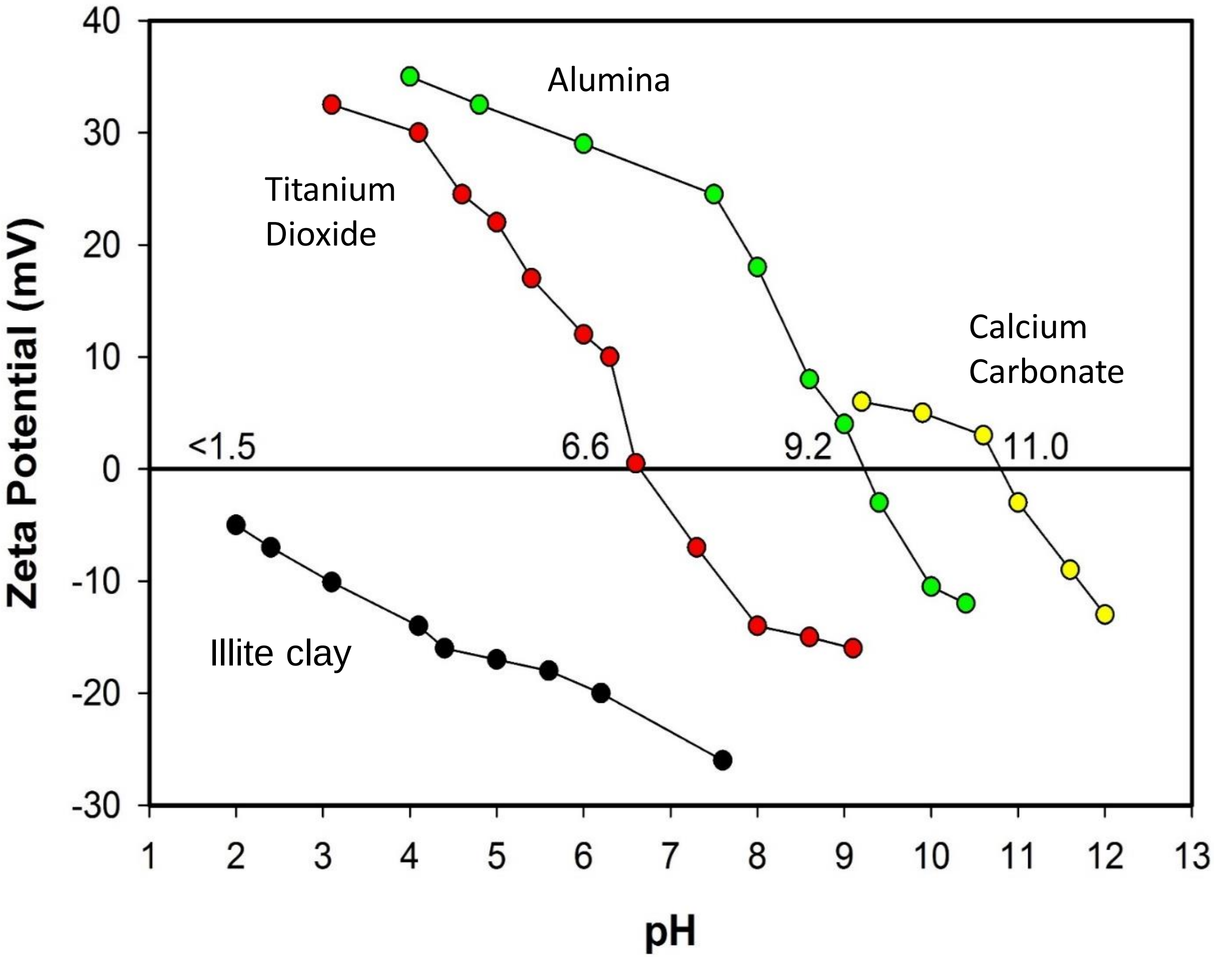
For nano-size systems **surface charge effects** play a dominant role in determining the physicochemical properties (surface chemical activity and catalysis) of the system as a whole
Zeta potential measurement is vital!

Effect of pH on Particle Charge



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

Aqueous Isoelectric Points (IEP)

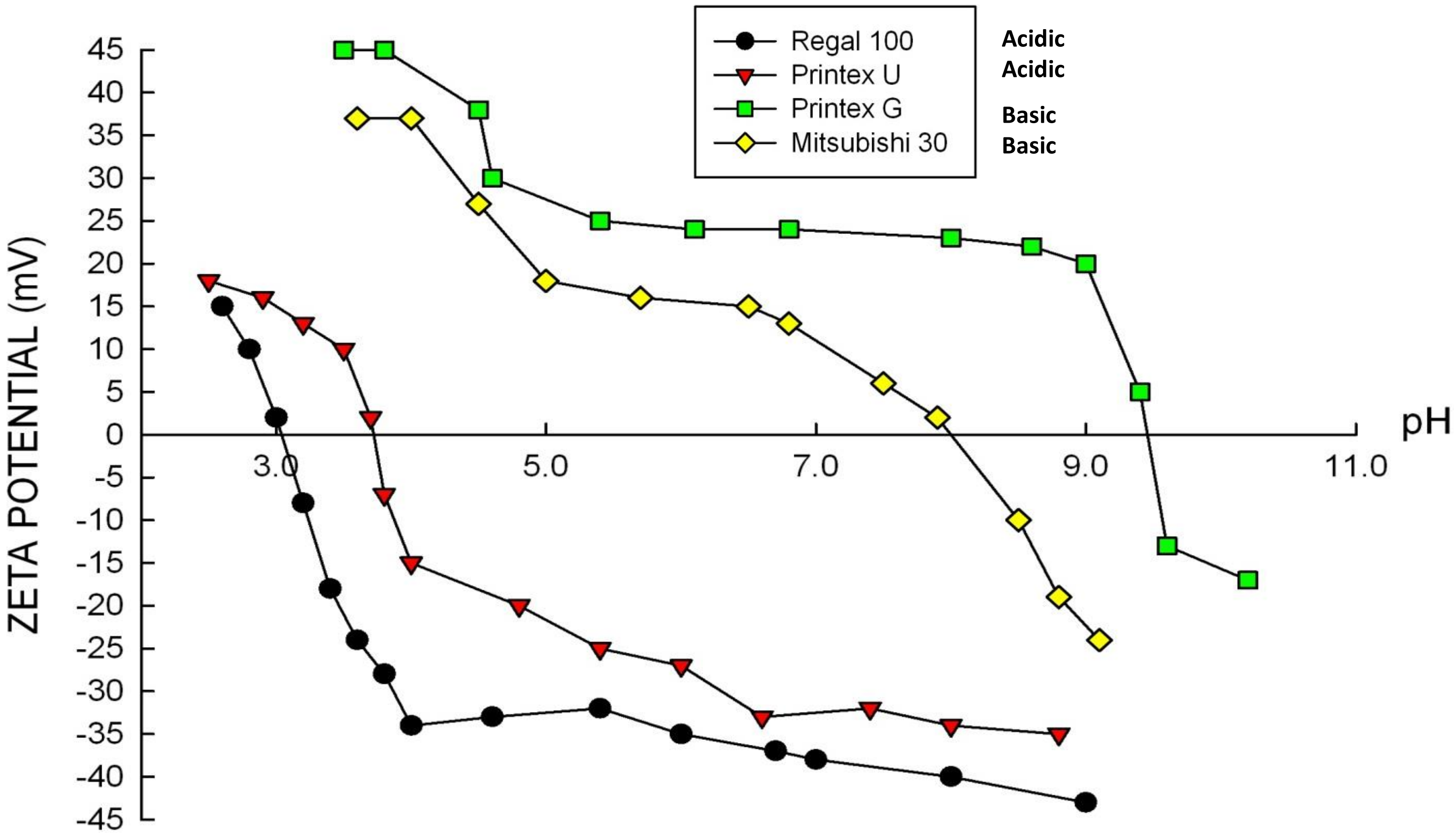


Mineral Oxide	I.E.P (pH)
Quartz (SiO_2)	2
Baddeleyite (ZrO_2)	4
Pyrolusite (MnO_2)	5
Cassiterite (SnO_2)	6
Rutile (TiO_2)	7
Hematite (Fe_2O_3)	8
Bauxite (Al_2O_3)	9
Tenorite (CuO)	10
Litharge (PbO)	11
Periclase (MgO)	12

Ionic Solid	I.E.P (pI)
Fluorite (CaF_2)	pCa3
Barite ($BaSO_4$)	pBa7
Silver Chloride (AgCl)	pCl8

Profile impacts precision of solution pH
Mixed oxide suspensions!

Zeta Potential of Commercial Carbon Blacks



Impacts choice of dispersant

The Nature of Surface Charge of Oxides in Water

Metal Oxides and Hydroxides

- difficult to control surface chemistry in manufacture and processing
- grinding not only reduces size but exposes new surface
  - reactant impurities

Mineral oxide crystal lattices are anisotropic

- charge development because of *n* and *p* defects in crystal structure
- results in hydroxyl groups (-OH)
  → reaction with either H^+ or OH^-

Metal Oxide in Water

Adsorption of protons and hydroxyl ions

$$MOH_2^+ \overset{H^+}{\leftrightarrows} MOH \overset{OH^-}{\leftrightarrows} MO^- + H_2O$$

Dissociation driven by pH
→ avoid swings in pH

Formation of hydroxylated species

$$M^{n+} + xOH^- \leftrightarrows M(OH)_x^{(n-x)+}$$

$$M(OH)_x^{(n-x)+} + OH- \leftrightarrows M(OH)_{x+1}^{(n-x-1)+}$$

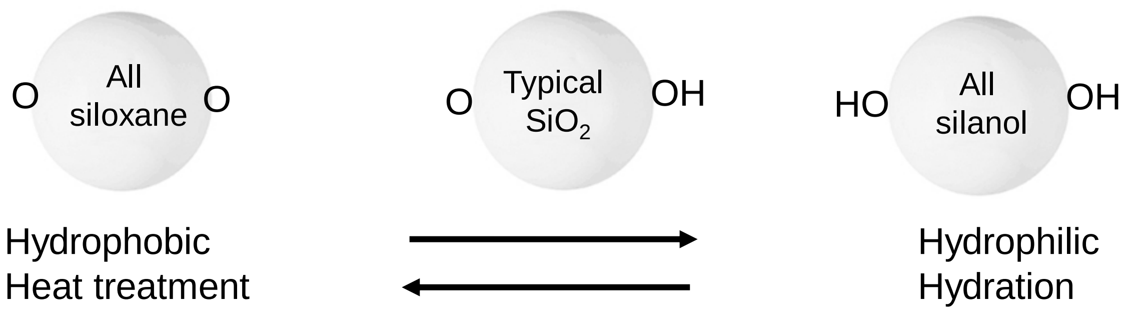
$$M(OH)_{x+1}^{(n-x-1)+} + H+ \leftrightarrows M(OH)_{x-1}^{(n-x+1)+}$$

Equilibria driven by particle concentration
→ constant %solids

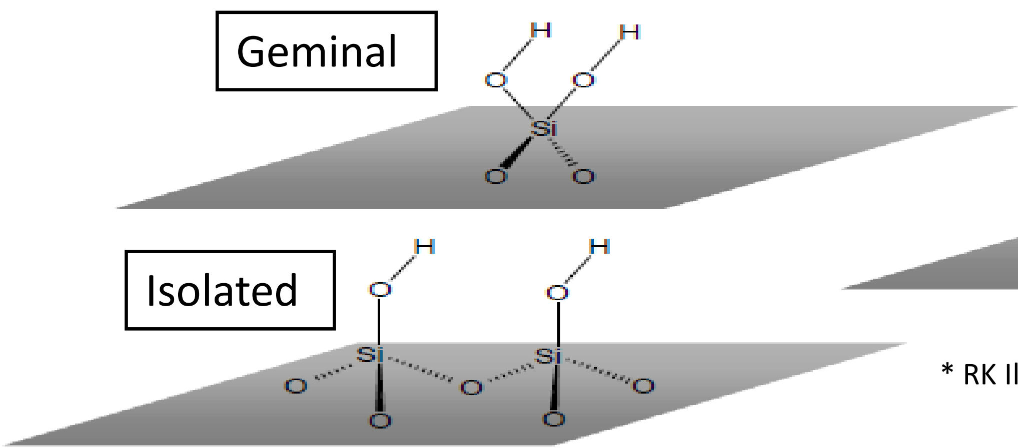
Beware hydrolysis!

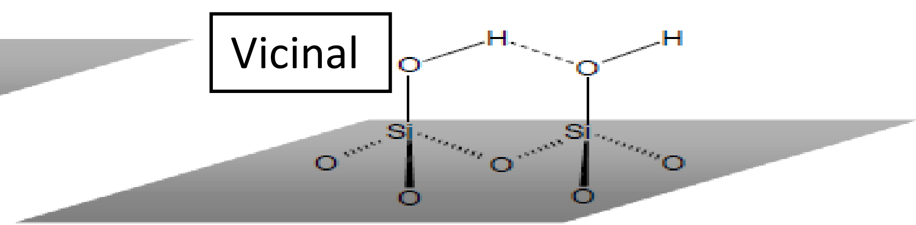
Silica Surface Chemistry

Different ratio: silanol to siloxane groups



Different types of silanol groups*

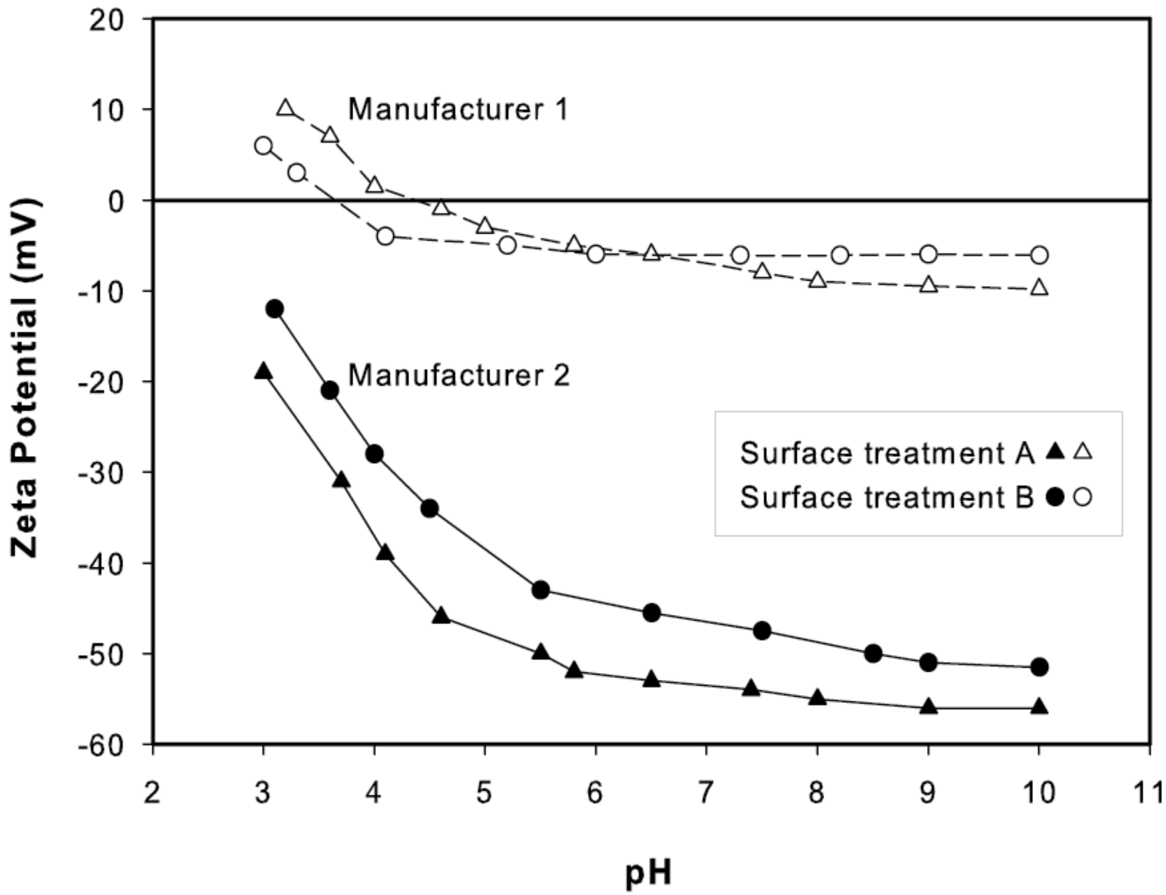




* RK Iler *Chemistry of Silica*, Wiley-VCH Verlag, Weinheim (1979)

The Zeta Potential will be different for each silica type
→ impacted by degree of hydration

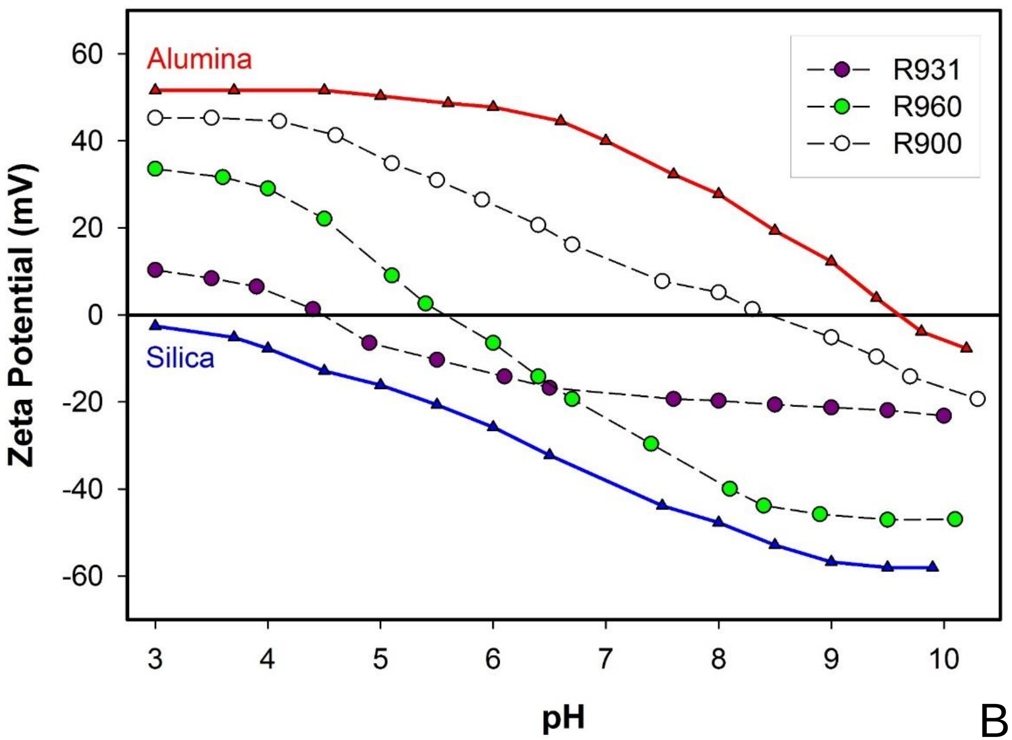
Zeta Potential of Commercial Silicas



Surface treatments affect silicas differently. Be careful of substitution of material from different suppliers without first checking ZP!

Surface Modification

Manufacturer Label: "Ti-pure Rutile" RXXX



Bulk % Coating		IEP (pH units)
SiO_2	Al_2O_3	
-----	-----	6.6
-----	4.5	8.4 (R900)
6.5	3.5	5.8 (R960)
8.0	8.0	4.6 (R931)

Types of Surface Modification

Inorganic	Organic
Metal oxides	Fatty acids/amines
Silicones	Organosilanes

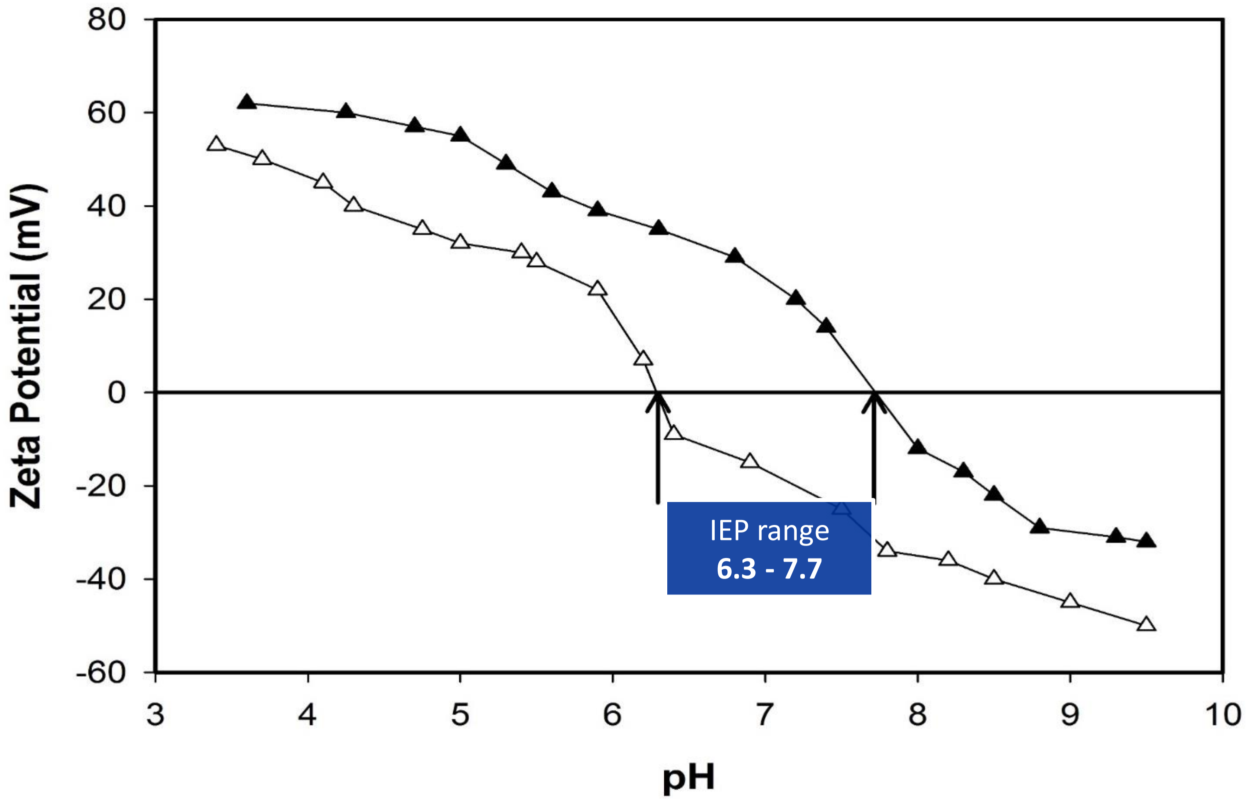
Bulk percentages (elemental analysis) of each chemical coating not reliable indicator of how the **surface** will behave in solution → measure the ZP!

Read the MSDS → Trust but verify!

Care needed when dispersing!

Zeta Potential of Commercial Pigmentary Grade* Titanium Dioxide

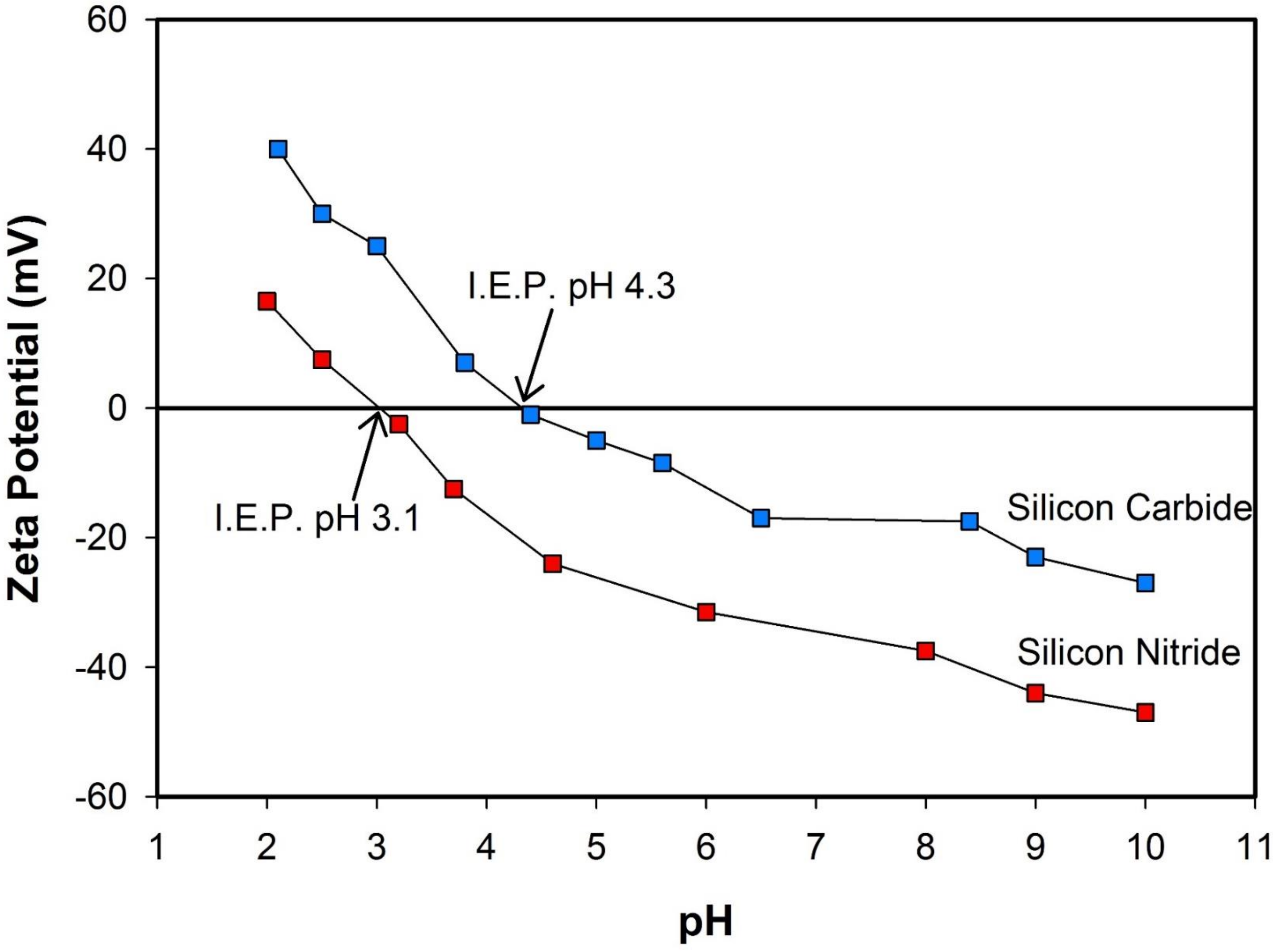
Batch-to batch and lot-to-lot variation over a 5-year period



Important to QC incoming material!

*Mean particle size: 260nm

Zeta Potential of Non-oxides

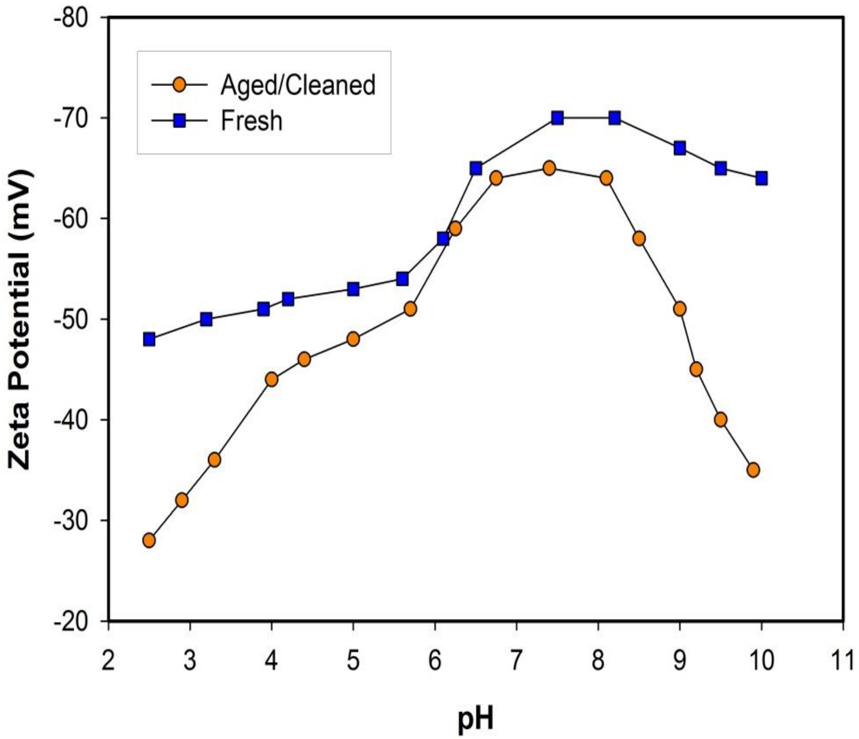


Surface impurities and contamination matters!

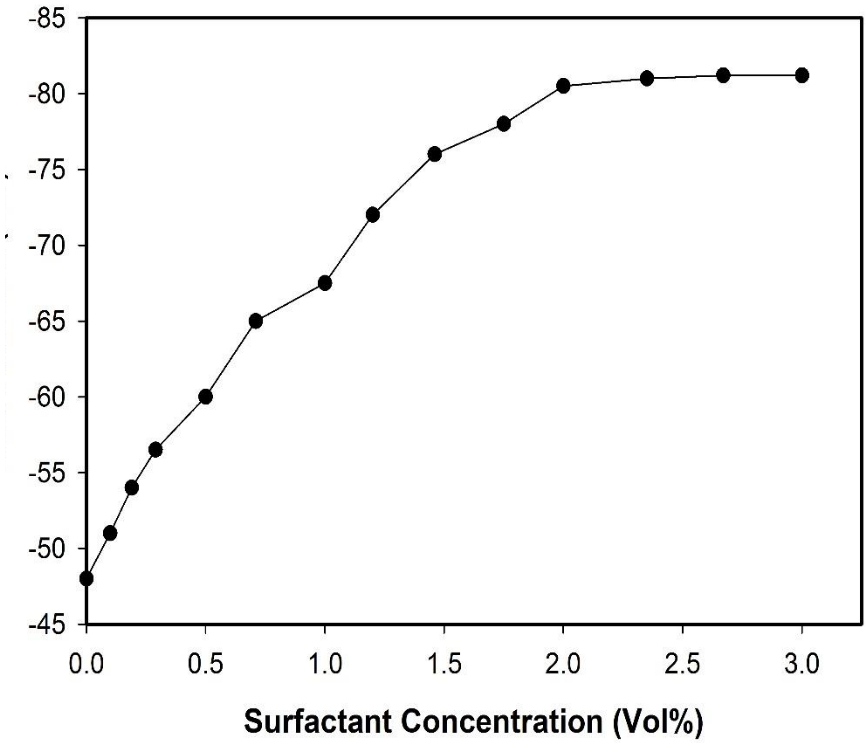
Zeta Potential of Commercial Polymer Latices

Poly Ethyl Acrylate

Fresh and Aged

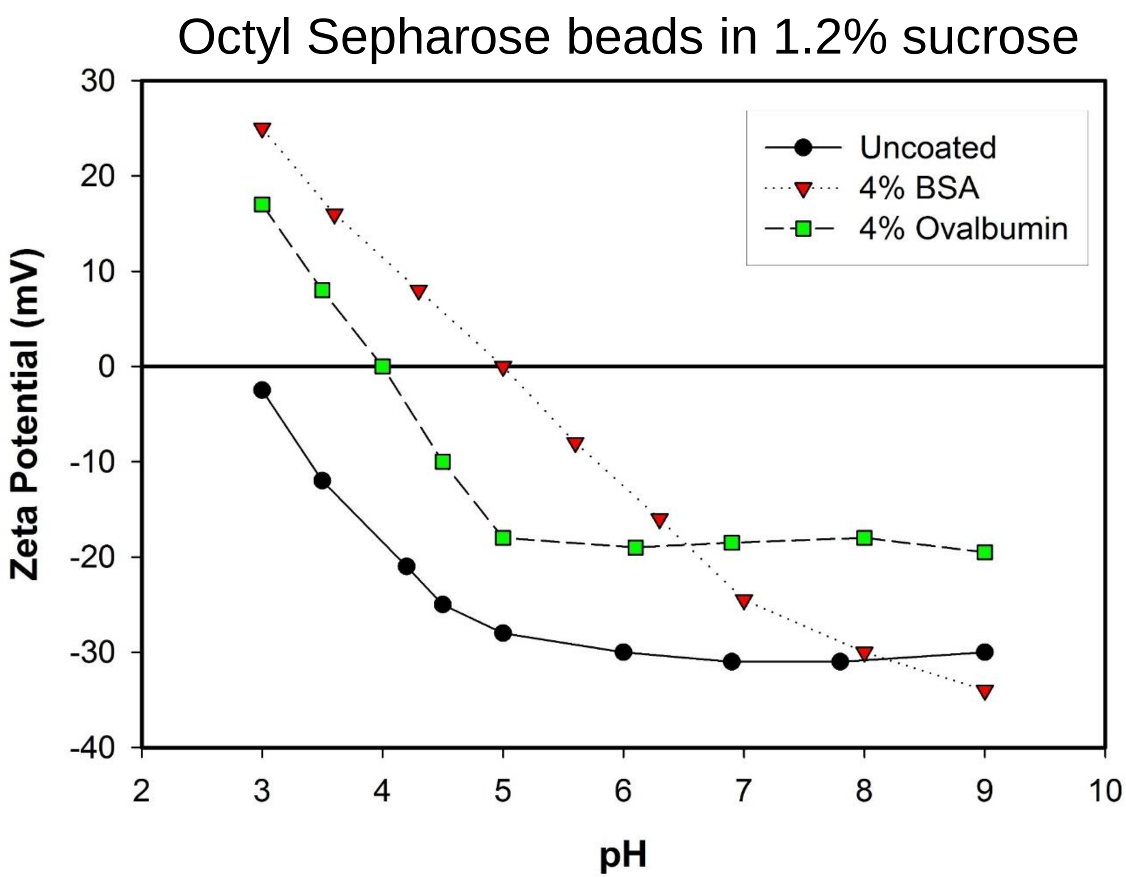


Adsorption of surfactant



Storage stability!

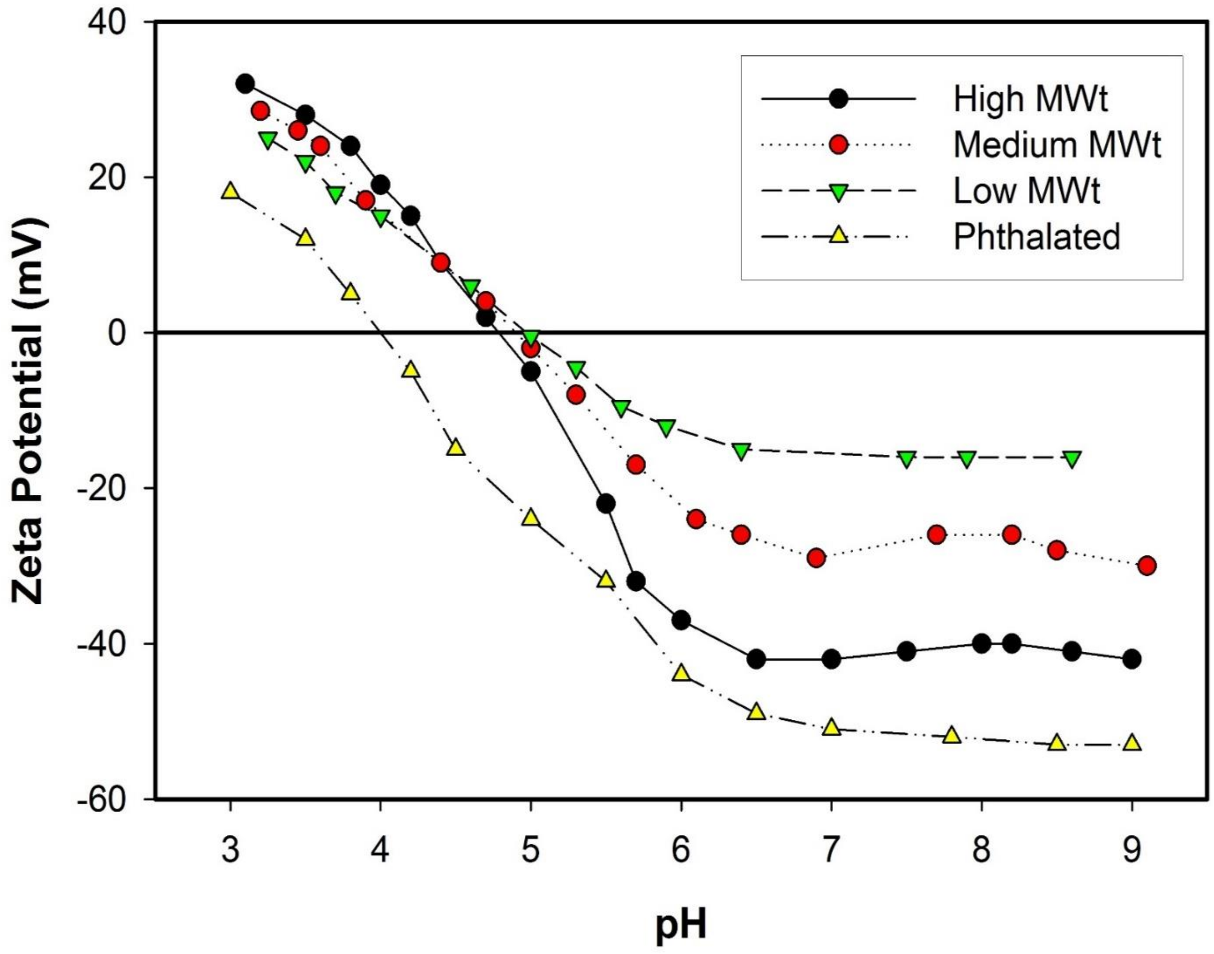
Zeta Potential of Proteins



Protein	pI
Avidin	10.5
Ribonuclease	9.5
Rapeseed 12S	7.0
Lactoglobulin	5.3
BSA	5.0
Strepavidin	5.0
Gelatin	4.8
Casein	4.6
Soy 18S	4.6
Ovalbumin	4.0

The IEP of any adsorbed species is important!

Zeta Potential of Gelatins



Bloom Number	Avg Molar Mass
Low (50-125)	20K-25K
Med (175-225)	40K-50K
High (225-325)	50K-100K

Maximum ZP directly related to COOH concentration

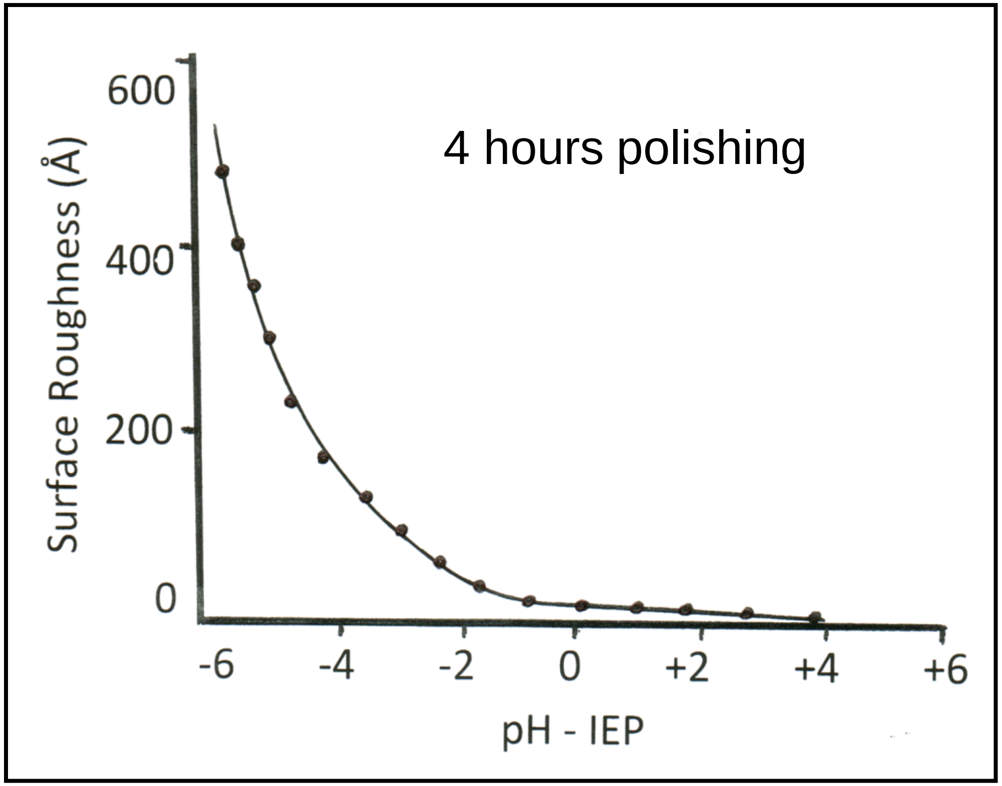
The Polishing of Optical Glass: Slurry Zeta Potential

Glass: Corning 7940 Fused Silica (IEP: 3.5)
Polishing agents: CeO_2, ZrO_2 (monoclinic) and Al_2O_3 (nanocrystalline)

Polishing Agent	IEP	Surface Charge at pH 4	Surface Charge at pH 7	Surface Charge at pH 10
ZrO_2	6.3	++	-	- - -
CeO_2	8.8	++++	++	- -
Al_2O_3	9.3	+++++	+++	-

The zeta potential of the polishing slurries varies with solution pH
→ positive or negative depending upon the metal oxide IEP

The Polishing of Optical Glass: Glass Surface Roughness



The glass surface roughness depends upon the **difference** in fluid pH and the IEP of the polishing agent. The more **positive** the difference the smoother the surface

Solution pH must be > the polishing agent IEP
Choose CMP agent whose IEP < Fluid pH

Preparation of Béarnaise Sauce

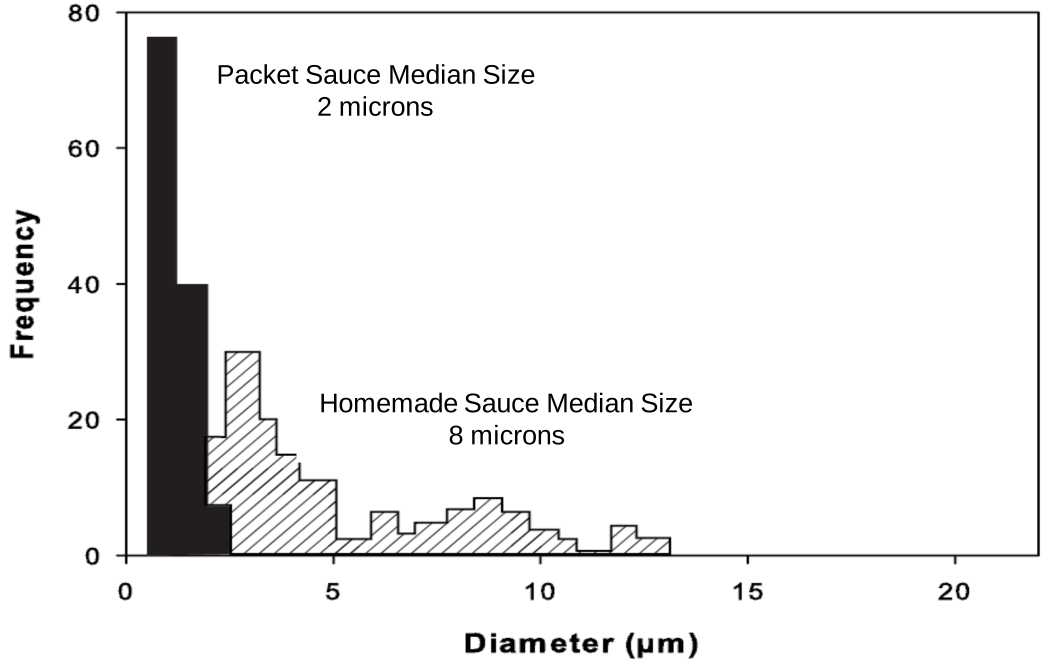
Monique's* Recipe for Béarnaise Sauce

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 chervil. 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 .

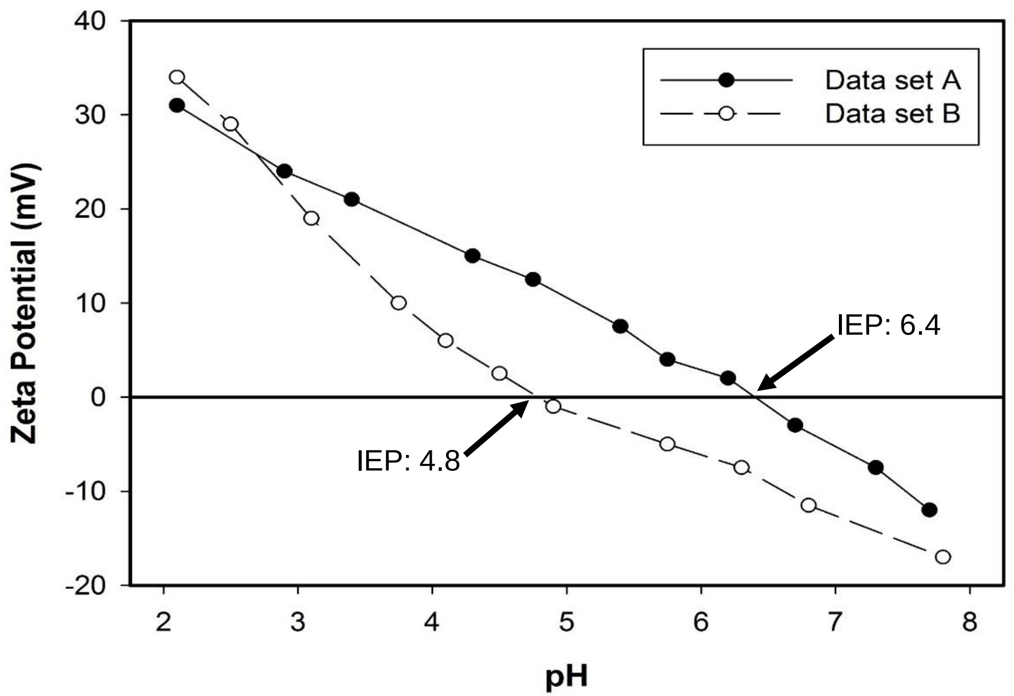
*Monique de Jaeger

Egg yoke complex mixture: components include carotenes, phospholipids, proteins and lecithin (emulsifier)

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



Emulsion Droplet Size Distribution determines sauce mouthfeel/texture



Egg Yoke Zeta Potential determines sauce stability!

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THANK YOU!

For more information, to send samples, to arrange a demonstration at your facility, or to speak to a technical applications specialist, please contact:

labinfo@horiba.com

1-800-446-7422

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