

The Utility of Zeta Potential Measurements in the Characterization of CMP Slurries



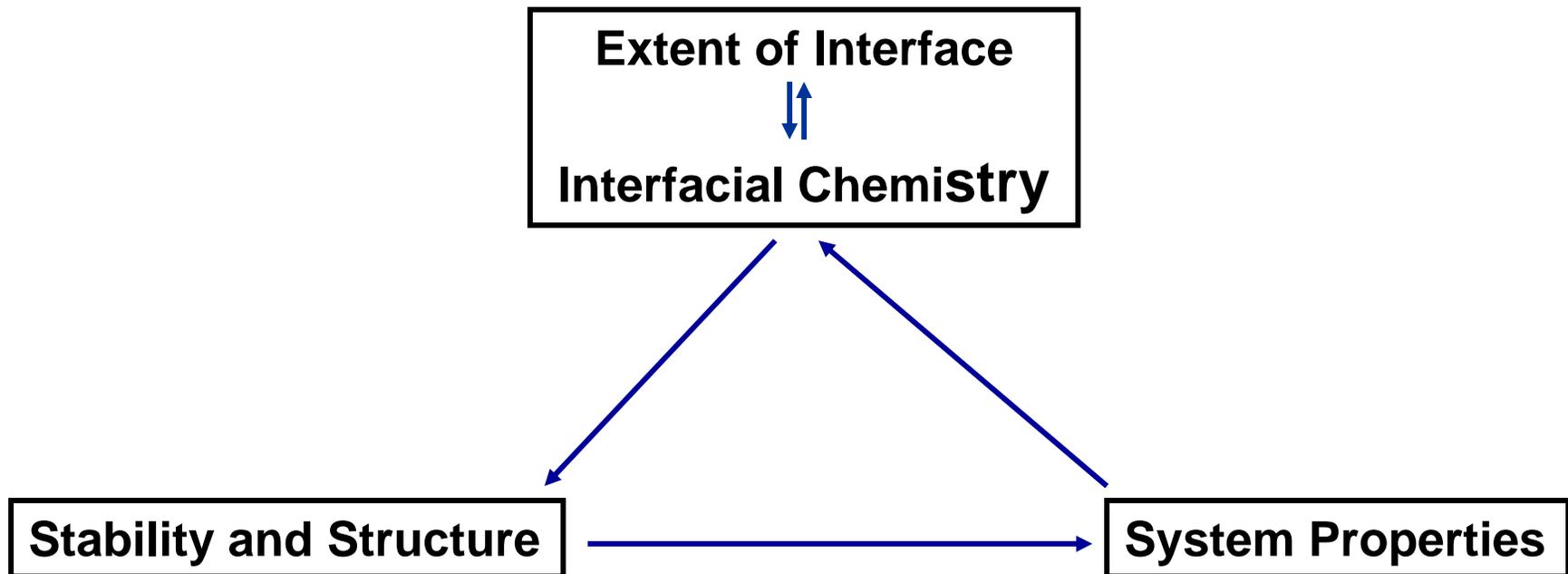
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HORIBA Scientific
Webinar
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Dispersed Systems

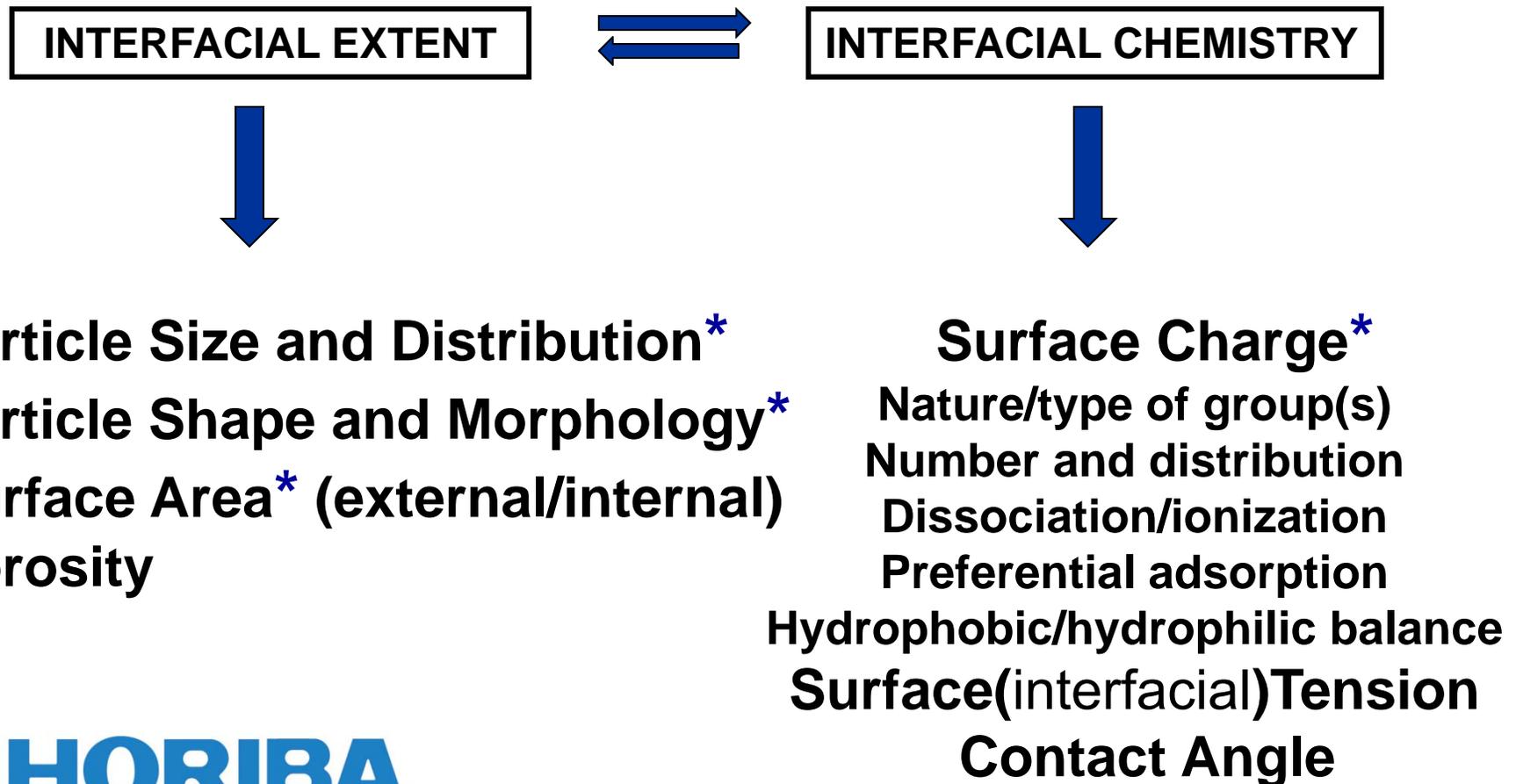
An **interface** always exists when one component (phase I) is dispersed in a state of subdivision in a medium (phase II)

Two fundamental parameters control the nature and behavior all dispersed systems



The interfacial extent and interfacial chemistry are not independent parameters

Measurement Techniques used to Characterize Particulate Suspensions



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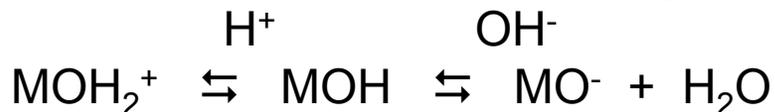
The Nature of Surface Charge in Water

Mineral oxide crystal lattices are anisotropic

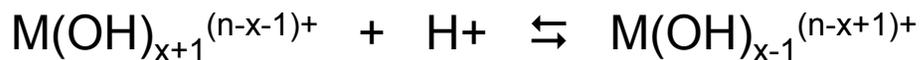
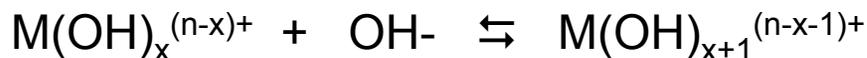
- ❑ charge development because of n and p defects in crystal structure
- ❑ results in hydroxyl groups (-OH) \oplus can undergo reaction with either H^+ or OH^-
- ❑ difficult to control surface chemistry in manufacture and processing
 - ❑ reactant impurities

Metal Oxide Surfaces in Water

Adsorption of protons and hydroxyl ions \oplus



Formation of hydroxylated species



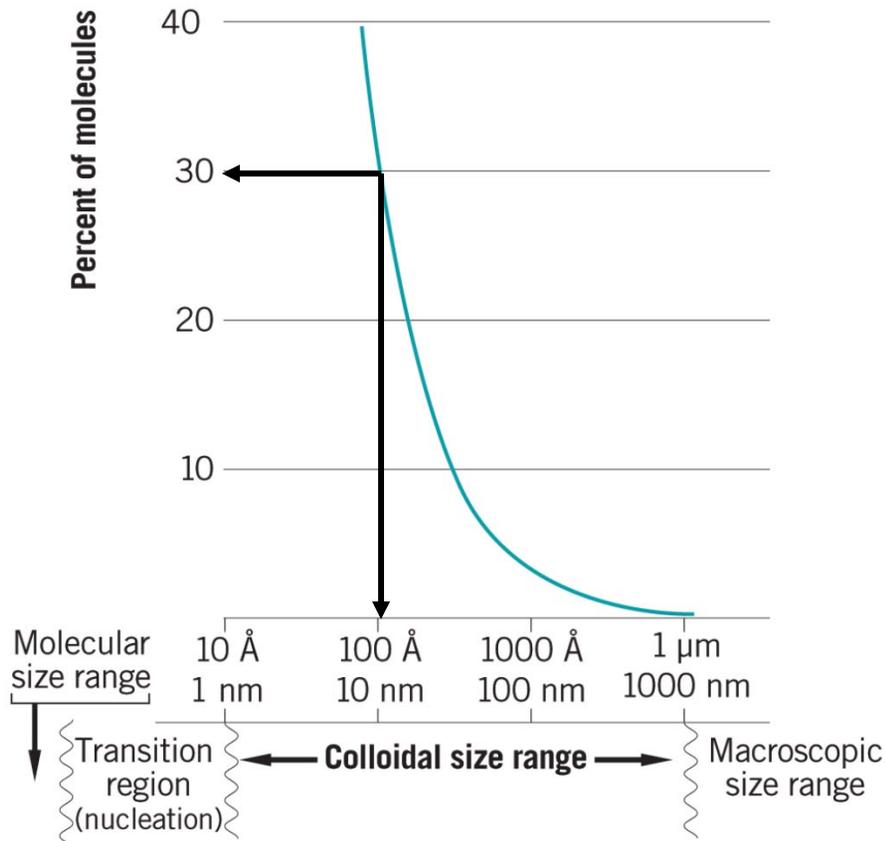
Dissociation driven by pH

\oplus avoid swings in pH

Equilibria driven by
particle concentration

\oplus constant %solids

Nanoparticle Surface Chemistry



10nm particle size:

ca 30% of molecules/atoms that comprise the molecular structure become “surface moieties”

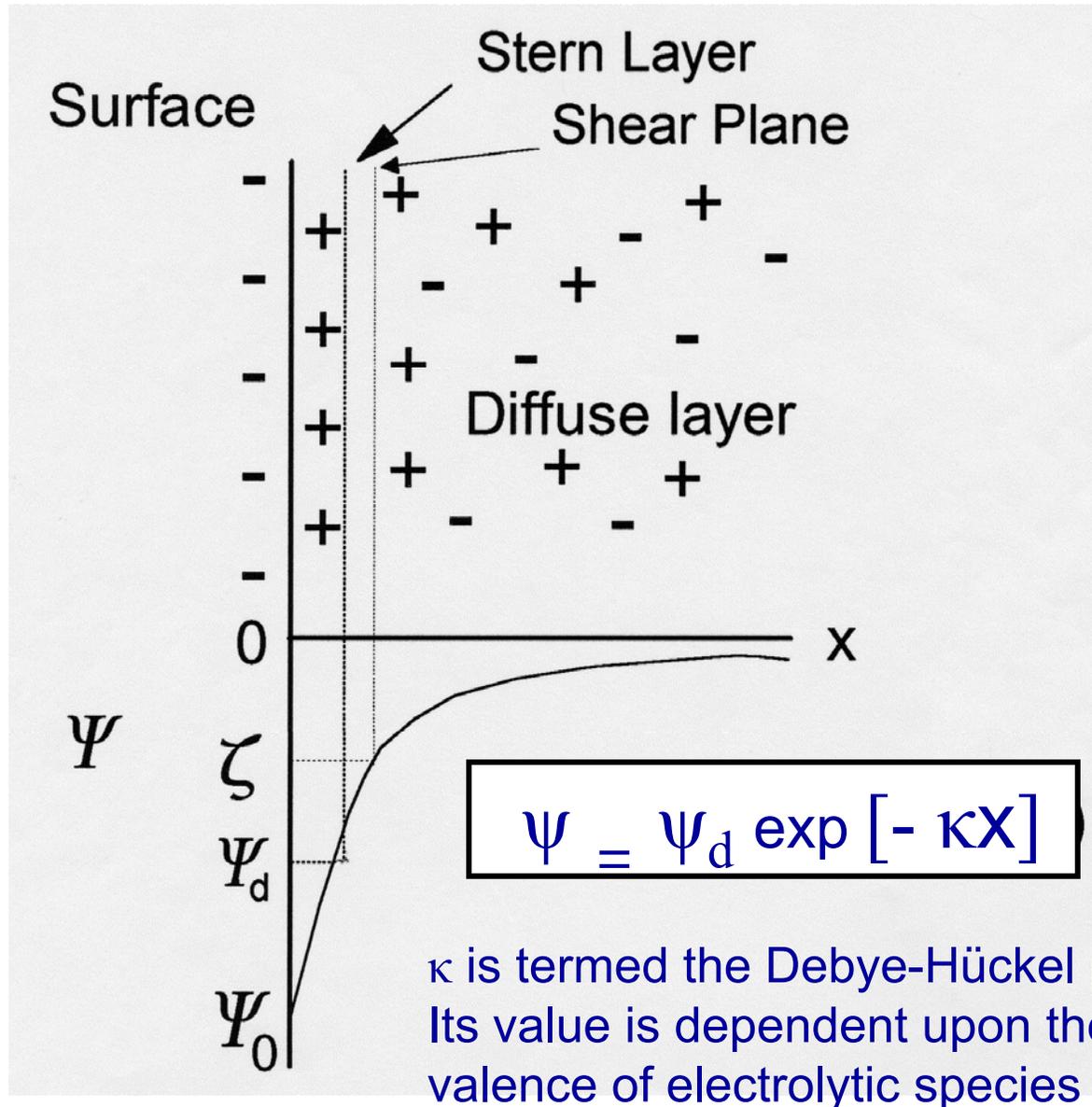
1nm particle size:

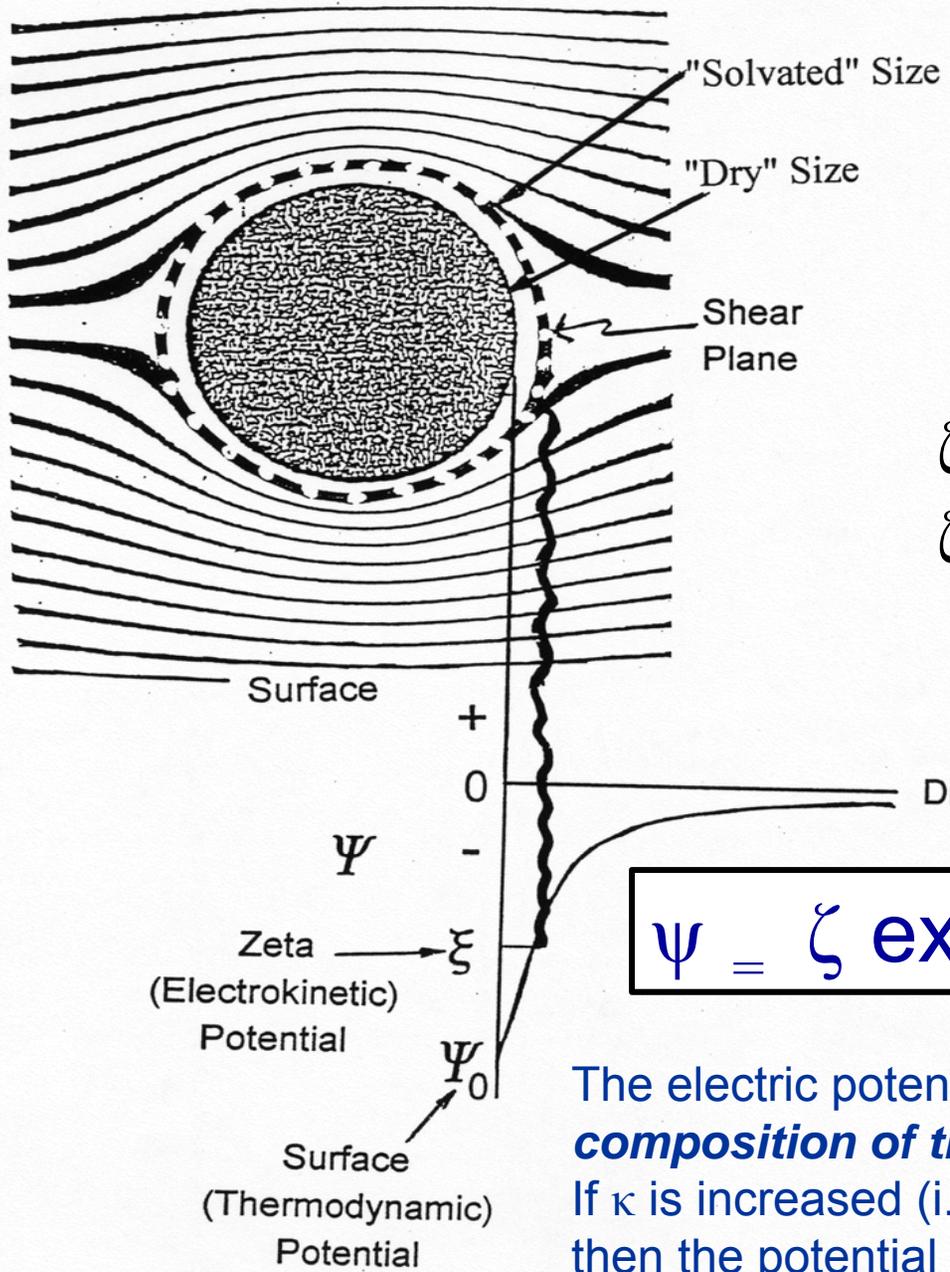
80% of the atoms are on the surface

A typical micellar solution containing 0.1M amphiphile has $\sim 4 \times 10^4$ m² of micellar-water interfacial area per liter of solution!

For nano-size systems **surface charge effects** play a dominant role in determining the physicochemical properties (surface chemical activity) of the system as a whole

The Electric Double Layer





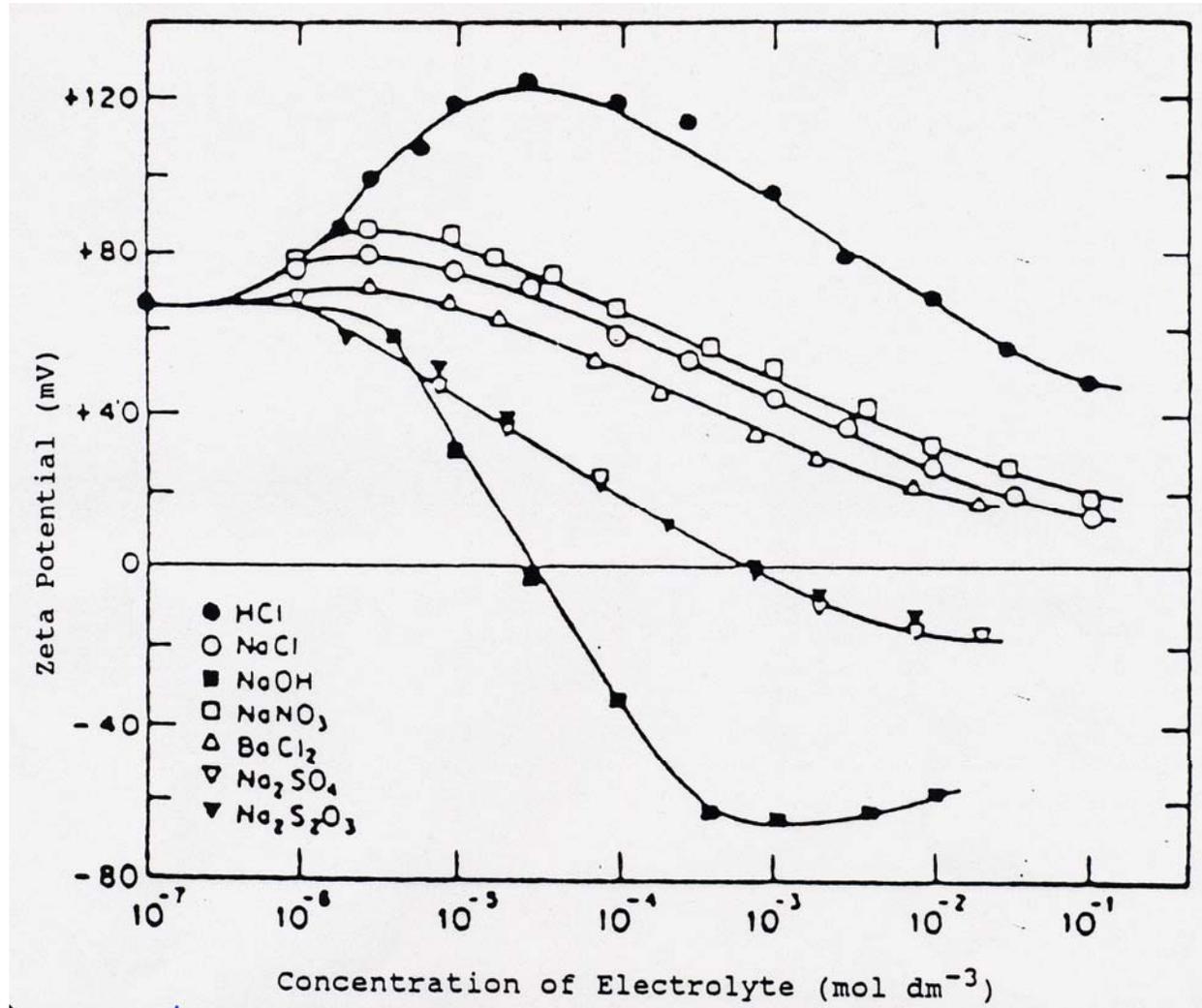
Ψ_0 - cannot be measured
 Ψ_d - mathematical concept

ζ - experimental parameter
 $\zeta \approx \Psi_d$

$$\Psi = \zeta \exp[-\kappa x]$$

The electric potential *depends* (through κ) **on the ionic composition of the medium.**
 If κ is increased (i.e. the electric double layer is "compressed") then the potential must decrease

Zeta Potential of Corundum (Al_2O_3) in Solution of Various Electrolytes



Zeta Potential: The “Effective” Surface Charge in solution

Depends upon:

- Fundamental “surface” sites – how many, what type
- Solution conditions – temperature, pH, electrolyte concentration

Useless to quote a zeta potential value without specifying suspension conditions

Calculation of the zeta potential

ζ is not determined directly

Most common measurement technique:
microelectrophoresis (ELS/PALS)



SZ-100
nano particle analyzer

Electrophoretic mobility,

$$U_E = V_p / E_x$$

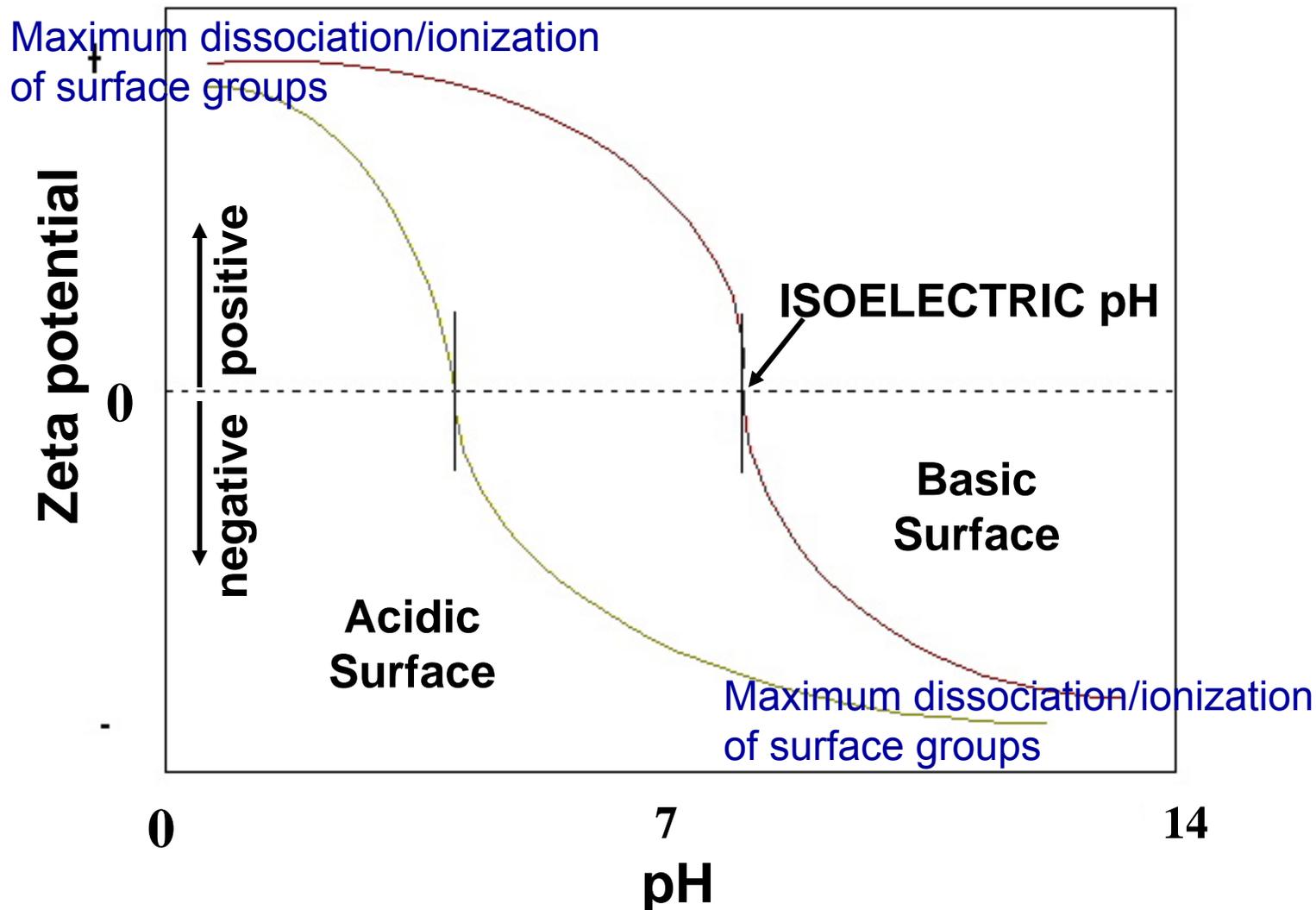
V_p is the particle velocity ($\mu\text{m/s}$) and E_x is the applied electric field (Volt/cm)

Relation between ζ and U_E is non-linear: $U_E = 2\varepsilon\varepsilon_0 \zeta F(\kappa a) / 3\eta$

The Henry coefficient, $F(\kappa a)$, is a complex function of ζ

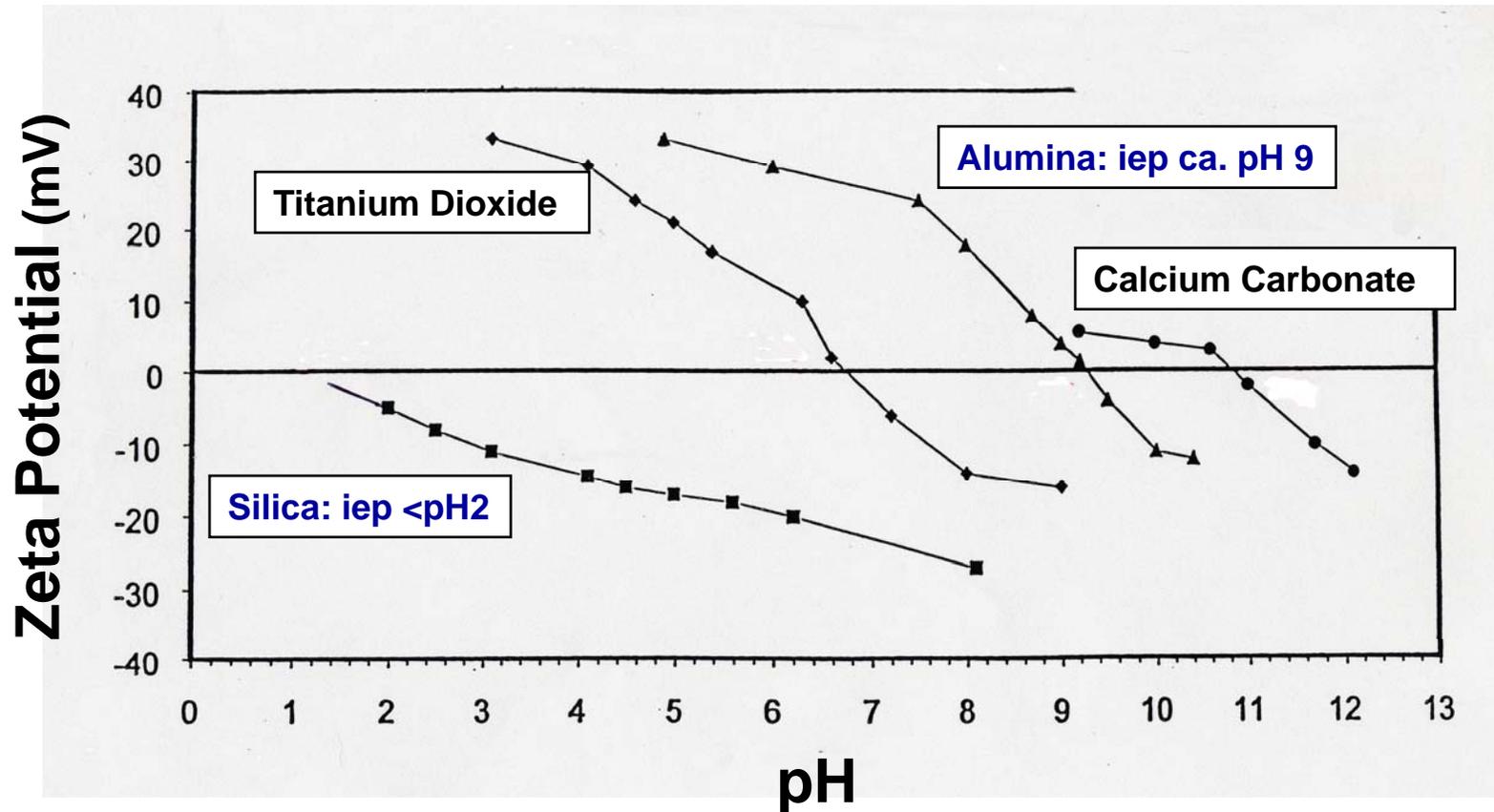
All modern commercial instruments provide both the measured electrophoretic mobility and an estimation of the zeta potential

The Effect of pH on Zeta Potential



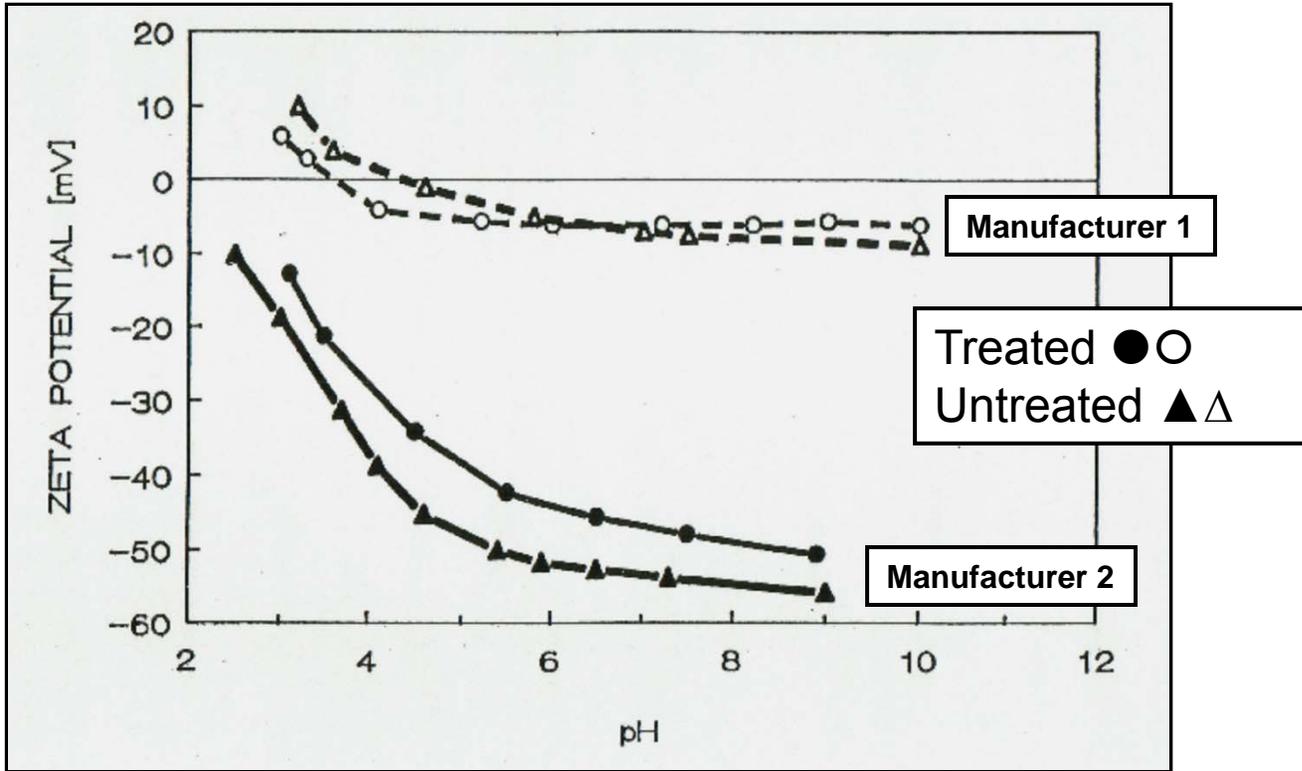
Imperative to determine ZP vs pH profile for any CMP agent prior to use

Aqueous Isoelectric Points of Silica and Alumina



The IEP can vary batch-to-batch and lot-to-lot

Zeta Potential of Two Commercial Colloidal Silicas



Always check ZP/pH profile when substituting material from different suppliers

Slurry Zeta Potential and the Polishing of Optical Glass

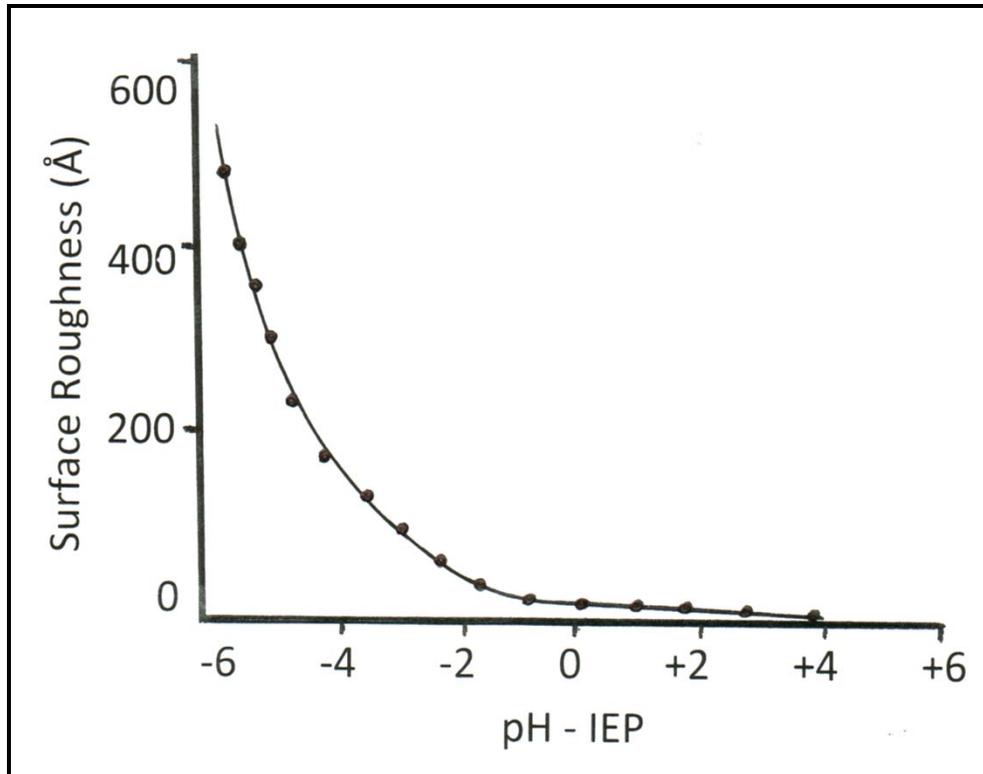
Glass: Corning 7940 Fused Silica (IEP: 3.5)

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 ZP of the polishing slurries varies with solution pH
⊕ positive or negative depending upon the metal oxide IEP

Slurry Zeta Potential and Glass Surface Roughness

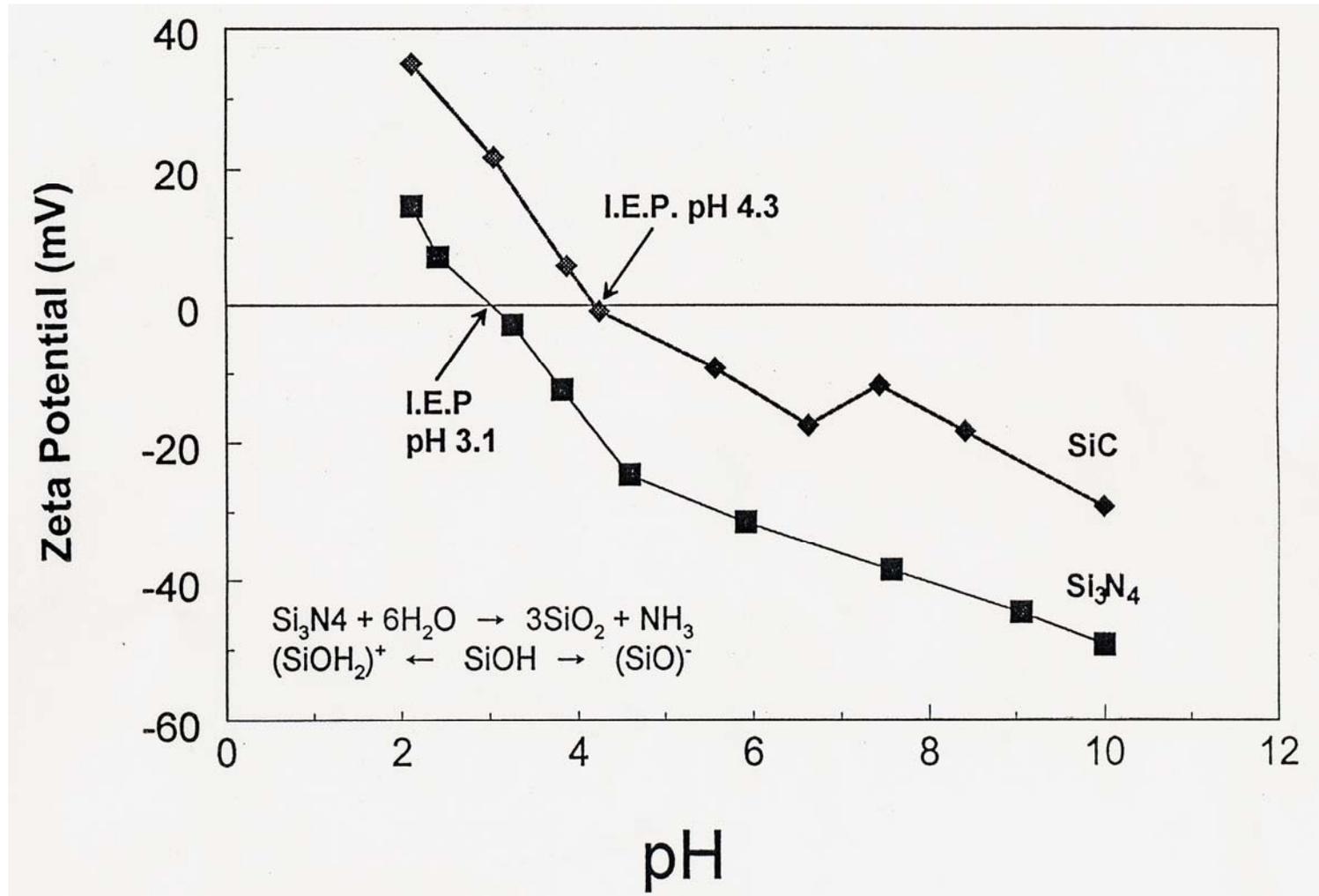


The glass surface roughness depends upon the difference in fluid pH and the IEP of the polishing agent

The more positive the difference the smoother the surface

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

Zeta Potential of Non-oxides



The ZP value affected by presence of surface impurities and contamination

In Conclusion

Surface Charge is a fundamental parameter that impacts the performance of CMP agents

The polishing efficiency of CMP slurries is dependent upon not just the metal oxide particle size but also the hydroxyl [OH] concentration and state of dissociation

The Zeta Potential of aqueous suspensions of metal oxide polishing agents critically impacts polishing efficiency. It should be a basic QC measurement for all incoming material

In practice, either the CMP IEP must be $<$ fluid pH or the solution pH must be adjusted to a value $>$ CMP IEP



Q&A

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Thank you

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