

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



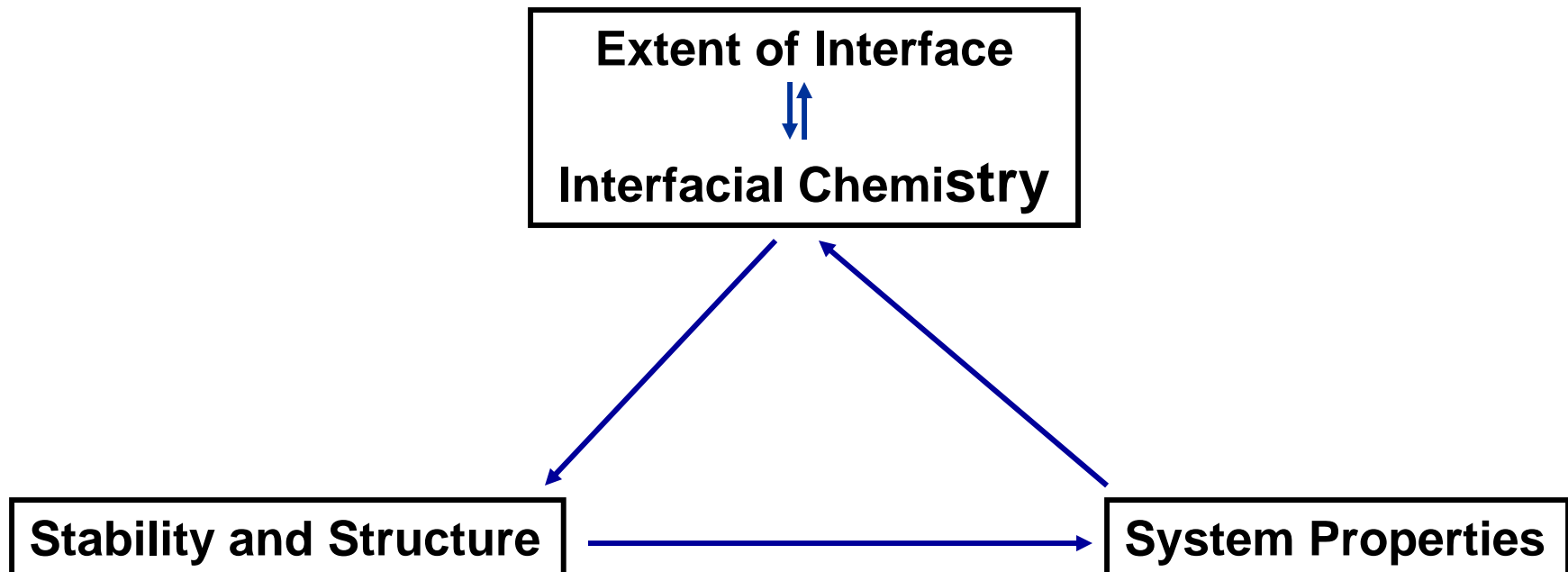
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**Colloid Consultants, Ltd**

HORIBA Scientific  
Webinar  
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# Dispersed Systems

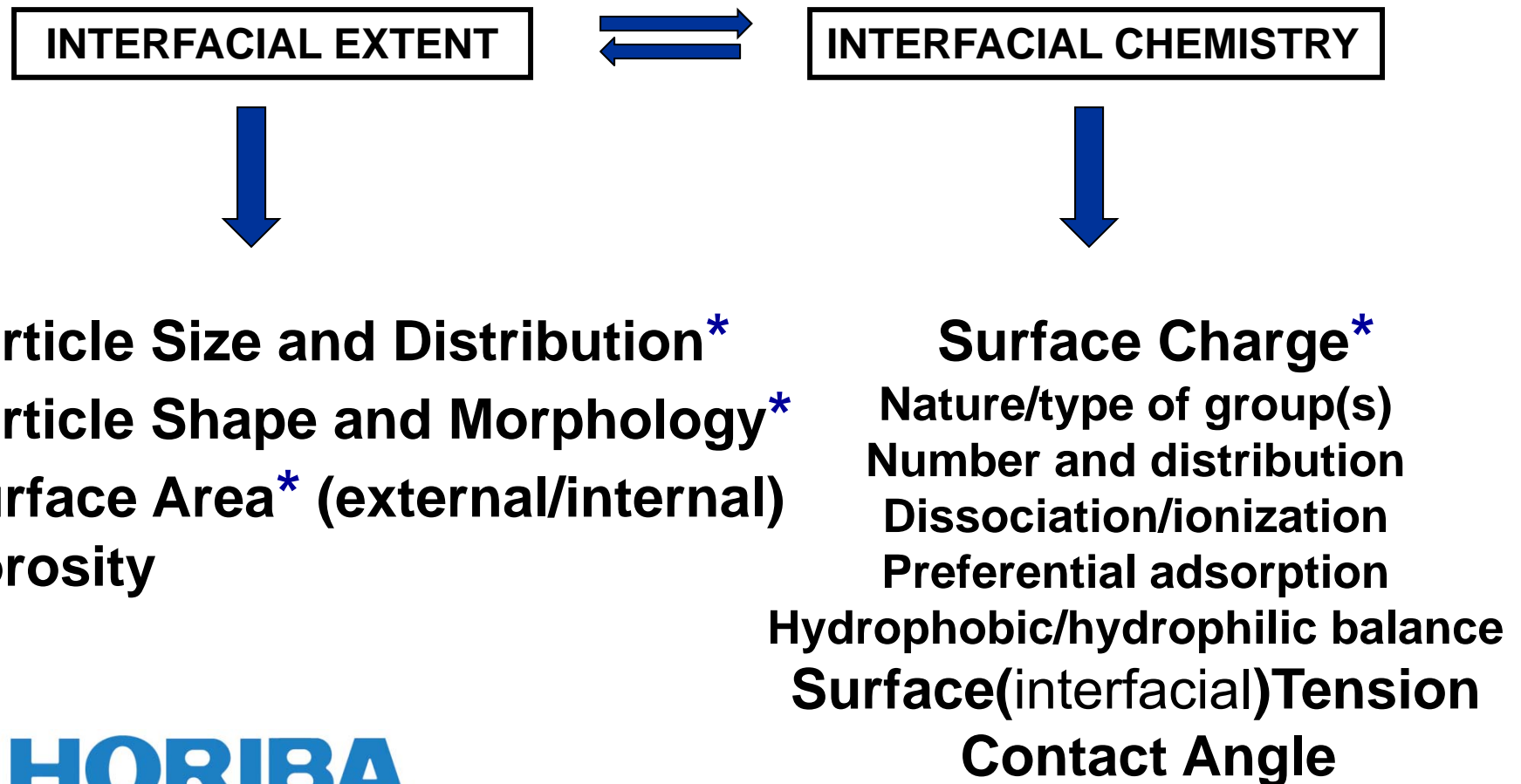
An **interface** always exists when one component (phase I) is dispersed in a state of subdivision in a medium (phase II)

**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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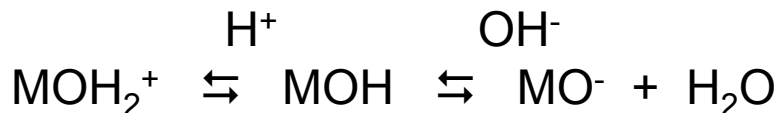
# The Nature of Surface Charge in Water

## Mineral oxide crystal lattices are anisotropic

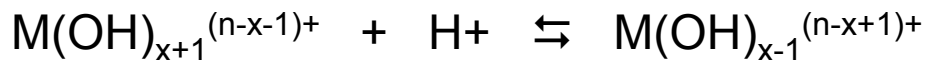
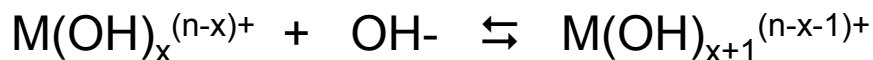
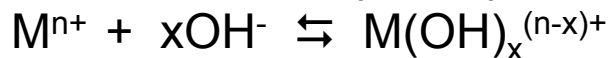
- ❑ charge development because of  $n$  and  $p$  defects in crystal structure
- ❑ results in hydroxyl groups (-OH)  $\oplus$  can undergo reaction with either  $H^+$  or  $OH^-$
- ❑ difficult to control surface chemistry in manufacture and processing
  - ❑ reactant impurities

## Metal Oxide Surfaces in Water

Adsorption of protons and hydroxyl ions  $\oplus$



Formation of hydroxylated species



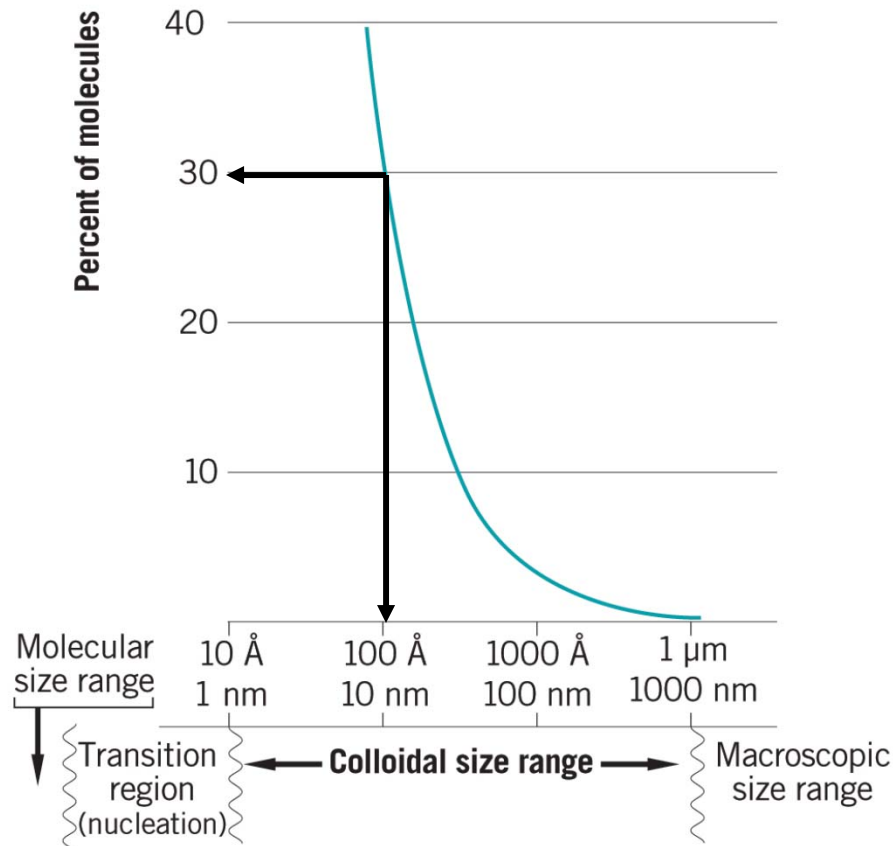
Dissociation driven by pH

$\oplus$  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”

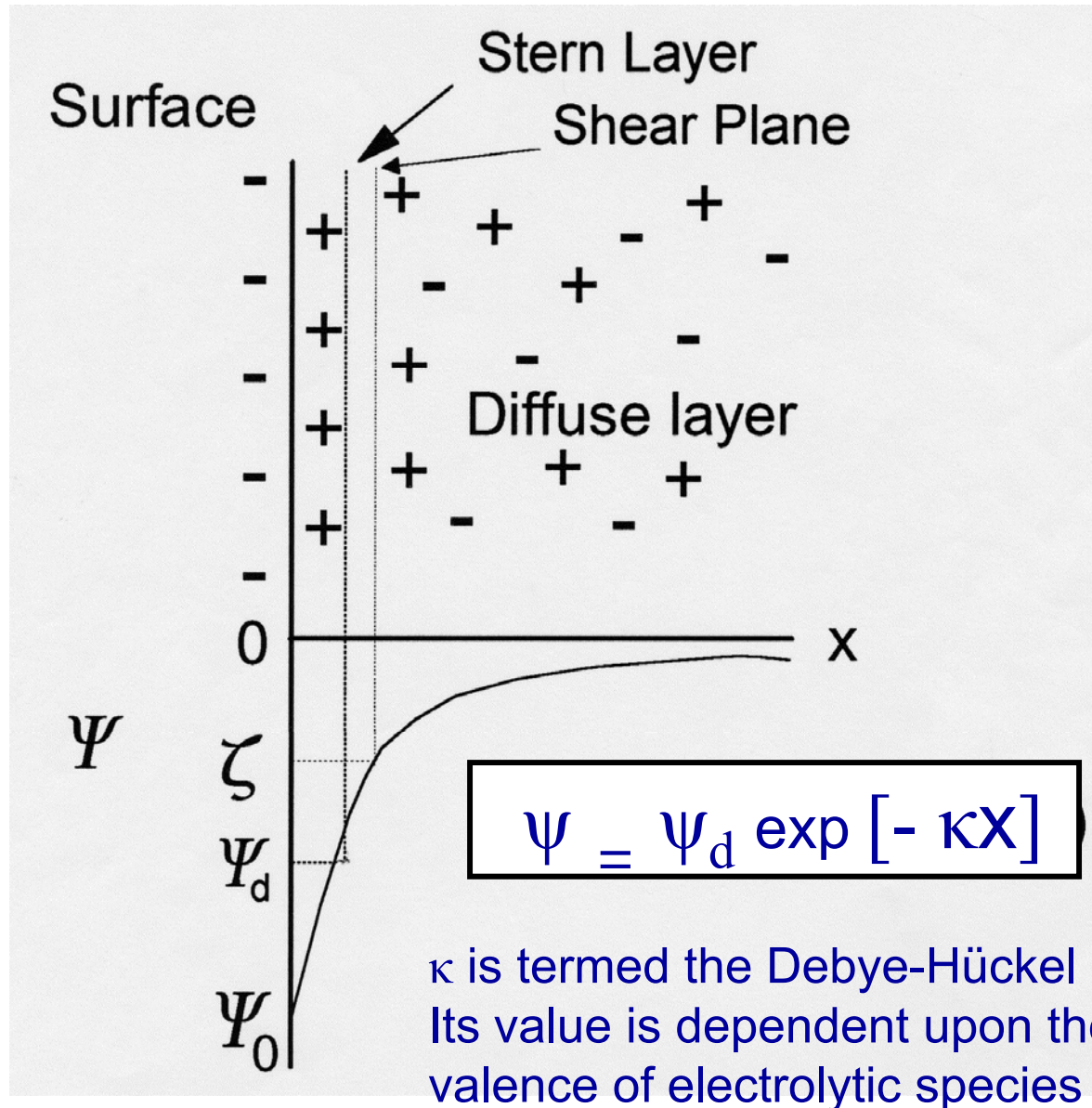
## 1nm particle size:

80% of the atoms are on the surface

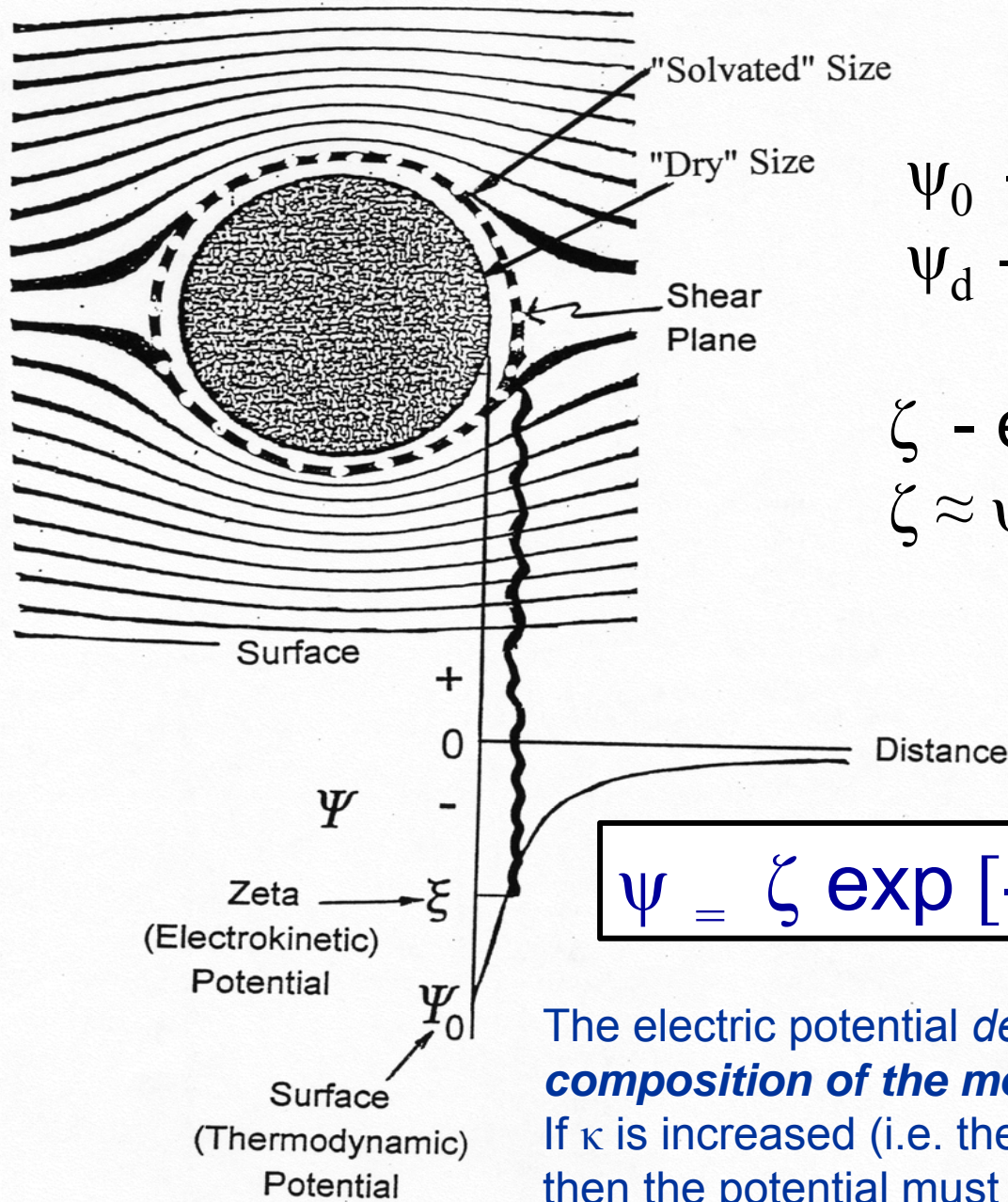
A typical micellar solution containing 0.1M amphiphile has  $\sim 4 \times 10^4 \text{ m}^2$  of micellar-water interfacial area per liter of solution!

**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







$\psi_0$  - cannot be measured  
 $\psi_d$  - mathematical concept

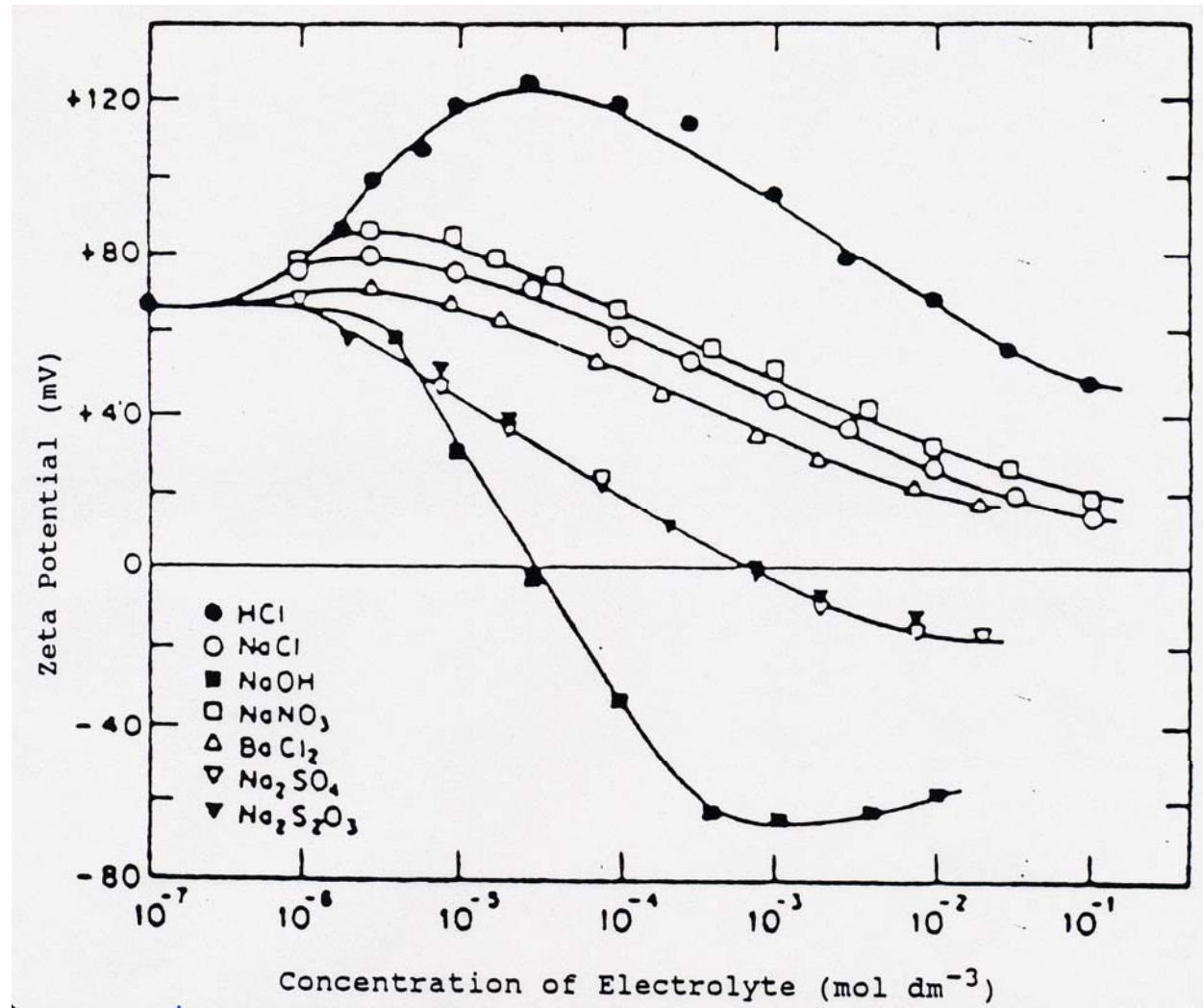
$\zeta$  - experimental parameter  
 $\zeta \approx \psi_d$

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

The electric potential *depends* (through  $\kappa$ ) ***on the ionic composition of the medium.***

If  $\kappa$  is increased (i.e. the electric double layer is "compressed") then the potential must decrease

# Zeta Potential of Corundum ( $\text{Al}_2\text{O}_3$ ) 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

$\zeta$  is not determined directly

Most common measurement technique:  
microelectrophoresis (ELS/PALS)

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

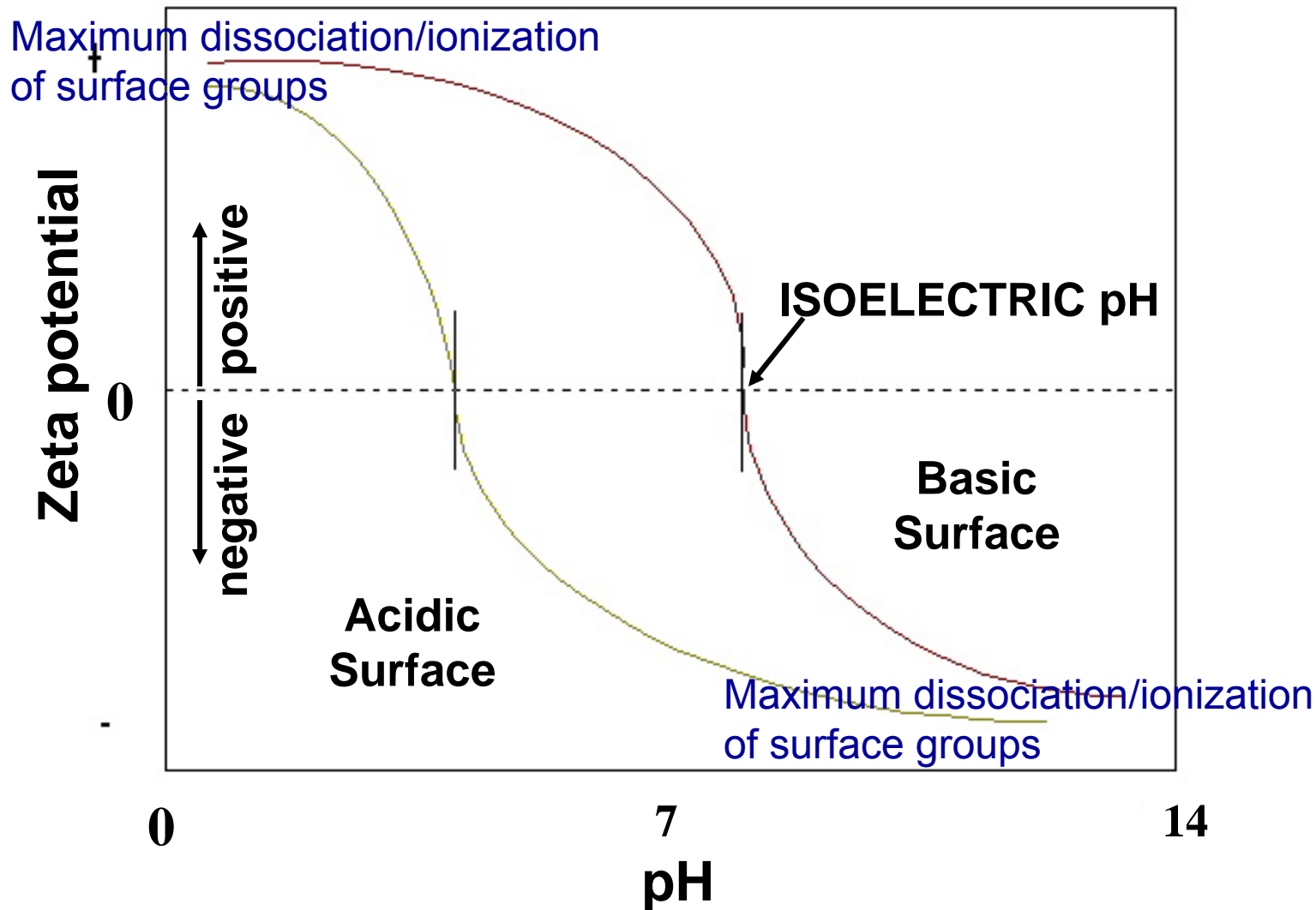
The Henry coefficient,  $F(\kappa a)$ , is a complex function of  $\zeta$



**SZ-100**  
nano particle analyzer

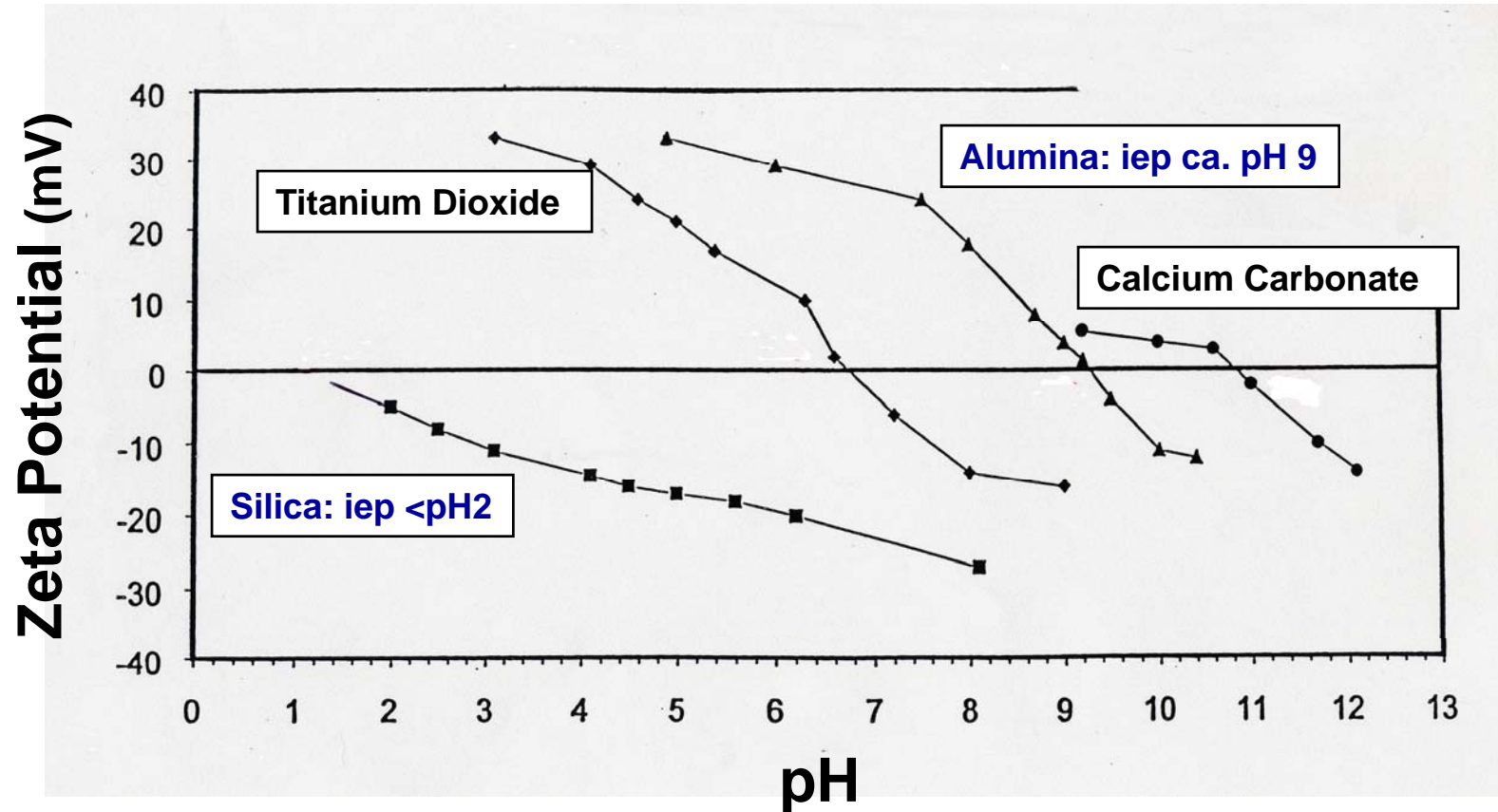
All modern commercial instruments provide both the measured electrophoretic mobility and an estimation of the zeta potential

# The Effect of pH on Zeta Potential



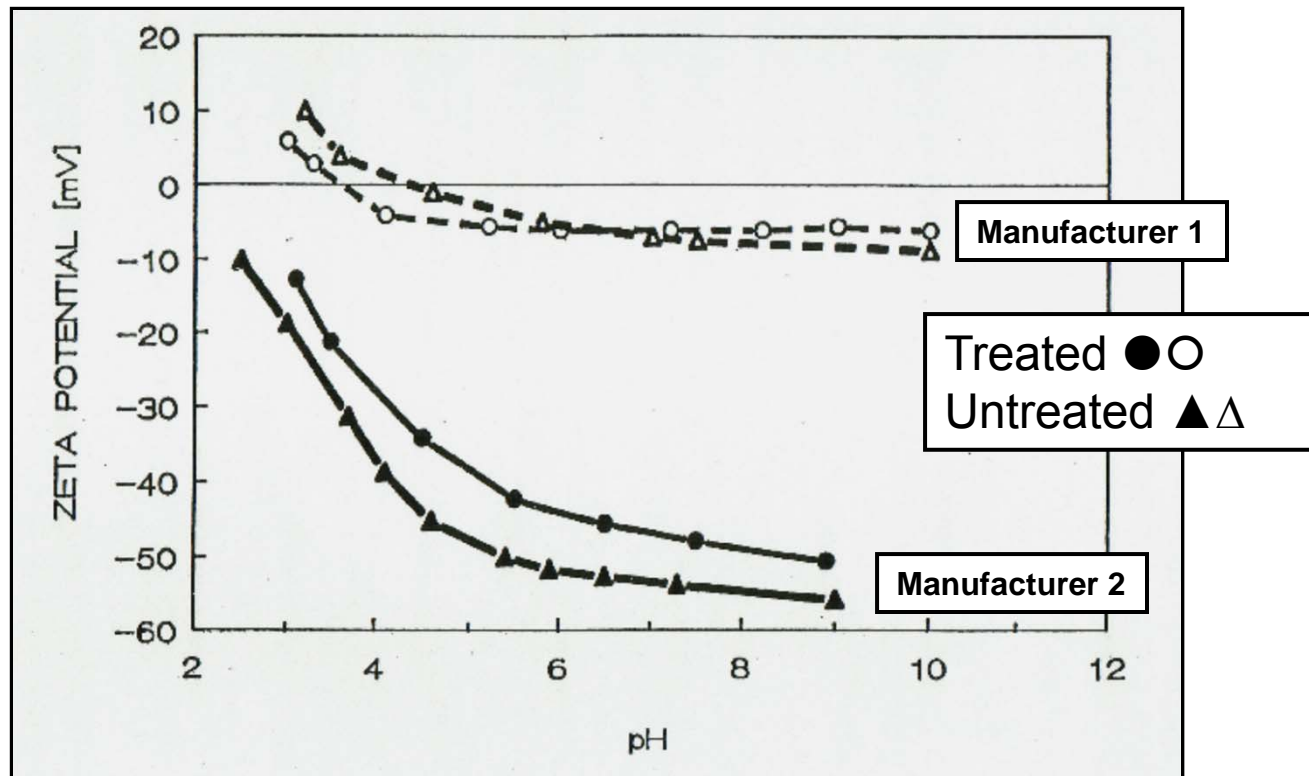
Imperative to determine ZP vs pH profile for any CMP agent prior to use

# 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

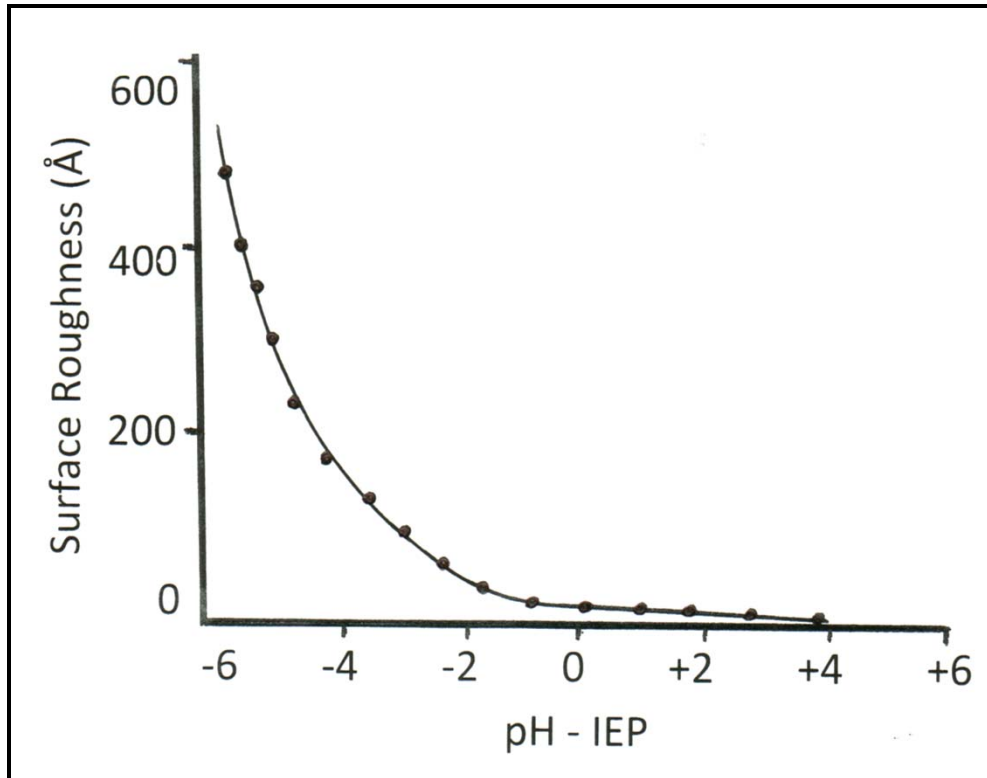
Glass: Corning 7940 Fused Silica (IEP: 3.5)

Polishing agents:  $\text{CeO}_2$ ,  $\text{ZrO}_2$  (monoclinic) and  $\text{Al}_2\text{O}_3$  (nanocrystalline)

Polishing Agent	IEP	Surface Charge at pH 4	Surface Charge at pH 7	Surface Charge at pH 10
$\text{ZrO}_2$	6.3	++	-	- - -
$\text{CeO}_2$	8.8	++++	++	- -
$\text{Al}_2\text{O}_3$	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

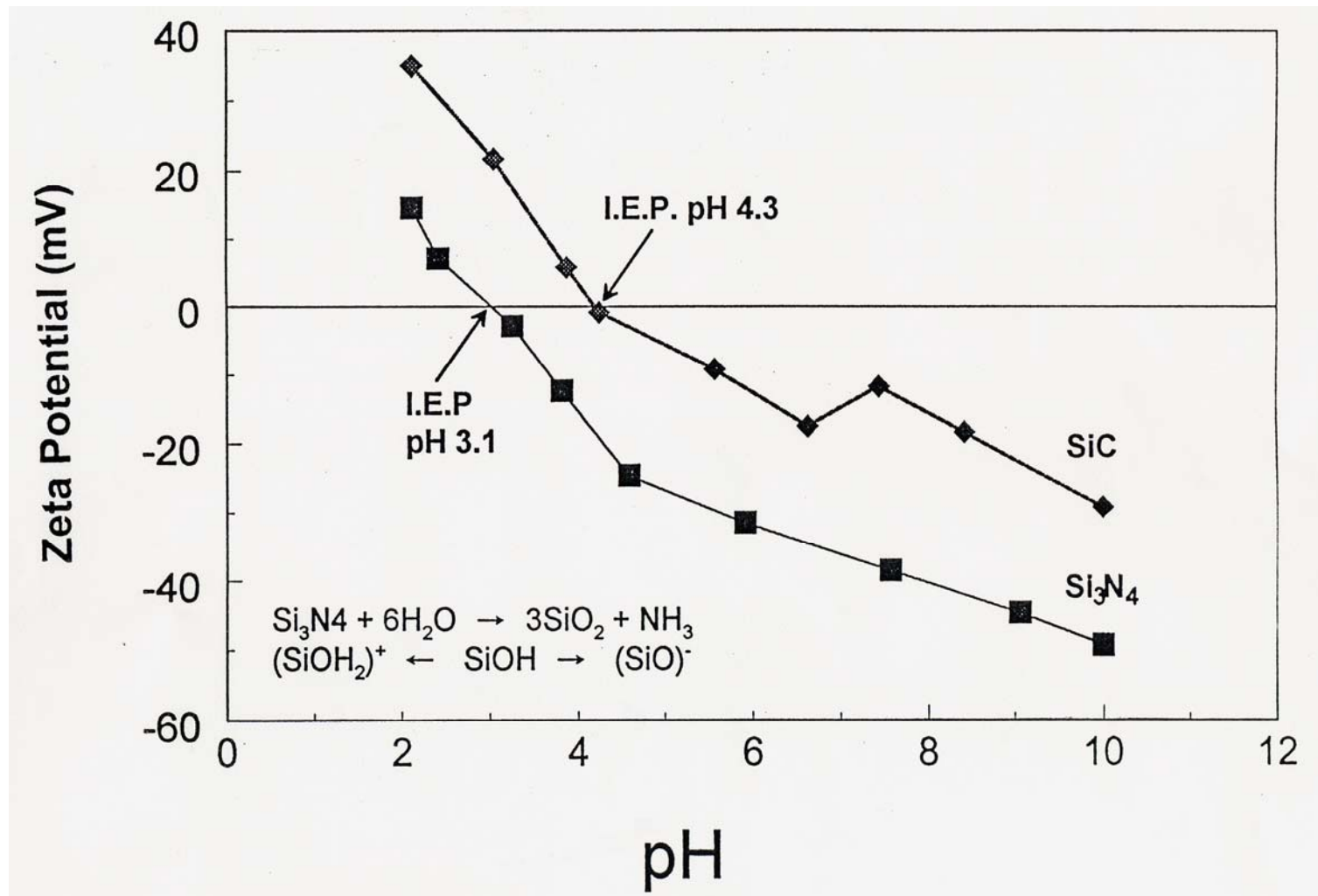


The glass surface roughness depends upon the difference in fluid pH and the IEP of the polishing agent

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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