An Overview of the Concept, Measurement, Use and Application of Zeta Potential

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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

How Particle Surfaces Acquire a Charge in Water

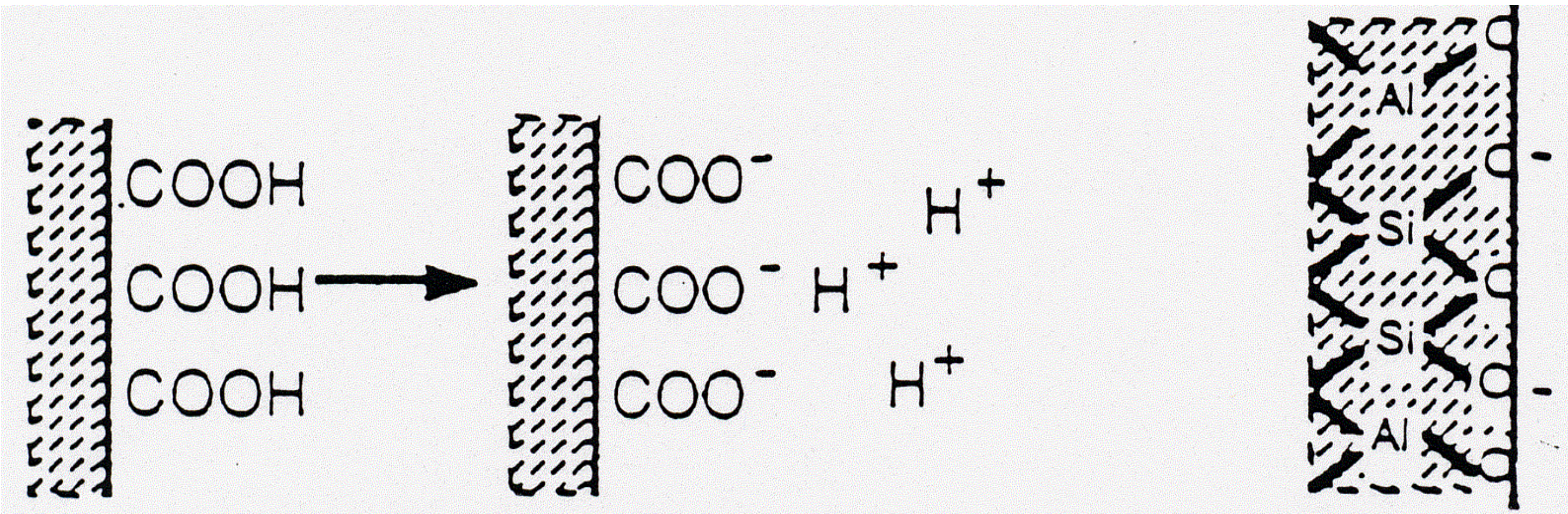
(a) Differential ion solubility

Net positive surface charge

Net negative surface charge

How Particle Surfaces Acquire A Charge in Water

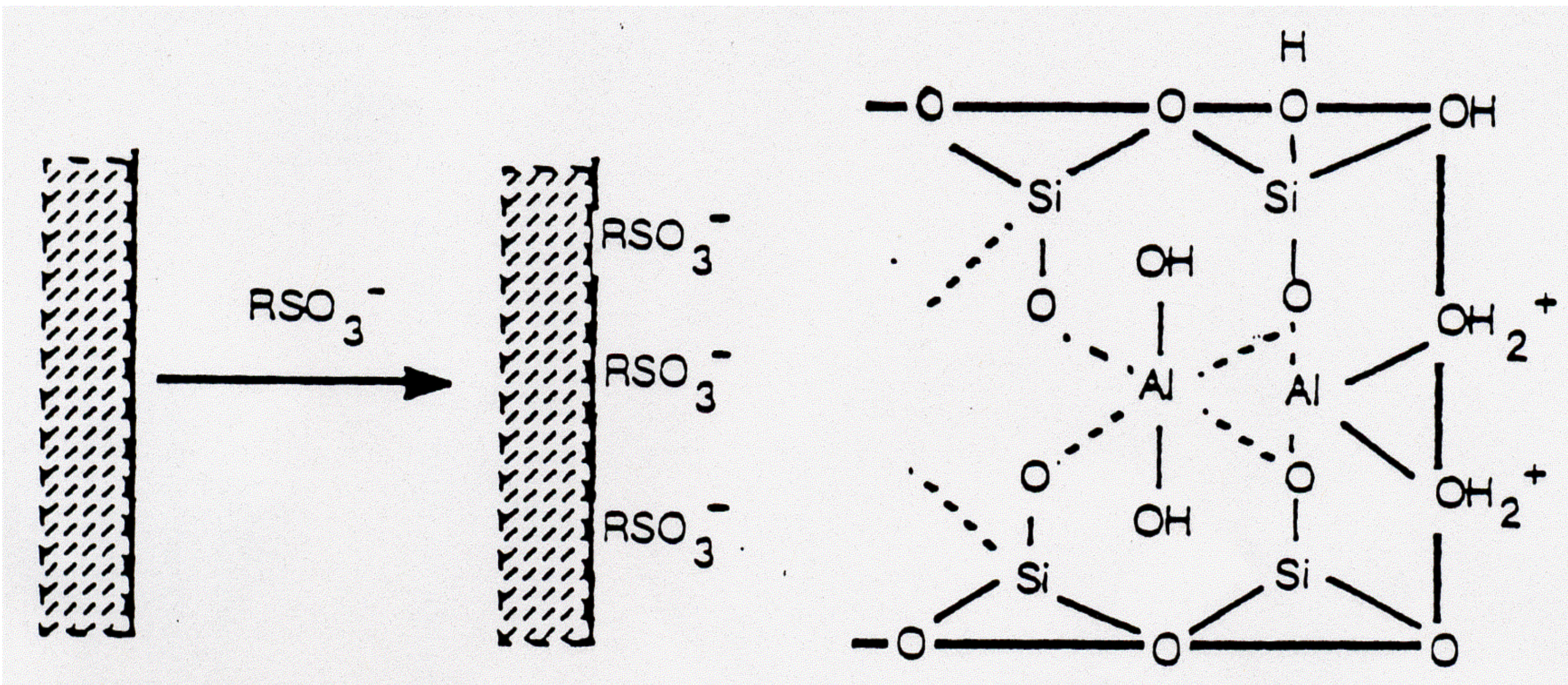
(b) Direct ionization of
surface groups



(c) Isomorphous ion
substitution

How Particle Surfaces Acquire a Charge in Water

(d) Specific ion adsorption



(e) Anisotropic crystals

Origin of Charge in Clays

Isomorphic Substitution	**FACE**
Lattice Imperfections	**-ve**
Broken Bonds	**EDGE**
Exposed Structural OH	**+ve**

In neutral water, *net* charge will usually be *negative*

Particle Association: **F – F E – F E – E**

Many structures are possible

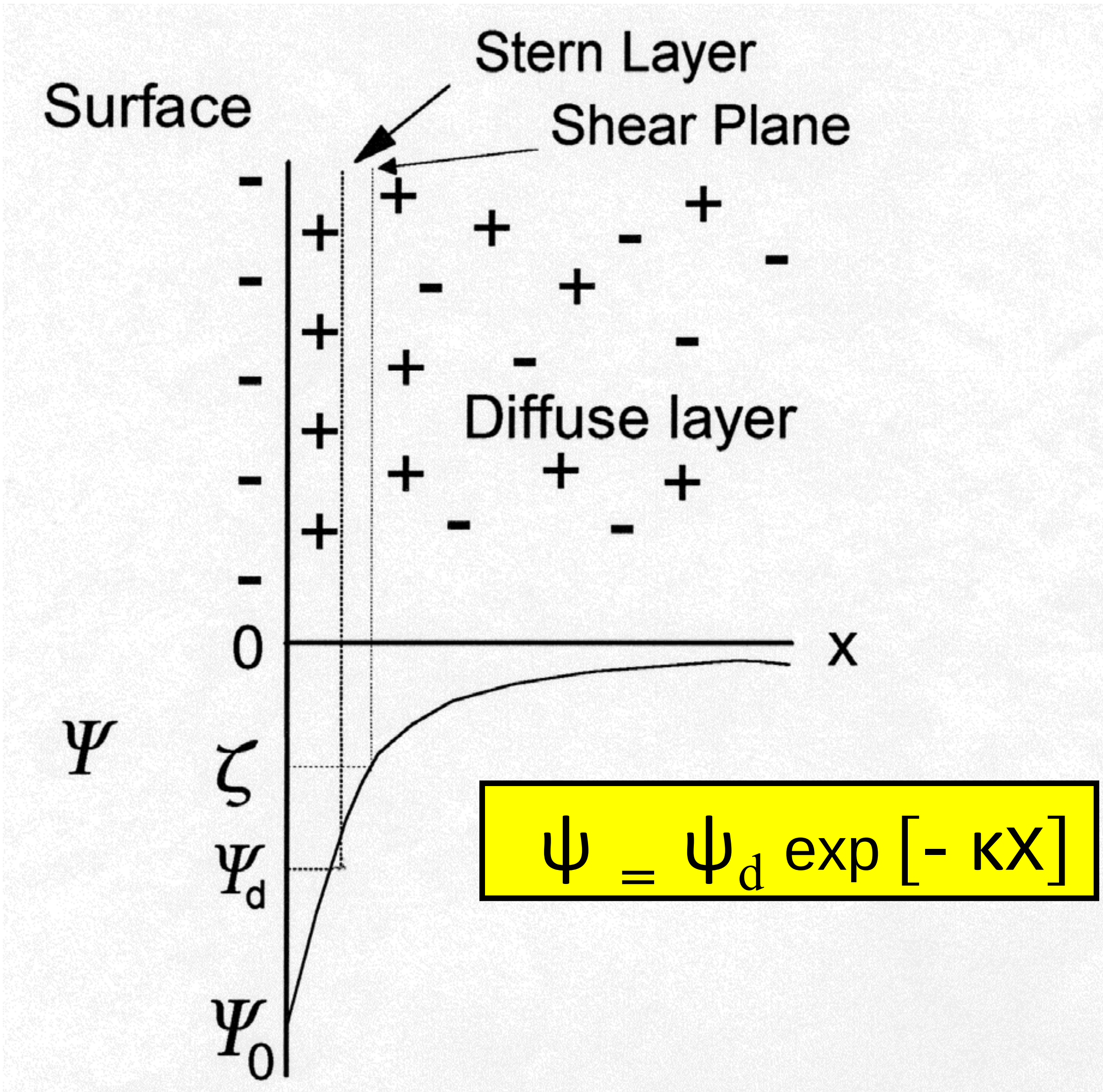
Particle Charges of Various Surfaces in Neutral Water

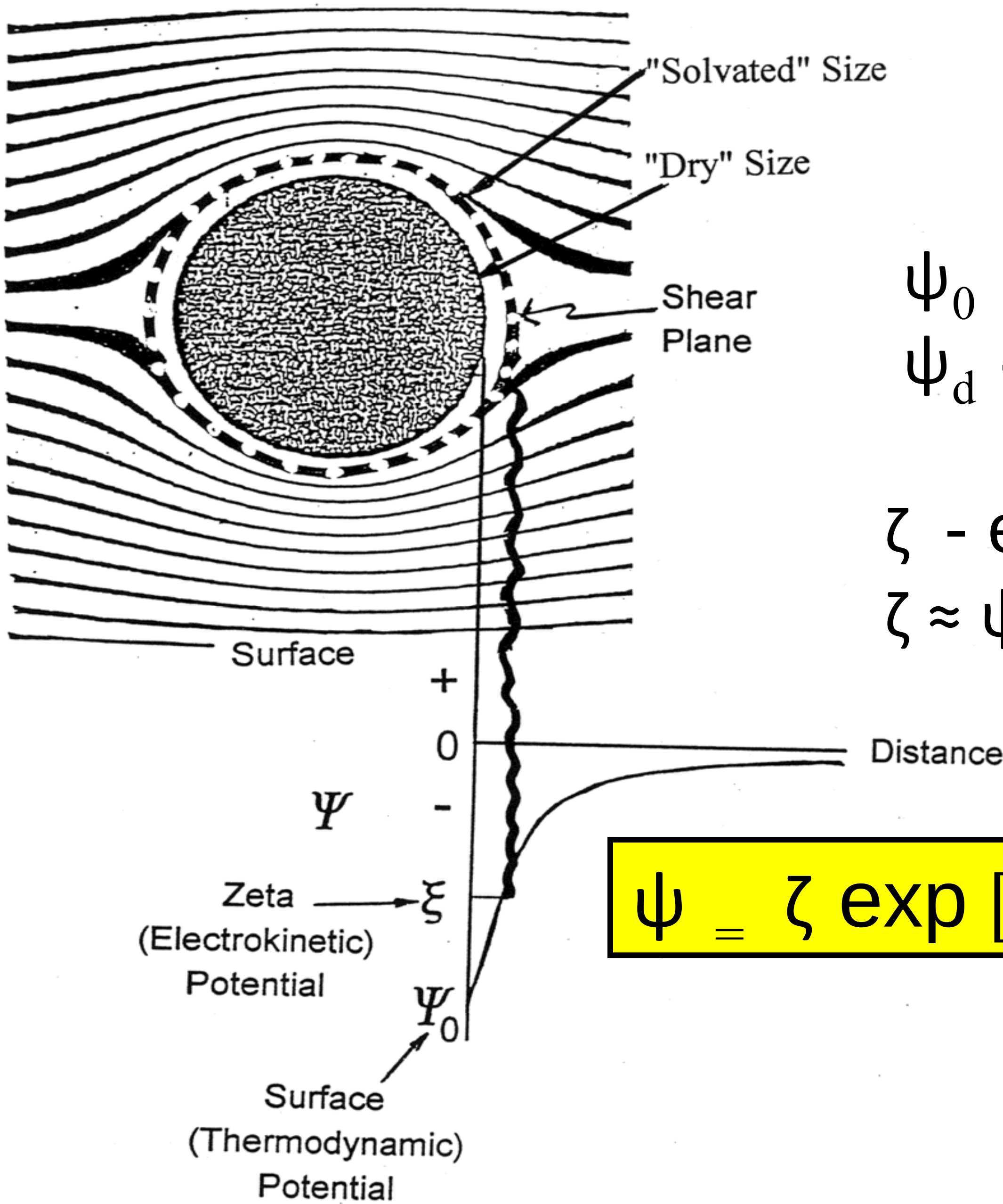
Positive	Negative
Ferric Hydroxide	Silicon Dioxide
Aluminium Hydroxide	Au, Ag, Pt, S, Se
Chromium Hydroxide	As_2S_3, PbS, CuS
Thorium Oxide	Acidic Dyes
Zirconium Oxide	(Congo Red)
Basic Dyes	Acid Protein
(Methylene Blue)	(Casein, BSA)
Base Proteins	Viruses, Microbes
(Protamines, Histones)	Air bubbles

Charge in non-aqueous media often opposite in sign!

(Electron Donor - Acceptor Theory)

The Electric Double Layer





ψ_0 - cannot be measured

ψ_d - mathematical concept

ζ - experimental parameter

$\zeta \approx \psi_d$

$$\boxed{\psi = \zeta \exp[-\kappa x]}$$

The Debye-Hückel parameter, κ , defined as:

$$\kappa = [2e^2 N_A c z^2 / \varepsilon\varepsilon_0 k_b T]^{1/2}$$

The Debye length, κ^{-1} is a measure of the "electric double layer thickness"

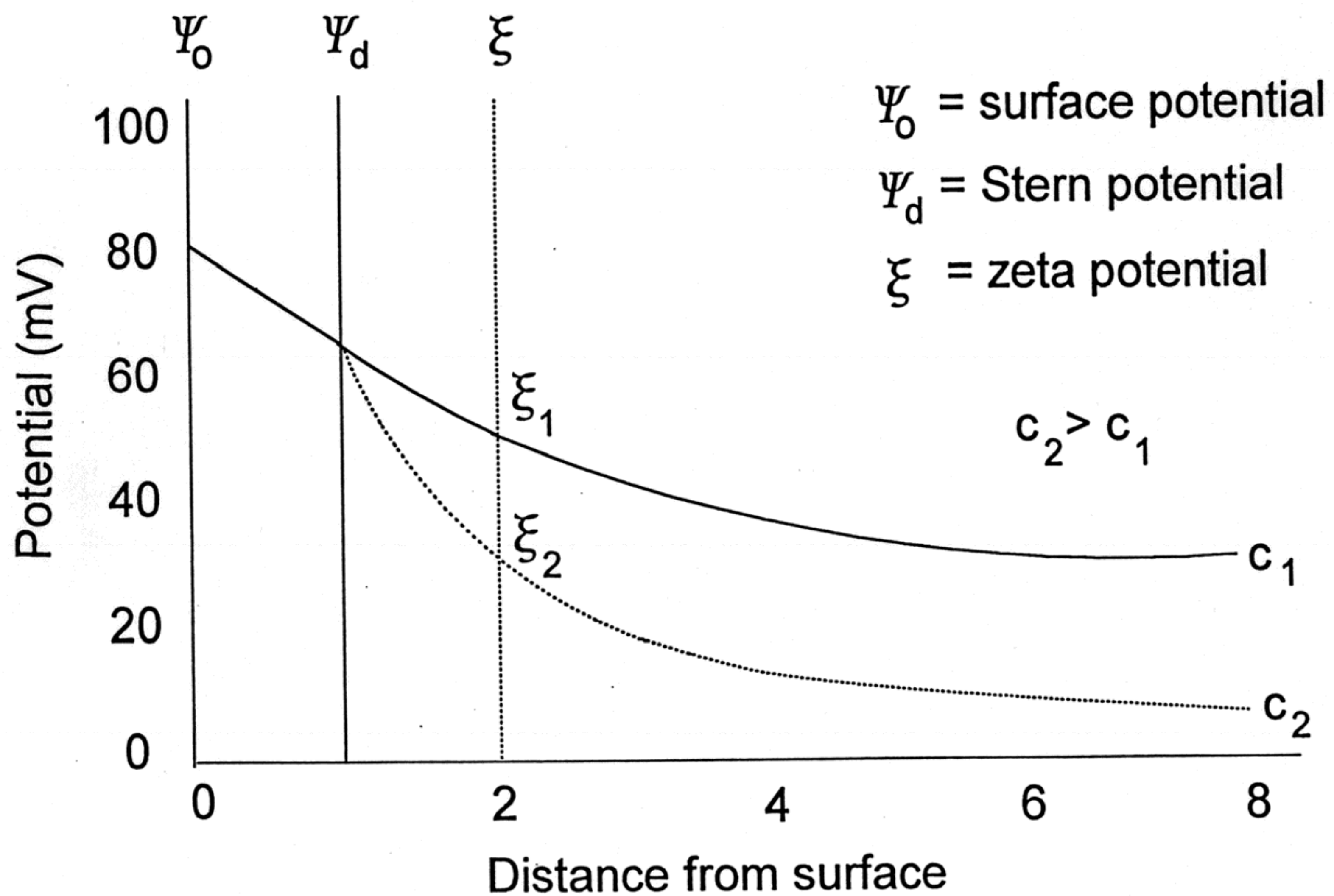
For single symmetrical electrolyte:

$$\boxed{\kappa^{-1} = 0.3041/\, Z\, C^{1/2}}$$

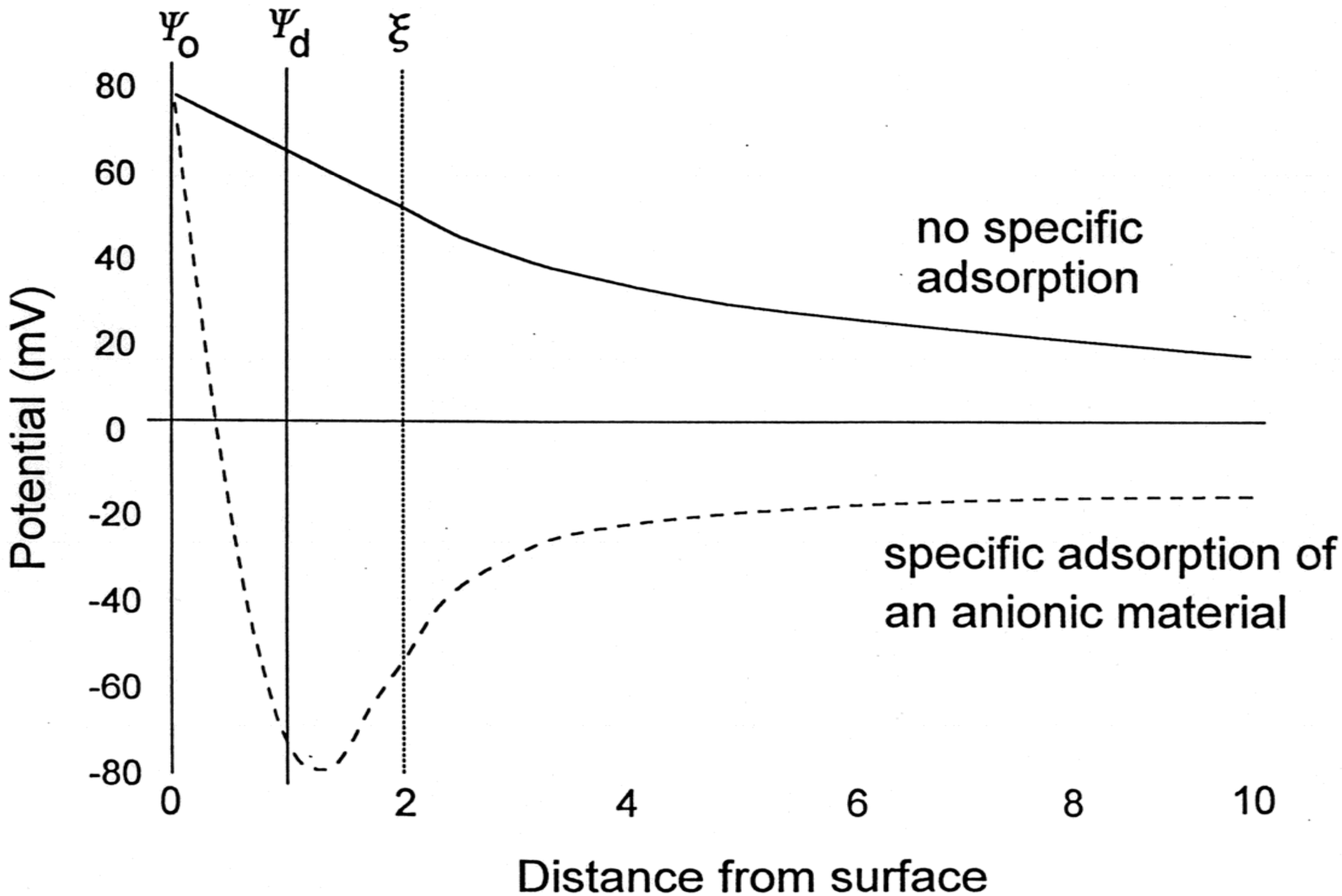
c is the concentration of electrolyte of valence, z

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.

Effect of addition of electrolyte on the zeta potential



Effect of specific adsorption of an anion on the zeta potential of a cationic surface



Zeta Potential is the “effectiveness” of the 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 technique:
microelectrophoresis (ELS/PALS)

SZ-100
nano partica **analyzer**

Electrophoretic mobility,
$U_E = V_p/E_x$

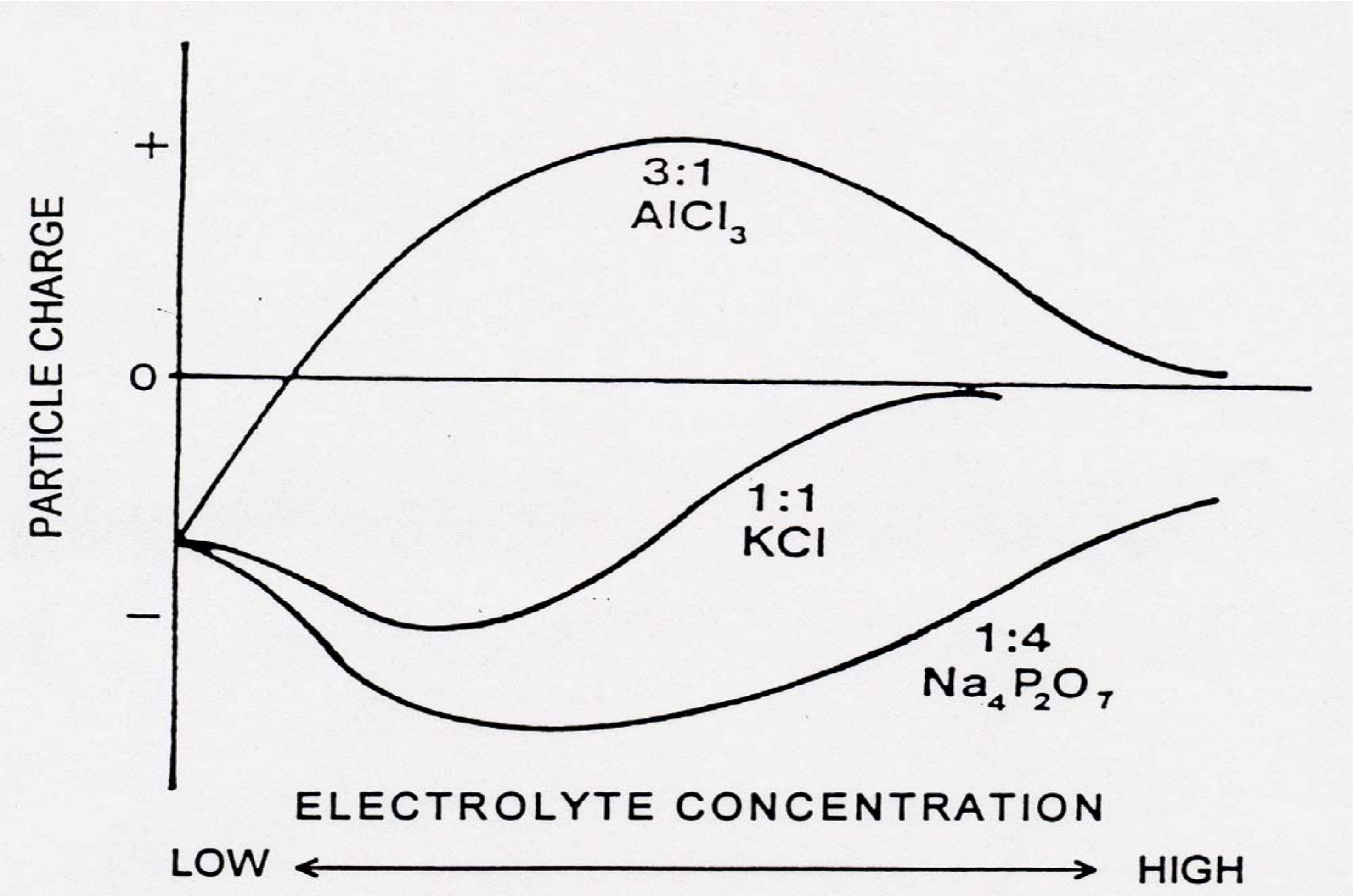
V_p is the particle velocity (μm/s) and E_x is the applied electric field (Volt/cm)

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

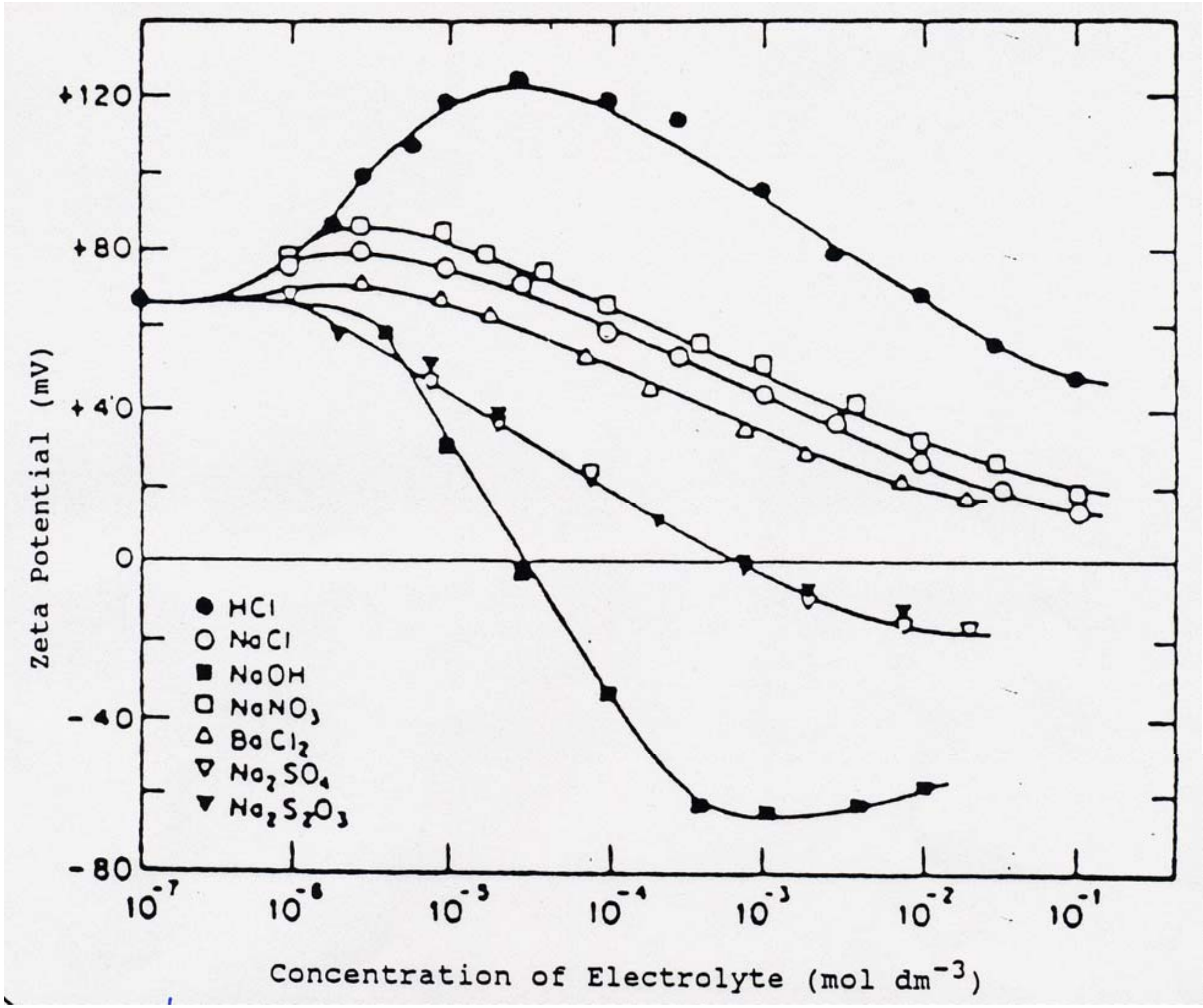
The Henry coefficient $F(\kappa a)$ is a complex function of ζ

Simplest solution: use electrophoretic mobility, U_E as the measurement metric

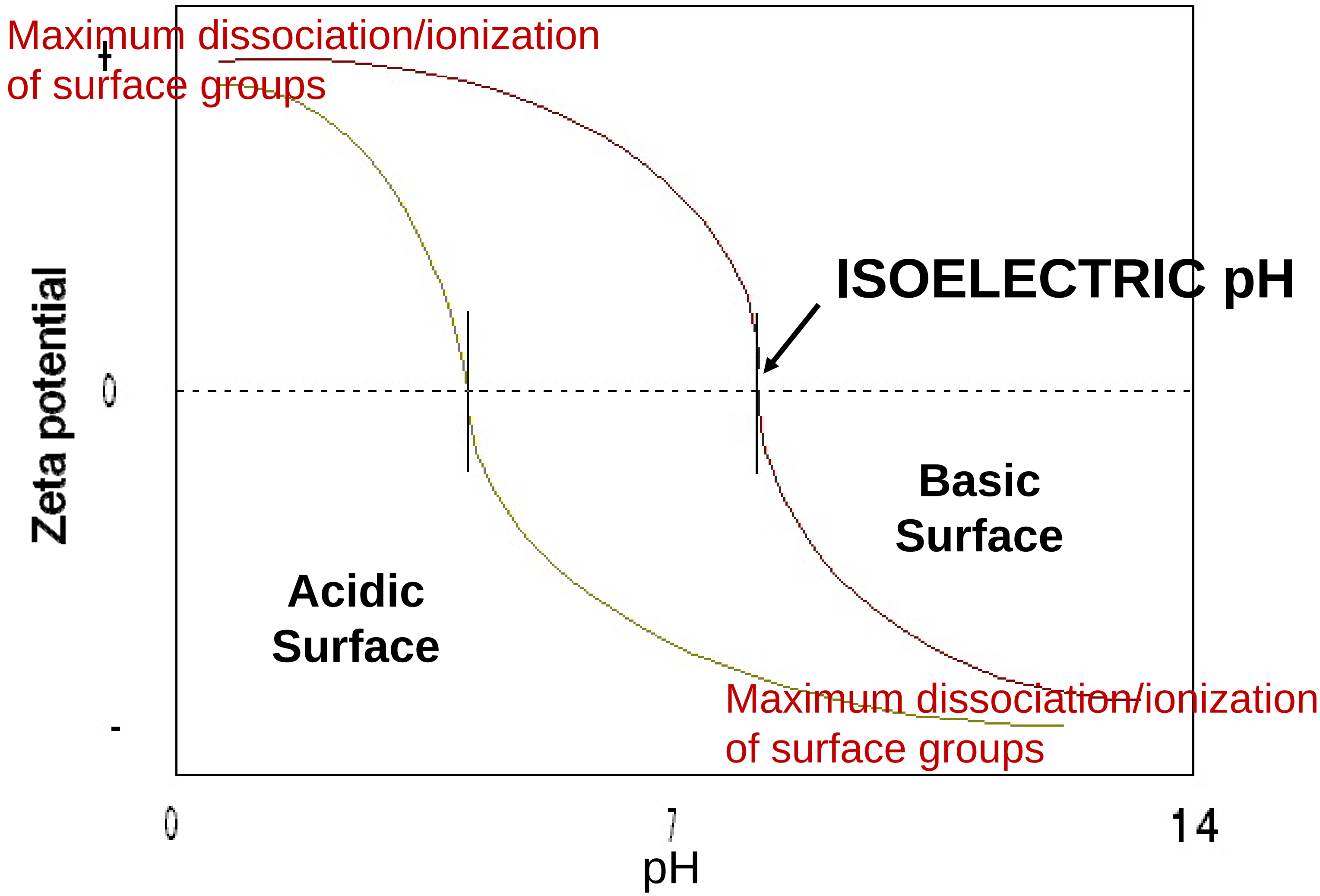
Effect of Electrolyte Concentration on Particle Charge



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

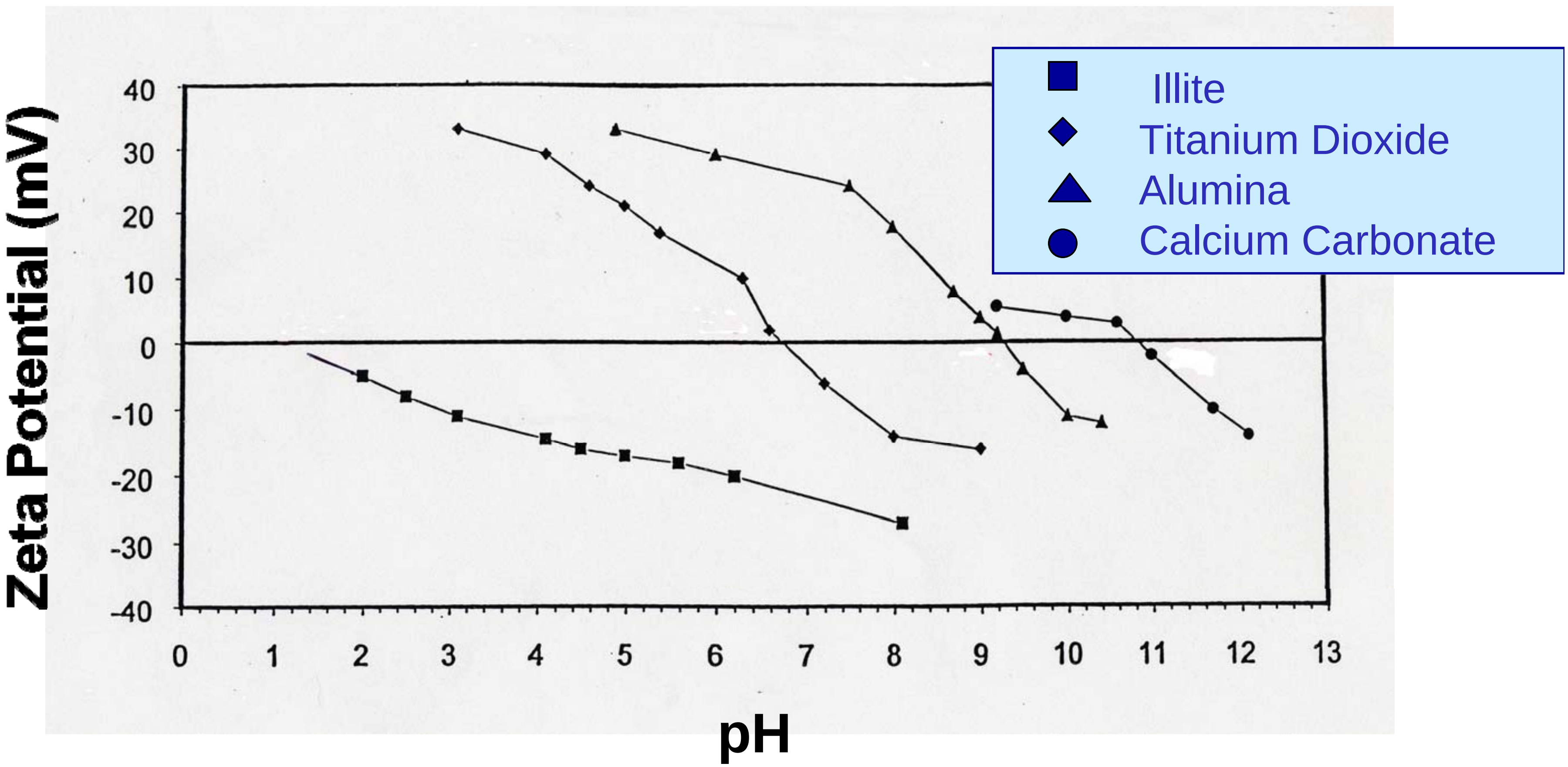


Effect of pH on Particle Charge



Sign of Zeta potential: pH(iep) – pH(solution)

Aqueous Isoelectric Points



Isoelectric Points of some Oxides

Oxide	pH value of I.E.P.
Silicon Dioxide	2
Manganese Dioxide	3
Zirconium Dioxide	4
Titanium Dioxide (Rutile)	6
Chromium Oxide	7
Iron Oxide	8
Aluminium Oxide	9
Lead Oxide	10
Cadmium Oxide	11
Magnesium Oxide	12

Force of Repulsion

$$V_R \approx D\ a\ \zeta^2 \exp(-K H)$$

D is a constant related to the permittivity (dielectric constant) of the material.

a is the particle or droplet radius.

ζ is a measure of the surface potential (charge).

K is proportional to the ionic strength ("conductivity").

H is the distance between particle surfaces.

For a fixed medium, particle size and zeta potential: repulsive force decreases as the ionic strength increases

For a fixed medium, particle size and ionic strength: repulsive force becomes larger with increase in zeta potential

Zeta potential and stability

Positive
zeta potential

STABLE

+10mV

Critical ZP range: NOT STABLE

-10mV

STABLE

Negative
zeta potential

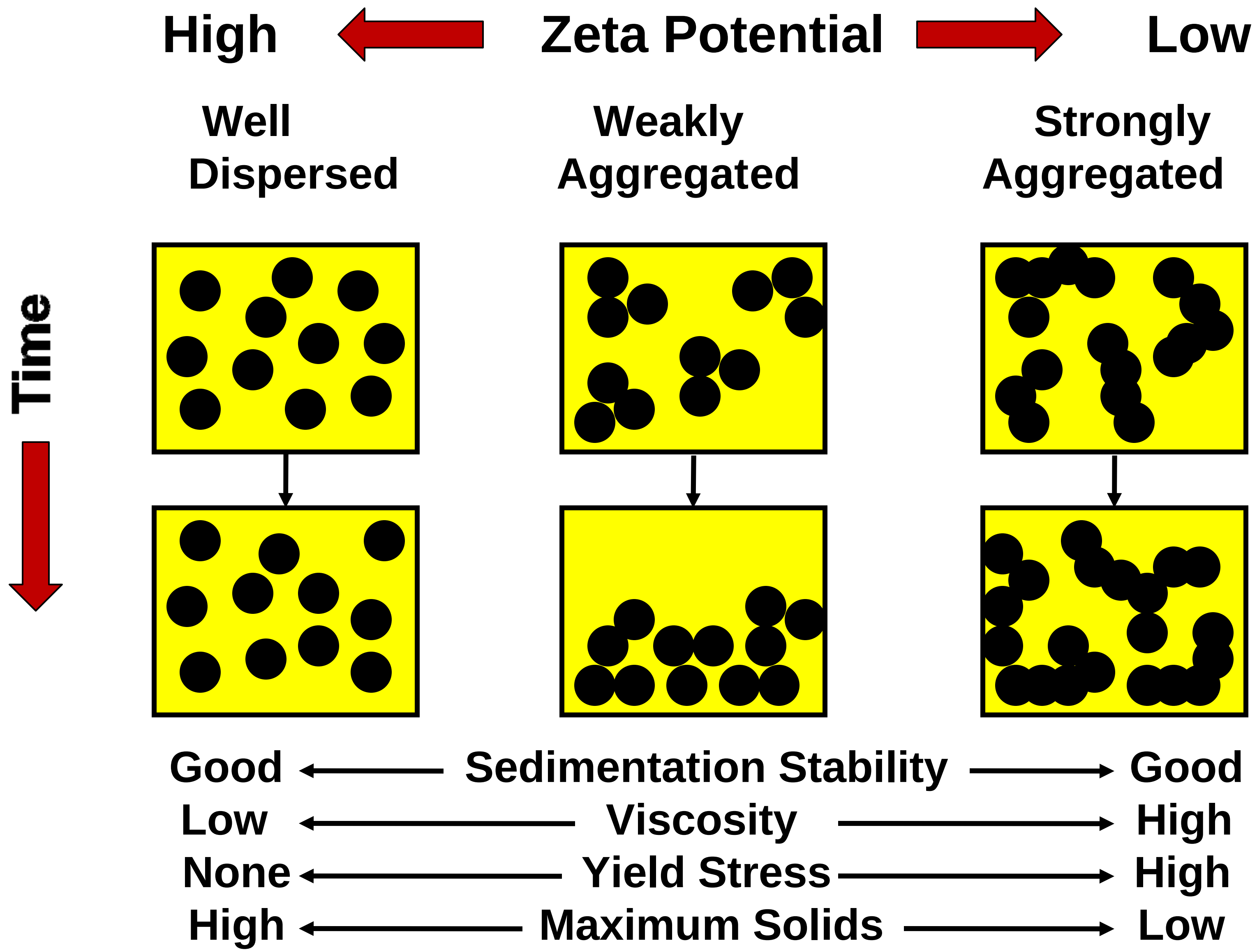
Electrostatic Stabilization	
Material	**ZP (mV)**
O/W emulsions	>15
Polymer Latices	>20
Metal oxides	>40
Metal Sols	>70

Critical Coagulation Concentration

$$\mathbf{ccc \approx \zeta^4 / z^2}$$

z is electrolyte *counterion* valence

Effect of Zeta Potential on Suspension Properties



Stabilization

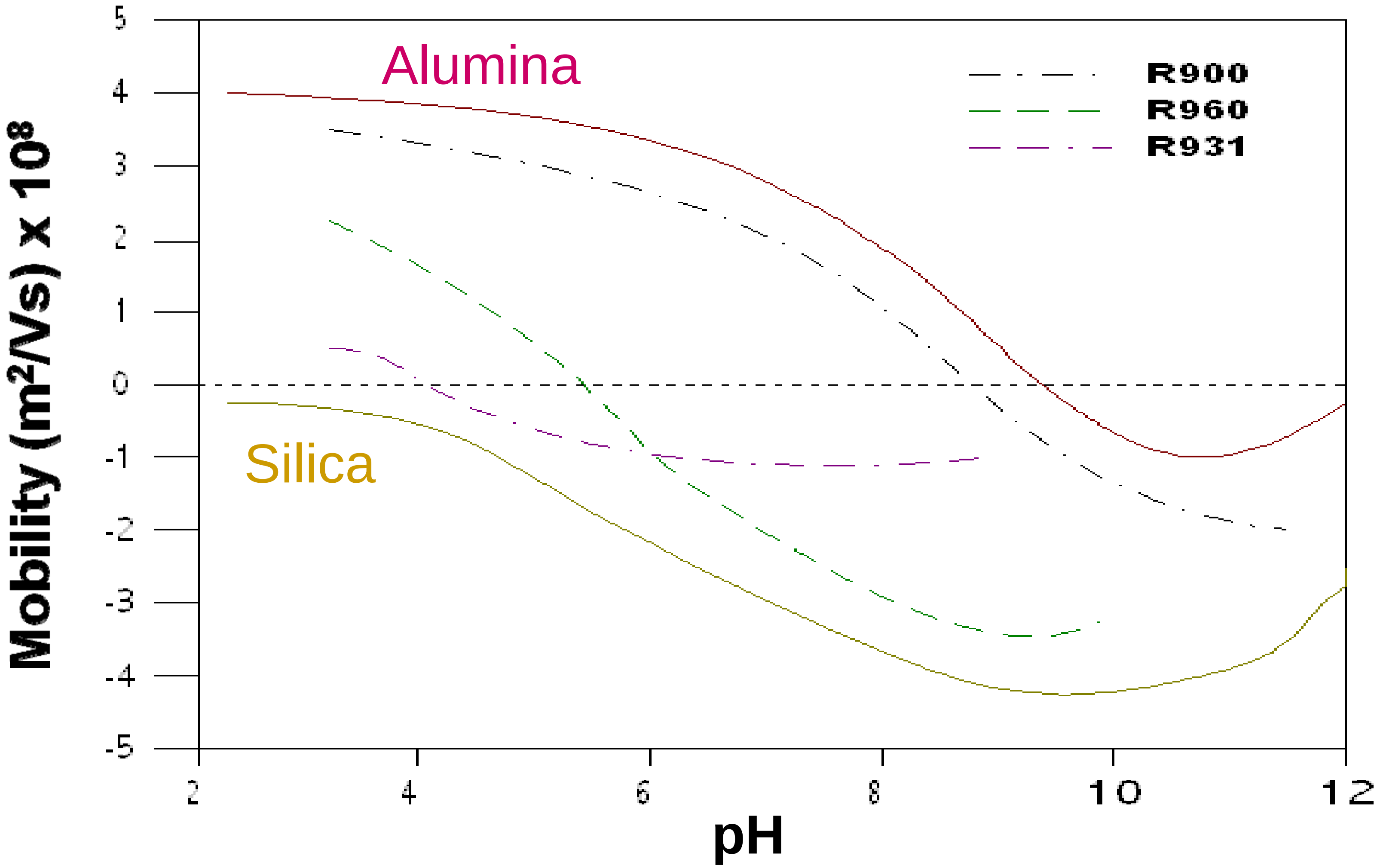
Any material added into solution can affect suspension stability

Water soluble polymers – “thickeners’, viscosity modifiers.

Presence in solution affects Repulsive Potential via the DIELECTRIC term:

$$V_R \propto D\ a\ \zeta^2\ \ [\text{Geometric term}]$$

Surface Modification



Care needed when dispersing!

Effect of Surface Modification on the 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

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

Surface Modification

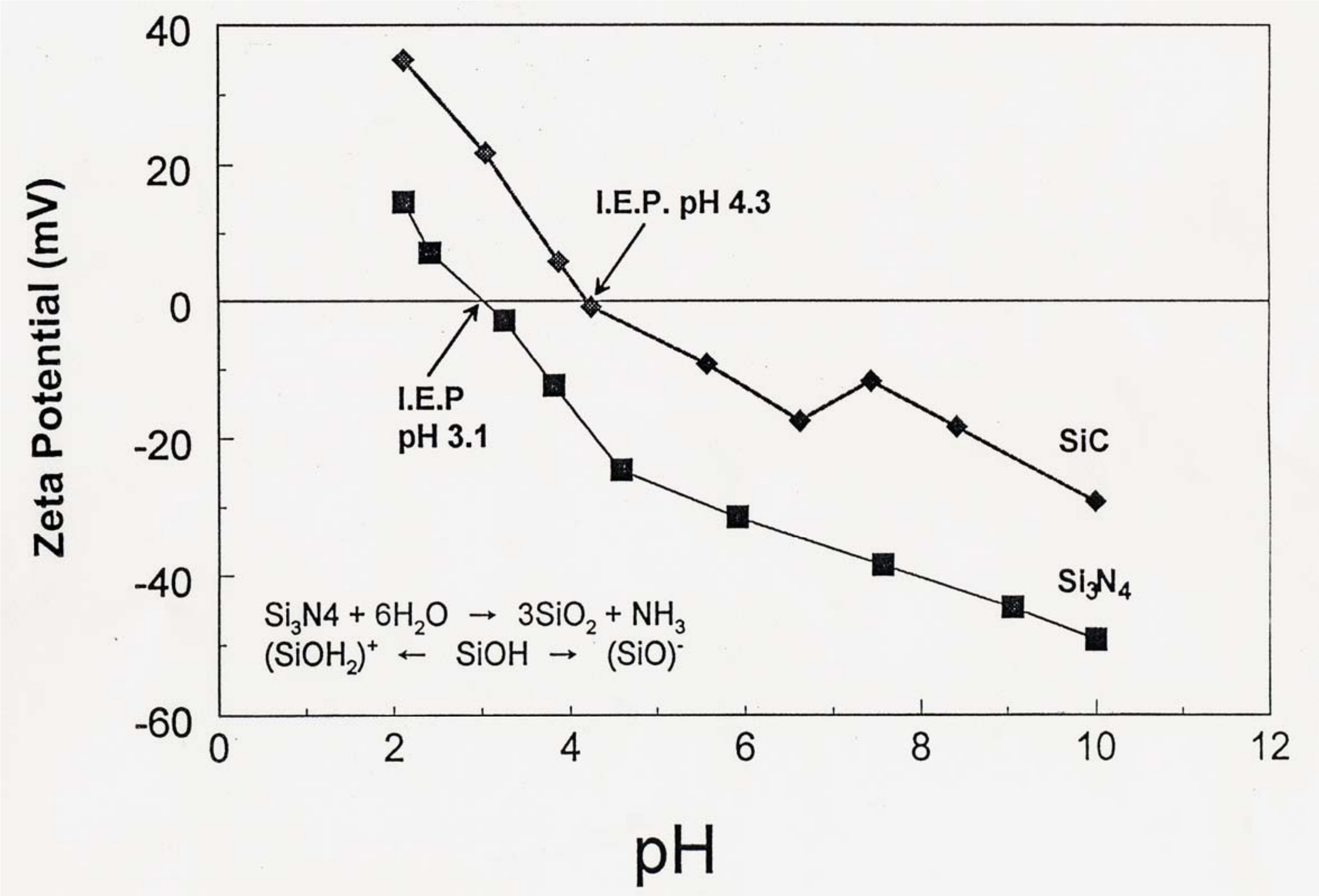
Typical “coatings” on TiO_2

Inorganic	Organic
Metal oxides	Fatty acids
Silicones	Organosilanes

Check the material MSDS!

Care needed in choice of dispersing aids!

Zeta Potential of Non-oxides



Surface impurities and contamination

In Conclusion

Zeta potential (ζ) measurement very useful technique

- ❑ provides information about the material surface-solution interface
- ❑ knowledge of ζ used to predict and control stability of suspensions/emulsions
- ❑ Measurement of ζ often key to understanding dispersion and aggregation processes
- ❑ The presence/or absence of surface charged moieties on materials (revealed by their ζ) directly affect their performance and processing characteristics in suspension
- ❑ The sign and magnitude of ζ affects process control, quality control and product specification
- ❑ at simplest level: help maintain a more consistent product
- ❑ at complex level: can improve product quality and performance

Q&A

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Thank you

Thank-you