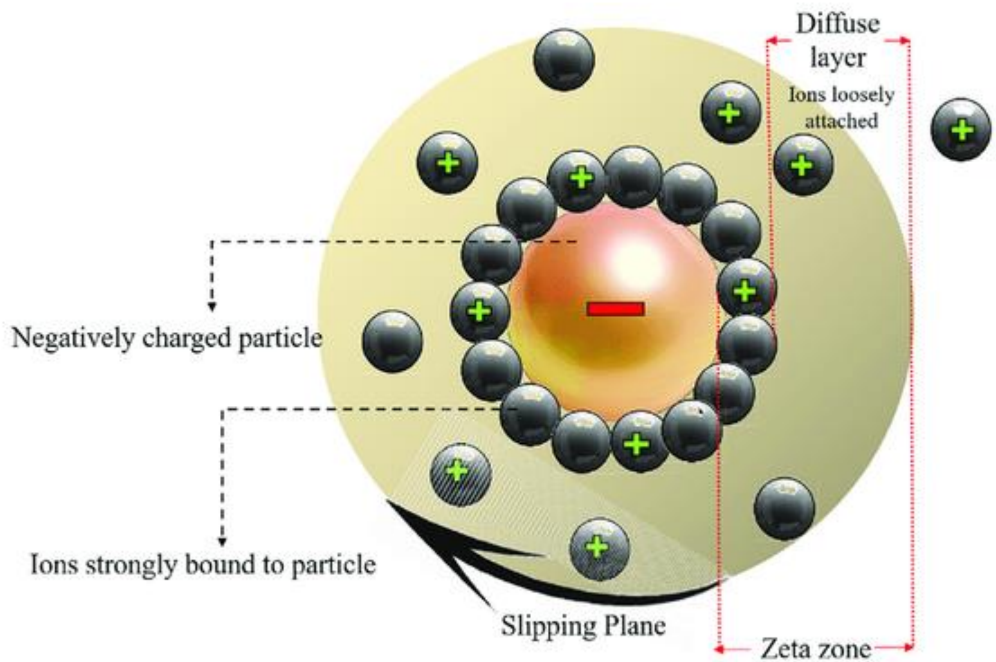
Part II:
An introduction to Zeta potential measurements



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Pessac, 21 Février 2022

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spécialité Métrologie Chimique et Nucléaire

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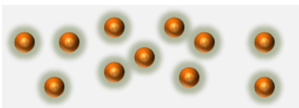
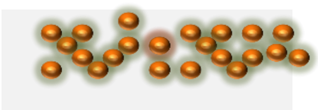
Colloidal suspension stability ?

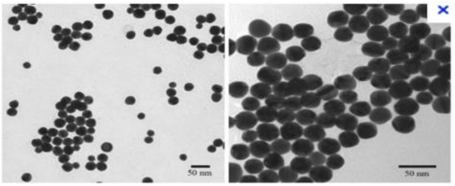
Colloid: dispersion of one or more substances suspended in a liquid, forming a system with 2 separate phases. It is a heterogeneous mixture of particles ranging in size from nm to µm

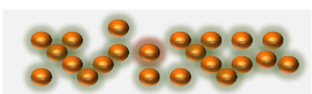


Stable systems

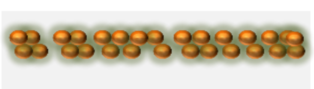


Aggregation/agglomeration

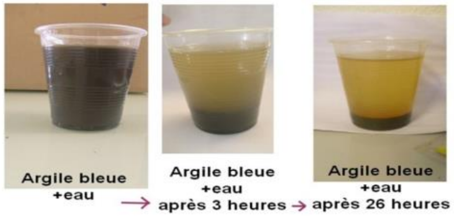


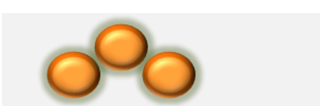


Flocculation

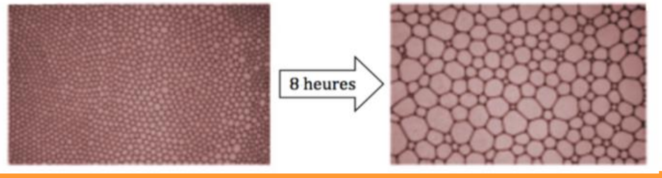


Sedimentation





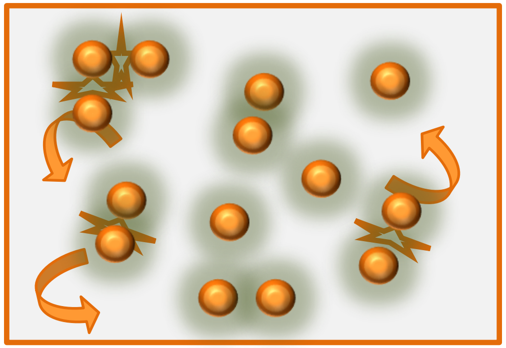
Emulsion:
Coagulation/coalescence

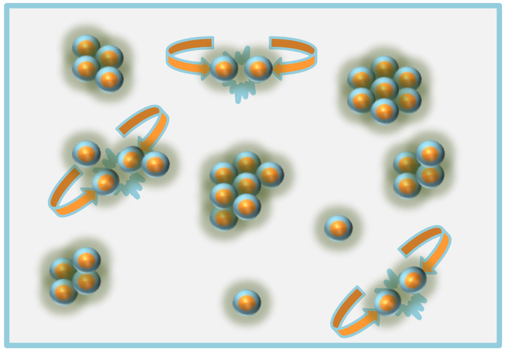


The origin colloidal stability/instability

Charged particles in liquids repel each other (**Coulomb force**)

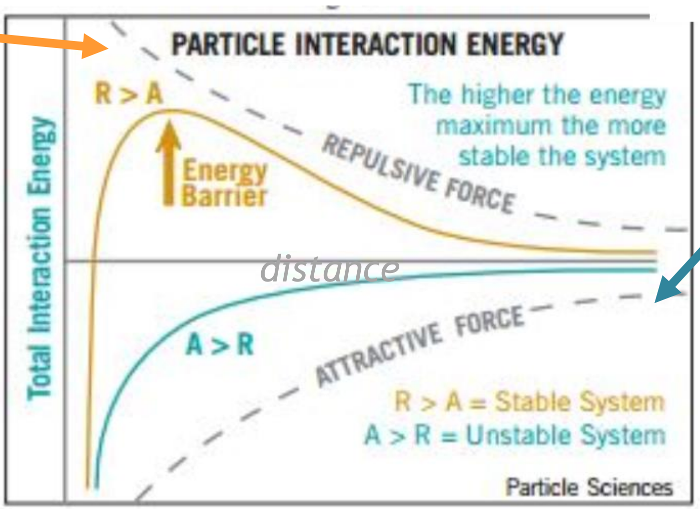
Particles are attracted by dipolar interaction (**Van der Walls forces**)





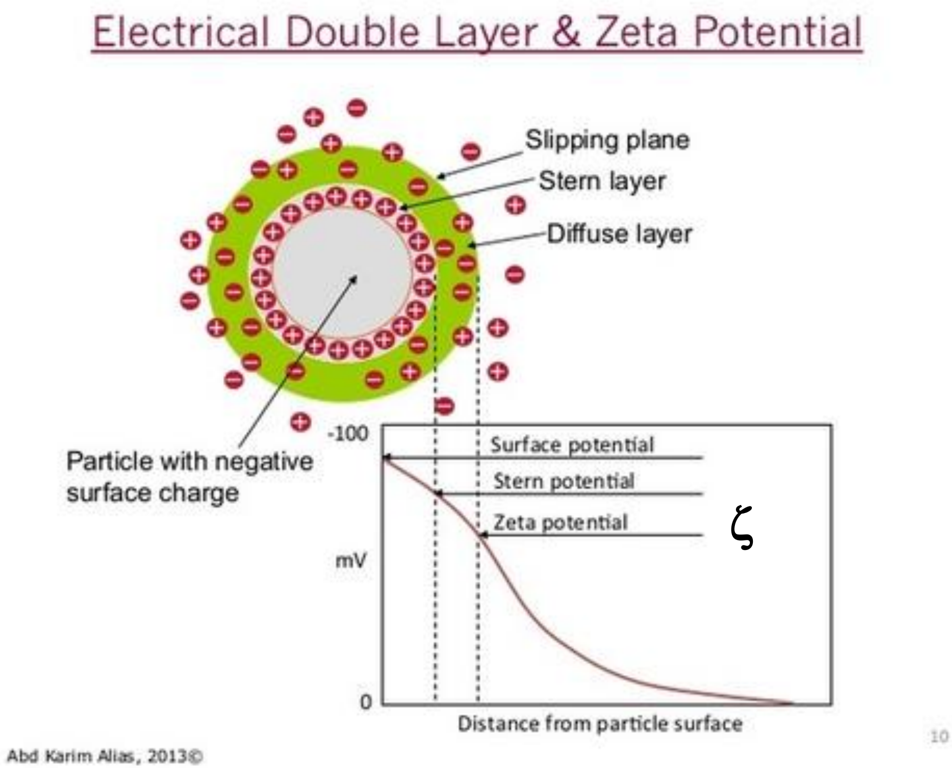
Repulsive forces

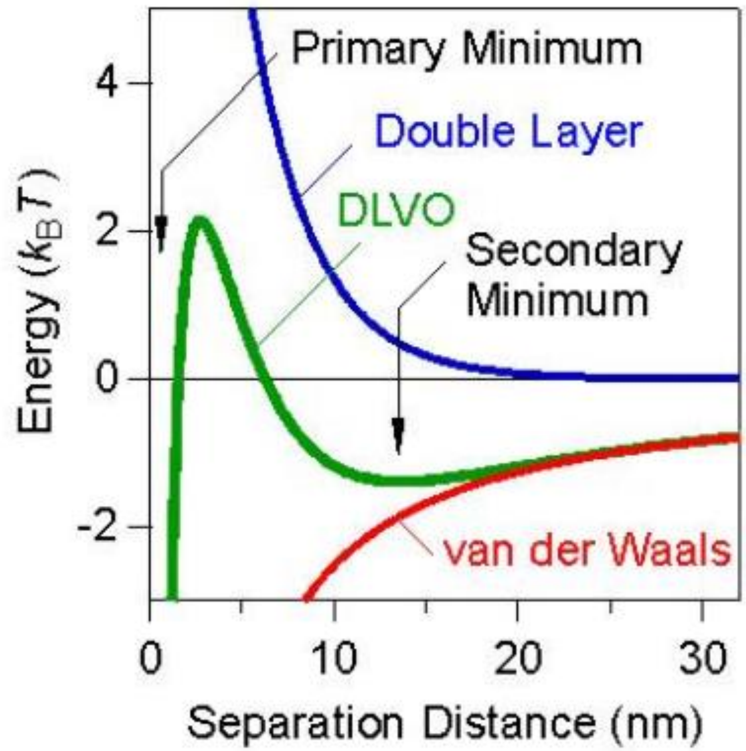
Attractive forces



- Colloid Stability depends on the balance between repulsive and attractive forces

Zeta Potential: a phenomenological approach of surface charge





▪**DLVO Theory & Double layer Model** : stern layer (ions attached to the NP surface) and diffuse layer counterions in a double electric layer separated by Slipping/shear plane

▪**Zeta Potential** ζ = potential (mV) at slipping plane

Zeta Potential determination

$$\zeta = \mu_e \frac{\eta}{\varepsilon} f(\kappa.a)$$

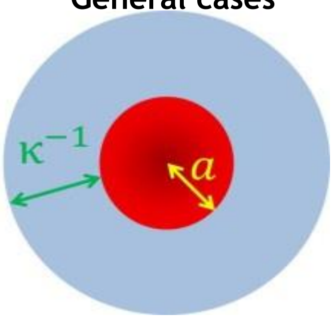
- ζ → Calculated
- μ_e → Measured
- η, ε → Solvent data base

ζ: Zeta Potential (mV)
μ_e: electrophoretic mobility (m2/V/Sec)
ε: medium permittivity
η: medium viscosity (Cp)
a: particle radius (m)
κ: invert of double layer thickness
κ^{-1} : Debye length (m)
$f(\kappa.a)$: Henry's function

Zeta is dependent of the $\kappa.a$ factor value
κ is dependent of the solvent

99% cases !!!

General cases

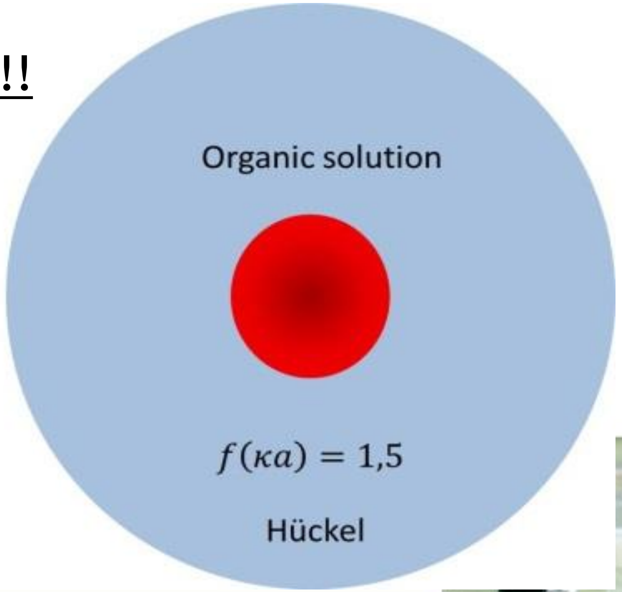


$1 \leq f(\kappa.a) \leq 1.5$

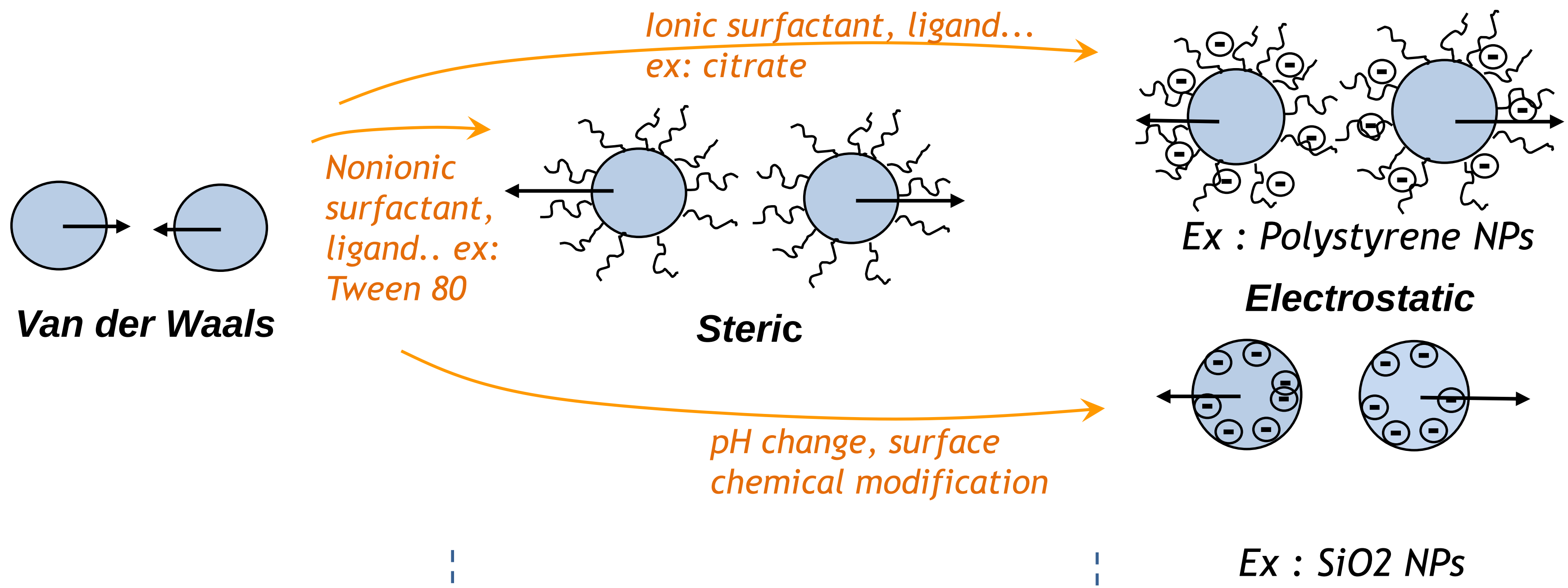
Aqueous solution

$f(\kappa a) = 1$

Smoluchowski



Colloids stabilzation



Attractive forces

Unstable

$\zeta = 0$

Repulsive forces
(short range)

Limitation of irreversible agregation/coalescense

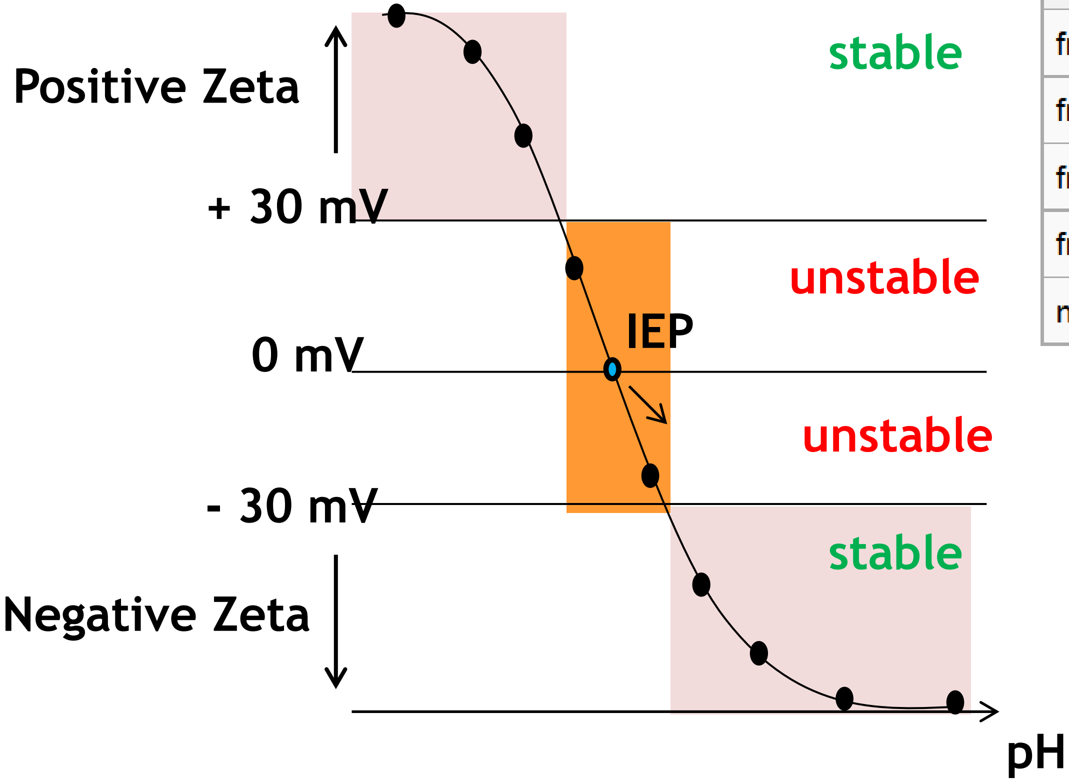
$\zeta = 0$

Repulsive forces
(long range)

stable

$|\zeta| > 30$

Colloid stability and Zeta potential value



Zeta potential [mV]	Stability behavior of the colloid
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

IEP : IsoElectric Point

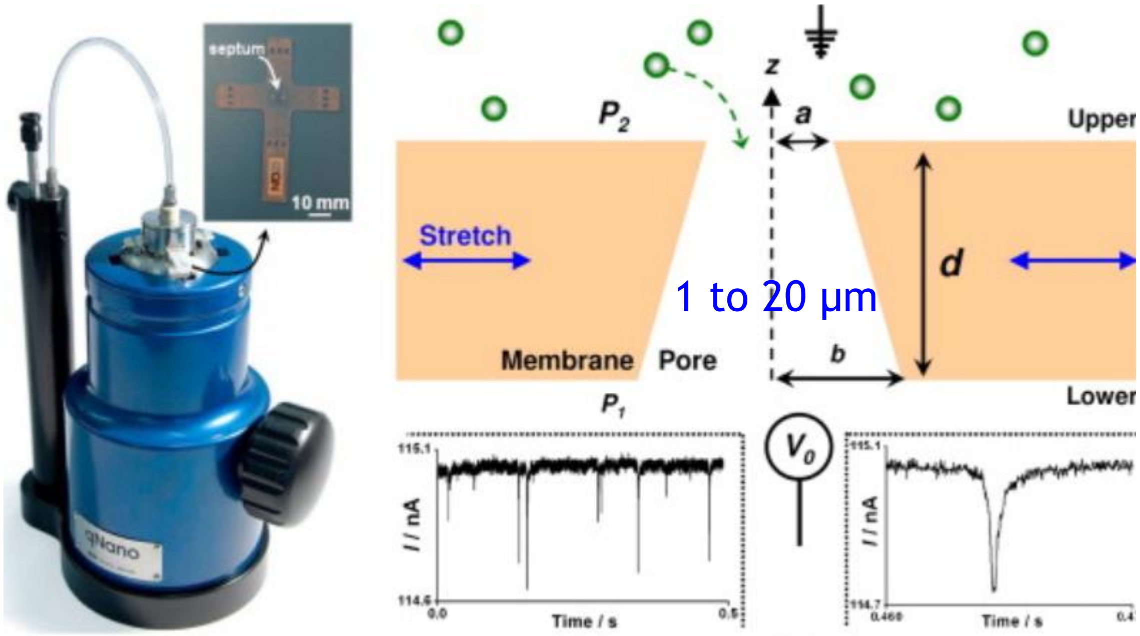
- The higher the Zeta potential (absolute value) the more stable is the suspension
- For aqueous suspension, stability is obtained for |ζ pot|>30 mV
- For oil/water emulsion stability is obtained for |ζ pot|>5 mV

Measuring Zeta potential: principle & implementation

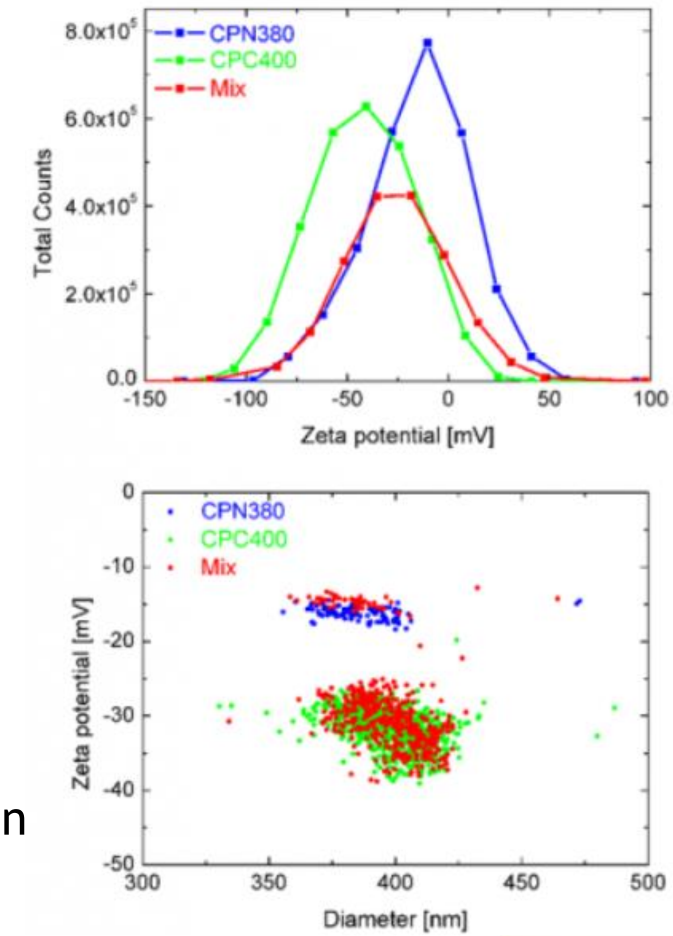
Main types of techniques used in the labs:

- Tunable Resistive Pulse Sensing (TRPS) technique:
  - ➢ Single particle charcaterisation
- Electro-Acoustic Techniques (CVP/CVI, ESA):
  - ➢ Statistical, for **Concentrated** samples
- Optical techniques (LDE/PALS, Particle tracking)
  - ➢ Statistical, for **Diluted** samples

Tunable Resistive Pulse Sensing (TRPS)



(a) (b)



- Based on Membrane electrical impedance variation
- Individual particle measurement
- Only for diluted samples
- Min size range >50 nm up to 10 µm

Electro-acoustic effect on cololoids

Effect prediction (Debye 1933) and observation (Rutgers, Zana 1940) :

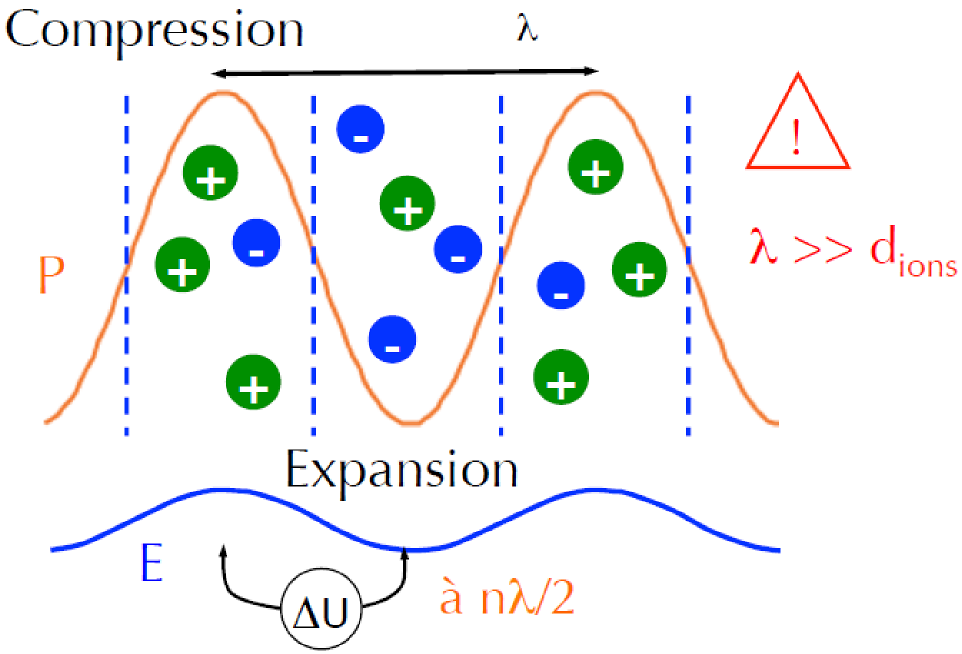
Travelling acoustic wave

Pressure modulation ΔP

Charge species displacement= f(mass/density)

Modulated charge density

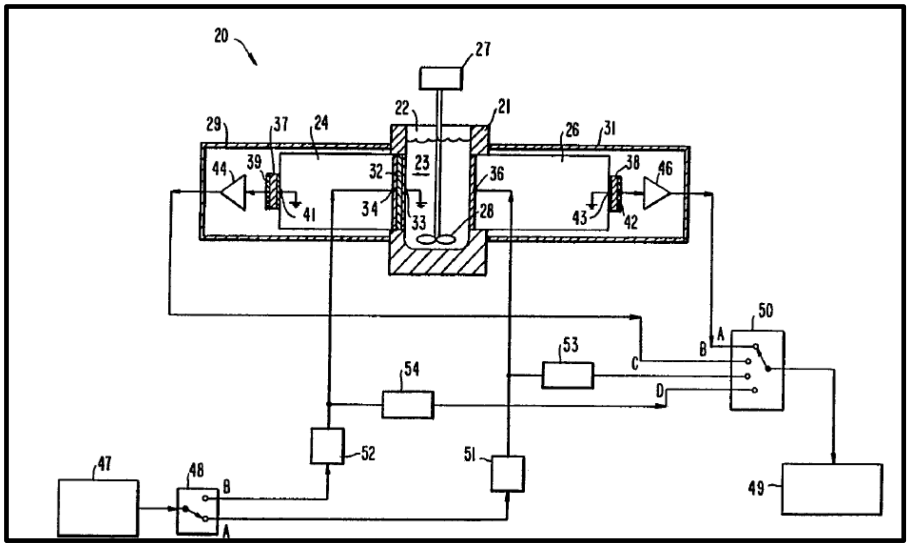
Electrical signal(CVP/CVI) /Applied burst voltage/Field

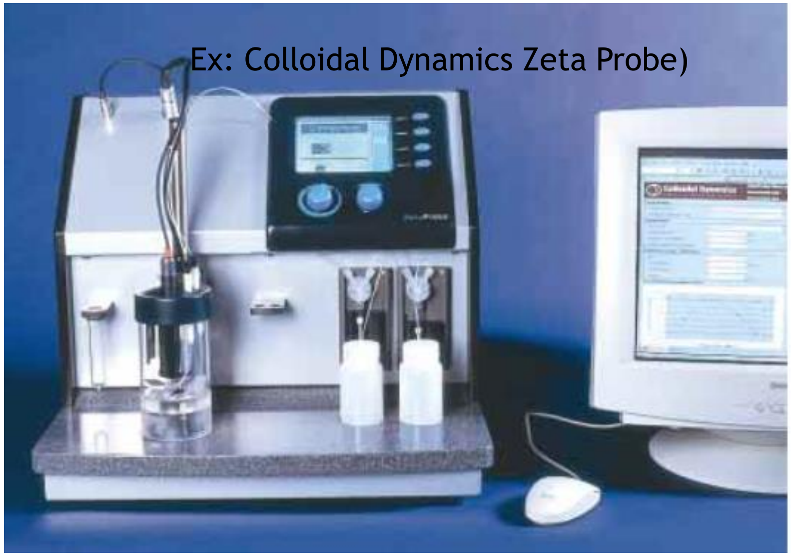


Acousto phoresis: The ESA Approach

Electric Sonic Amplitude (*ESA*): pulsed Electric field Stimulation & Acoustic wave monitoring

Eletric field/voltage → Acoustic signal





Normalised potential

Particle Density

Accoustic impedance term

Mobility

$$\mu_d = A_{ESA} \frac{\rho_m}{\varphi(\rho_p - \rho_m)} \frac{1}{A(\omega)F(Z)}$$

Vol fraction

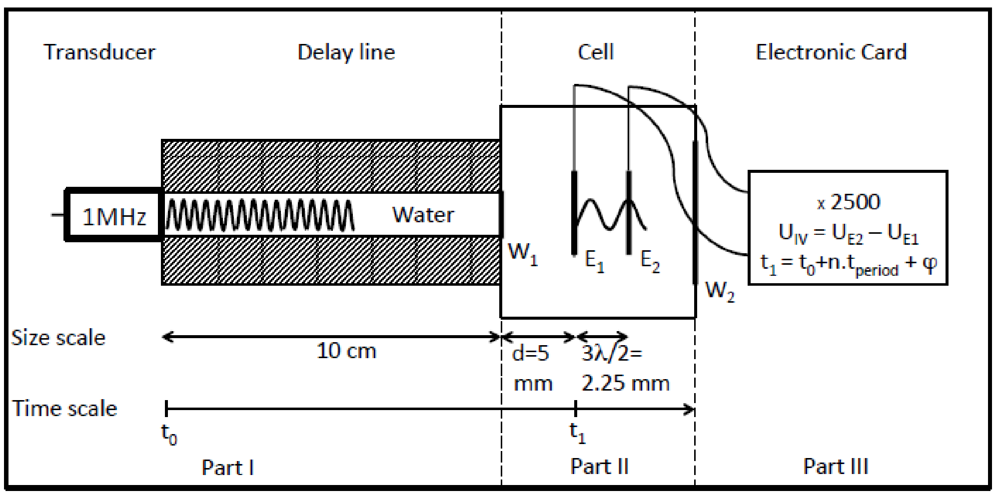
Solvant Density

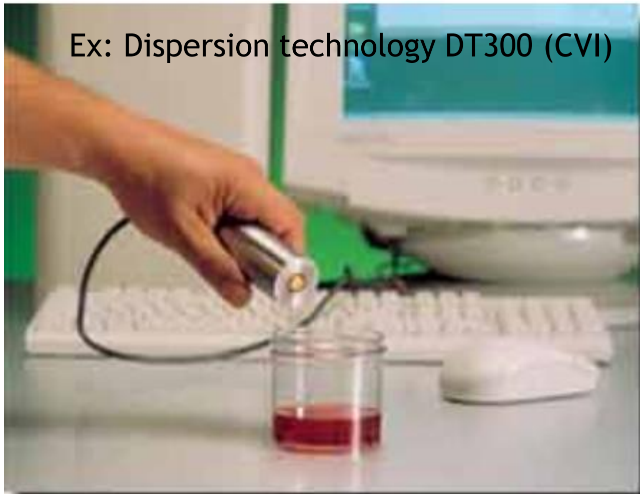
Cal function

Acousto phoresis: The CVI approach

Colloidal Vibrational Potential/current (CVP/CVI): Apply a pulsed acoustic wave and monitor an induced voltage/current at different modulation Frequency

Acoustic wave ➡ Electric(V/I) signal



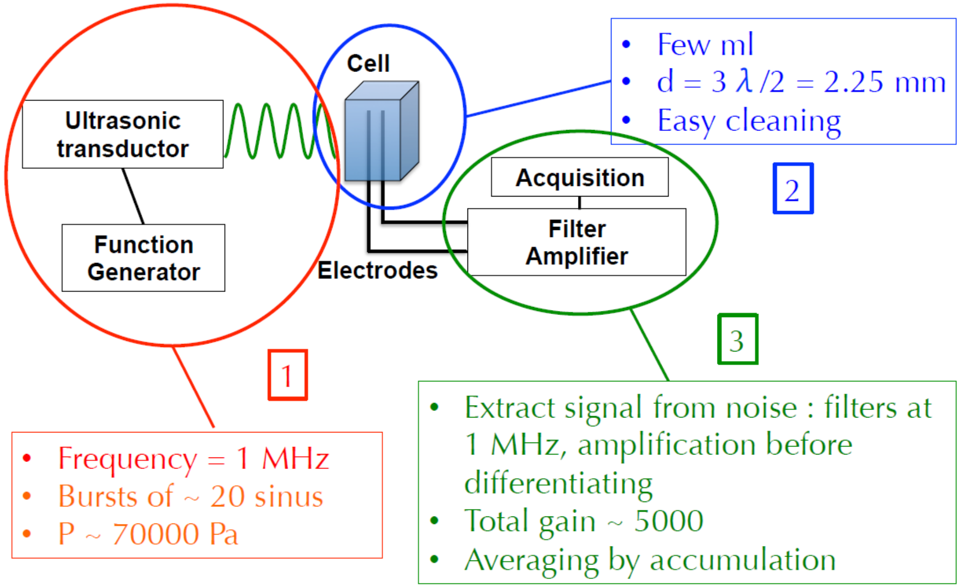


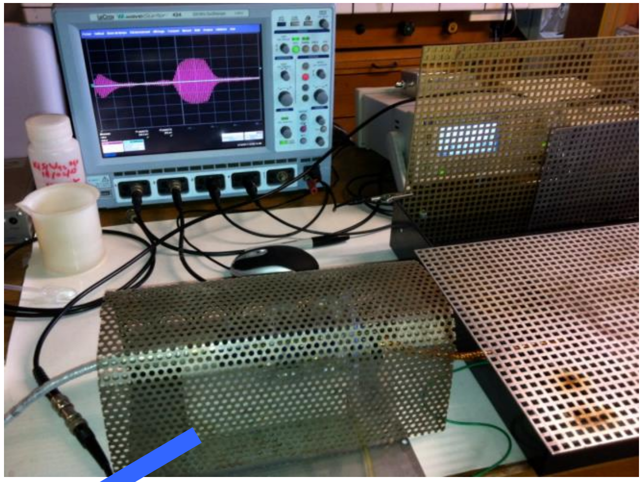
Normalised cureent — Particle Density — Accoustic impedance term — Mobility

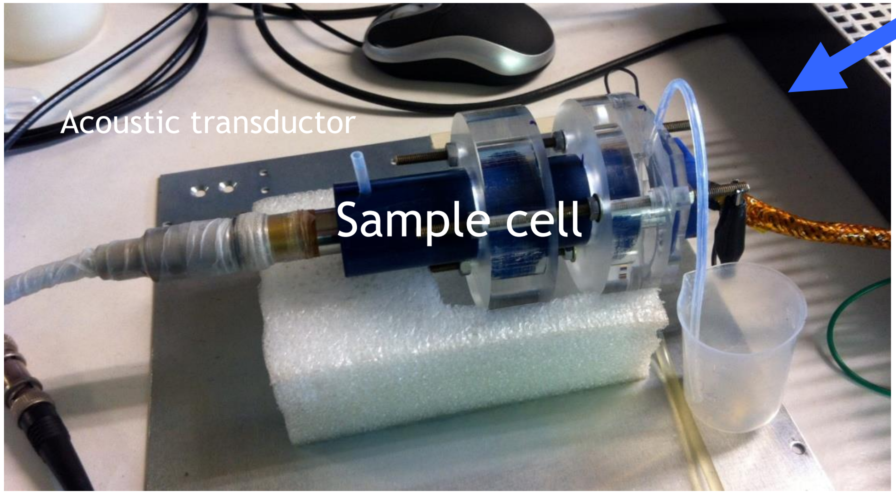
$$\mu_d = I_{CVI} \frac{\rho_m}{\varphi(\rho_p - \rho_m)} \frac{1}{A(\omega)F(Z)}$$

Vol fraction — Solvant Density — Cal function

Acoustophoresis CVP technique: implementation







- Acoustic Modulation at 1 MHz
- Electrodes spacing : $(2n+1)\lambda_{ac}/2$
- Acoustic delay line: 8-10 cm
- Sample volume : 2 ml
- Signal level few μV to mV

Acoustophoresis Measurements

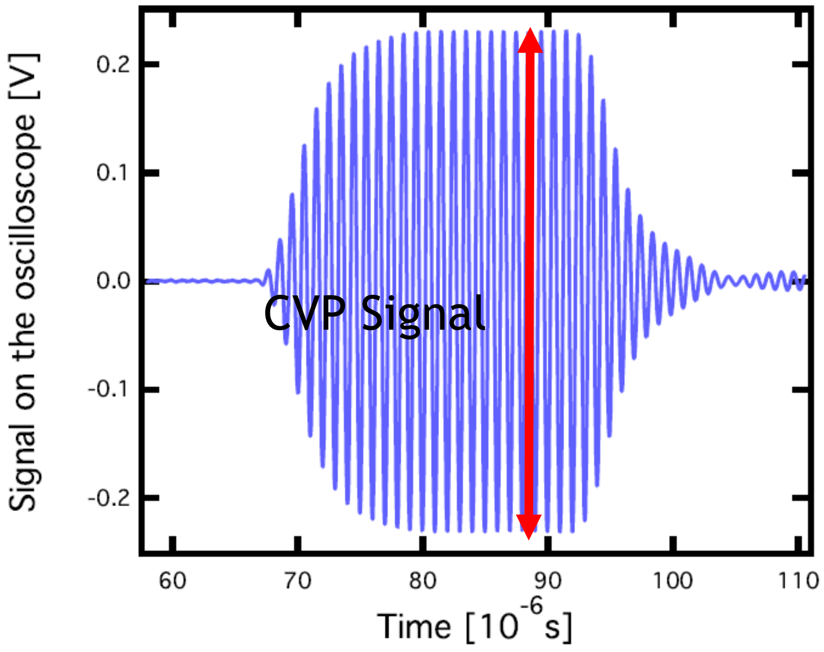
NPs density

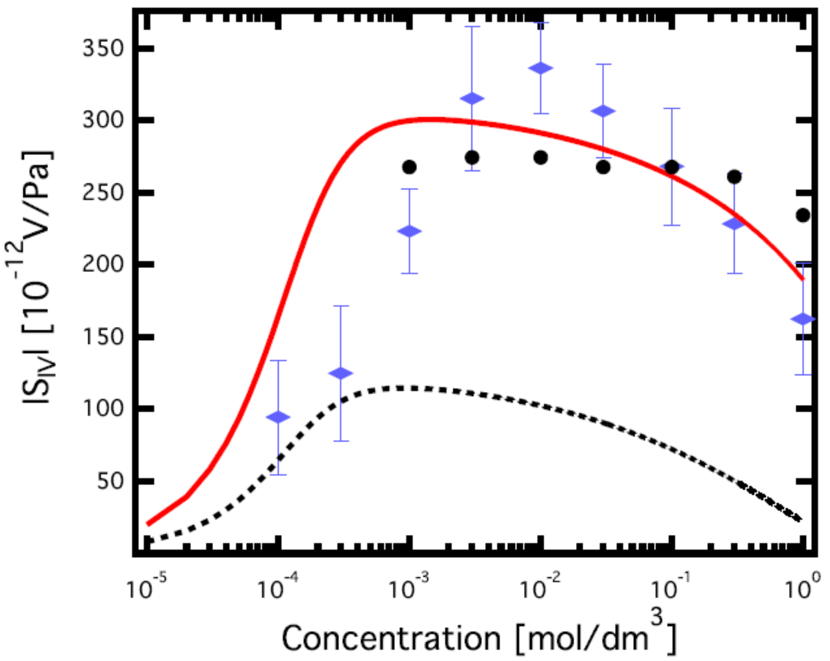
Conductivity at 1 MHz

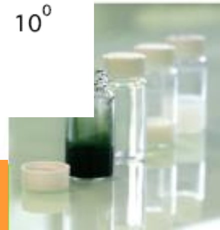
$$[\mu_e] = \frac{\rho_{NPs}}{\emptyset_{WT} * (\rho_{NPs} - \rho_{solvent})} [CVP] * K$$

Massique concentration

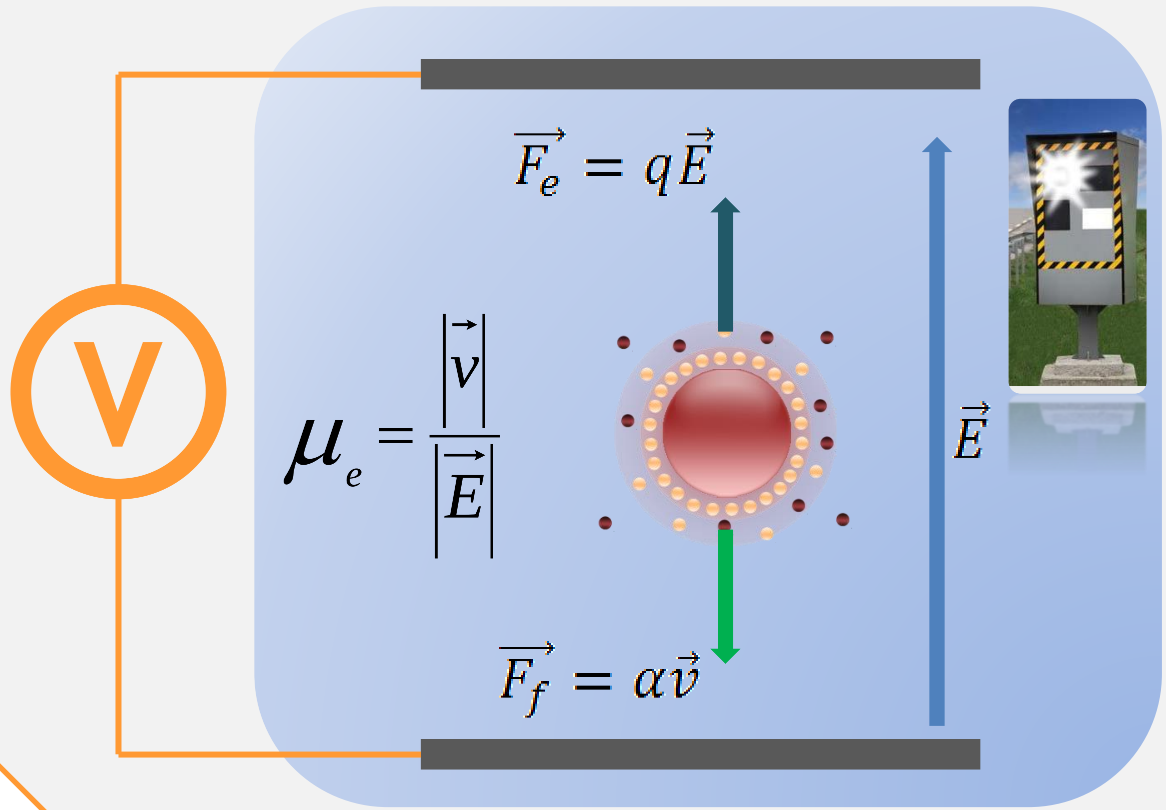
Solvent density







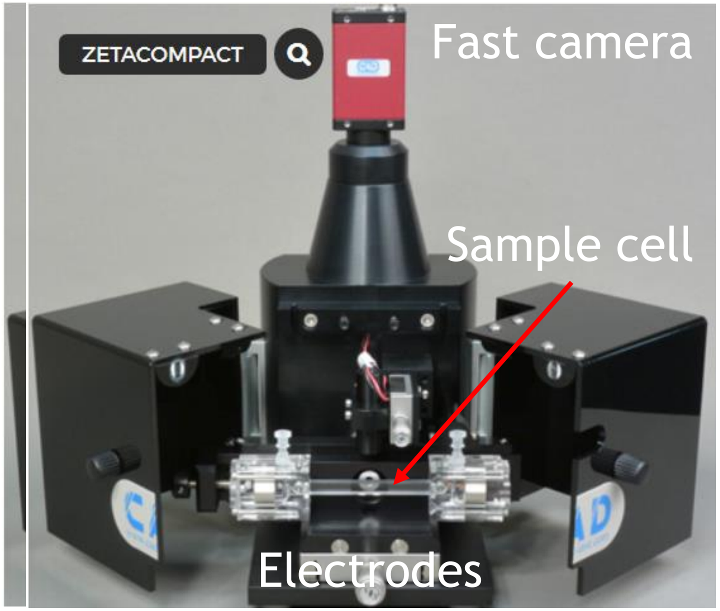
Electrophoresis & Electrophoretic mobility

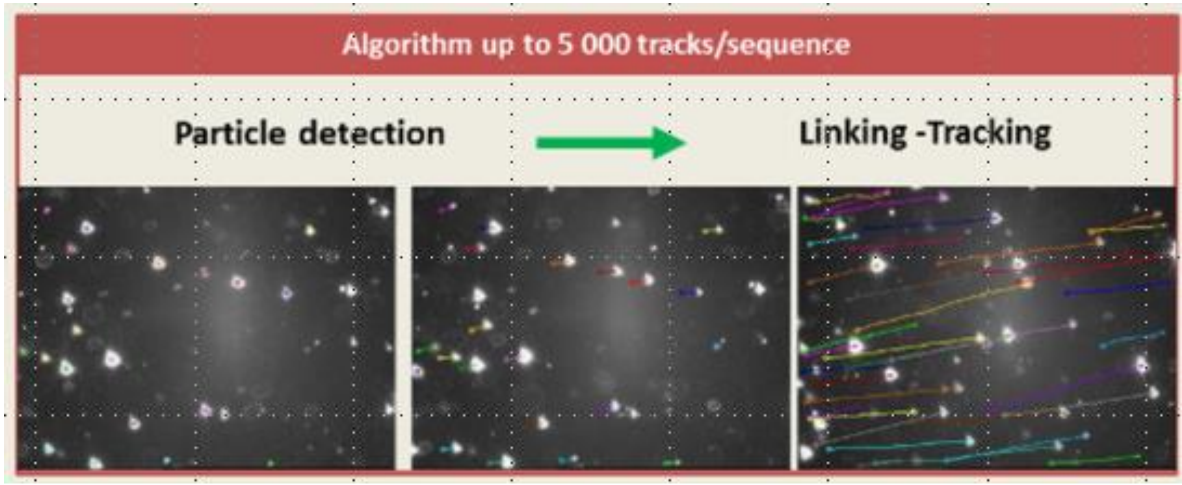


μ_e: electrophoresis mobility
E: electric field
V : voltage applied
q : electric charge
F_e : electric force
F_f : friction force

- Applying an Electric field: the particles move with its surrounding layers.
- Particle velocity directly related to its electrophoretic mobility and E

Nano Particle tracking electrophoresis

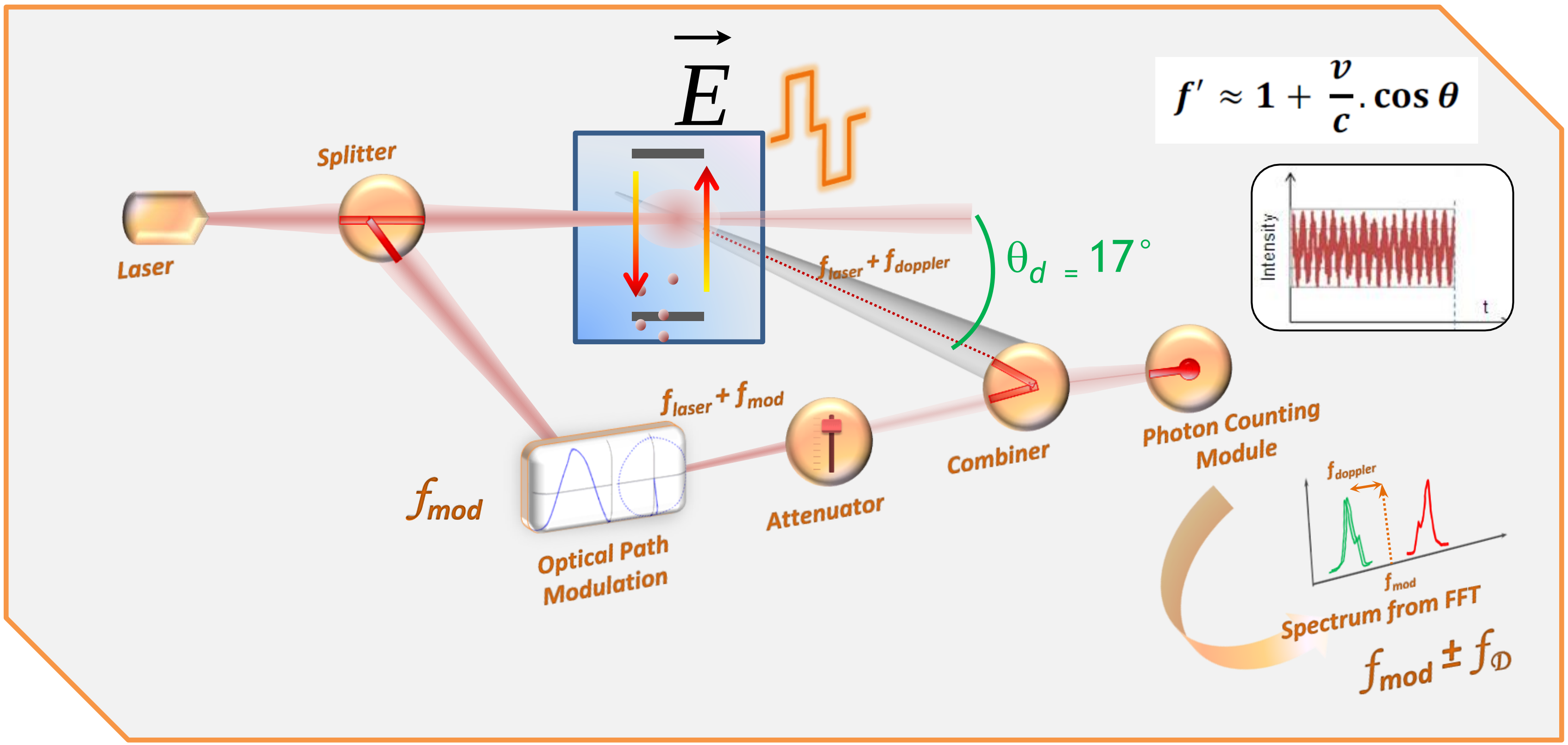




- Particle tracking image : particle speed calculation from trajectory analysis
- Limitations: works Only for diluted samples and particle >30 nm

Laser Doppler Electrophoresis (LDE)

Heterodyne optical Interferometer : retrieving doppler low frequency



$$\mu_e = \frac{\lambda_{laser}}{E \sin \theta_d} f_D$$

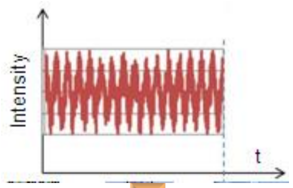
μe: electrophoretic mobility (μmcm/Vs)

E : applied electric field

f_D : Doppler frequency

Measurement Steps

Heterodyning Signal



FFT

Doppler shift

f_D

Measured

Electrophoretic Mobility

μ_e

By ***LDE***
(Laser Doppler Electrophoresis)

Double Layer model

Huckel ?
Smoluchowski ?

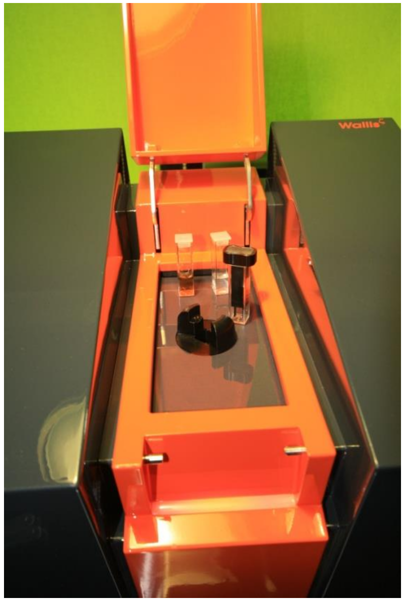
$f(\kappa.a)$
Henry function

Computed

Zeta Potential

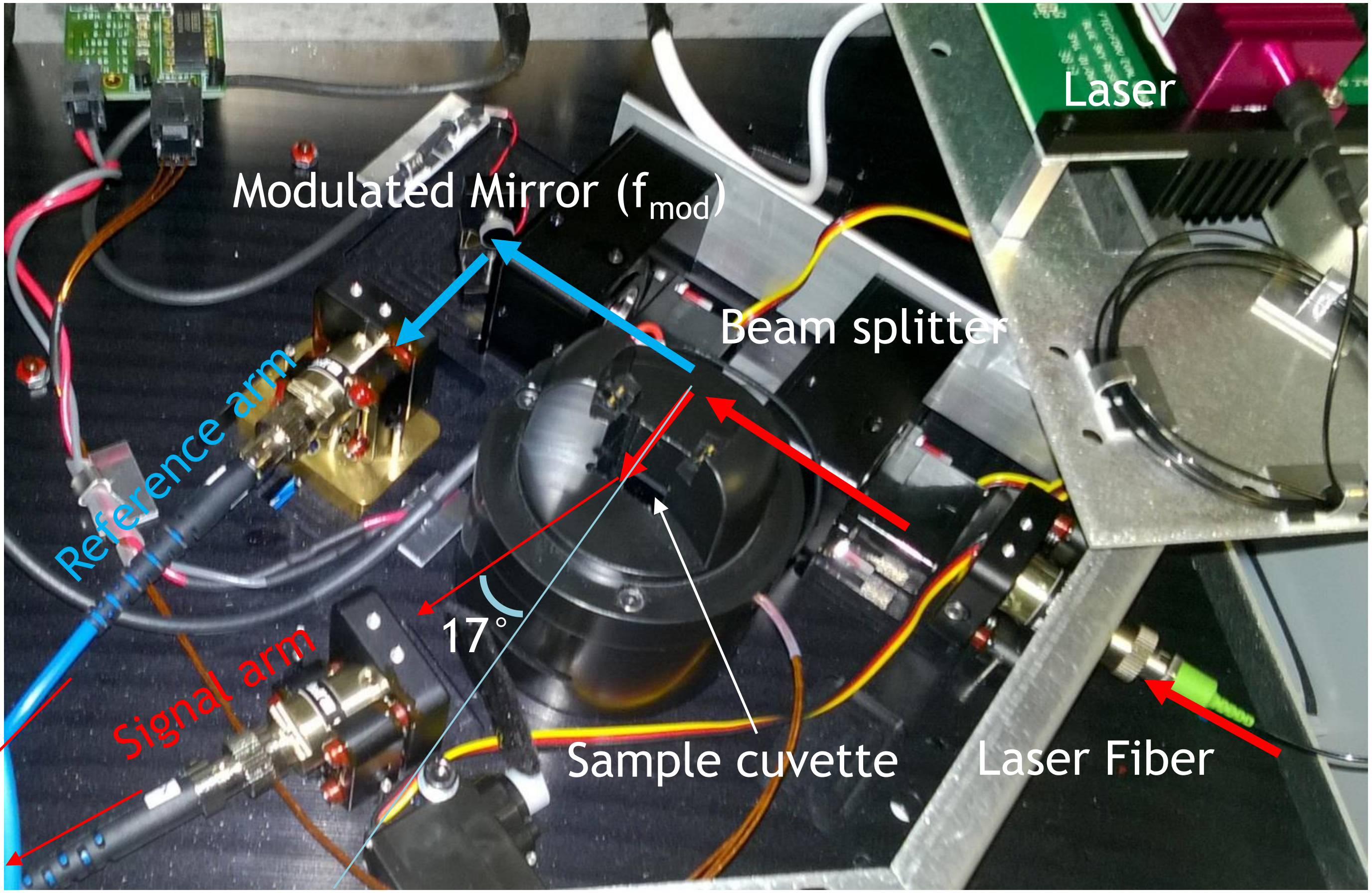
ζ

WALLIS ζ: an example of High-Resolution Zeta Potential Analyser



- Purely designed and optimized for Charge/Zeta potential measurement
- Based on Laser Doppler electrophoresis
- Complementary tool to VASCO for colloid characterization
- High resolution analysis down to 0.5 mV

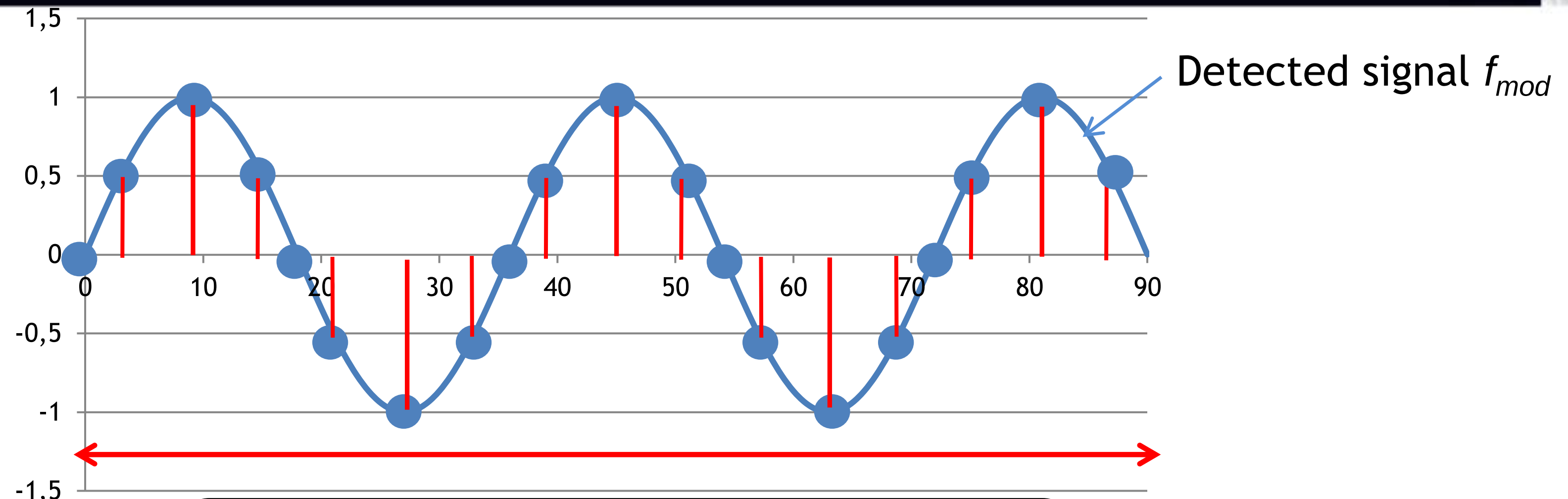
LDE optical interferometer



To fiber combiner

- Piezo electric modulator
- Laser wavelength: 635 nm
- Detection angle 17°

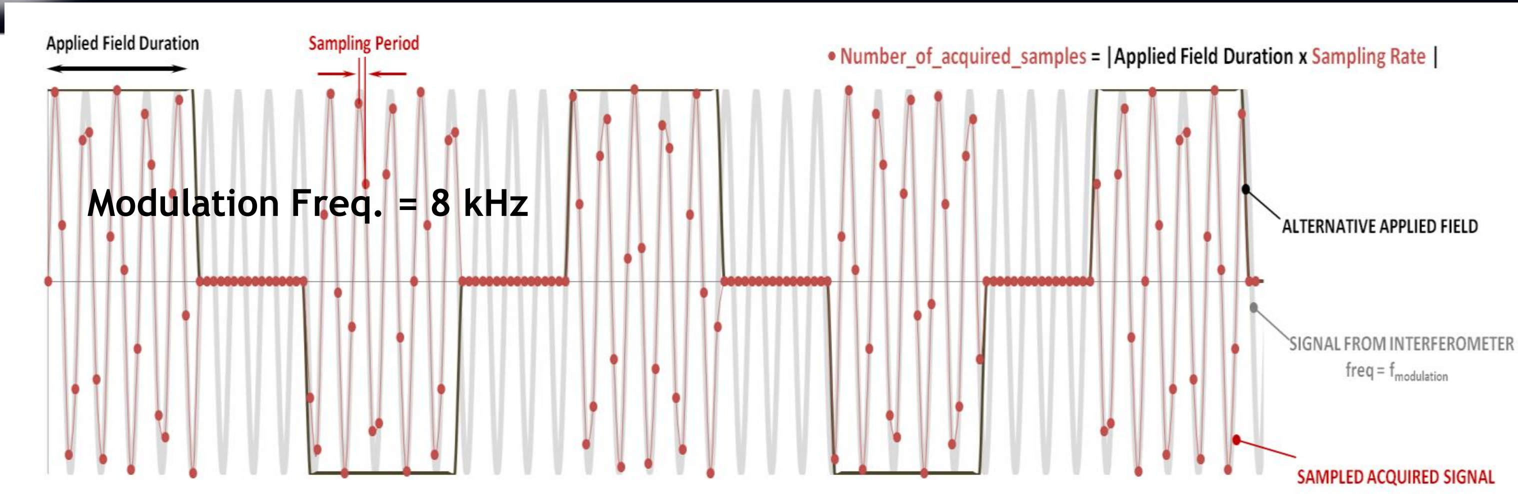
measurement resolution consideration



$$Resolution \propto \frac{Sampling\_Freq}{Number\_of\_samples}$$

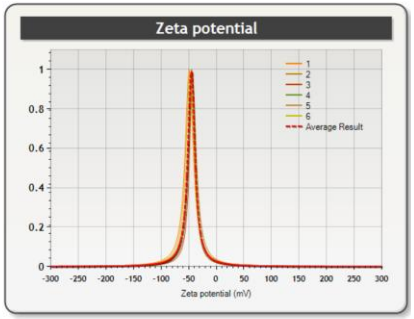
- Sampling Freq ≥ 2 x f_{mod} (Shannon/Nyquist criteria)
- Nber of sampling points limited by : memory buffer size, acquisition duration, sampling freq, calculation time
- Applied electric field duration optimized to avoid electrolysis, electrodes polarization & joule effect

WALLIS Hi resolution measurements



- Mirror modulation frequency: Fmod 8 kHz
- Electric field frequency : ~ 1 Hz (duration ON hundreds of ms)
- Measured Doppler shift: from 0 to 100 Hz

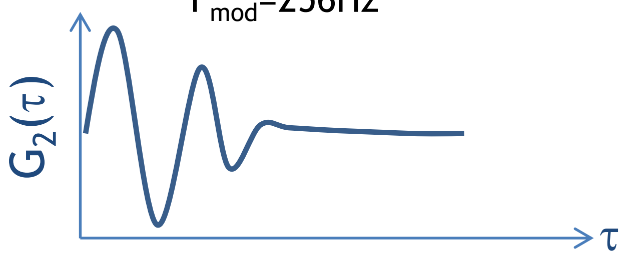
Mode	Res. (Hz)	E field duration (ms)
LOW	5	100
MEDIUM	1.5	420
HIGH	0.6	850

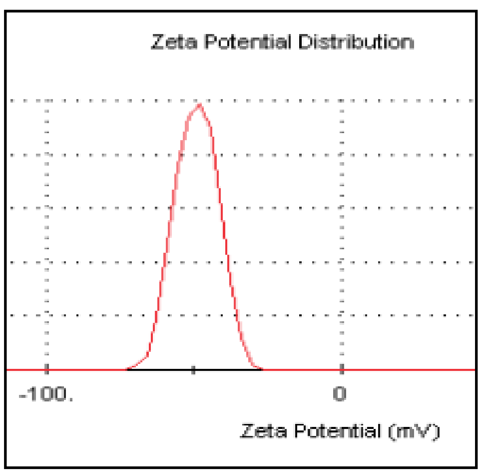


Measurement resolution in practice

Correlator
(2 in 1 concept Zeta+DLS other supplier)

256 to 1024 channels
F_{mod}=256Hz



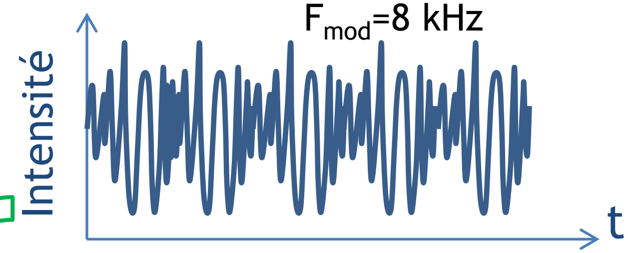


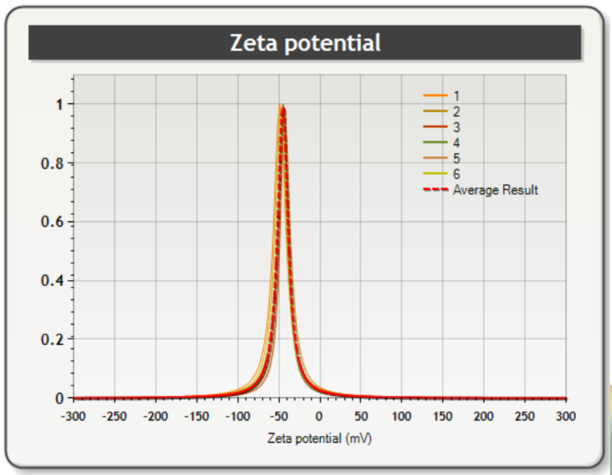
Resolution 3-5 mV

FFT

High-speed digital acquisition: Wallis

8192 sampling points
F_{mod}=8 kHz

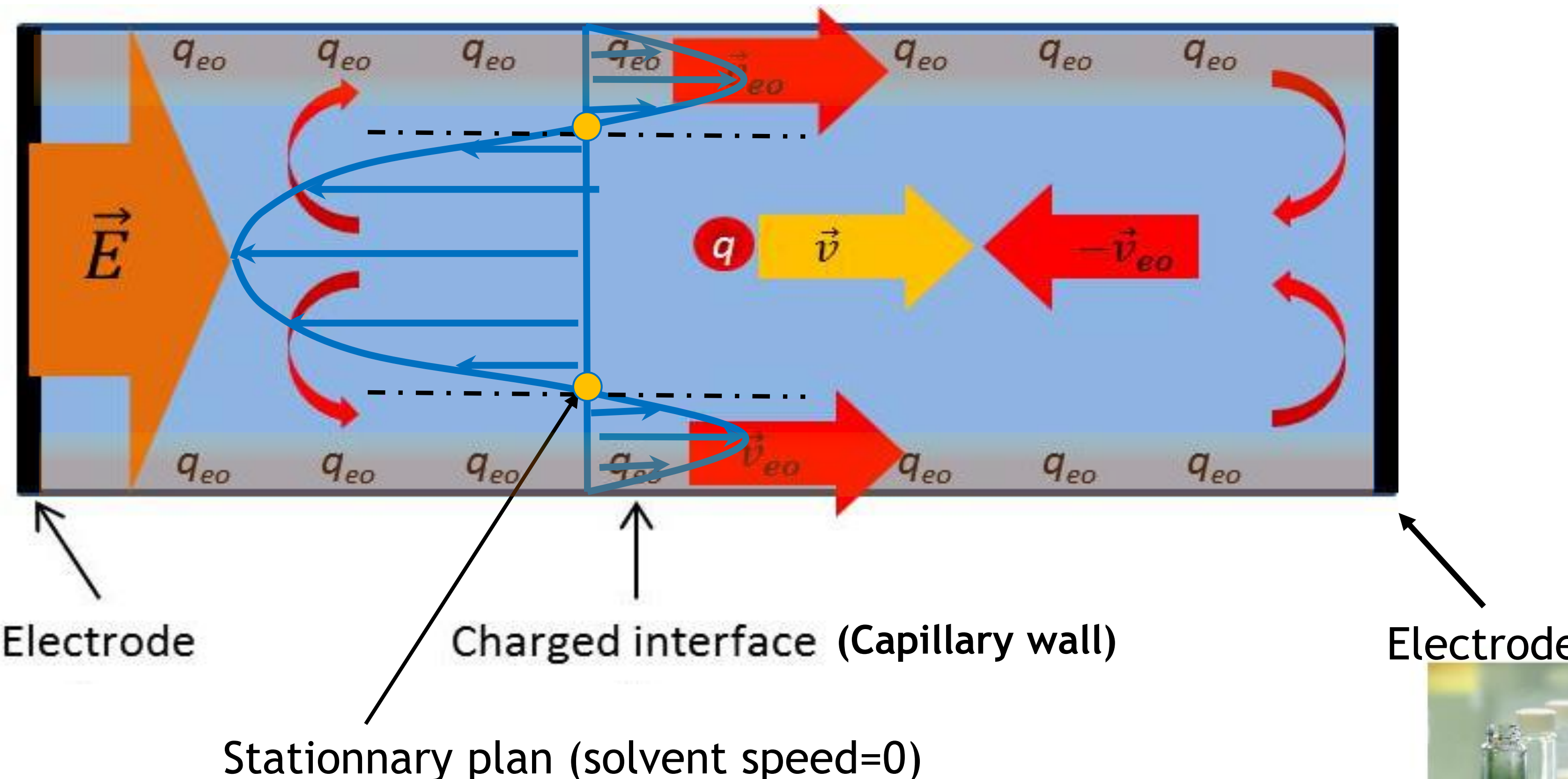




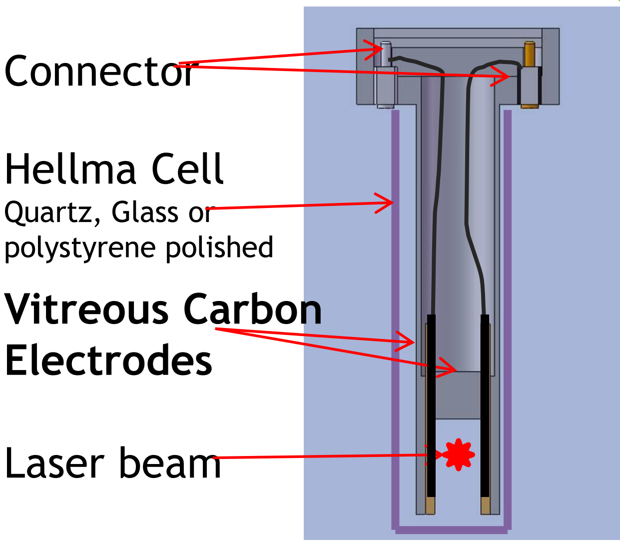
Resolution < 0.5 mV

Electro-osmosis effect:

« Phénomène qui résulte du mouvement d'un fluide (qui peut être l'eau déionisée ou un électrolyte ou un fluide organique) lorsque l'on applique un champ électrique tangentiel dans la couche diffuse, Un champ électrique engendre la force de Coulomb qui met en mouvement les charges libres dans la couche diffuse. Le mouvement de ces charges, via les liaisons visqueuses, entraîne le fluide »



Dip cell configuration

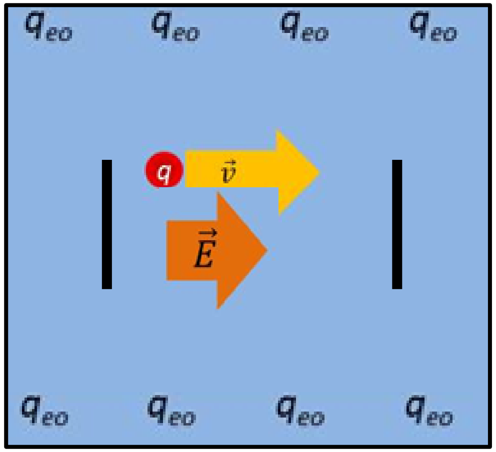


- No electro-osmosis
- Field proven concept
- Custom made electrodes

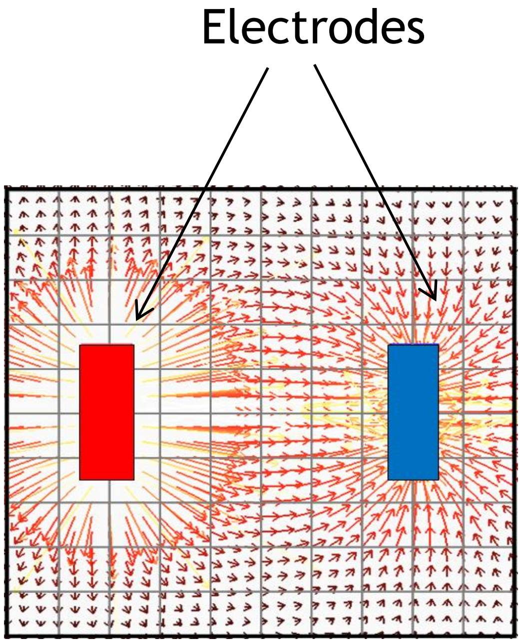
- Easy to handle
- Easy filling, no risk of bubbles ! (vs capillary cell/viscosity)
- Stand alone electrode holder-> easy to replace
- Vitreous carbon electrodes: extreme chemical resistance (No oxidation); low electrical resistance
- Easy cleaning of electrodes (rinsing and ultra sound bath tub)->No cross contamination

- Reusable quartz cell-> no consumable
- Easy to clean
- Excellent optical quality
- Compatible with organic solvent
- Compatible with standard cell (10x10 mm^2) …
- Sample volume ≈750µL

Dip cell design against electro-osmosis



Dip cell 10 x 10 mm (WALLIS)



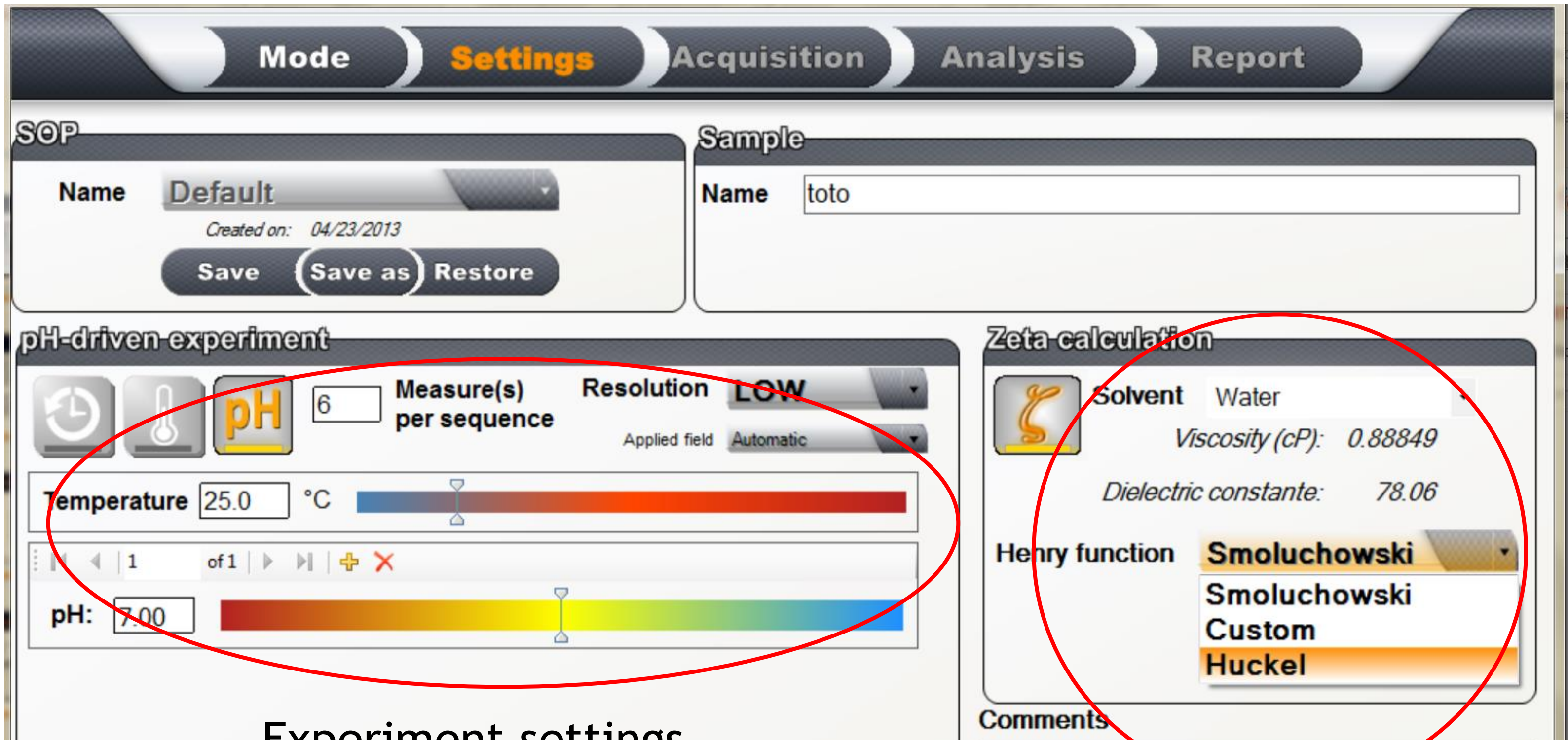
Electric field 2D map

Electric field negligible close to the cell wall + samle cell geometry=>No solvent motion, no electro-osmosis

ZetaQ software for Zeta potential measurement

- Unique and proprietary software
- User-friendly and intuitive GUI
- SOP and programmable experiments (Time, T°, pH)
- Experiment storage in data base
- Many other advanced functionalities

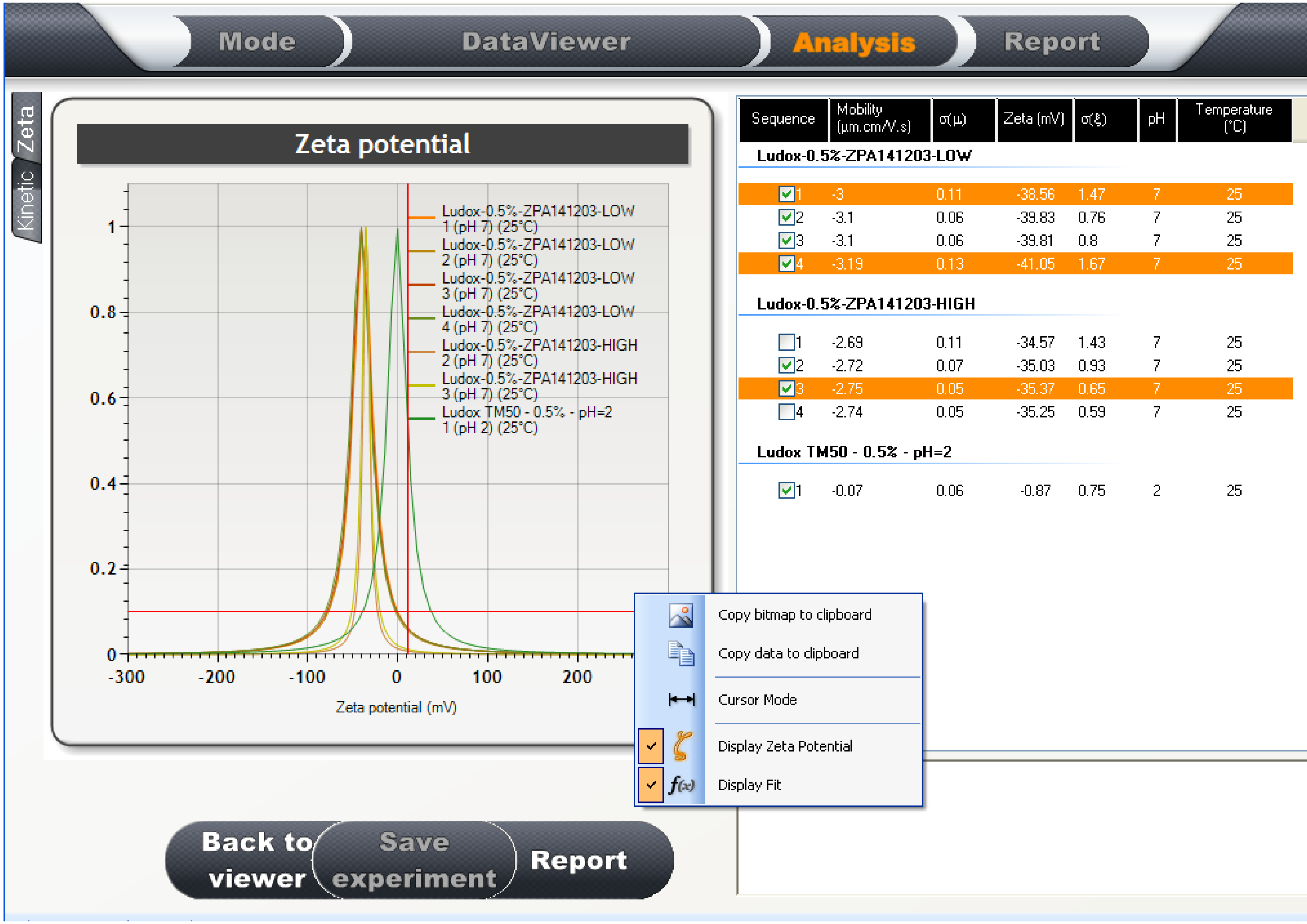
Software overview (1): experiment settings



Experiment settings

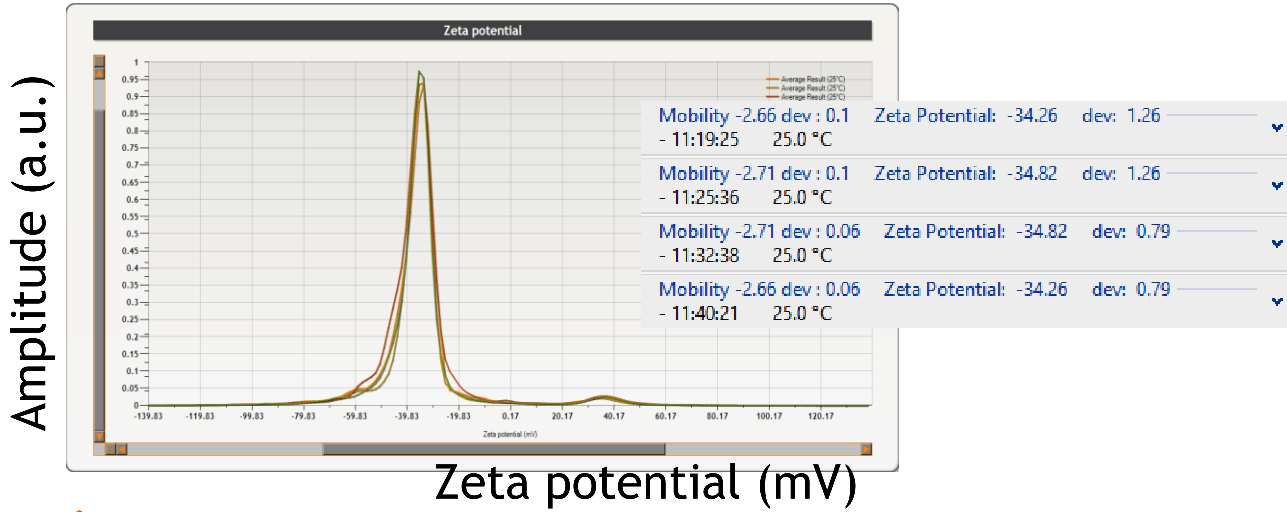
Zeta Model settings

Software overview (2): analysis

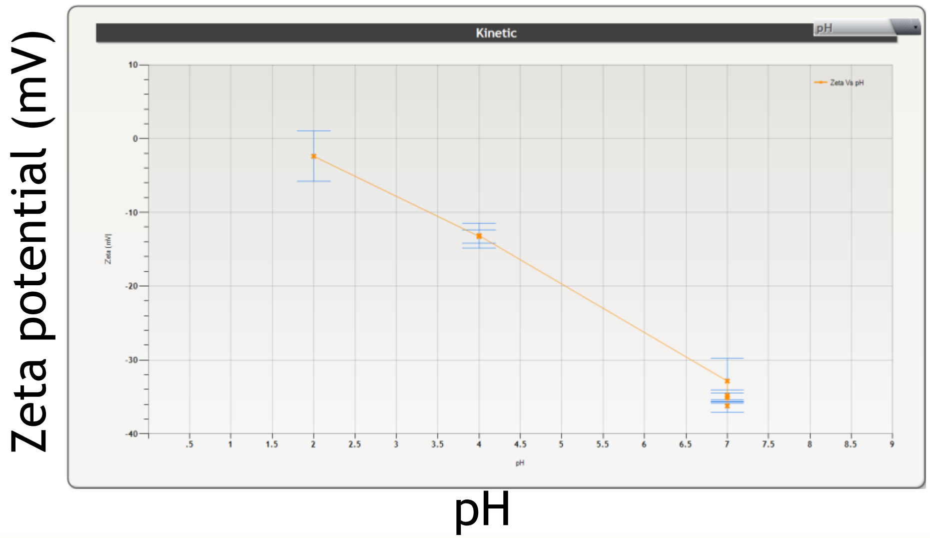


Experiment example on Ludox TM50 0.5% - 22nm

Reproducibility



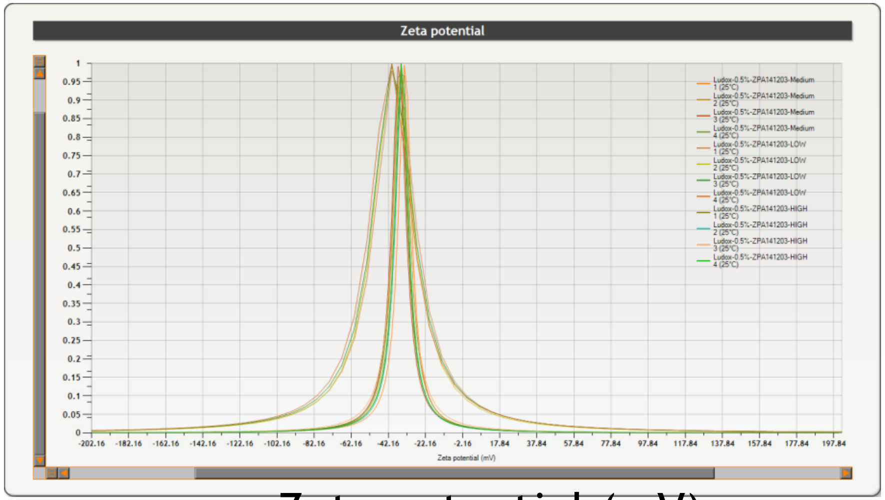
Isoelectric point location



Experiment example on Ludox TM50 0.5% - 22nm

Resolution mode comparison

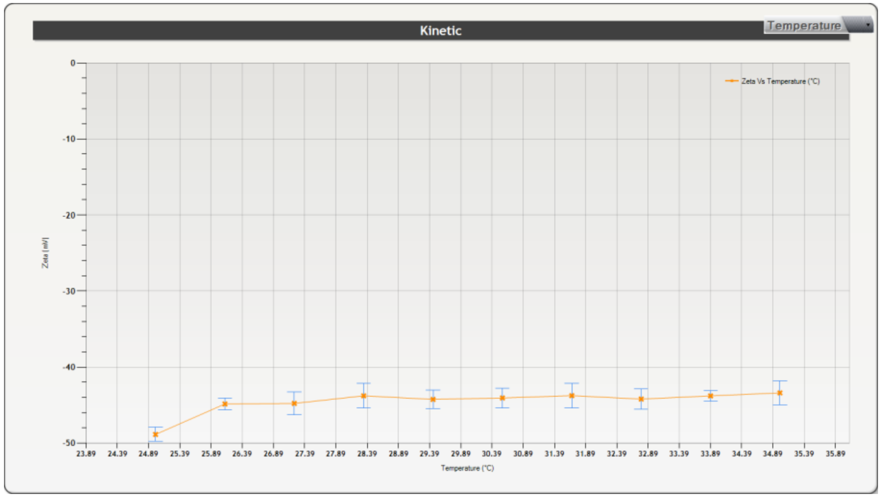
Amplitude (a.u.)



Zeta potential (mV)

Temperature Kinetics mode

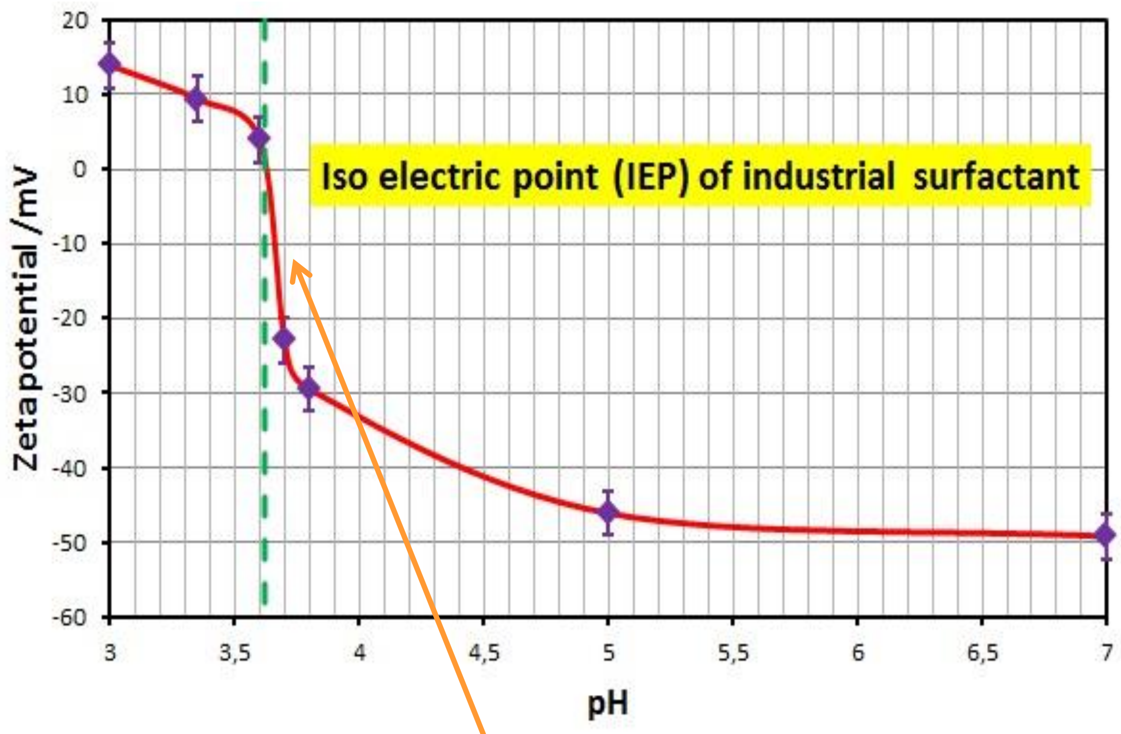
Zeta potential (mV)



Temperature(°C)

Performances example #2

IEP characterization of an industrial surfactant

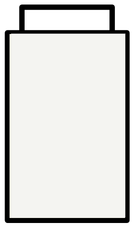


WALLIS High resolution allows precise measurement of IEP even with sharp Zeta transition !

Good practice for Sample preparation for LDE

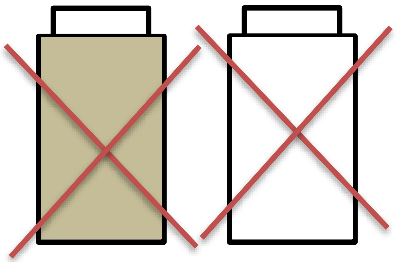
Homogeneity:

- sonication
- centrifugation
- filtration

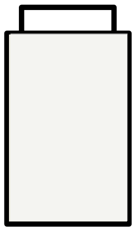


One homogenous phase

Concentration:



- dilution

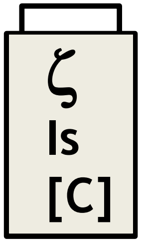


Transparent sample

pH and ionic force:

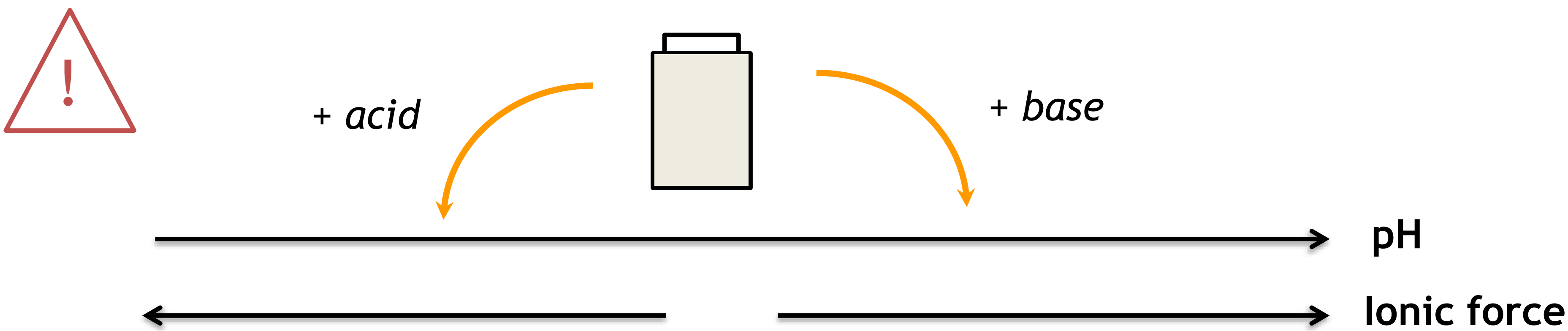
ζ function of pH and ionic strength!

- +base or acid solutions
- +salt buffer
- Dilution (if high cond)

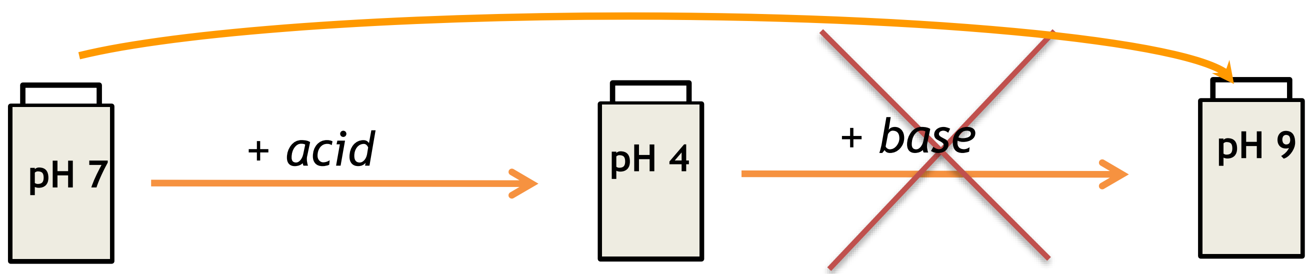


Sample preparation: pH and ionic force

- Addition of basic or acid solutions induces a change in the suspension ionic force.



- Addition of basic and acid in the same suspension produces a lot of salt



*Ex: $NaOH + HCl \rightarrow H_2O$ + **$NaCl$***

(always start pH adj. from Mother suspension)

Further reading!

[0] Tharwat Tadros ; General Principles of Colloid Stability; Colloids and Interface Science Series, Vol. 1

[1] Hunter R, Zeta potential in colloidal science; Academic press, New York, 1981

[2] Reliang Xu; Particle Characterization: light scattering methods; Kluwer Academic Publishers

[3] ISO13099B1,Colloidal systems—Methods for Zeta potential determination Part 1:Electroacoustic and electrokinetic phenomena

[4] V. DELGADO et al.; measurement and interpretation of electrokinetic phenomena; IUPAC Technical Report , Pure Appl. Chem., Vol. 77, No. 10, pp. 1753–1805, 2005

[5] R. Pusset et al,; Non-ideal effects in electroacoustics of solutions of charged particles: combined experimental and theoretical analysis from simple electrolytes to small nanoparticles

Thank you of your attention!

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