Part II: Nano particle charge/zeta potential measurement
Colloidal suspension stability?

- Stable systems
- Aggregation/agglomeration
- Flocculation
- Sedimentation
- Coagulation/coalescence
Repulsive forces: Charged particles in liquids repel each other (Coulomb force)

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

Colloid Stability depends on the balance between repulsive and attractive forces
Zeta Potential definition

\[ \zeta = \mu e \frac{\eta}{\varepsilon} f(\kappa \cdot a) \]

- \(\zeta\): Zeta Potential (mV); \(\mu\): electrophoretic mobility (m²/V·Sec); \(\varepsilon\): medium permittivity; \(\eta\): medium viscosity (Cp); \(a\): particle radius (m); \(\kappa\): inverse of double layer thickness; \(\kappa^{-1}\): Debye length (m); \(f(\kappa \cdot a)\): Henry’s function (depends on solvent)

Calculated \quad Measured \quad Solvent data base

99% cases !!!

- General cases
  - \(1 \leq f(\kappa \cdot a) \leq 1.5\)
  - \(f(\kappa \alpha) = 1\) Smoluchowski
  - \(f(\kappa \alpha) = 1.5\) Hückel
The higher the Zeta potential (absolute value) the more stable is the suspension.

For aqueous suspension, stability is obtained for $|\zeta \text{ pot}| > 30 \text{ mV}$.

For oil/water emulsion stability is obtained for $|\zeta \text{ pot}| > 5 \text{ mV}$. 

<table>
<thead>
<tr>
<th>Zeta potential [mV]</th>
<th>Stability behavior of the colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>from 0 to ±5</td>
<td>Rapid coagulation or flocculation</td>
</tr>
<tr>
<td>from ±10 to ±30</td>
<td>Incipient instability</td>
</tr>
<tr>
<td>from ±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>from ±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>more than ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>

IEP : IsoElectric Point
**Colloids stabilization**

**Van der Waals**

**Attractive forces**

Unstable

\[ \zeta \approx 0 \]

**Steric**

**Repulsive forces**

(Short range)

Limitation of irreversible aggregation/coalescence

\[ \zeta \ll 0 \]

**Electrostatic**

**Repulsive forces**

(Long range)

Stable

\[ |\zeta| > 30 \]

**Ionic surfactant, ligand... ex: citrate**

**Nonionic surfactant, ligand... ex: Tween 80**

**pH change, surface chemical modification**

**Ex : Polystyrene NPs**

**Ex : SiO2 NPs**
Main types of techniques used in the labs:

- Tunable Resistive Pulse Sensing (TRPS) technique:
  ➢ Single particle characterisation

- 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)

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

- Blockade magnitude is directly proportional to the volume of each particle.
- Blockade duration changes with the velocity of the particle and can be used to calculate the surface charge of each particle.
- Blockade frequency is used to determine particle concentration.

1 to 20 µm
Electro-acoustic basics

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

- Travelling acoustic wave
- Pressure modulation $\Delta P$
- Charge species displacement $= f(\text{mass/density})$
- Modulated charge density
- Electrical signal (CVP/CVI)

/AIDS: Applied burst voltage/Field
Acoustophoresis: The ESA Approach

Electric Sonic Amplitude (ESA): Apply a pulsed electric field and monitor an acoustic wave

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

- Mobility
- Normalised potential
- Particle Density
- Accoustic impedance term
- Vol fraction
- Solvent Density
- Cal function

Ex: Colloidal Dynamics Zeta Probe)
Acoustophoresis: 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

\[
\begin{align*}
\mu_d &= I_{CVI} \\
&= \frac{\rho_m}{\varphi(\rho_R - \rho_m)} \frac{1}{A(\omega)F(Z)}
\end{align*}
\]

- Normalised current
- Particle Density
- Mobility
- Vol fraction
- Solvent Density
- Cal function
- Acoustic impedance term

Ex: Dispersion technology DT300 (CVI)
Acoustophoresis CVP technique: implementation

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

**Sample cell**
- Frequency = 1 MHz
- Bursts of ~ 20 sinus
- \(P \approx 70000\) Pa
- Few ml
- \(d = 3 \frac{\lambda}{2} = 2.25\) mm
- Easy cleaning

**Extract signal from noise**:
- Filters at 1 MHz, amplification before differentiating
- Total gain \(\approx 5000\)
- Averaging by accumulation
Acoustophoresis Measurements

\[ [\mu_e] = \frac{\rho_{\text{NPs}}}{\phi_{\text{WT}} \ast (\rho_{\text{NPs}} - \rho_{\text{solvent}})} [CVP] \ast K \]

- NPs density
- Conductivity at 1 MHz
- Massique concentration
- Solvent density

![Graph showing CVP Signal](signal-graph)

![Graph showing Concentration vs. Signal](concentration-graph)
• Applying an Electric field: the particles move with its surrounding layers.

• Particle velocity directly related to its electrophoretic mobility and $E$

\[ \mu_e = \frac{v}{E} \]

\[ \vec{F}_e = q\vec{E} \]

\[ \vec{F}_f = \alpha \vec{v} \]

$\mu_e$: electrophoresis mobility

$E$: electric field

$V$: voltage applied

$q$: electric charge

$F_e$: electric force

$F_f$: friction force
Nano Particle tracking electrophoresis

Particle tracking/image analysis: particle speed calculation
-> Only for diluted samples and particle >30 nm
Laser Doppler Electrophoresis (LDE): principle

Heterodyne optical Interferometer: retrieving doppler low frequency

\[ f' \approx 1 + \frac{v}{c} \cdot \cos \theta \]

\[ \theta_d = 17^\circ \]

\[ \mu_e = \frac{\lambda_{\text{laser}}}{E \sin \theta_d} f_D \Rightarrow f(\kappa \cdot a) \Rightarrow \zeta \]
Purely designed and optimized for Charge/Zeta potential measurement
Based on Laser Doppler electrophoresis (LDE)
Complementary tool to particle size characterization
High resolution analysis down to 0.5 mV
LDE interferometer

Mirror modulation frequency: 8 kHz
Laser wavelength: 635 nm
Sample cell design consideration: 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 »
Reusable quartz cell -> no consumable
• Easy to clean
• Excellent optical quality
• Compatible with organic solvent
• Compatible with standard cell (10x10 mm²) ...
• Sample volume ≈750 µL
• Field proven concept
• Custom made electrodes
• No electro-osmosis

Measurement Dip cell configuration

- Connector
- Hellma Cell
  - Quartz, Glass or polystyrene polished
- Vitreous Carbon Electrodes
- Laser beam

Vitreous Carbon Electrodes

Dip cell 10 x 10 mm (WALLIS)

Electric field 2D map
Other cell/electrodes configuration:

- Compatible with standard cell
- U/Omega disposable cell

- Electrode materials: amorphous carbon, Paladium, gold coated Iron
- Electrode spacing: from few mm up to several cm
- Sample volume: 20µl to 1 ml
Measurement resolution: some experimental considerations

<table>
<thead>
<tr>
<th>Mode</th>
<th>Res. (Hz)</th>
<th>E field duration (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOW</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>MEDIUM</td>
<td>1.5</td>
<td>420</td>
</tr>
<tr>
<td>HIGH</td>
<td>0.6</td>
<td>850</td>
</tr>
</tbody>
</table>

Electric Field Modulation profile

\[ F_{mod} \pm F_D \]

8192 sampling points
\[ F_{mod} = 8 \text{ kHz} \]
Good practice for sample preparation for LDE:

**Homogeneity:**
- sonication
- centrifugation
- filtration

**Concentration:**
- dilution

**pH and ionic force:**
- +base or acid solutions
- +salt buffer
- Dilution (if high cond)

\[ \zeta \text{ is a function of pH and ionic strength!} \]
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: \( \text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl} \)  
(\textit{always start pH adj. from Mother suspension})
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

![Zeta potential analysis](image)

**Table: Zeta Potential Data**

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Mobility (μm²/V·s)</th>
<th>σ(ω)</th>
<th>Zeta (mV)</th>
<th>σ(ζ)</th>
<th>pH</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ludox 0.5% ZPA141203-LOW</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.1</td>
<td>0.11</td>
<td>-38.52</td>
<td>1.47</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>3.11</td>
<td>0.06</td>
<td>-39.63</td>
<td>0.76</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>3.1</td>
<td>0.06</td>
<td>-39.81</td>
<td>0.8</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>3.19</td>
<td>0.13</td>
<td>-41.05</td>
<td>1.57</td>
<td>7</td>
<td>25</td>
</tr>
</tbody>
</table>

**Ludox 0.5% ZPA141203-HIGH**

| 1        | 2.63                | 0.11 | -34.57     | 1.43 | 7  | 25               |
| 2        | 2.72                | 0.07 | -35.03     | 0.60 | 7  | 25               |
| 3        | 2.75                | 0.05 | -33.37     | 0.83 | 7  | 25               |
| 4        | 2.74                | 0.05 | -35.25     | 0.59 | 7  | 25               |

**Ludox TM50 - 0.5% - pH=2**

| 1        | 0.07                | 0.06 | -0.67      | 0.75 | 2  | 25               |

[**Copy bitmap to clipboard**]
[**Copy data to clipboard**]
[**Cursor Mode**]
[**Display Zeta Potential**]
[**Display Fit**]
Performances example #1

with correlator (other suppliers)

Résolution : 3.7 mV !!!

with fast acquisition (WALLIS)

Résolution < 0,5 mV !!!
Experiment example on Ludox TM50 0.5%

- **Resolution mode comparison**
- **Temperature Kinetics mode**
- **Reproducibility**
- **Isoelectric point location**
Performances example #2

IEP characterization of an industrial surfactant

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

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


Thank you of your attention!

www.cordouan-tech.com

Follow Cordouan Technologies on Twitter!