Introduction to Zeta Potential Measurement with the SZ-100

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What is Zeta Potential?

- Zeta potential is the charge on a particle at the shear plane.

Shear plane

Bulk liquid
How do Surfaces Acquire Charge?

Ionization of surface groups

-COO^-  -COO^-H^+  -COO^-  -COO^-  -COO-H^+  -COO^-  -COO^-  -COO^-  -COO^-  -COO^-  -COO^-  -COO^-  -COO^-
How do Surfaces Acquire Charge?

Differential loss of ions from surface
e.g., AgI,
Ag+ dissolves preferentially

$$\begin{align*}
\text{Ag}^+ & \quad \text{I}^- \\
\text{Ag}^+ & \quad \text{surface} \\
\text{Holes from dissociated ion} & \\
\text{Ag}^- & \quad \text{Ag}^+ \\
\end{align*}$$
How do Surfaces Acquire Charge?

Specific adsorption of ions, e.g. ionic surfactants

\[ \text{Anionic surfactant} \]

\[ \text{H}^+ \]
Why Zeta Potential?

- Good way of evaluating electrostatic stabilization of suspensions
- Can use to predict interactions

![Graph showing Zeta Potential vs pH](image)
How to Measure Zeta Potential:

- Acoustic techniques (use sound to probe particle response)
- It is much more popular to use light scattering to probe motion of particles due to an applied electric field. This technique is known as electrophoretic light scattering.
- Used for determining electrophoretic mobility, zeta potential.
Other Light Scattering Techniques

- **Static Light Scattering:** over a duration of ~1 second. Used for determining particle size (diameters greater than 10 nm), polymer molecular weight, 2\textsuperscript{nd} virial coefficient, \(R_g\).

- **Dynamic Light Scattering:** use scattered light to probe random motion of particles. If this motion is due to Brownian motion the technique can be used to determine particle size.
How to Measure? With the SZ-100

- Single compact unit that performs size, zeta potential, and molecular weight measurements: the SZ-100
How to determine zeta potential

- Apply an electric field and probe response of particles to applied field.
- You need to see Doppler shift in scattered light due to particle motion with respect to fixed electrodes.

\[ \omega_0 + \omega_d \]
Optical System

Use optical mixing to extract motion of particles relative to electrodes.
Optical Mixing

Frequencies differ by 3%

Sum of waves has easy to see oscillation
Data Analysis

- Analyze observed spectrum.

- $\omega_D$

- shifted due to motion of particles.

- broad due to diffusion
Doppler Shift Calculations

\[ \omega_D = q \cdot V \]

- \( \omega_D \) = frequency (Doppler) shift, measured
- \( q \) = scattering vector
- \((4\pi n/\lambda)\sin(\theta/2)\), known
- \( V \) = particle velocity
- \( E \) = electric field strength, known
- \( \mu_e \) = electrophoretic mobility (desired result)
Zeta Potential Calculation

- Need to use a model to obtain zeta potential (desired quantity) from mobility (measured quantity).
- Most common is Smoluchovski (shown here)

\[ \mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta(T)} \]

- \( \varepsilon_r \) = relative permittivity (dielectric constant)
- \( \varepsilon_0 \) = permittivity of vacuum
- \( \zeta \) = zeta potential
- \( \eta \) = viscosity (function of temperature)
Ceramics; Ludox® Silica

<table>
<thead>
<tr>
<th>Silica</th>
<th>Ludox Silica® TM-50 with 0.01M KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Preparation</td>
<td>100 ppm</td>
</tr>
</tbody>
</table>

- **Conditions**
  - Temperature: 25°C
  - Solvent: Water
  - Refractive Index: 1.333
  - Distribution base: Scattering light

- **Results**
  - Mobility (μm·cm/V·s): -3.02
  - Zeta Potential (mV): -31.8

From GRACE’s catalogue
Application (Zeta Potential)

Iso Electric Point of Coffee Mate

<table>
<thead>
<tr>
<th>Iso-electric point</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4.0</td>
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</table>

If you want to bind Ludox HS (IEP ~pH 2) to Coffee Mate, what pH should you choose?
Using Zeta Potential to Predict/Control Particle Interactions

- Note size maximum at IEP due to flocculation.
- If you mix Al₂O₃ with Fe₂O₃, what happens?
  - At pH 2, both are positive: no interaction
  - At pH 6, Al₂O₃ is positive and Fe₂O₃ is negative: particles stick together.
  - At pH 9, both are negatively charged, no interaction.

Data from Berg et al., Nanotoxicology, Dec. 2009; 3(4): 276-283
Zeta Practical Tips
Impurities

- Zeta is a **surface property**.
- Result is sensitive to surface active impurities.
  - Soaps/detergents
  - Specific ions (e.g., Cl\(^-\), TSPP)
  - Grease/oil/fingerprints (hydrophobic materials will go to surfaces of aqueous suspension)
- Keep everything extremely clean
- Keep surfactant additives in mind when interpreting data.
Electrolyte

- Recall that potential is a function of ionic strength.
- Pure water has an ionic strength of \(~10^{-7}\) M.
- A little bit of CO\(_2\) from the air can raise ionic strength by a factor of 10 or 100 to \(10^{-5}\) M.
- Use 1 mM electrolyte instead of no electrolyte to keep electrolyte levels (and therefore results) consistent from sample to sample.
- This doesn’t apply for samples that already have substantial electrolyte.
Electrolyte Continued

- Titration is popular.
- Remember that acid and base will add to system ionic strength. pH 3 corresponds to $10^{-3}$ M electrolyte.
- Adding acid or base will increase ion concentration.
- Start with a 10 mM ($10^{-2}$ M) salt ($\text{KNO}_3$) concentration to keep acid/base concentration from affecting results.
Why Zeta Potential?

- Use measured surface charge to predict colloidal stability
- Use measured surface charge to predict particle-particle interactions
Q&A

Ask a question at labinfo@horiba.com

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Visit the Download Center to find the video and slides from this webinar.

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Thank-you