Interfacial Engineering

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Lecture-39

Electrokinetic phenomena

Electrophoresis; Electroosmosis: Zeta Potential; Electrokinetic models such as Huckel, Helmholtz-Smoluchowski, and Henry demonstration particle size and zeta potential measurements using zetasizer

Welcome back. So, in this video lecture, we will look at what electrokinetic phenomena are known. So, under this umbrella called electrokinetic phenomena, various scientists have carried out several studies. One of them is very widely used, and that is nothing but electrophoresis studies. So, electrokinetic phenomena based on electrophoresis study are often used by colloidal scientists in determining the electrophoresis or the elliptic mobility of the charged particle. Hence, this is also helpful in deciding zeta potential right we are going to look at you see why we measure zeta potential we are going to address question on you know why we will measure we measure zeta potential why not surface potential right so those things we will see in details in this video lecture let's begin.

Time: 1.20 mins

What Are Electrokinetic Phenomena?

Movement of ions or particles with respect to electrical phenomena

1. Electrophoresis: This refers to movement of a particle (and double layer attached to the surface of the particle) relative to a stationary liquid under the influence of an applied electric field.

2. Electroosmosis: Here, the liquid (an electrolyte solution) moves past a charged surface (e.g., the surface of a capillary tube or through a porous plug) under the influence of an electric field. Thus, electroosmosis is the complement of electrophoresis. The pressure needed to balance the electroosmotic flow is known as *electroosmotic pressure.*
Application: Dewatering of soils for construction purposes, dewatering of waste sludges, etc.

3. Sedimentation potential: Electric potential generated when the charged particles are forced to move relative to a stationary liquid. This phenomena is inverse of electrophoresis.

4. Streaming potential: Generation of electric potential by the movement of a liquid (electrolyte) along a solid surface. This is also known as reverse electroosmosis.

Electro kinetic phenomena in the context of colloid & surface chemistry refers to phenomena that ca[...]ed to measure zeta potentials and charges of colloidal species.

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Yes, so as we described, there are several electrokinetic phenomena. Let's say electrophoresis, electroosmosis, right? Sedimentation potential, steaming potential.

So these four techniques are being used in electrokinetic phenomena. What is more, I mean, electrophoresis is widely used by colloid scientists, right? So this is nothing but the movement of charged particles in a liquid electrolyte under the influence of an electric field. That is nothing but an electrophoresis study. Electroosmosis is quite different.

Here, the charged particle will be stationary, whereas the liquid electrolyte will be a mobile phase, right, under the electric field. So this study is nothing but an electroosmosis study. In various applications, this study is used, such as dewatering soils for construction purposes, waste sludges, sedimentation potential, streaming potential, and other electrokinetic phenomena. They are nothing but the inverse of electrophoresis or the inverse   of   electroosmosis.

For example, in the case of sedimentation potential, we are not applying electric potential. Still, electric potential is generated when a charged particle is moving, forced to move relative to the stationary phase. Here, the stationary phase is nothing but the electrolyte. On the other hand, streaming potential is nothing but a study where electric potential is generated by the movement of liquid electrolyte when the solid is stationary. This is also nothing but reverse electroosmosis.

Time: 3.20 mins

What Are Electro kinetic Phenomena?

Movement of ions or particles with respect to electrical phenomena

Electrophoresis
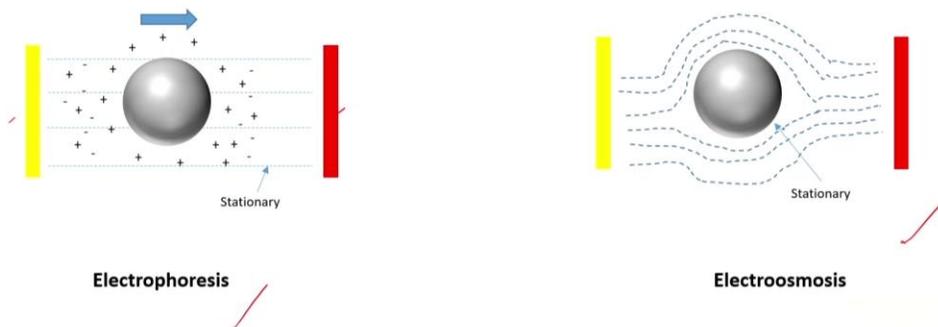
Electroosmosis
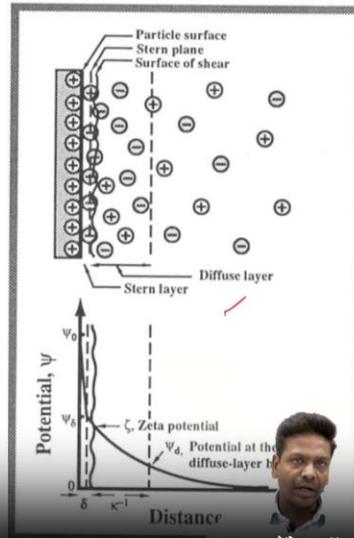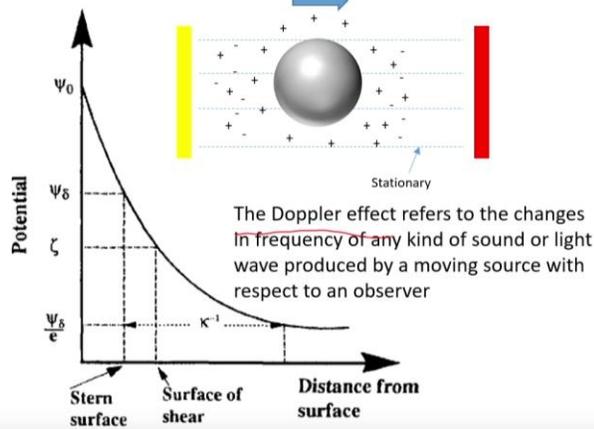
But here we will see electrophoresis and electrosmosis in a more detailed way.

I have illustrated both electrophoresis and electrosmosis phenomena as schematics over here. Electrophoresis is nothing but movement of the charged particle under the influence of electric field. Here, these two electrodes are essential. So when electric field is applied this will induce the movement of charged particle but there will be electrolyte. So this particle will be surrounded by the electrolyte.

Here, electrolyte is stationary phase. Charged particle is the mobile phase. On the other hand, electroosmosis, here, the charged particle, I have not shown the electrical double layer here, but you can assume there is electrical double layer. So here, the particle is stationary, whereas the liquid electrolyte is the mobile, right, mobile phase, right? So that is the difference between electrophoresis and the electroosmosis.

Time: 4.30mins

Zeta Potential

The Doppler effect refers to the changes in frequency of any kind of sound or light wave produced by a moving source with respect to an observer

➤ Zeta potential is the key indicator of stability of the colloidal systems.

Doppler shift based technology is helpful in tracking spacecraft velocity as f(d)

10:23 / 27:23

Now, why it is so important? How does this electrophoresis study movement of charged particle under the influence of electric field in the presence of electrolyte is essential? That is precisely what we are going to look at in this slide. It is essential.

We need to understand what is nothing but the... a Doppler shift okay how we can measure or determine the electrophoretic mobility how this is useful in determining the zeta potential that is precisely what we are looking at in this slide so here if you look at you know that whenever we introduce a charged object right in the into the electrolyte medium so three kinds of counter ions emerge right firmly bound counter ion, weakly bound counter ion and diffuse counter ion. The firmly bound counter ion and weakly bound counter ion form the stern and shear layers right.

So, the strongly bound counter ion contributes to the stern layer whereas the weakly bound counter ion contributes to the shear layer. and the diffuse counter ion contribute to the diffuse layer. Hence, there are only three layers whenever you introduce the charged particle the electrical double layer is developed okay it consists of three layer stern layer shear layer and diffuse layer right Now, the stern layer and the shear layer is rigid. OK, that is something you must know. Keep in mind. So the stern layer and the shear layer form the rigid layer, whereas the diffuse layer is a porous layer.

So when I say porous, meaning it can allow the light to pass through, but the rigid layer will not allow the light to pass through. If I shine a laser light onto the particle surface, you may imagine the light will strike the particle surface, but not. fundamentally they will not strike the particle surface they will strike the outermost layer that is the shear layer that's

why whenever you measure the potential we don't call it as a surface potential because the potential that we measure is at the boundary between shear and the diffuse layer okay So this is why we say that whatever we measure, potential that we measure is zeta potential, not the surface potential. So we know that there are three layers. So the stern layer and shear layer form the rigid layer, whereas diffuse layer is the porous layer that will allow the light to pass through.

Now, what is known as Doppler effect is what is, you know, very useful for us to measure the electrophoretic mobility. So what happens is whenever you shine a laser light, because the particle is under the, you know, movement continuously under the influence of electric field. After all, the laser light is now striking the particle's surface when the particle is subject to movement under the electric field. So that creates a shift in the frequency of laser light. That is nothing but Doppler shift. and because it creates a change in the frequency we can record, collect this information as a function of distance and eventually this shift in the frequency as a result of the particle's movement is you know a process you know to get details such as electrophoretic mobility.

When I say electrophoretic mobility it is not just the velocity It is velocity per unit electric field, okay? That is what exactly we measure. As we move on, you will know how this electric field is helpful for us to measure the zeta potential, right? Sorry, the electrophoretic mobility. Now, you will be.

.. So... you will be able to understand how this is useful in determining the zeta potential, which is the potential measured at the boundary between shear and the diffuse layer, right? Now, you will be wondering to know that, you know, this Doppler technology is what being used in the Chandrayaan, the recent spacecraft that we sent to moon, right, in India's mission, one of the successful missions. One of the reasons for achieving the soft landing is the Doppler shift technology. This helps determine the spacecraft velocity as a distance function, so you can track the speed. at which the spacecraft is approaching the land right, you will be able to control the speed of the spacecraft as well. Hence, this is you know housed in the space in the spacecraft right such that so that you that i mean because of that we were able to track the speed of the spacecraft velocity when it was approaching the moon land right Right. So this is very interesting technology.

Right. So this is what exactly we are going to look at. So next slide, we will look at how we can get the fundamental, governing equation as a function of. So we will be able to measure zeta potential by knowing the electrophoretic mobility. That is what exactly we are going to look at now. So we will start from here.

Time : 10.29mins

❑ An isolated ion in an electric field experiences a force directed toward the oppositely charged electrode.

Electric force, F_{El}

Viscous force, F_{vis}

Assuming Stokes's regime
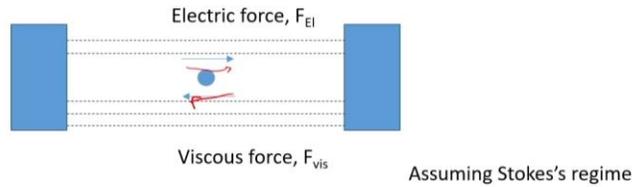
$F_{El} = qE$ (1)

$F_{vis} = fv = 6\pi\eta R_s v$ (2)

At stationary state, $F_{el} = F_{vis}$

$$u = \frac{ze}{6\pi\eta R_s}$$ (5)

$q = C = \frac{J}{v}; E = \frac{v}{m}$ and hence $F_{El} = N$

$qE = 6\pi\eta R_s v$ (3)

$\left(\frac{v}{E}\right) = \frac{ze}{6\pi\eta R_s}$ (4)

$u = \frac{v}{E} = \frac{m}{s} \cdot \frac{2}{v}$

12:17 / 27:23

So the governing equation for this problem is starting from the force balance. That is, there are two counteracting forces acting in this. One is whenever you suspend a charged particle. There will be two contracting forces when it is subject to the movement under the electric field in the presence of electrolyte medium. One will be force due to electric field because the particle is charged.

There is electric field. So the particle is under the movement concerning electric field. So there will be force experienced by the particle that is due to electric field. That is nothing but:

Q × E

where E is the electric field,
and Q is the charge.

On the other hand, when a particle is subject to movement under the electric field, there will be a counteracting force due to the viscosity of the medium. So, there will be a viscous force in the opposite direction.

If the particle moves in one direction, there will be a counteracting force in the opposite direction due to the medium's viscosity.

So, you will have a viscous force acting against it.

At equilibrium or stationary state, these two forces are equal and balance.

So if I equate these two forces:

$Q \cdot E = 6 \cdot \pi \cdot \eta \cdot R_s \cdot V$

V / E is nothing but U, which is the electrophoretic mobility.

Also, $Z \cdot e = Q$, so we have:

$Z \cdot e \cdot E = 6 \cdot \pi \cdot \eta \cdot R_s \cdot V$

This is the governing equation for this scenario.

Time: 12.23mins

Relationship between surface or zeta potential and mobility

Potential distribution around a spherical particle

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = \frac{-\rho^*}{\varepsilon_0 \varepsilon_r}$$

$$\Psi = \frac{q}{4\pi\varepsilon r} e^{-kr}$$

At large k^{-1} or small k ⟶ $\zeta = \Psi$

$$\zeta = \frac{q}{4\pi\varepsilon r} \cdot \frac{1}{e^{kr}} = \frac{q}{4\pi\varepsilon r} \frac{1}{(1+kr)}$$

if k is small such that $kr \ll 1$

$$\zeta = \frac{q}{4\pi\varepsilon r} \cdot \frac{1}{e^{kr}} = \frac{q}{4\pi\varepsilon r}$$

Analogues to flow streamline

$$\zeta = \frac{ze}{4\pi\varepsilon r}$$

From eq. 5

More elaborate theory shows that the eq. is valid.

$$\zeta = \frac{u 6\pi\eta r}{4\pi\varepsilon r}$$

Thick EDL

$$u = \frac{2\varepsilon\zeta}{3\eta}$$

Hückel equation

valid when $kr < 0.1$

Helmholtz- Smoluchowski equation

$$u = \frac{\varepsilon\zeta}{\eta}$$

valid when $kr > 100$

$$u = C\frac{\varepsilon\zeta}{\eta} \qquad C = 1; C =$$

Thin EDL

2/3 factor is not needed

Hiemenz, P. C., & Rajagopalan, R. (2016). Principles of Colloid and Surface Chemistry, revised and expanded. CR'

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Now, a very interesting analogy we need to go through. Let's say we have the streamlines or potential lines.

If we suspend a charged particle with different particle sizes, assume two particles of different radii but with the same Debye length (κ^{-1}). In one case, $\kappa \cdot R_s$ is very small, and in the other, $\kappa \cdot R_s$ is very large.

Note: $\kappa = 1 / (\kappa^{-1})$, so if κ is small, κ^{-1} is large, and vice versa. But in this analogy, we keep κ^{-1} constant and vary R_s.
- Small $R_s \rightarrow \kappa \cdot R_s$ is small
- Large $R_s \rightarrow \kappa \cdot R_s$ is large

When $\kappa \cdot R_s$ is small, the potential lines remain undisturbed near the particle; the streamline

is uniform. In contrast, when $\kappa \cdot R_s$ is large, the potential field deforms around the particle.

Thus:
- When $\kappa \cdot R_s \ll 1 \rightarrow \zeta \approx \psi_0$ (zeta potential $\approx$ surface potential)
- When $\kappa \cdot R_s \gg 1 \rightarrow \zeta \neq \psi_0$ (zeta, Stern, and surface potentials differ)

Consider a spherical particle and assume a one-dimensional case in spherical coordinates. Solving the governing equation gives:
$\psi(r) = (Q / (4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r)) \cdot \exp(-\kappa \cdot r)$

This is similar to the planar case from the Poisson-Boltzmann equation.

If κ^{-1} is large (i.e., thick double layer), then $\psi \approx \zeta$, and we can replace ψ with ζ in the above equation.
Expanding the exponential for small $\kappa \cdot r$:
$\exp(-\kappa \cdot r) \approx 1 - \kappa \cdot r + (\kappa \cdot r)^2 / 2 - \ldots \approx 1 - \kappa \cdot r$ (neglecting higher-order terms)

So:
$\psi \approx Q / (4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r)$

Now, $Q = Z \cdot e$, and substituting mobility:
$U = (2 / 3) \cdot (\varepsilon \cdot \zeta / \eta)$, where $\varepsilon = \varepsilon_0 \cdot \varepsilon_r$

This is known as the Huckel equation, valid for $\kappa \cdot R_s < 0.1$.

When $\kappa \cdot R_s \gg 1$ (thin double layer), use the Helmholtz–Smoluchowski equation:
$U = (\varepsilon \cdot \zeta) / \eta$

Generalized form:
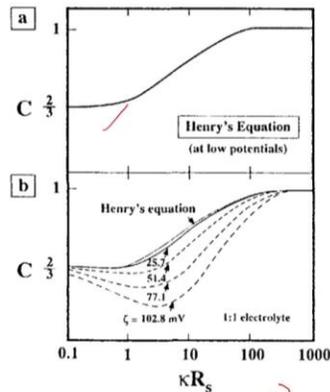$U = C \cdot (\varepsilon \cdot \zeta / \eta)$, where:
- $C = 2 / 3 \rightarrow$ Huckel ($\kappa \cdot R_s \ll 1$)
- $C = 1 \rightarrow$ Smoluchowski ($\kappa \cdot R_s \gg 100$)

If $\kappa \cdot R_s$ is in between, this is the most interesting and complex case.
In practice, electrophoretic mobility (U) is measured (e.g., via zeta sizer), substituted into the appropriate equation, and ζ is determined.

Time: 20.42 mins

$$u = \frac{2 \epsilon \zeta}{3 \eta} f(\alpha)$$

where

$$f(\alpha) = \left(1 + \frac{1}{16}\alpha^2 - \frac{5}{48}\alpha^3 - \frac{1}{96}\alpha^4 - \frac{1}{96}\alpha^5 \right.$$
$$\left. - \left[\frac{1}{8}\alpha^4 - \frac{1}{96}\alpha^6\right] \exp(\alpha) \int_{\infty}^{\alpha} \frac{e^{-t}}{t} dt\right) \quad \text{with} \quad \alpha = \kappa R_s < 1$$

For $\kappa R_s > 1$, the function $f(\alpha)$ becomes (see Hunter 1981)

$$f(\alpha) = \left(\frac{3}{2} - \frac{9}{2}\alpha^{-1} + \frac{75}{2}\alpha^{-2} - 330\,\alpha^{-3}\right)$$

Variation of the constant C with kr, (log scale): (a) at low potentials according to Henry's equation; and (b) for various potentials

Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded.* CRC

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Let's say it is between point one to hundred. Debye-Hückel Parameter
The Debye-Hückel parameter, denoted as κ^2 (k squared), is defined as:
$\kappa^2 = (e^2 / (\epsilon\, k\_B\, T)) \times \Sigma(z_i^2 \times n_i^\infty)$

Where:
- z_i is the valence of the i-th ion
- n_i^∞ is the bulk concentration

It is often useful to express n_i^∞ in terms of molarity:
$n_i^\infty = 1000 \times N\_A \times M_i$

Where:
- M_i is the molarity (mol/L)
- N_A is Avogadro's number (constant)

The factor 1000 converts mol/L to mol/m³ (SI units).

Debye Screening Length
The inverse of κ, $1/\kappa$, is the Debye screening length.

This length characterizes the thickness of the diffuse boundary layer in an electrostatic system.
Beyond this length, electrostatic potential due to the surface charge becomes negligible.

A charged surface (e.g., negatively charged solid) attracts counter-ions.

- Near the surface: strongly bound counter-ions
- Further out: diffuse layer of ions

Beyond a distance of $1/\kappa$, the influence of the charged surface is effectively zero. No significant interaction occurs between ions beyond this zone and the surface charge.

Henry's Equation and Electrokinetics
For $0.1 < \kappa R_s < 100$, Henry's equation applies:
$$\mu_e = (2\varepsilon\zeta / 3\eta) \times f(\alpha)$$

- $f(\alpha)$ is Henry's function, which changes depending on κR_s
- For $\kappa R_s < 1$: use one expression for $f(\alpha)$
- For $\kappa R_s > 1$: use another expression for $f(\alpha)$

At low potential ($\zeta < 25$ mV), the mobility (μ_e) vs. potential graph is linear.
For $\zeta > 25$ mV, the graph becomes nonlinear, dependent on κR_s.

General form:
$$\mu_e = (\varepsilon\zeta / \eta) \times C$$
C is derived from plots for different κR_s.

Model Selection Based on κR_s
- If $\kappa R_s < 0.1$, use Hückel model:
  $$\mu_e = (2\varepsilon\zeta / 3\eta)$$
- If $\kappa R_s > 100$, use Smoluchowski model:
  $$\mu_e = (\varepsilon\zeta / \eta)$$
- For intermediate values, use Henry's model.

Electrokinetic Potential and Layers
When a charged particle is introduced in electrolyte:
- Strongly and weakly bound counter-ions form the Stern and shear layers
- Diffuse ions form the diffuse layer (porous and optically active)

Laser light in electrophoresis interacts with the shear layer, not the particle surface. Measured zeta potential corresponds to the potential at shear-diffuse layer boundary.

Surface vs Zeta Potential
- For small κR_s, surface potential $\approx$ zeta potential.
- For large κR_s, exact expressions (e.g., Smoluchowski's) are needed.

Summary:
- Hückel Equation: approximation for small κR_s (C = 2/3)
- Smoluchowski Equation: large κR_s (C = 1)
- Henry's Equation: interpolation for intermediate κR_s

Conclusion
Electrokinetic phenomena and zeta potential measurement are crucial in colloid science.
Henry's equation bridges the Hückel and Smoluchowski models.
Understanding κ, κ^{-1}, and κR_s is essential for accurate experiment interpretation.

End of lecture.

Three kinds of counter ions will emerge: strongly bound, weakly bound and diffuse counter ion. The strongly bound, weakly bound contributes to stern layer, shear layer. And the diffuse counter ion contribute to diffuse layer diffuse layer is the porous layer, which will allow the light to pass through. In contrast, the stern layer and shear layer are strong and rigid layer that will not allow any light to pass through so whenever you shine a laser light it is not striking the particle surface remember that this is very important concept It is striking the outermost layer that is nothing but your, you know, shear layer. So whatever potential you measure is the potential at the boundary between the shear and diffuse layer.

Okay. It is not the surface potential. Right. So, this concept you must know. So, because we are not measuring the surface potential, we are using this analogy called KRS, which is small, KRS, which is large. When KRS is small, you are still allowed to, I mean, we can safely use the surface potential equation as a zeta potential equation by substituting surface for zeta potential. Right when krs is large then the problem comes so for that there is a you know a detailed derivation by shown by you know helmer smolohowski so one has to go through this textbook okay there it is given in details so the final and compact equation in that case will be that is also same as the zeta potential. Still, your c factor will be different if it is one instead of two by three. So once you know that, you know on one hand you have the Huckel equation because it comes from the approximation.

On the other hand, you have Smoluchowski's equation. And although we have not shown the detailed derivation here, you can go through the textbook. The other one is the Henry equation that is in between, right? So, these things should be very clear. And this electrokinetic phenomenon is a very interesting topic. And people often use this electrophoresis study nowadays to solve many problems, okay? And I hope these things are very clear now.

We will stop here. We will continue from the following lecture. Thank you.