Ceramic Processing
5 Colloidal Processing Fundamentals

Introduction

❑Colloidal suspension - contains two distinct phases

- A continuous **liquid** or dispersion phase or medium
- Fine, dispersed **particulate** phase or disperse phase, often with size ~1-1000 nm

Slip-casted clay pot

https://britehub.com/manufacturing/casting/slip-casting

❑Ceramic processing via (colloidal) suspension

- Advantages over processing of dry/semidry powders
  - Capability to process complex shape/high aspect ratio
  - Better microstructural control and uniformity

Tape-casted green ceramic tape

http://www.cgcri.res.in/page.php?id=43

❑Issues with stability of colloidal suspension

- Gravity of particles causing sedimentation
  - Less significant for colloidal suspension with particle size <1 μm
- Attraction between particles that cause them to flocculate/form agglomerates
  - Need to introduce repulsive force

❑Additional aspects of interest

- Rheology – movement of suspension when subject to stress
- Electrophoresis - motion of particles in suspension when subject to electrical field

Rahaman (2003), p. 181-182

Van der Waals Forces

- **Secondary bonding force existing between all atoms, molecules, and particles**
- **Categories**
  - Force between permanent dipoles - Keesom forces
    - e.g., between H_2O or HF molecules
  - Force between permanent dipole and a induced (transient) dipole - Debye forces
    - e.g., between HF and H_2 molecules
  - Dispersion force, i.e., forces between induced (transient) dipole – London forces
    - e.g., between H_2 and H_2 molecules
- **Magnitude**

  Potential energy for van der Waals force generally satisfy

$$V \propto \frac{1}{x^6}$$

Rahaman (2003), p. 183-184

https://en.wikipedia.org/wiki/Van_der_Waals_force

Van der Waals Forces between Particles (1)

❑Description

- Assumption: Interactions (specifically attraction) between two particles is the sum of the interactions between one small unit in one particle with one small unit in the other particle
- Define

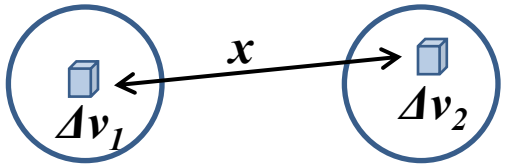
Δv_1 Infinitesimally small volume unit in particle 1

Δv_2 Infinitesimally small volume unit in particle 2

n_1 Atom number density in particle 1

n_2 Atom number density in particle 2

x Distance between the two small units



The potential energy between the two small units $\delta V = -\frac{C}{x^6} n_1 \Delta v_1 n_2 \Delta v_2$

The total interactive energy between the two particles

$$V_A = \int -\frac{C}{x^6} n_1 n_2 dv_1 dv_2$$

Rahaman (2003), p. 185-190

Van der Waals Forces between Particles (2)

❑ **Continue from previous page**

Rahaman (2003), p. 185-190

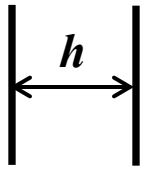
Hamaker showed

$$V_A = -\frac{A}{\pi^2}\int\frac{dv_1 dv_2}{x^6}$$

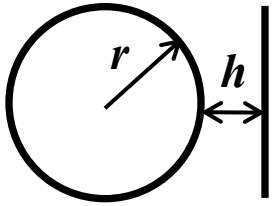
Material/system specific Geometric term

A is called Hamaker constant and it is material/system specific

❑ **Special cases**

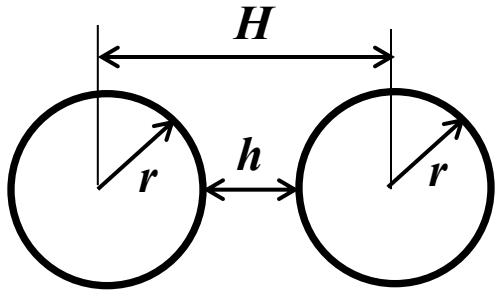


$$V_A = -\frac{A}{12\pi h^2}$$



When r >> h

$$V_A = -\frac{Ar}{6h}$$



When h << r $V_A = -\frac{Ar}{12h}$

When h >> r $V_A = -\frac{16Ar^6}{9h^6}$

Practical Hamaker Constant

- Hamaker constant usually in the range of 10^{-20}-10^{-19} J (or 2.5-25 kT) at room temperature
- Hamaker constant decreases when there is medium compared with air or vacuum

Material	Crystal Structure	A in vacuum (10^{-20} J)	A in water (10^{-20} J)
α-Al_2O_3	Hexagonal	15.2	3.67
$BaTiO_3$	Tetragonal	18	8
C (diamond)	Cubic	29.6	13.8
$CaCO_3$	Trigonal	10.1	1.44
KCl	Cubic	5.51	0.45
MgO	Cubic	12.1	2.21
6H-SiC	Hexagonal	24.8	10.9
SiO_2 (quartz)	Trigonal	8.86	1.02
TiO_2	Tetragonal	15.3	5.35

Rahaman (2003), p. 185-190

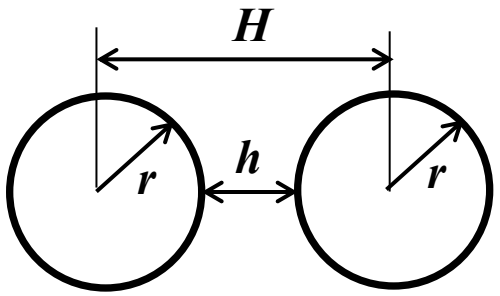
Van der Waals Forces between Particles vs. Thermal Energy

❑For colloidal suspension of similar particles

Assuming the equation for potential energy is valid down to contact, and if

- Particle separation distance h = 0.3 nm
- Hamaker constant A = 10^{-20} J

Then van der Waals energy will be:



$$\textit{When } h << r \quad V_A = -\frac{Ar}{12h}$$

when particle radius r = 200 nm

$$V_A = -\frac{10^{-20}\,J \times 200nm}{12 \times 0.3nm} = -5 \times 10^{-19}\,J$$

when particle radius r = 20 nm

$$V_A = -\frac{10^{-20}\,J \times 20nm}{12 \times 0.3nm} = -5 \times 10^{-20}\,J$$

The negative sign represents **attraction** force between particles

❑Thermal energy

At room temperature, thermal energy on the order of KT

$$KT = 1.38 \times 10^{-23}\,J/K \cdot 298K = 4 \times 10^{-21}\,J$$

Either case, $KT << |V_A| \rightarrow$

Rahaman (2003), p. 190-191

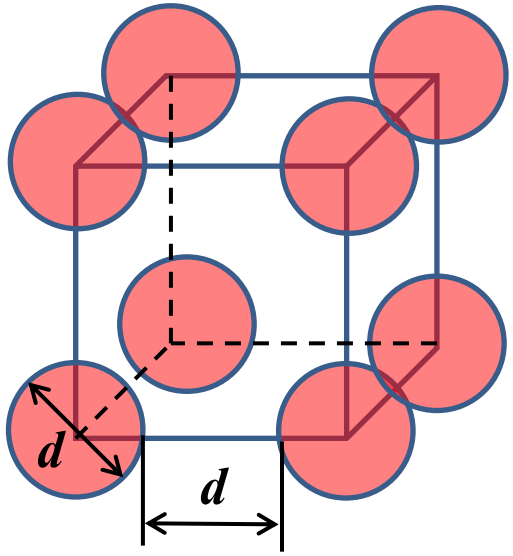
Colloidal particles tend to stick together in suspension!

Estimation of Volume and Weight Fraction

- **Assuming SOLID particles of diameter d arranged in suspension like simple cubic fashion and with separation $h = d$ (i.e., center to center distance of $H = 2d$)**
  - Please calculate the volume fraction of the SOLID particle in the suspension

$$V_S\% = \frac{V_{Solid\ particles}}{V_{repeat\ unit}} = \frac{8\times\frac{1}{8}\times V_{sphere}}{V_{cube}} = \frac{8\times\frac{1}{8}\times\frac{1}{6}\pi d^3}{(2d)^3}$$

$$= \frac{\pi}{48} \approx 6.5\%$$



  - Please calculate the weight fraction of particle in the above suspension assuming density of particle is 4 g/cm^3 and density of solvent is 1 g/cm^3

$$w_S\% = \frac{W_S}{W_S + W_L} = \frac{V_S\% \cdot \rho_S}{V_S\% \cdot \rho_S + (1 - V_S\%) \cdot \rho_L} = \frac{0.065 \times 4}{0.065 \times 4 + 0.935 \times 1} \approx 21.8\%$$

In practical colloidal suspension, average interparticle **distance** is often **NOT large**!

Three Ways to Achieve Stabilization of (Colloidal) Particle Suspensions

- **Fine particles in suspension tend to flocculate due to van der Waals forces larger than thermal energy**
- **Need to introduce repulsive force between particles to stabilize colloidal particle suspension**

- **Electrostatic stabilization**
  Repulsion between particles due to electrostatic charges on particle surface

- **Steric stabilization**
  Repulsion between particles due to uncharged polymer chains adsorbed on particle surface

- **Electrosteric stabilization**
  Combination of electrostatic and steric repulsion

Rahaman (2003), p. 191

Ways to Develop Charge on Oxide Particles Surface in Aqueous Solution

- **Particles could develop surface charge in aqueous solution in several different ways**
  - **Preferential ion adsorption** from (electrolyte) solution
    - Adsorption of H^+ or OH^- from solution
    - Adsorption of other ions from (electrolyte) solution
  - **Non-stoichiometric dissolution** (including Isomorphoric substitution)
  - **Adsorption of charged polymers** (polyelectrolytes)

Rahaman (2003), p. 191

Surface Charge Development (1) – Preferential Ion Adsorption from Solution

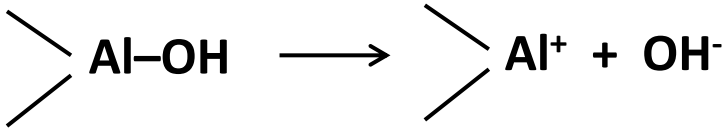
❑ Preferential adsorption of H^+ or OH^-

- Oxide particle surface often has surface groups such as OH, which preferentially adsorb proton H^+ or hydroxyl ion OH^-, which determines potential and charge on surface
- For M ion*s* such as Ba^{2+}, Al^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, etc., the process could be:

$$MOH + H^+ \overset{K_1}{=} MOH_2^+$$

$$MOH \overset{K_2}{=} MO^- + H^+ \quad \text{or} \quad MOH + OH^- = MO^- + H_2O$$

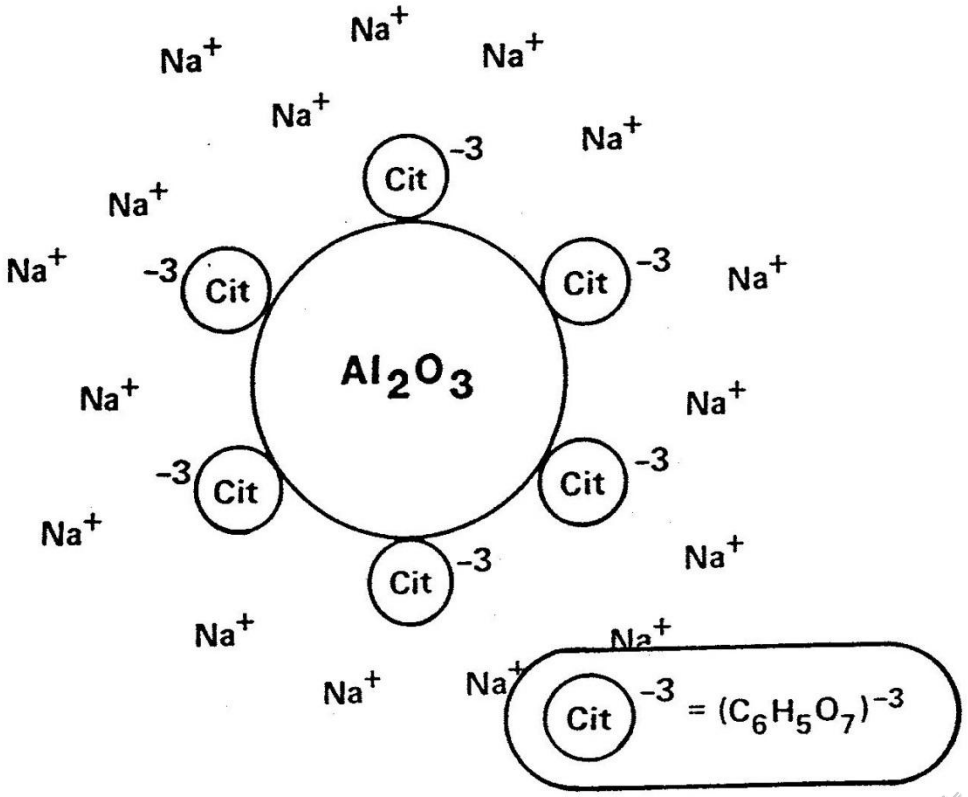
- Example: edge of clay particles



Surface Charge Development (1') – Preferential Ion Adsorption from Solution

❑ Preferential adsorption of other ions

- Apart from H^+/OH^-, other ions may also preferentially adsorb onto ceramic particle surface and become potential-determining ions
- Example: Citrate ion adsorption on Al_2O_3
  - Sodium citrate is the electrolyte and Na^+ is the counter ion
  - If initially surface neutral, preferential adsorption of citrate ion lead to negatively charged surface



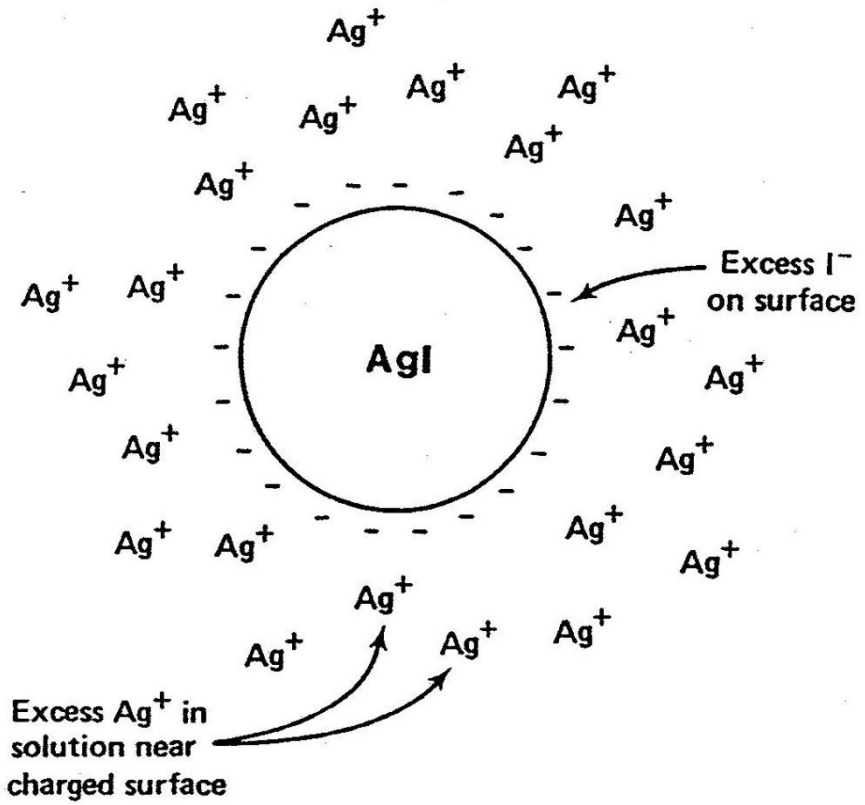
Rahaman (2003), p. 194-197
MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Surface Charge Development (2) – Nonstoichiometric (or Preferential) Dissolution

❑Description

- Certain solid experiences non-stoichiometric dissolution, i.e., preferred dissolution of one type of ion from the particle surface, leaving the surface rich in the counter ions, which gives it surface charge
- **Example**: AgI in water

  AgI may go through non-stoichiometric dissolution in aqueous solution:
  - When solution contain too little Ag^+, (or too much I^-), excess dissolution of Ag^+ from AgI surface will occur, leading to excess I^- on surface and it become negatively charged
  - When solution contain too little I^-, excess dissolution of I^- from AgI surface will occur, leading to excess Ag^+ on surface and it become positively charged



Rahaman (2003), 193-194; Reed (1994), 150-151

MD Sacks, (2001), Class notes, *Fine Particle Technology*

Surface Charge Development (2') – Isomorphoric Substitution

❑Description

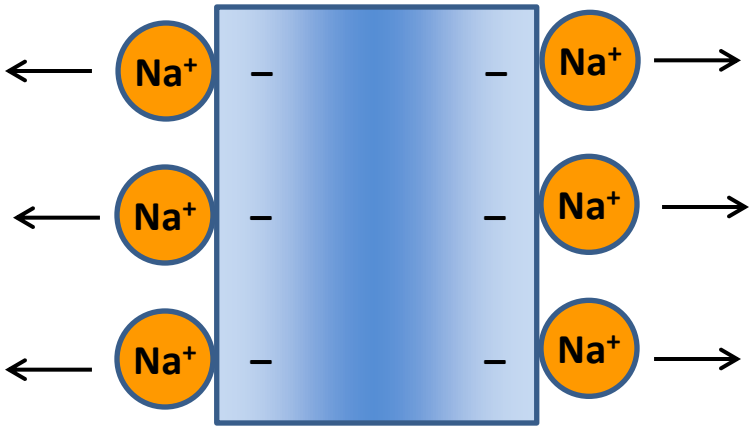
Rahaman (2003), 193-194; Reed (1994), 150-151

- High valence ions (e.g., Al^{3+}, Si^{4+}) replaced by low valence ions (e.g., Mg^{2+}), leading to extra cations (e.g., Na^{+}) adsorbed on surface for charge balance, often for clays particles:

$$Si^{4+}_{lattice} \ \underline{\text{replaced by}} \ Al^{3+}_{lattice} + Na^{+}_{surface}$$

$$Al^{3+}_{lattice} \ \underline{\text{replaced by}} \ Mg^{2+}_{lattice} + Na^{+}_{surface}$$

- Upon dispersion in water, the extra adsorbed ions on the surface dissolve and leave the particle surface to become negatively charged.



- Example:

$$Al_2(Si_2O_5)_2(OH)_2 \rightarrow Na_{0.33}(Al_{1.67}Mg_{0.33})(Si_2O_5)_2(OH)_2$$

Point of Zero Charge (PZC)

❑Description

A concept that describes the condition when total electrical charge (area) density on surface is zero. Generally, it is the negative decimal logarithm of the **activity** of potential-determining ion in solution when the net charge density is zero.

- When H^+/OH^- are potential-determining ions, it is the pH value at which adsorbed H^+ balance absorbed OH^- and the particle surface has zero net charge and be effectively neutral
- When other ions are potential-determining ions, it is the **negative** decimal logarithm of that ion activity (concentration) for which the net charge density is zero

Rahaman (2003), p. 194-197

Material	PZC	Material	PZC
SiO_2	pH~2-3.7	CaF_2	pCa~3
SnO_2	pH~4-6	AgI	pAg~5-6
TiO_2	pH~4-6	AgCl	pAg~4
ZrO_2	pH~4-6	Ag^2S	pAg~10
CeO_2	pH~6-7		
Fe_2O_3	pH~8-9		
Al_2O_3	pH~8-9		
ZnO	pH~9		
NiO	pH~10-11		
MgO	pH~12.0		

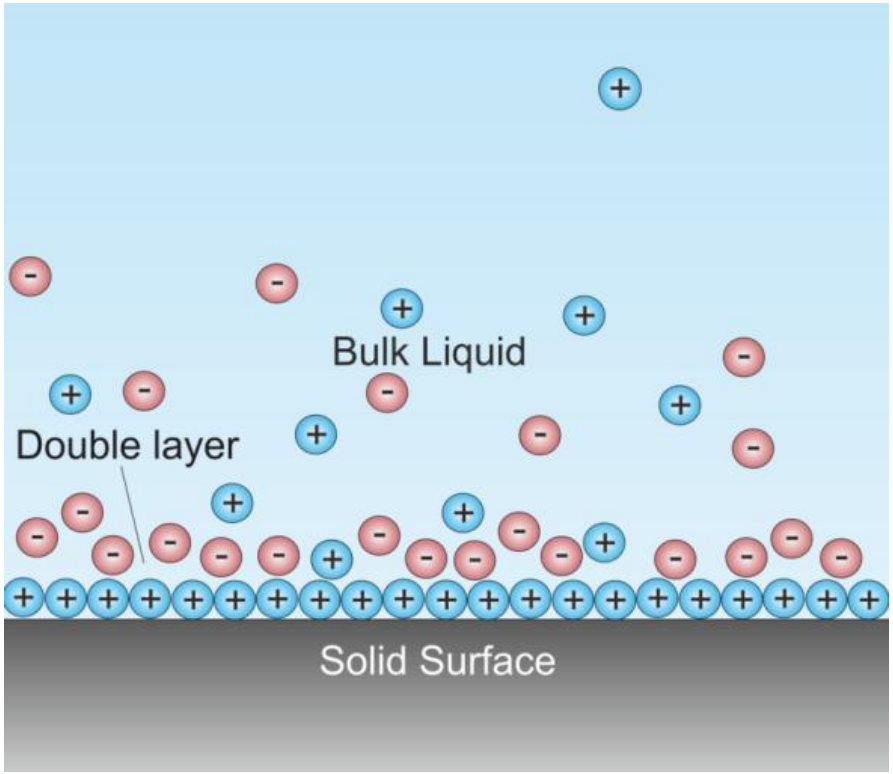
Electrical Double Layer (EDL)

❑Formation

Rahaman (2003), p. 198-202

In solution, if particle surface has fixed surface charges, to maintain overall charge neutrality, oppositely charged species will preferentially surround the charged particle, often in a diffuse way

"The combination of two separated, but associated, charged regions is called electrical double layer or EDL" (MD Sacks, class notes, 2001)



https://en.wikipedia.org/wiki/Double_layer_(interfacial)#/media/File:Double_Layer.png

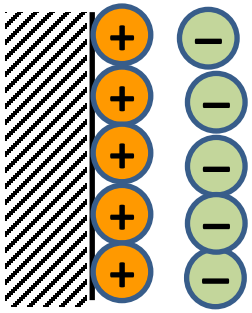
❑Mechanism for repulsion

- When charged particles come together, the diffuse layers with charge will start to overlap. The interaction between the EDL give the repulsive force.
- If repulsive force greater than van der Waals, suspension will be stable

Electrical Potential for EDL (1)

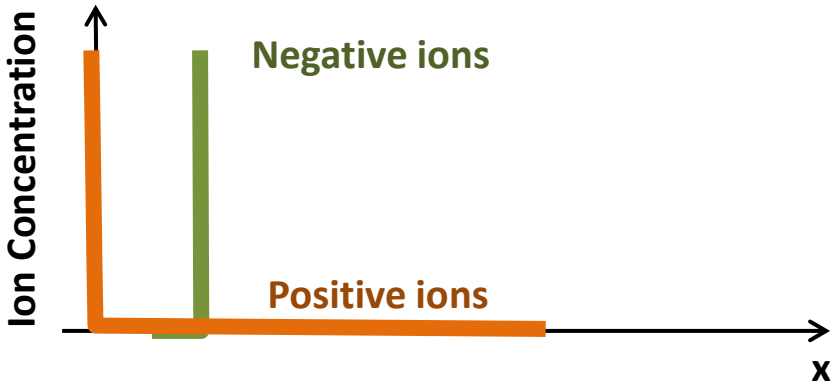
- **Helmholtz model: Linear potential distribution**

  Fixed charge on particle surface countered by densely packed opposite charges



Φ_0 Electrical potential at the surface (x=0)

- Zero potential outside the double layer:
- Thickness t hard to define
- **Oversimplification** and **not realistic** as it does not consider any thermal distribution effect for counter charges



Rahaman (2003), p. 198-202

Electrical Potential for EDL (2)

- **Gouy-Chapman model: Exponential potential distribution**

  Fixed charges on surface balanced by diffuse, opposite charges in solution

  For low potential, electrical potential at distance x from surface is approximated by:

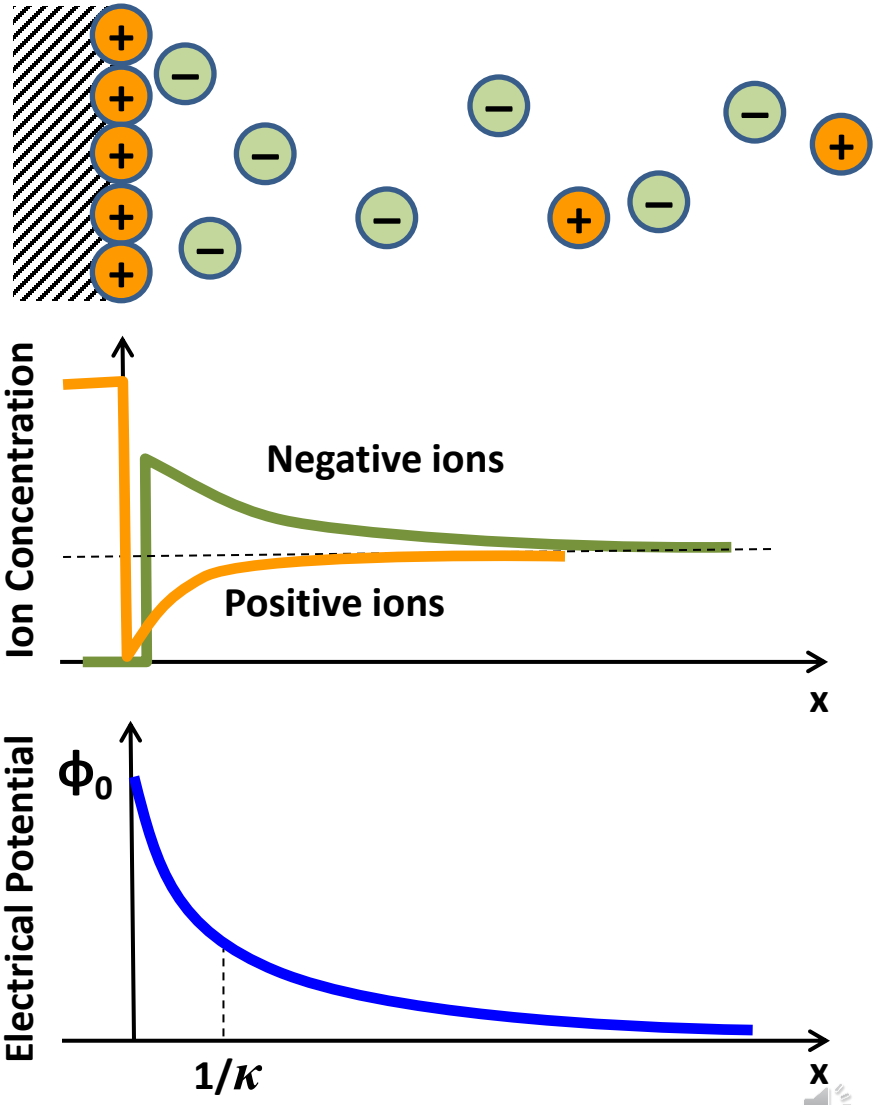
$$\phi = \phi_0 \exp(-\kappa x)$$

  Φ_0 Electrical potential at the surface (x=0)

  $1/\kappa$ Debye length, which can be used to approximately represent double layer thickness → at $1/\kappa$, the electrical potential drops to 1/e of surface potential Φ_0

  - Fast ("exponential") decay of potential as distance away from surface

  Rahaman (2003), p. 198-202



Impacts of Solution Ionic Strength on Debye Length

- **Debye length can be approximated by**

$$\frac{1}{\kappa} \approx \left(\frac{\varepsilon_r \varepsilon_0 kT}{2e^2 N_A I} \right)^{1/2}$$

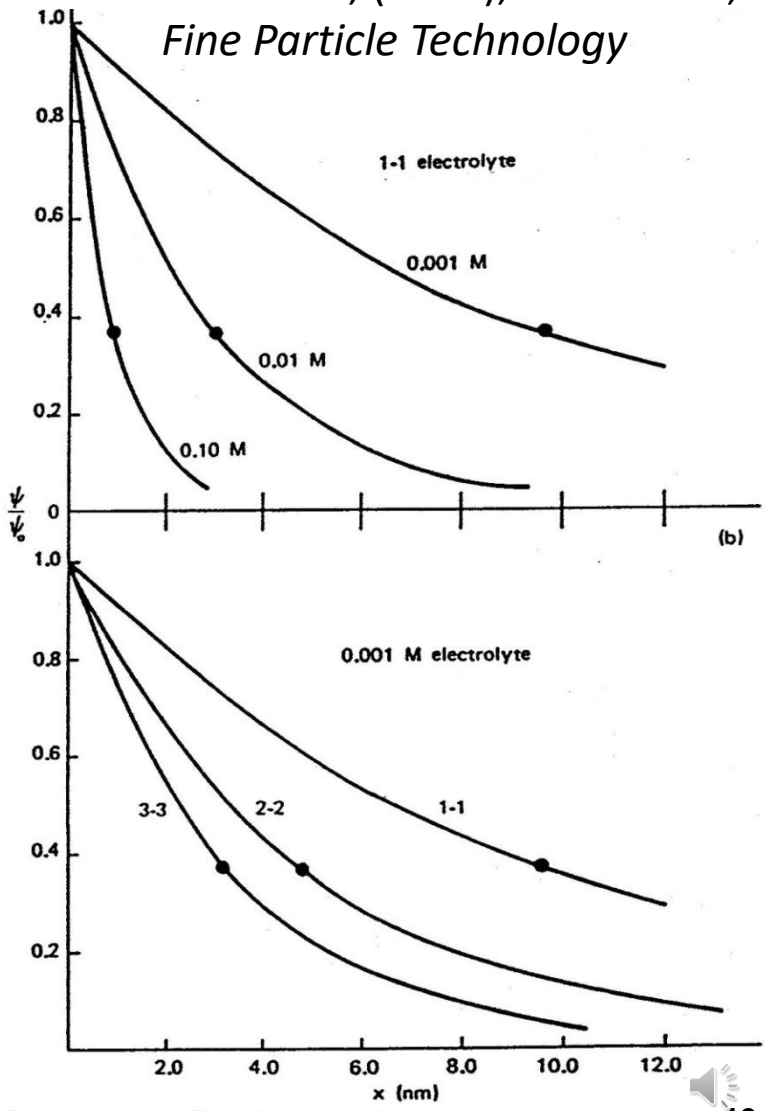
in which

$$I = \frac{1}{2} \sum_j z_j^2 M_j$$

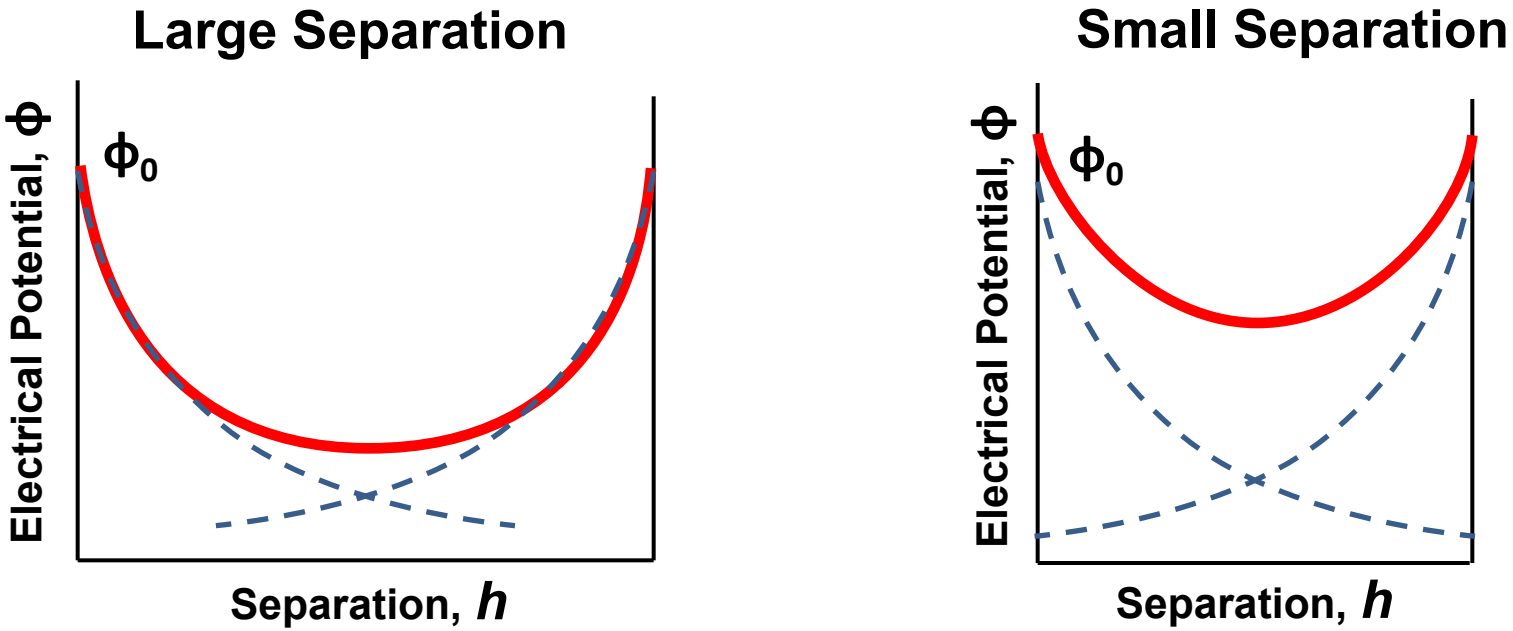
N_A	Avergadro's number 6.02x10^{-23} mol^{-1}
e	Electron charge 1.60x10^{-19} C
k	Boltzman constant 1.38x10-23 J • mol^{-1} • K^{-1}
ε_0	Vacuum permittivity 8.85x10^{-12} F• m^{-1}
ε_r	Relative dielectric constant
T	Temperature in K
I	Ionic strength for the solution
z_j	Valence for ion j in the solution
M_j	Molar concentration of ion j, in mol/m^3

Higher ionic strength leads to **reduced** Debye length ($1/\kappa$) and steeper potential decay

MD Sacks, (2001), Classnotes, *Fine Particle Technology*



Repulsion between Two Electrical Double Layers



- Ion concentration increases between particles

Rahaman (2003), p. 203-205

- If planar surface with small surface potential

$$V_R = 2\varepsilon\varepsilon_0\kappa\phi_0^2 \exp(-\kappa h)$$

- If spherical particles with small surface potential
  - For large double layer thickness ($1/\kappa > 0.2r$) $V_R \approx 2\pi r\varepsilon\varepsilon_0\phi_0^2 \exp(-\kappa h)$
  - For small double layer thickness ($1/\kappa < 0.1r$) $V_R \approx 2\pi r\varepsilon\varepsilon_0\phi_0^2 \ln[1+\exp(-\kappa h)]$

Surface Potential & Surface Charge Density

❑ **For low surface potential, surface charge density can be approximated:**

Rahaman (2003), p. 202-203

$$\sigma_0 = \frac{\varepsilon_r \varepsilon_0}{1/\kappa}\phi_0$$

in which

ε_r Relative dielectric constant of liquid

ε_0 Vacuum permittivity

$1/\kappa$ Debye length

Knowing capacitance

$$C = \frac{\varepsilon_r \varepsilon_0}{t}$$

For $t = 1/\kappa$, the above equation becomes

$$\sigma_0 = \frac{\varepsilon_r \varepsilon_0}{1/\kappa} \cdot \phi_0 = \frac{\varepsilon_r \varepsilon_0}{t} \cdot \phi_0 = C \cdot \phi_0$$

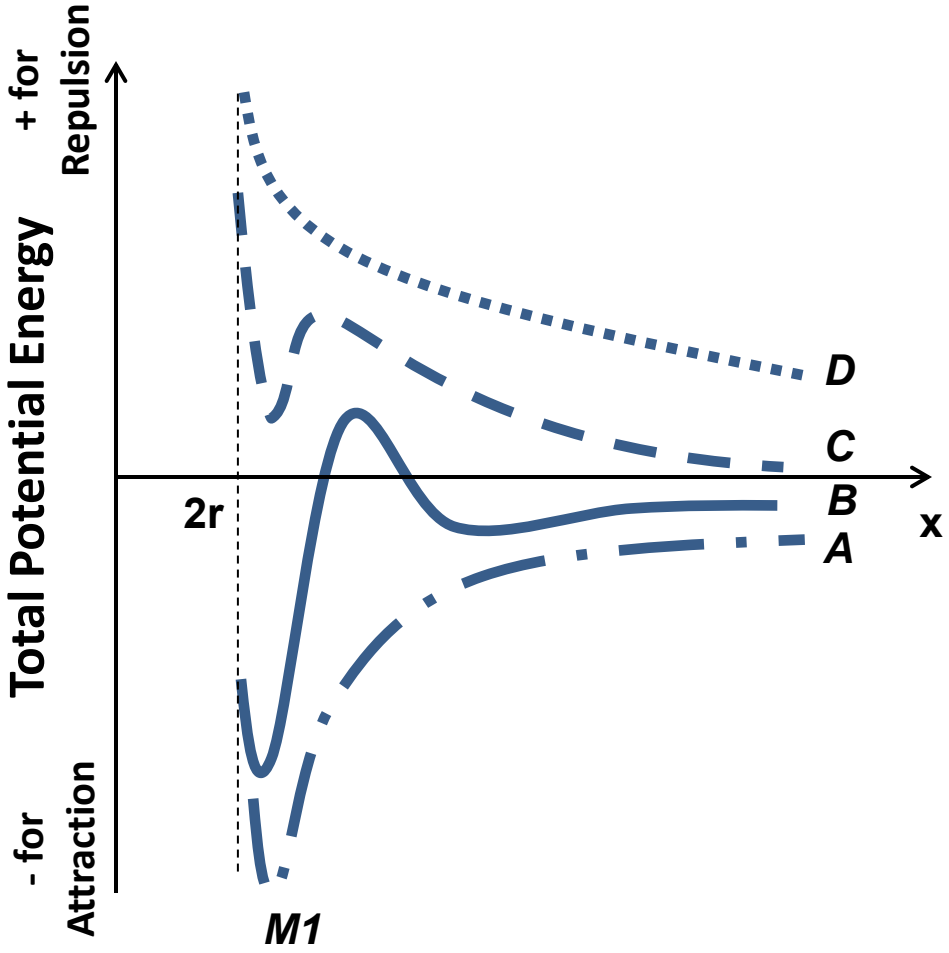
This means electrical double layer can be approximated as a **parallel capacitor** with effective thickness of $t = 1/\kappa$ and relative dielectric constant of ε_r

Stability of Electrostatically Stabilized Colloids

- **Total potential energy between particles is the sum of van der Waals attraction and electrostatic repulsion**

$$V_T = V_A + V_R$$

- **Major categories of behaviors**
  - A Repulsion is weak and particles attract one another and reach equilibrium at M1 – sedimentation with large separation
  - B Repulsion is stronger, but thermal activation can knock system into flocculation
  - C Repulsion large enough that form stable colloids
  - D Repulsion is so large that extreme stable colloids form that only allows low solid loading



Rahaman (2003), p. 206-208

Example of Debye Length and Electrostatic Stabilization

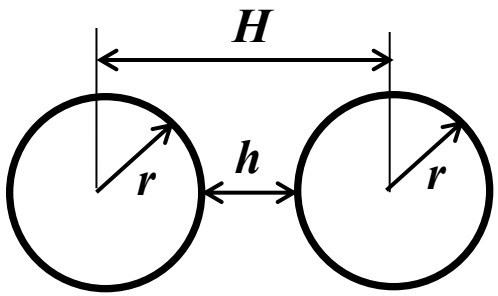
❑ **For 1:1 electrolyte dissolved in water with different concentration**

$$\frac{1}{\kappa} \approx \left(\frac{\varepsilon_r \varepsilon_0 kT}{2e^2 N_A I} \right)^{1/2}$$

$$I = \frac{1}{2} \sum_j z_j^2 M_j$$

Electrolyte concentration (mol/L)	Debye length (nm)
10^{-5}	97
10^{-4}	31
10^{-3}	10
10^{-2}	3

Assuming for charged particles r = 200 nm, Φ_0 = 0.05V, $1/\kappa$ =30 nm, h=30 nm



When h << r $V_A = -\frac{Ar}{12h}$

Van der Waals attraction energy

$$V_A = -\frac{10^{-20} J \times 200nm}{12 \times 30nm} = -5.5 \times 10^{-21} J$$

Thermal energy

$$KT = 1.38 \times 10^{-23} J/K \cdot 298 K = 4 \times 10^{-21} J$$

Electrostatic repulsion energy

$$V_R \approx 2\pi r \varepsilon \varepsilon_0 \phi_0^2 \ln\left[1 + \exp(-Kh)\right] = 6 \times 10^{-19} J$$

Therefore, the colloidal suspension will be stable against agglomeration

Electrophoresis, Mobility & Zeta Potential ζ (1)

❑Electrophoresis

When electric field is applied to a colloid suspension, charged particles will move under the electrical field

❑Mobility from electrophoresis

DC voltage V is applied to parallel electrodes at fixed distance l, particle velocity v can be observed (e.g., using a microscope)

For a particle with radius r and net charge q under electrical field E, driving force

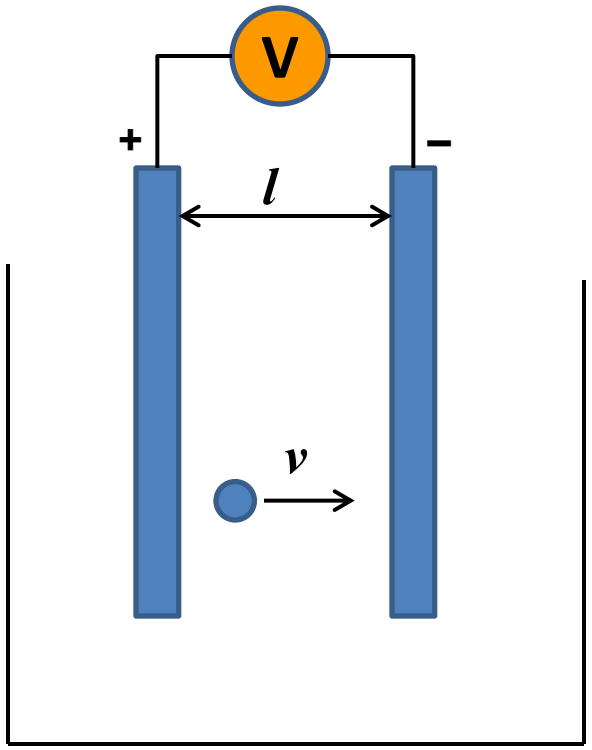
$$F = qE$$

In a viscous medium, terminal velocity is reached quickly, as determined by Stokes Law, we have

$$F = 6\pi\eta r v$$

η Viscosity of liquid

v Terminal velocity



Rahaman (2003), p. 209-211

Electrophoresis, Mobility & Zeta Potential ζ (2)

❑Continue from previous page

$$F = qE \qquad F = 6\pi\eta r v$$

Therefore, $qE = 6\pi\eta r v$

Mobility $$u = \frac{v}{E} = \frac{q}{6\pi\eta r}$$ which can be measured

❑Zeta Potential

As a charged particle moves in solution due to electrophoresis, it will drag solution and certain counter ions with it. The electrical potential at the **slippage plane or plane of shear**, i.e., the plane along which particle with adsorbed solution and ions actually moves, is called **zeta potential** ζ

Generally, $$\zeta = \frac{1}{f_{\kappa r}} \cdot \frac{u\eta}{\varepsilon\varepsilon_0}$$

For concentrated solution with $1/\kappa < 0.005r$ ($\kappa r > 200$), $f_{\kappa r} = 1$, $\zeta = \dfrac{u\eta}{\varepsilon\varepsilon_0}$

For very small colloidal or low ionic strength with $1/\kappa > 10r$ ($\kappa r < 0.1$), $f_{\kappa r} = 2/3$, $\zeta = \dfrac{3u\eta}{2\varepsilon\varepsilon_0}$

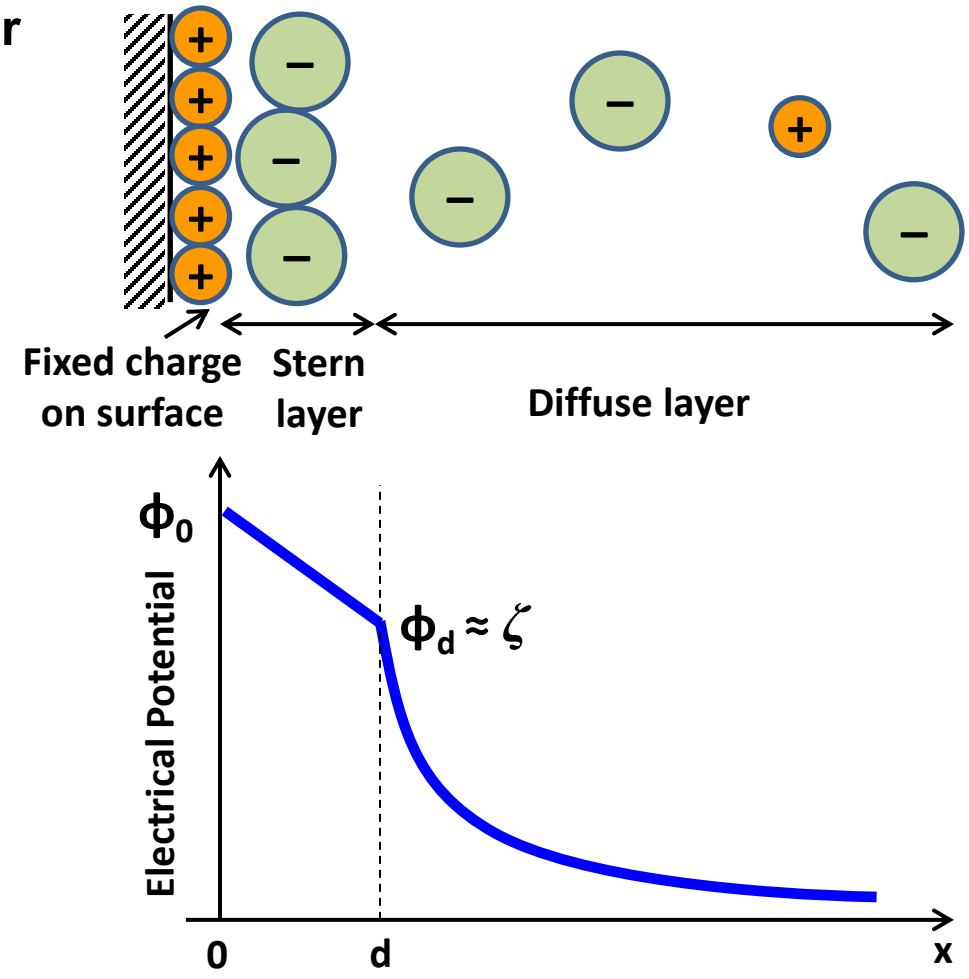
Stern Model for EDL & Zeta Potential ζ

❑ Stern Model: Stern – Diffuse Bilayer

Fixed charge on surface balanced by inner closely adsorbed layer and outer diffuse (Gouy) layer

Zeta potential ζ represent surface potential for the **electrokinetic unit** moving through the solution, which is approximated that at the interface between Stern layer and diffuse layer

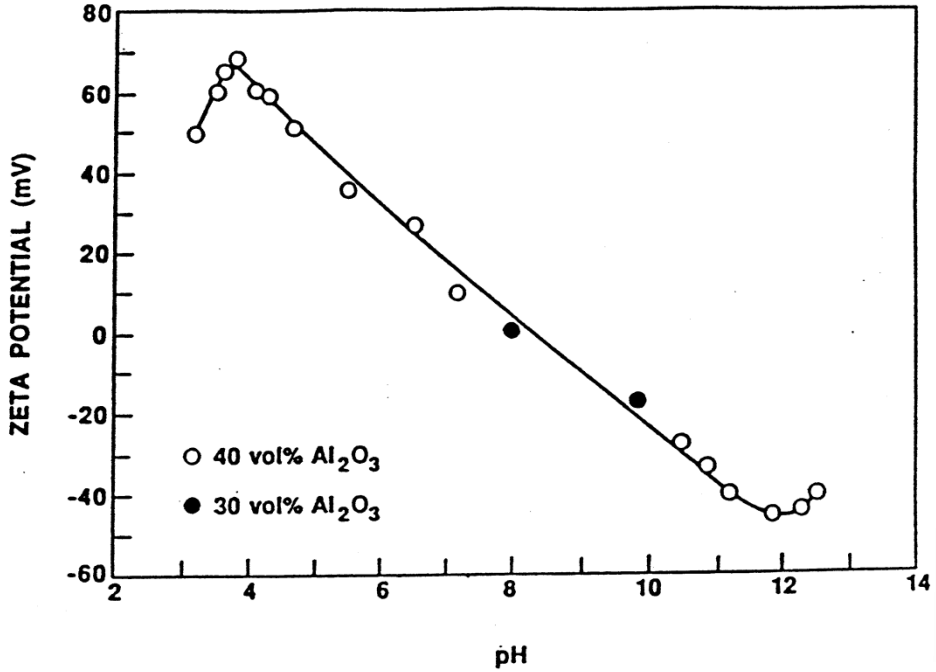
- Zeta potential is close to potential at the beginning of diffuse layer potential, Φ_d, but lower than that at particle surface, which is Φ_0
- Impacts phenomena that depend on electrical double layer
- **Independent of particle size**
- **Higher zeta potential** corresponds leads to **better stability** against flocculation, while lower zeta potential leads to fast flocculation
- At 20 °C, zeta potential of >~25 mV is needed to counter van der Waals attraction



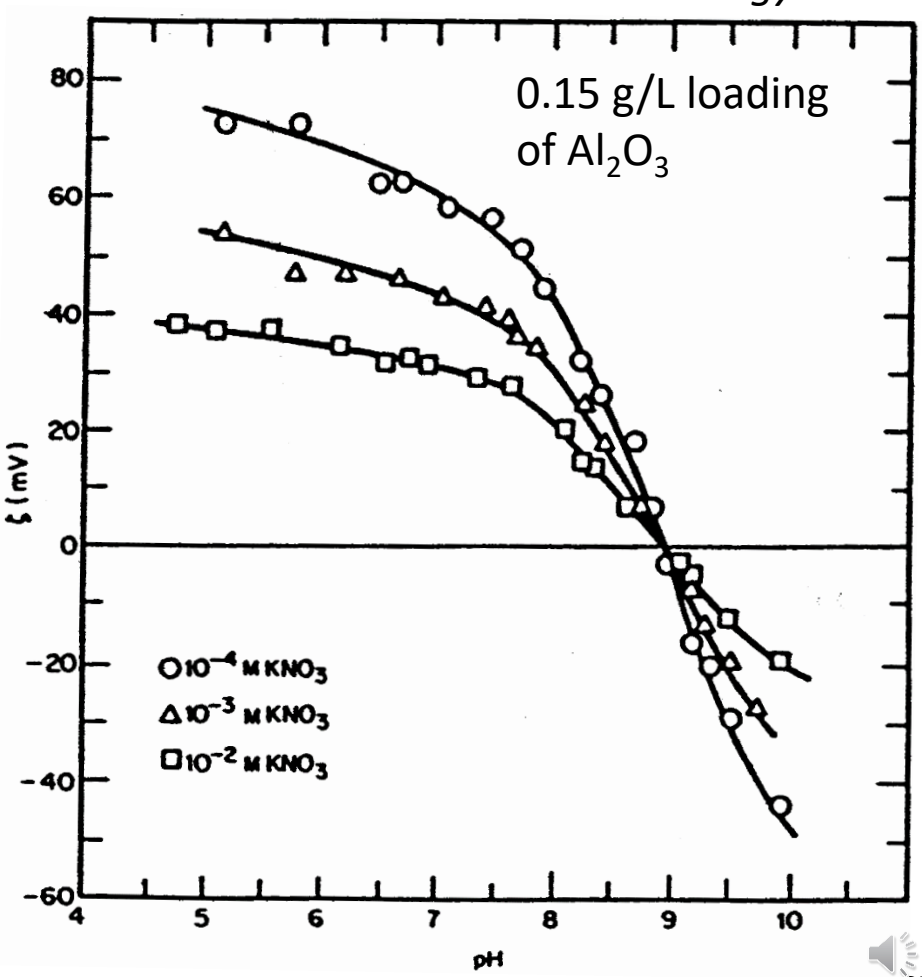
Impacts of Potential-determining Ion and Solution Ionic Strength on Zeta Potential (1)

❑Example 1: Al_2O_3 colloidal suspension in water

- Zeta potential ζ become more positive when pH decreases while more negative when pH increases
- As solution ionic strength I (e.g., [KNO_3]) increases, absolute value of zeta potential ζ become **smaller**



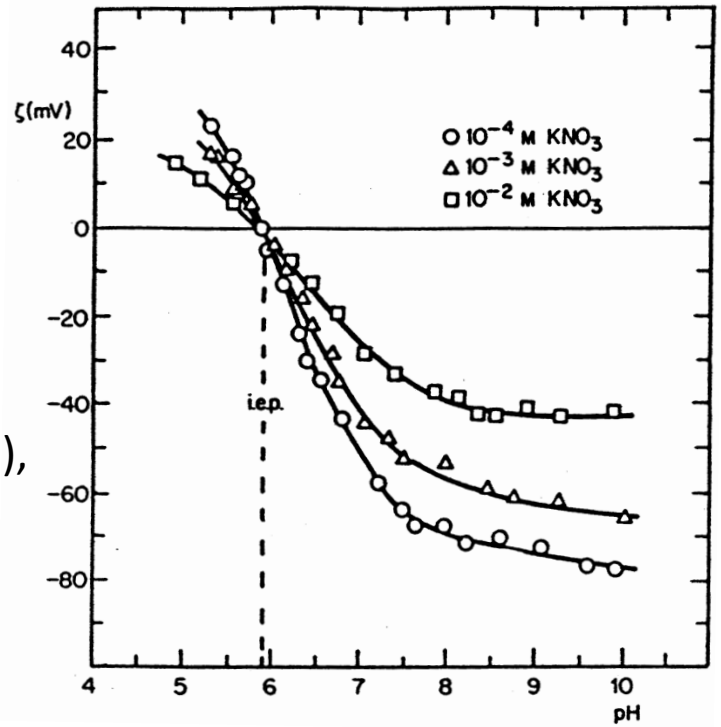
MD Sacks, (2001), Classnotes, *Fine Particle Technology*



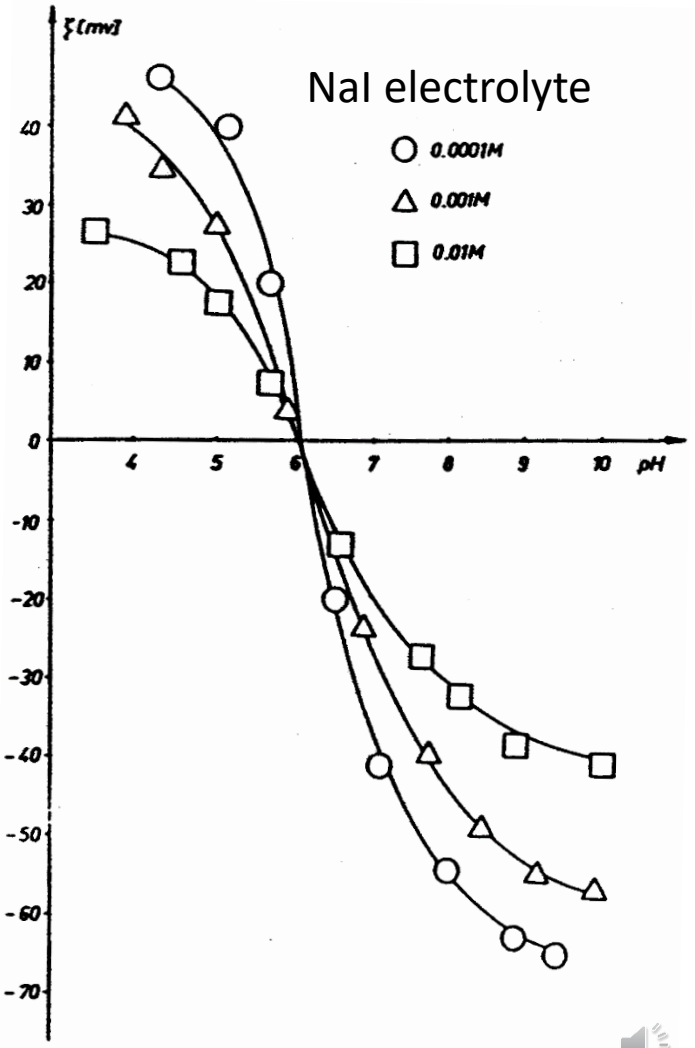
Impacts of Potential-determining Ion and Solution Ionic Strength on Zeta Potential (2)

❑Example 2: TiO_2 colloidal suspension in water

- Zeta potential ζ become more positive when pH decreases and more negative when pH increases
- As solution ionic strength I (e.g., [KNO_3] or [NaI]) increases, absolute value of zeta potential ζ become **smaller**



MD Sacks, (2001), Classnotes, *Fine Particle Technology*

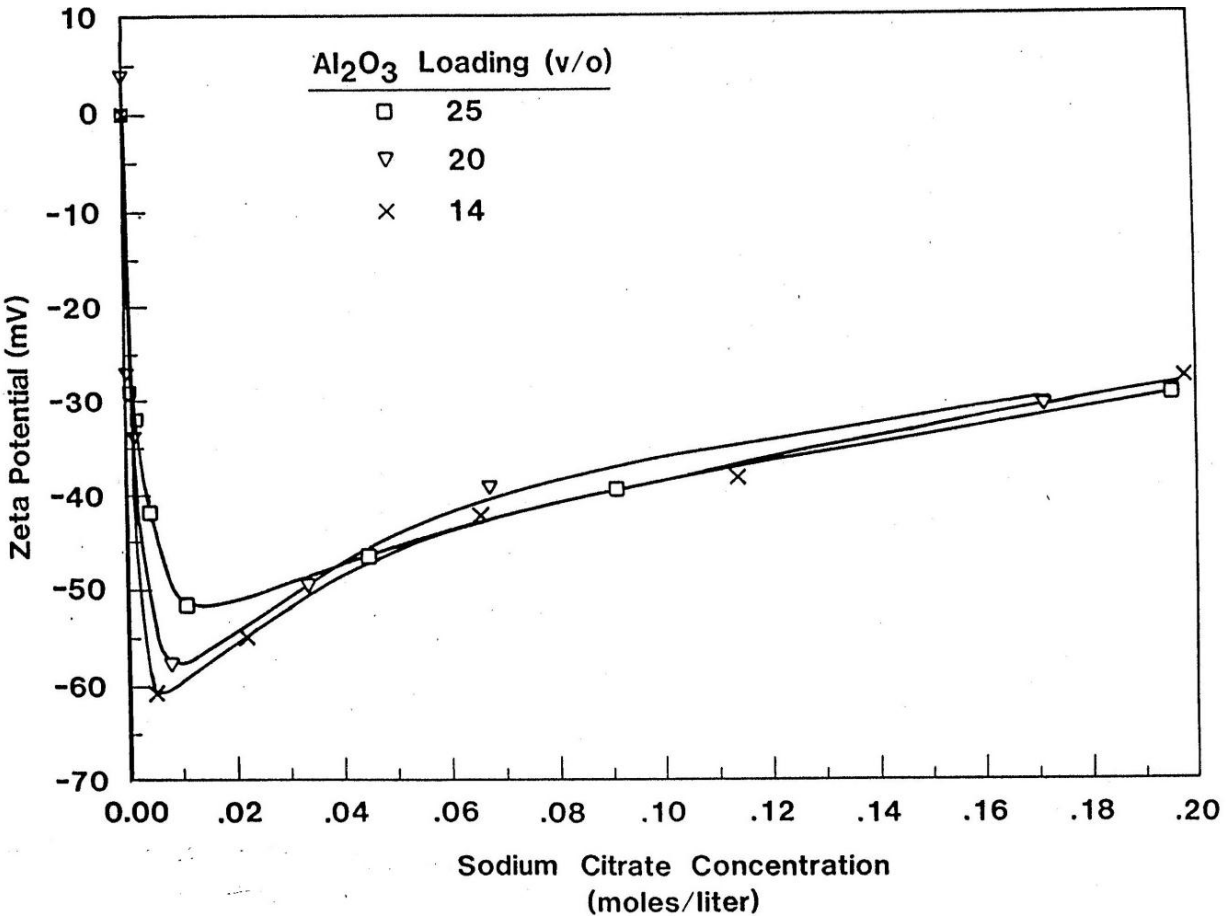


Impacts of Potential-determining Ion and Solution Ionic Strength on Zeta Potential (3)

❑Example 3: Al_2O_3 colloidal suspension with sodium citrate

As citrate ion (potential-determining ion) concentration increases,

- Initially, ζ become more negative as more citrate ions adsorb on Al_2O_3 surface
- After reaching highest value, ζ starts to decrease due to higher ionic strength I, which reduces Debye length $1/\kappa$ (i.e., compresses EDL)

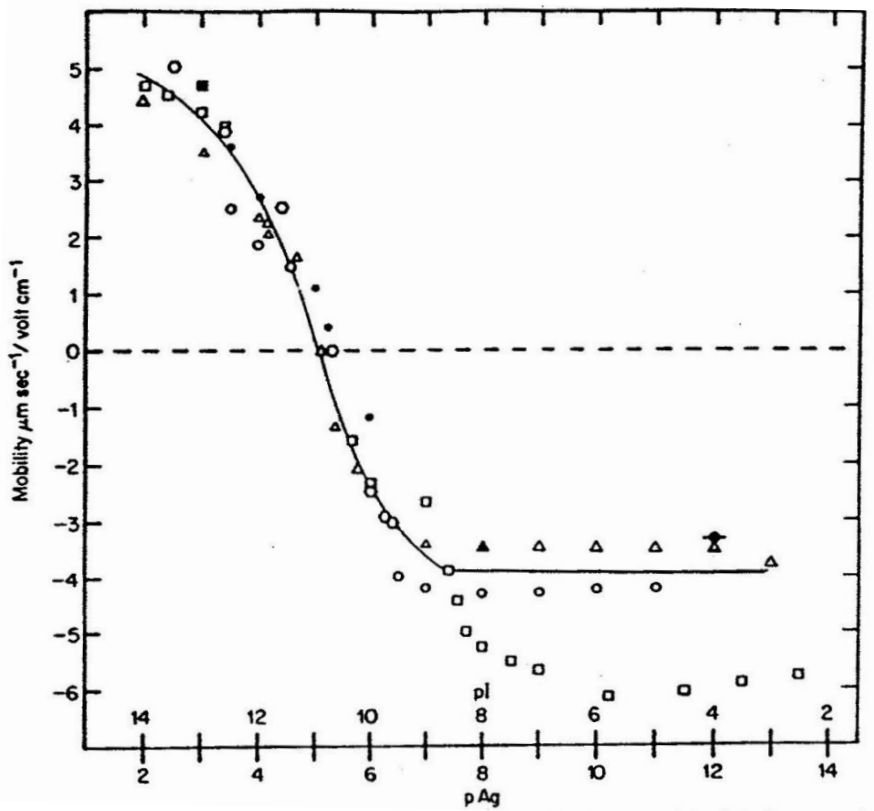


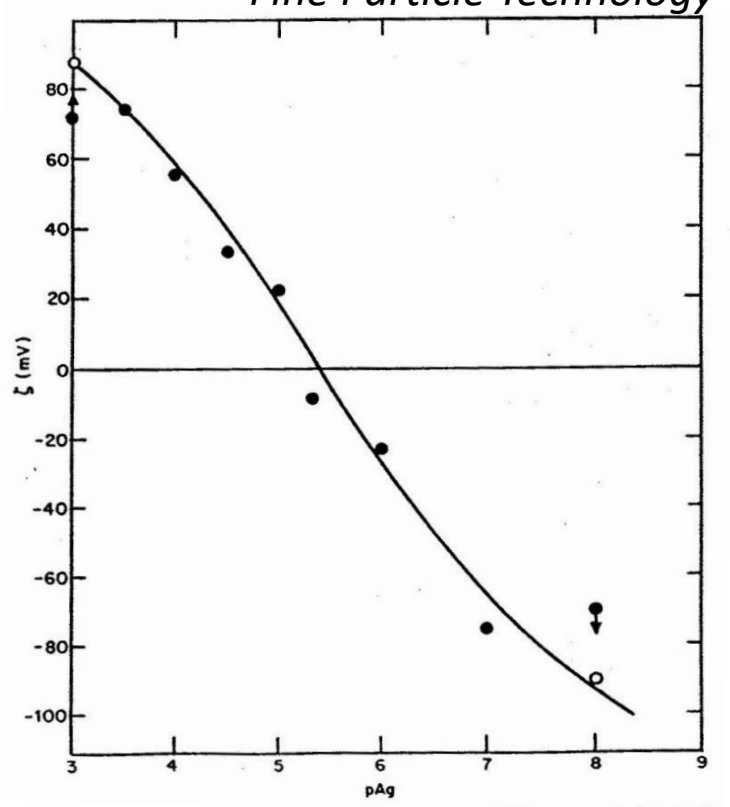
MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Impacts of Potential-determining Ion and Solution Ionic Strength on Zeta Potential (4)

❑ **Example 4: AgI colloidal suspension in water**

MD Sacks, (2001), Class notes, *Fine Particle Technology*





- pAg > PZC (pAg >> ~5, very low [Ag]), ζ <0 due to preferential Ag^+ dissolution (or I^- adsorption) and AgI surface become negative charged by excess I^- ions
- pAg < PZC (pAg << ~5, very high [Ag]), ζ >0 due to preferential I^- dissolution (or Ag^+ adsorption) and AgI surface become positive charged by excess Ag^+ ions`

Isoelectrical Point (IEP)

❑Description

- A concept that describes the condition (typically pH) when ζ zeta potential, which is the electrostatic potential at the plane of shear (or roughly the interface between Stern layer and diffuse layer) is zero
- Often it is the negative decimal logarithm of the activity of potential-determining ion in solution when the net charge density is zero
- Usually, **PZC ≈ IEP**

Rahaman (2003), p. 194-197

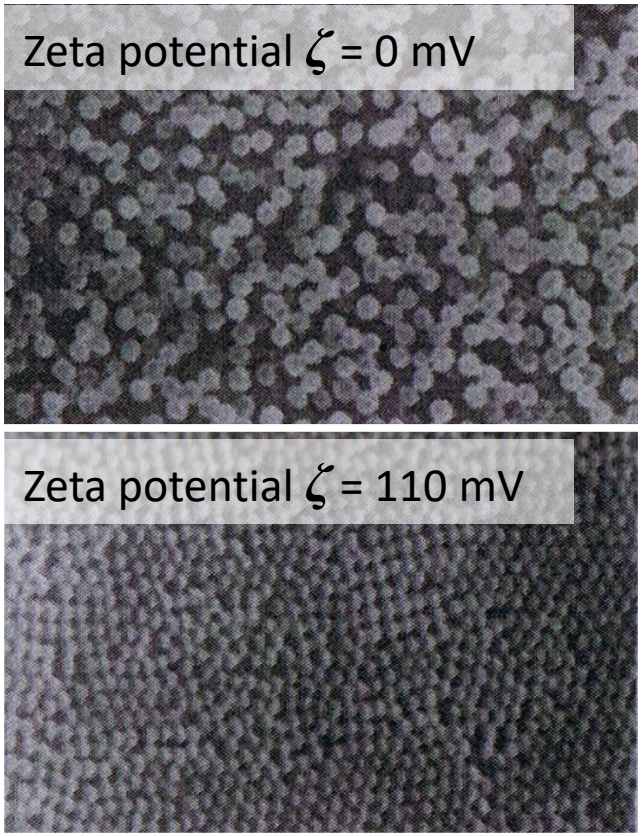
Zeta Potential on Structure of Powder Compacts from Colloidal Suspension (1)

- **When colloids is not stable due to low zeta potential**

  Flocculation/sedimentation happen quickly and the structure formed is loosely packed with high porosity

- **When colloids is stable due to high zeta potential**

  Flocculation/sedimentation happen very slowly and the structure formed is densely packed with low porosity and often has feature of ordering



Microstructure for powder compact formed from 0.7 μm colloid SiO_2 via centrifugal consolidation

MD Sacks, (2001), Class notes, *Fine Particle Technology*

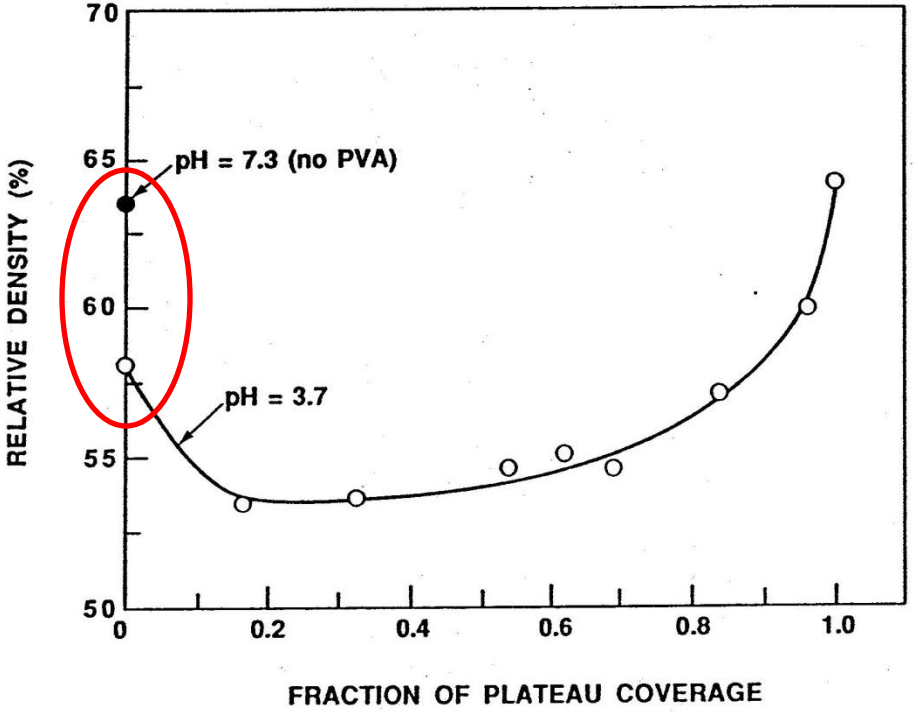
Zeta Potential on Structure of Powder Compacts from Colloidal Suspension (2)

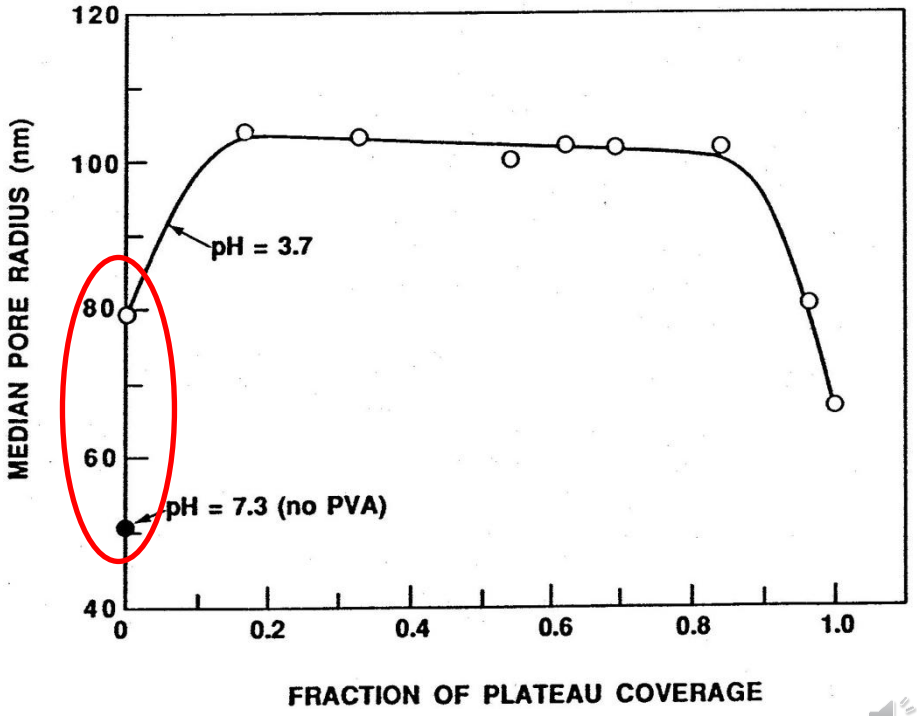
❑ **SiO_2 in water, IEP = PZC ≈ 3-4, PVA as dispersant**

MD Sacks, (2001), Class notes, *Fine Particle Technology*

When PVA concentration is zero (i.e., zero PVA coverage on SiO_2)

- pH=3.7: low surface charge density/small zeta potential → lower relative packing density (~58%) & larger pore size (~80 nm) due to SiO_2 particles agglomeration
- pH=7.3: negative charge on particle surface → higher (more negative) zeta potential and higher relative density (~63%) and smaller pore size (~50 nm)

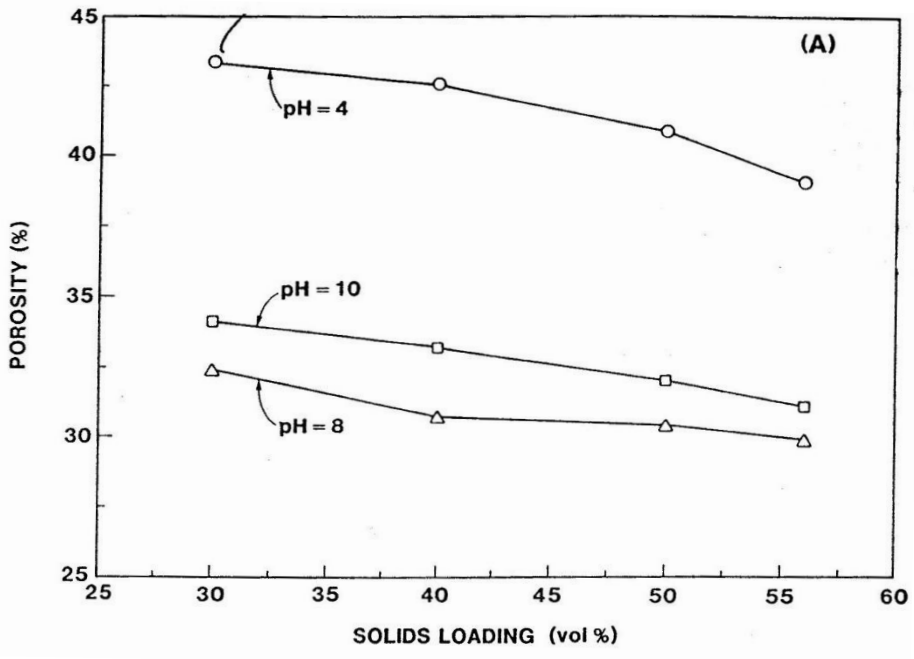


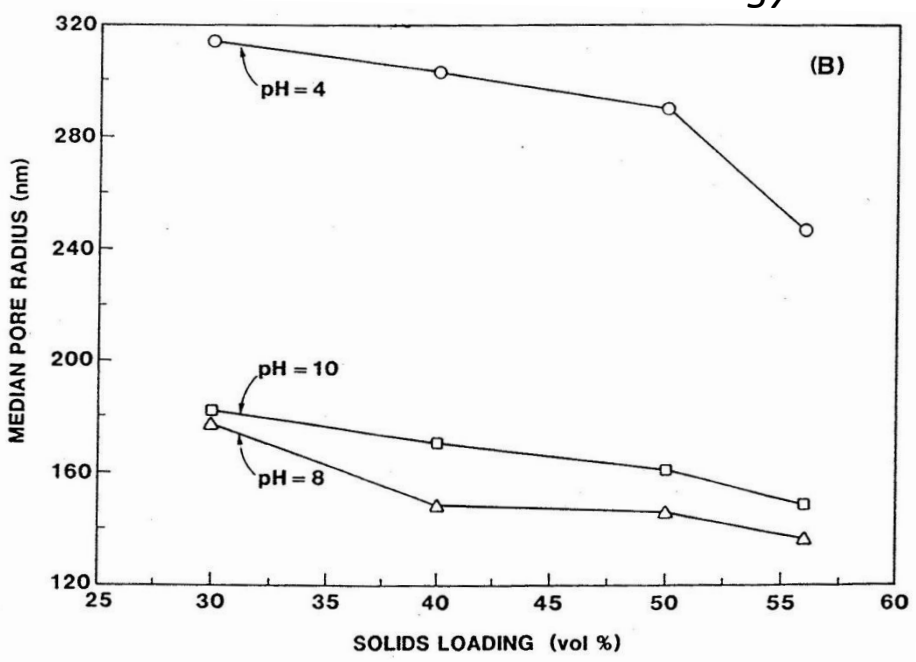


Zeta Potential on Structure of Powder Compacts from Colloidal Suspension (3)

❑For SiO_2, IEP = PZC ≈ 3-4

MD Sacks, (2001), Classnotes, *Fine Particle Technology*



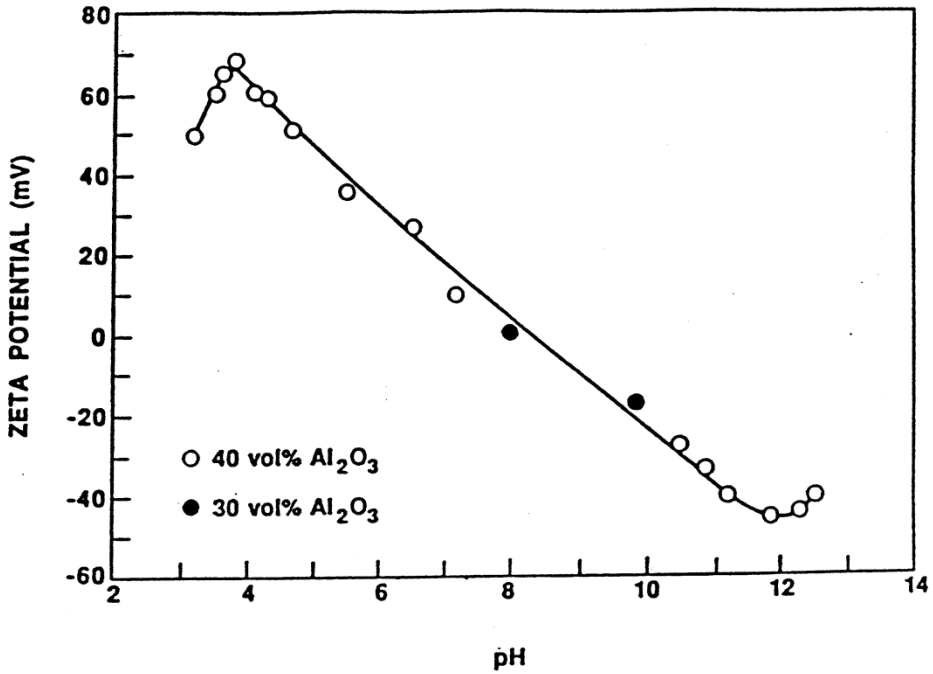


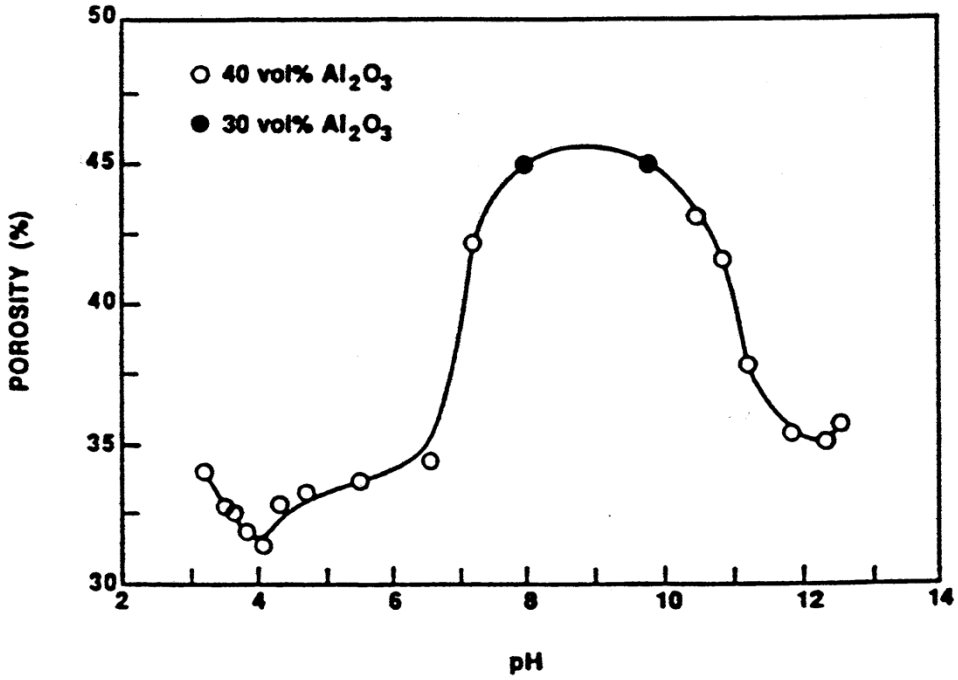
- pH = 4, no net surface charge & zeta potential ≈ 0 → porosity is higher while pore size is also larger due to severe agglomeration of SiO_2 colloidal particles
- pH = 8, significant negative charge on particle surface → more negative zeta potential and relative low green porosity and much smaller median pore size
- pH = 10, too high ionic strength I → compression of EDL (Debye length ↓) → weaker agglomeration and higher porosity and larger pore size (than pH = 8)

Zeta Potential on Structure of Powder Compacts from Colloidal Suspension (4)

- For Al_2O_3, IEP = PZC ≈ 8-9

MD Sacks, (2001), Classnotes, *Fine Particle Technology*





- pH ~7-10 → zeta potential absolute value is low, suspensions experience agglomeration & sediments' relative porosity is high
- pH << ~7 or pH >> ~10 → zeta potential absolute value high → suspension stable and the sediments porosity lower

Ways to Achieve Stabilization of (Colloidal) Particle Suspension

- **Fine particles in suspension tend to flocculate due to van der Waals forces larger than thermal energy**
- **Need to introduce repulsive force between particles to stabilize colloidal particle suspension**
  - **Electrostatic stabilization**
    Repulsion between particles due to electrostatic charges on particle surface
  - **Steric stabilization**
    Repulsion between particles due to uncharged polymer chains adsorbed on particle surface
  - **Electrosteric stabilization**
    Combination of electrostatic and steric repulsion

Rahaman (2003), p. 191

Polymers Structure in Solution

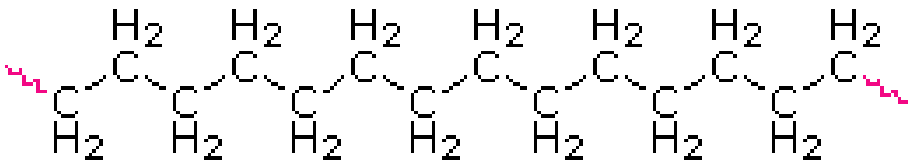
- **Structure of polymer chain in solution determined by two opposing factors:**
  - Van der Waals attraction between monomer units → leading to collapse of polymer to a small ball
  - Maximization of configurational entropy → leading to outward random spreading of polymer chain

  } Polymer chain in solution maintain open, random structure

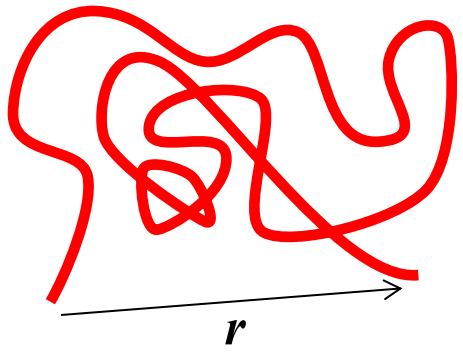
- **Size of polymer chain**

  Approximated by the "root-mean-square" end-to-end distance, given by

$$\left\langle r^2 \right\rangle^{1/2} = \sqrt{N} l$$



http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm



N Number of (repeating) units in the polymer

l Length for a (repeating) unit

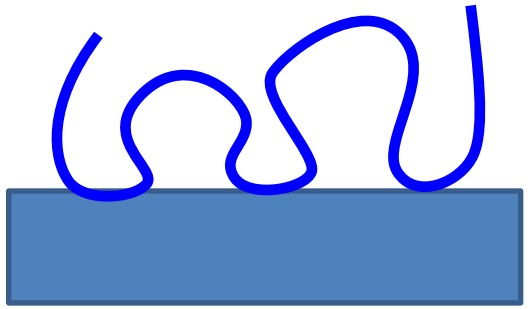
Example: l = 0.1 nm; N = 10^4, $\langle r^2 \rangle^{1/2}$ = 10 nm

Rahaman (2003), p. 212-215

Adsorption of Polymers from Solution

❑General configuration

Van der Waals force between polymers and particle surface leads to adsorption of polymer on particle surface with "anchor" points and loops/tails extend into solution

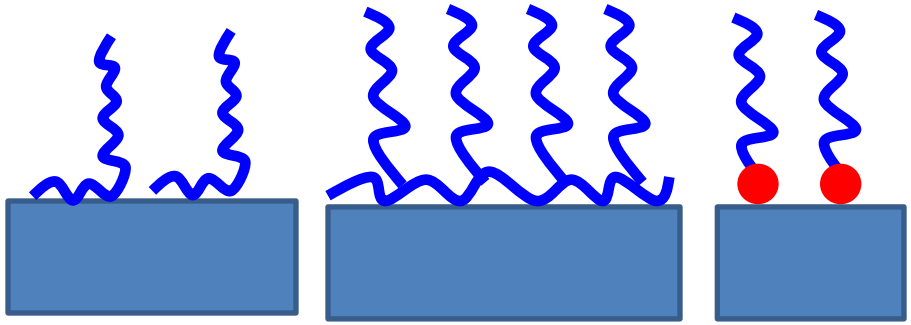


❑Approaches for improved anchoring effects

- Use graft/block copolymers

Some portions/blocks of the polymer has low solubility and attach to particle surface while other portions/blocks extend into solvent.

- Poly(vinyl pyrrolidone)/polystyrene (PVP/PS)
- Poly(ethylene oxide)/polystyrene (PEO/PS)



- Use polymers with polar head groups

The polar head groups adsorb strongly onto particle surfaces (e.g., via hydrogen bond or acid-base interactions) while the non-polymer tail extend into solvent

- Use polymers with function groups that react with surface sites

$$\text{Si-OH}_{\text{surface}} + \text{X-Si-[CH}_2\text{-CH}_2\text{]}_n\text{-R} \rightarrow \text{Si-O-Si-[CH}_2\text{-CH}_2\text{]}_n\text{-R}_{\text{surface}} + \text{HX}$$

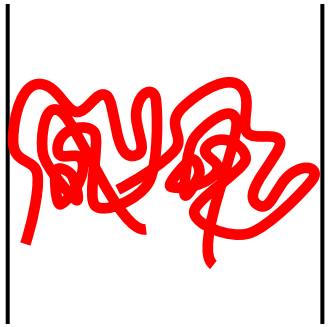
Rahaman (2003), p. 212-215

Interactions between Adsorbed Polymers over Particle Surface

- **Suppose h is inter-particle distance and L is thickness of adsorbed polymer layer, and $L \approx \langle r^2 \rangle^{1/2}$**
  - No interaction when $h > 2L$
  - **Mixing** effect when $L < h < 2L$

Adsorbed polymer molecule on one particle start to interpenetrate with adsorbed polymer molecule on another particle →

This may lead to attraction or repulsion depending on polymer molecule and solvent

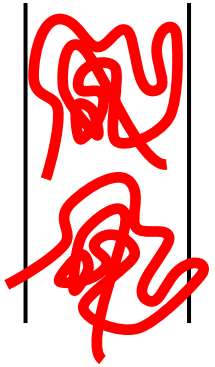


- **Elastic**/entropy effect When $h < L$

Adsorbed polymer molecule become compressed → This always leads to repulsion due to decreased entropy (also called volume restriction) effect

- Total interaction energy

Depend on the combination of the two factors: mixing + elastic

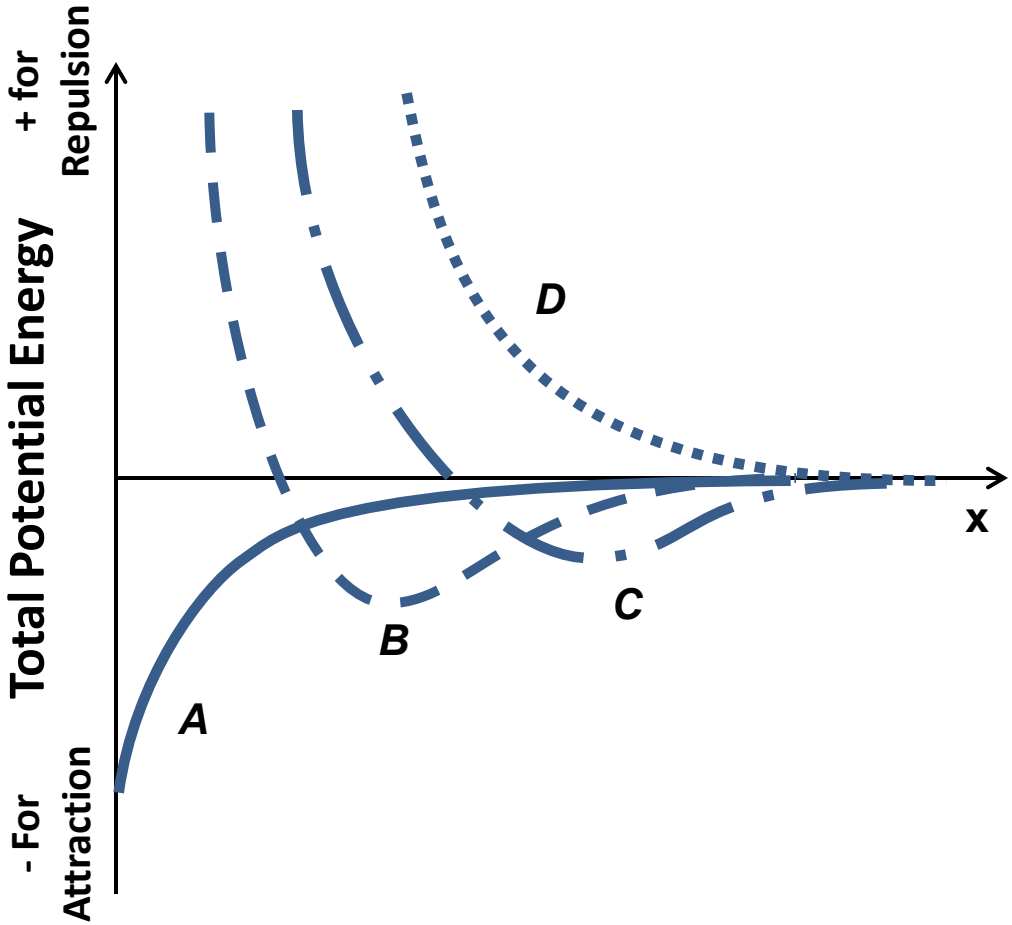


Rahaman (2003), p. 215-217

Origin for Steric Stabilization (2)

❑ **Different scenarios**

A. No polymer: only van der Waals attraction
B. With low polymer coverage, long-range attraction caused by polymer "bridging" effect → leading to "bridging flocculation
C. With slightly higher polymer coverage, long-range attraction become weaker while repulsion increases
D. At high coverage, only repulsion

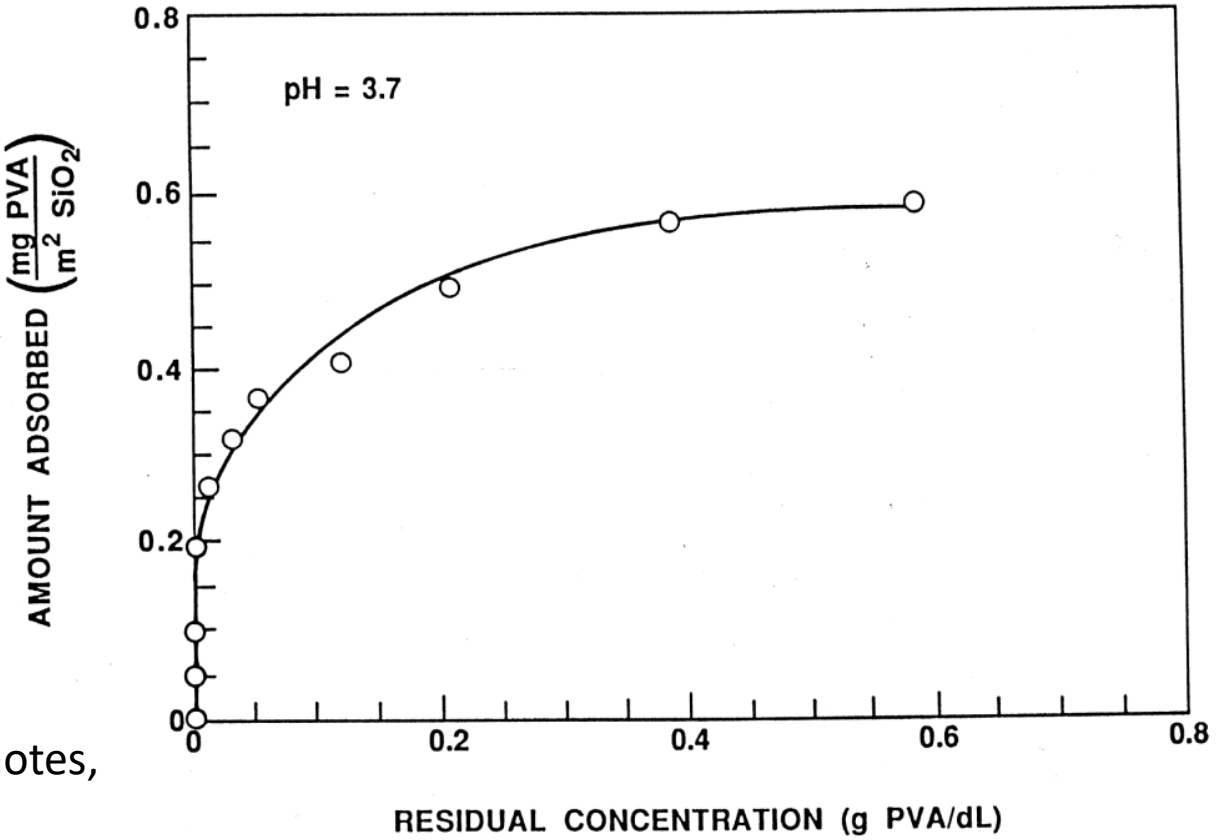


Rahaman (2003), p. 219-220

Adsorption of Polymer on Particle Surface – Polymer Concentration Effect

- **Higher polymer concentration leads to more adsorption until saturation**

  Example: PVA adsorption on SiO_2 in water at pH=3.7 (~IEP)

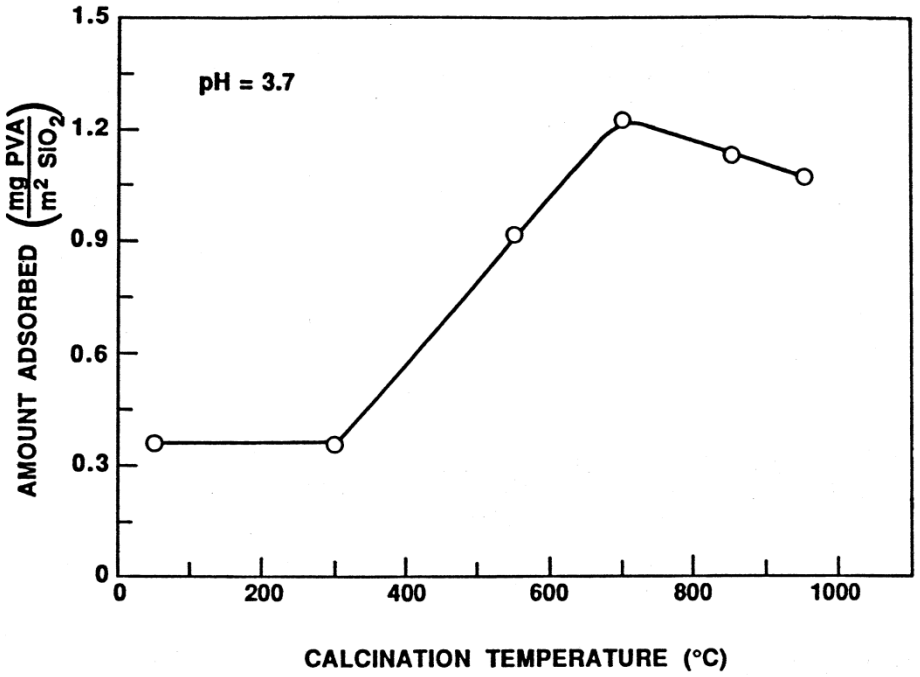


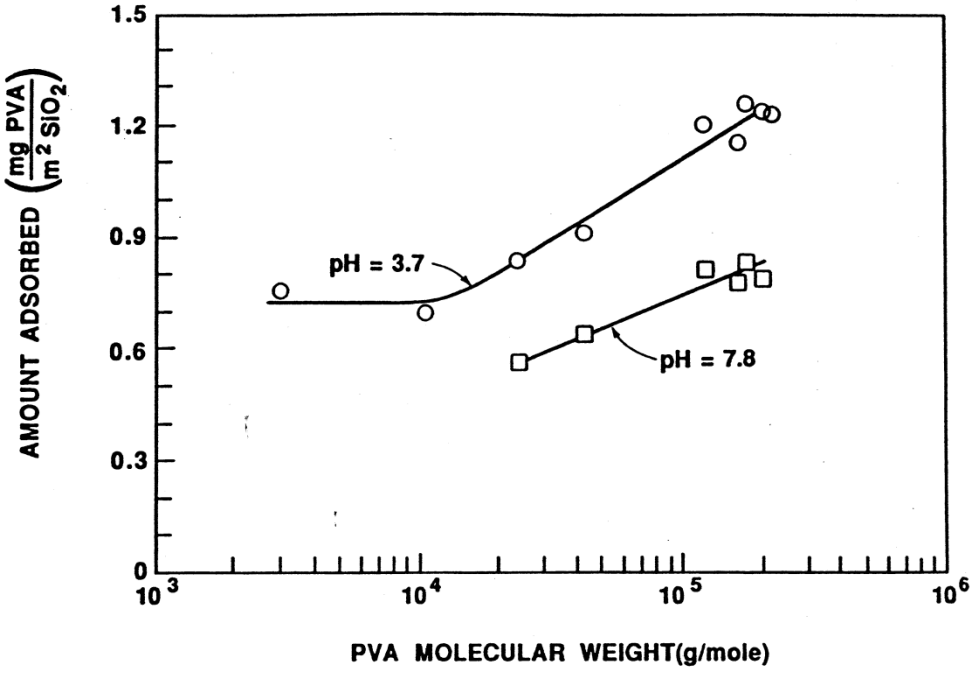
MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Adsorption of Polymer on Particle Surface – Particle Surface & Polymer MW Effects

- **Amount of polymer adsorbed on particle surface changes also with**
  - Surface condition: cleaner surface tends to adsorb more polymer
  - Molecular weight: higher molecular weight polymer tends to adsorb more

Example: PVA adsorption on SiO_2 in water at pH=3.7 (~IEP)





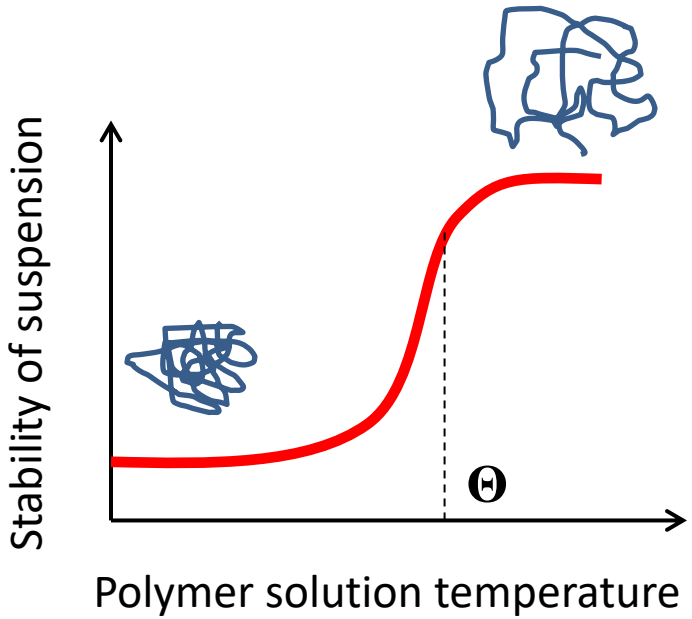
MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Solvent "Quality" & Temperature Effect

❑ Solvent "quality" & temperature also influence steric stabilization

For a polymer dissolved in solvent

- Above certain temperature, total free energy change due to polymer interpenetration is positive, solvent is referred to as "**good solvent**", and polymer tend to spread out more
- Below certain temperature, total free energy change due to polymer interpenetration is negative, solvent is referred to as "**poor solvent**", and polymer tend to coil tightly
- That temperature corresponds well with **critical flocculation temperature**



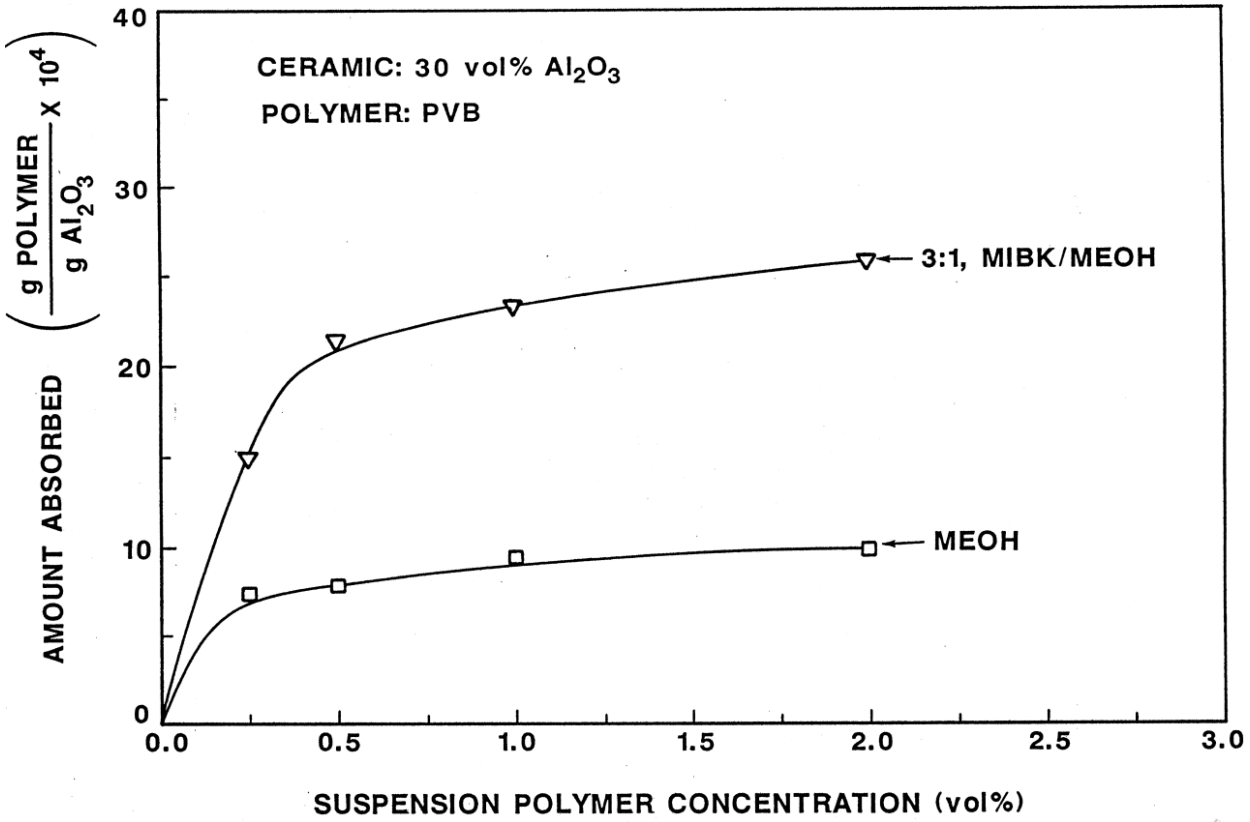
Rahaman (2003), p. 217-218

Adsorption of Polymer on Particle Surface - Solvent Quality Effect

- **Amount of polymer adsorbed on particle surface changes also with <u>solvent quality</u>: "good" solvent leads to more adsorption of polymer**

  Example: Non-polar polymer PVB adsorption over Al_2O_3 in polar solvent of methanol (MEOH) vs. mixture of MEOH & non-polar methanol-methyl isobutyl ketone (MIBK):

  - Adding less polar MIBK solvent to MEOH enhances PVB adsorption over Al_2O_3 surface

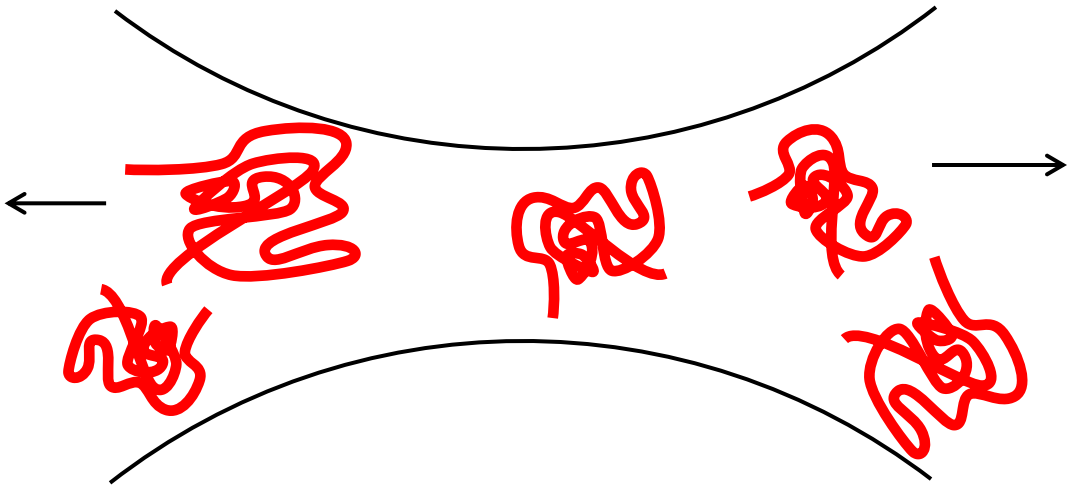


MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Additional Interactions Caused by Unadsorbed Polymers in Free Solution

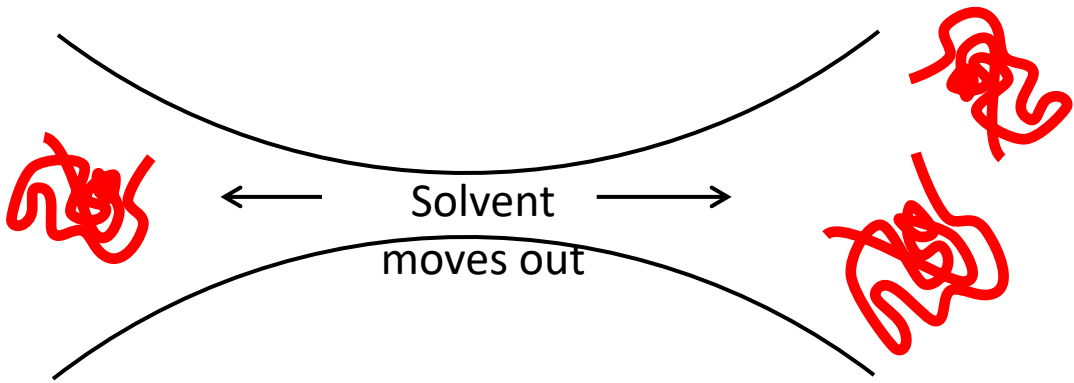
❑Depletion stabilization

Work must be done to drive polymer away from the region between particles, which leads to stabilization



❑Depletion flocculation

When particles become too close that is smaller than polymer cluster size, no polymer exist between particles and solvent between particles tend move to regions with higher polymer concentration, leading to flocculation

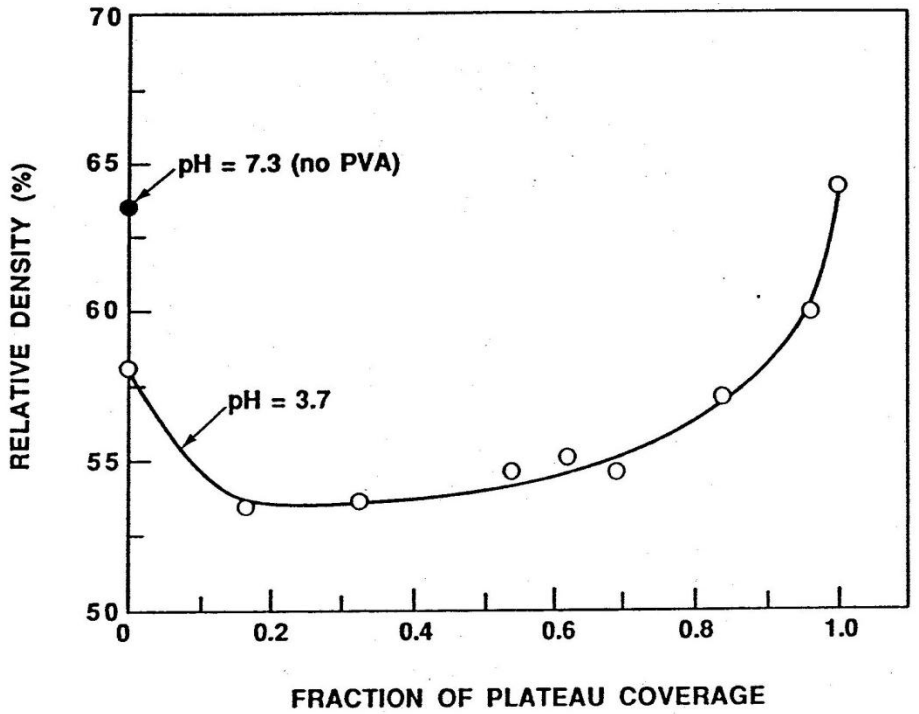


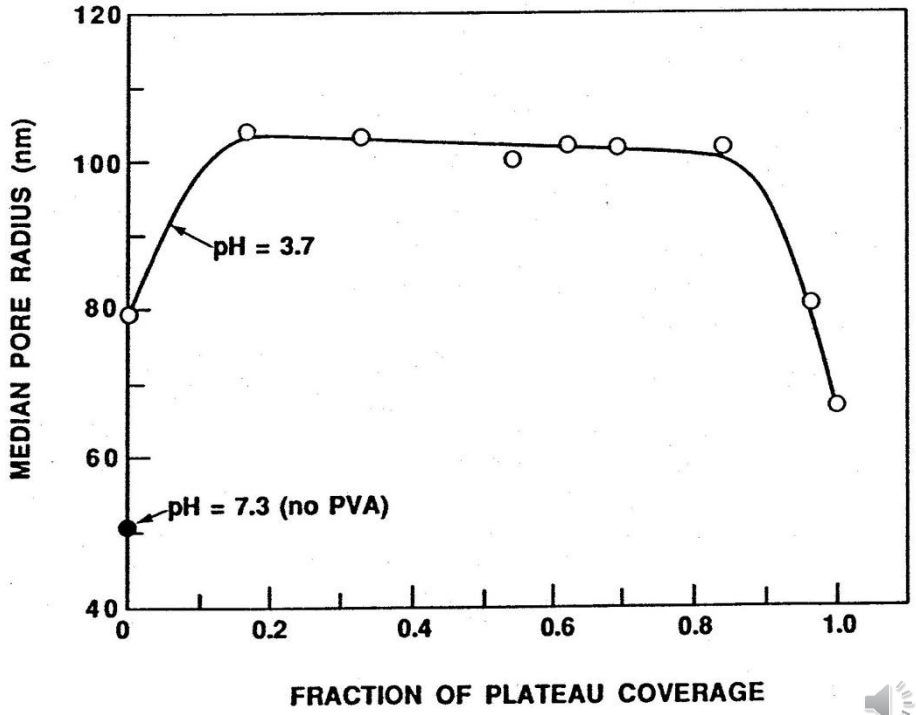
Rahaman (2003), p. 220-222

Steric Stabilization on Powder Compact Structure - Polymer Coverage Ratio Effect

MD Sacks, (2001), Class notes, *Fine Particle Technology*

- **For SiO_2, IEP ≈ 3-4**
  - At pH=3.7, with PVA polymer dispersant, initially, packing density decrease due to more agglomeration via bridging; then at higher PVA loading, steric stabilization come to play and packing density increases while pore size decreases
  - At pH=7.3, even without PVA, negative charges on SiO_2 surface lead to electro-static stabilization, resulting high packing density & small median pore size

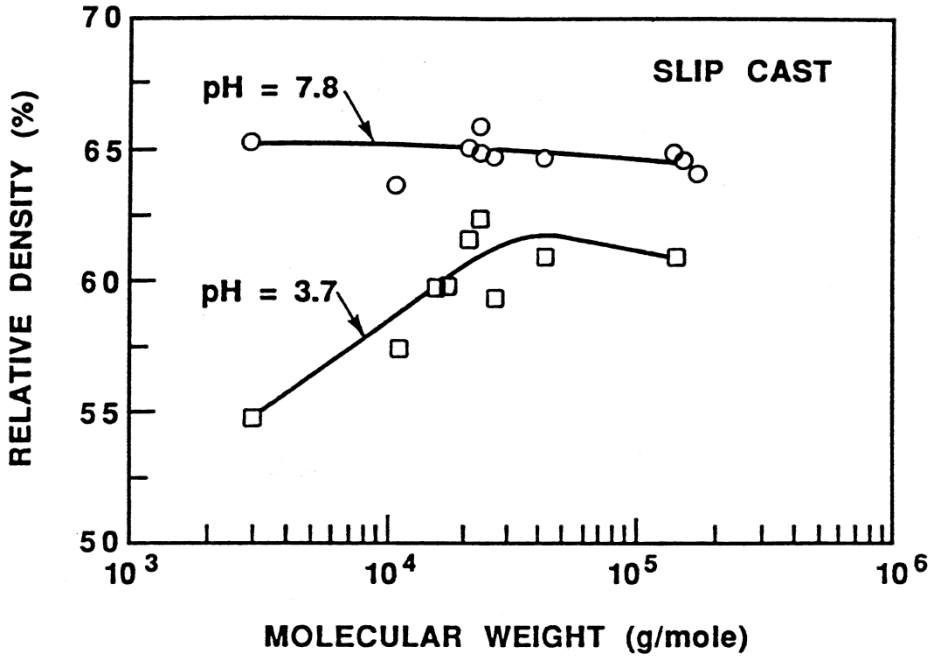


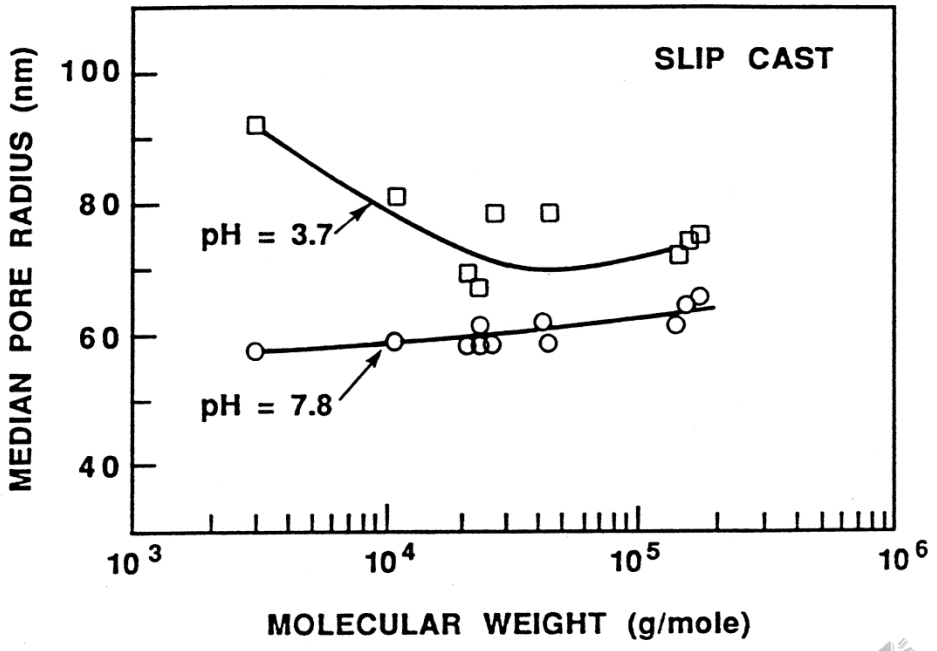


Steric Stabilization on Powder Compact Structure - Polymer Molecular Weight Effect

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

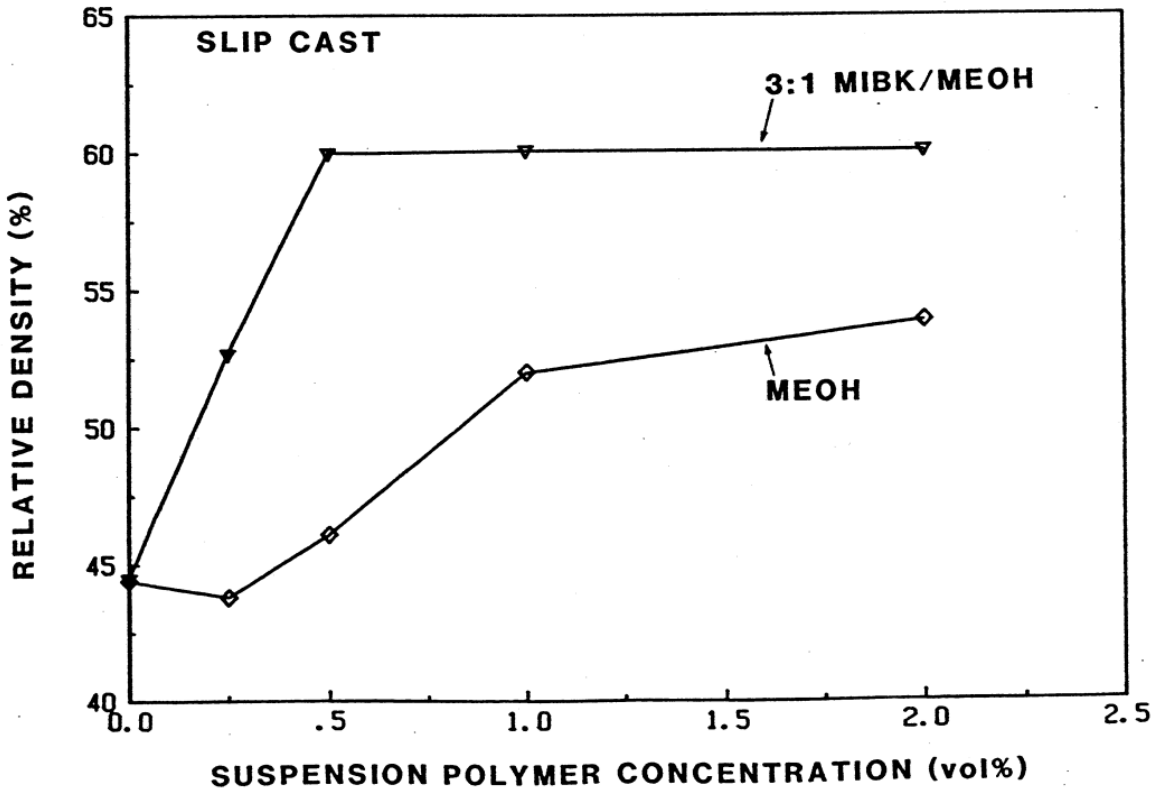
- **For SiO_2, IEP ≈ 3-4**
  - At pH=3.7, higher molecular weight PVA → longer interaction distance ***L*** (e.g., for MW=10^4, L ≈ 10 nm; MW=10^5, L ≈ 30 nm) → and particles are better stabilized and green density increase significantly while pore size decreases:
  - At pH=7.8, with high surface charge, larger polymer molecule size (via higher molecular weight PVA) does not increase packing density or decrease pore size





Steric Stabilization on Powder Compact Structure - Solvent Quality Effect

- **For Al_2O_3 in organic solvents with non-polar polymer dispersant**
  - With more polar solvent (i.e., methanol MEOH), PVB polymer packs denser and less dispersion of colloidal suspension and lower powder compact density
  - With addition of less polar solvent MIBK (e.g., 3:1 of MIBK-MEOH mixture), PVB polymer is more spread out, and better dispersion of colloidal suspension and higher powder compact density



MD Sacks, (2001), Classnotes, *Fine Particle Technology*

Ways to Achieve Stabilization of (Colloidal) Particle Suspension

- **Fine particles in suspension tend to flocculate due to van der Waals forces larger than thermal energy**
- **Need to introduce repulsive force between particles to stabilize colloidal particle suspension**
  - **Electrostatic stabilization**
    Repulsion between particles due to electrostatic charges on particle surface
  - **Steric stabilization**
    Repulsion between particles due to uncharged polymer chains adsorbed on particle surface
  - **Electrosteric stabilization**
    Combination of electrostatic and steric repulsion

Rahaman (2003), p. 191

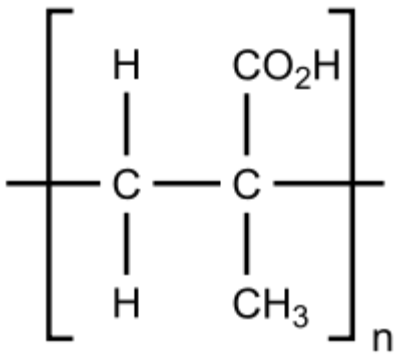
Dissociation of Polyelectrolytes in Solution

❑Polyelectrolyte dissociates in solvents

Example

- Poly methacrylic acid (PMAA)
  The $-CO_2H$ group may exist as acid group: it dissociates and releases H^+ and form charged group of $-COO^-$, which makes PMAA anionic polyelectrolyte

PMAA

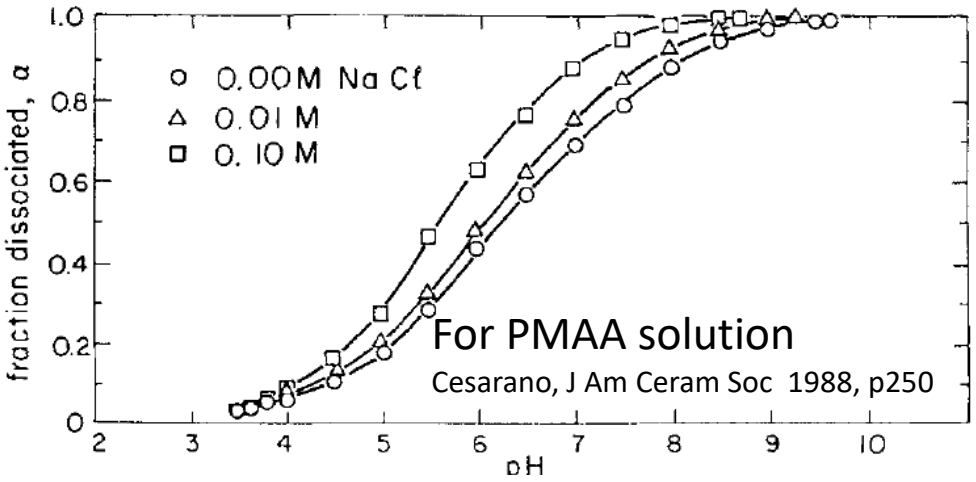


https://en.wikipedia.org/wiki/Poly(methacrylic_acid)

❑Extent of dissociation depends on pH and salt concentration

Example

- For PMAA, the higher the pH or higher Na salt concentration, the higher the extent of dissociation → the larger the polymer molecule cluster in solution



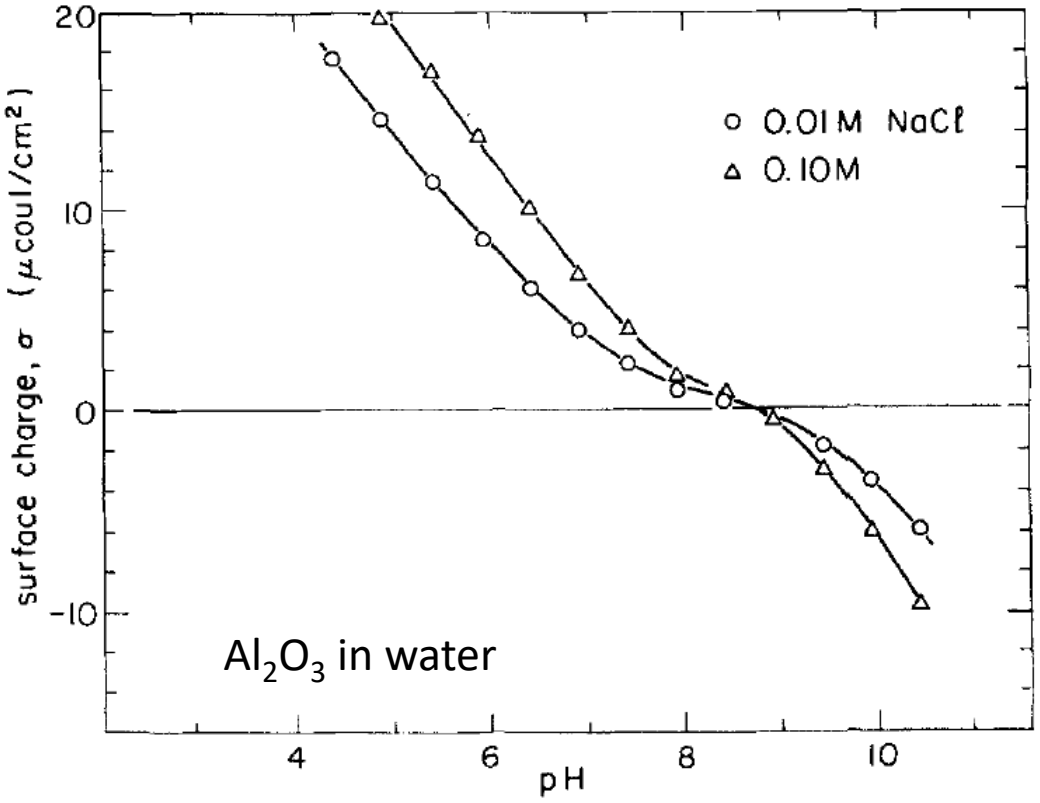
Rahaman (2003), p. 223-224

Adsorption of Polyelectrolytes from Solution

- **Electrostatic interaction leads to adsorption of polyelectrolytes from solution onto (charge) ceramic particle surface**

Example

- α-Al_2O_3 develops positive charge in pH <~9 while PMAA dissociates to form negatively charged groups at pH of 3.5-8.5, leading to electrostatic attraction.
  - The lower the pH, the PMAA polyelectrolyte becomes smaller and pack denser, and more polymer is needed to achieve monolayer coverage (saturation)

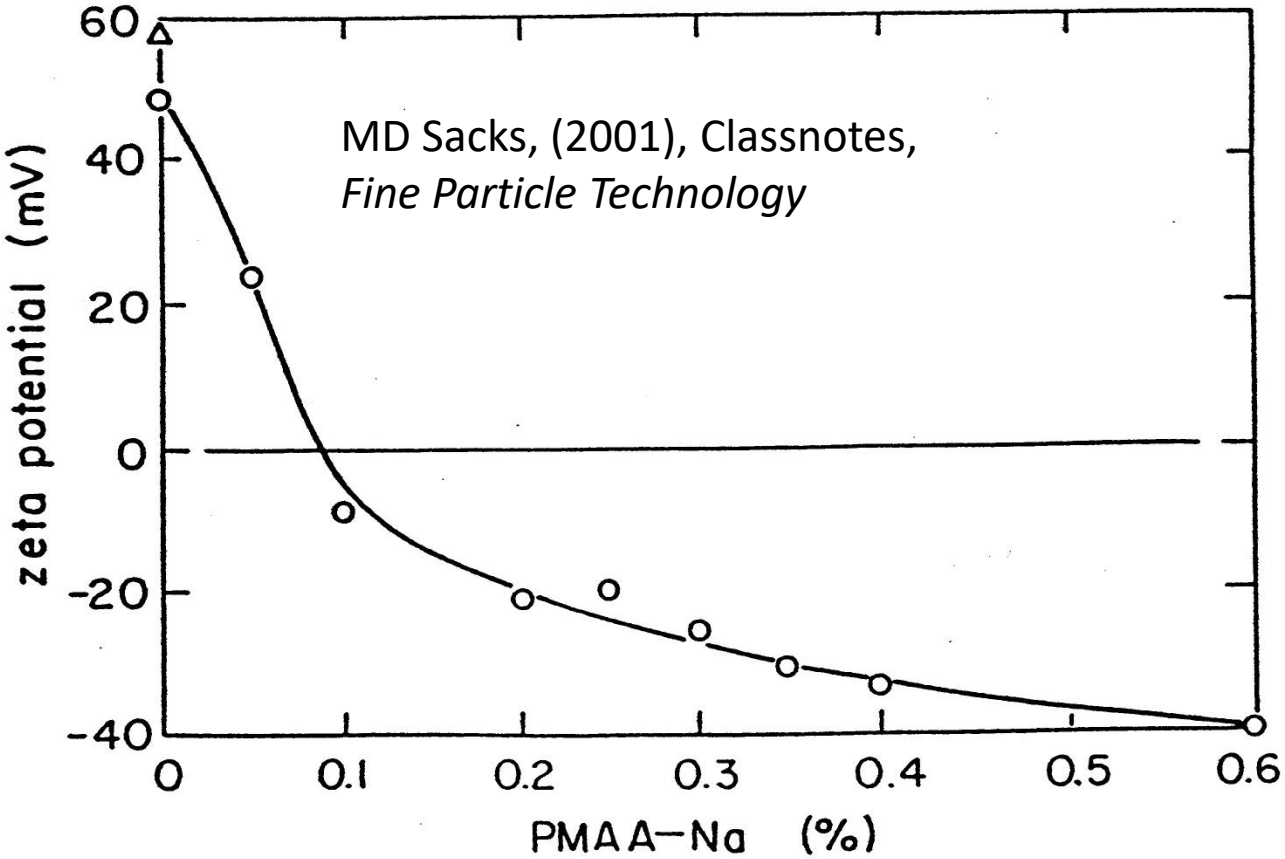


For PMAA solution

Cesarano, J Am Ceram Soc 1988, p250

Polyelectrolytes Effects on Zeta Potential

- **Example: Al_2O_3 (2 vol.% in water) colloidal solution with PMAA-Na**
  - IEP ~ 8-9 (or Al_2O_3 surface positively charged at pH of ~7)
  - As PMAA-Na electrolyte concentration increases, the Al_2O_3 particle selectively adsorb more negatively charged PMAA, and zeta potential changed from positive to negative



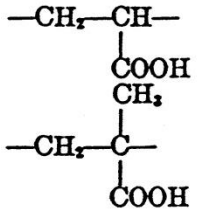
Common Polyelectrolytes

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

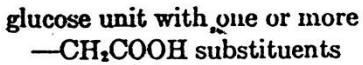
Weak polyacids

poly(acrylic acid)

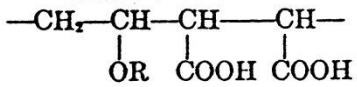
poly(methacrylic acid)



carboxymethylcellulose



vinyl alkyl ether–maleic acid copolymers

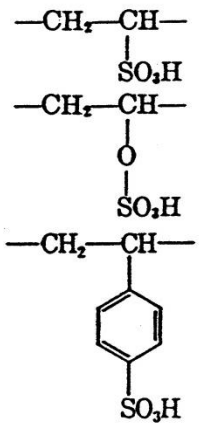


Strong polyacids

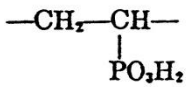
poly(ethylenesulfonic acid)

partially sulfated poly(vinyl alcohol) (sometimes called poly(vinyl alcohol sulfate) to denote residual unesterified —OH groups)

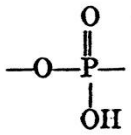
poly(styrenesulfonic acid)



poly(vinylphosphonic acid)



poly(phosphoric acid) (sometimes called poly-(*m*-phosphoric acid))

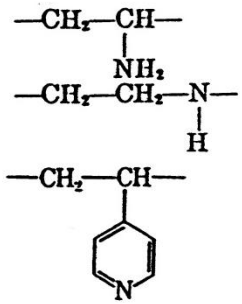


Polybases

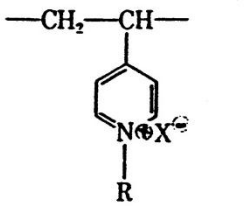
poly(vinylamine)

poly(ethylenimine)

poly(4-vinylpyridine)



poly(4-vinyl-*N*-alkylpyridinium halides)



Stability of Electrosterically Stabilized Solution

- **Stability depends on multiple factors**
  - Polyelectrolyte concentration
    - If too low, not enough electrosteric effect while bridging might actually cause flocculation
    - At higher concentration, electrostatic repulsion at larger inter-particle distance and steric repulsion at shorter distance
  - Solution pH
    - pH impacts the extent of polyelectrolyte dissociation and surface charge state of the ceramic particles

Rheology of Colloidal Suspension

❑Rheology

- "Study of the flow of matter, primarily in a liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force" https://en.wikipedia.org/wiki/Rheology
- (Plastic) deformation and flow characteristics of (liquid or soft) material in response to stress

❑Importance of rheology

- Key characteristics of colloidal suspension
- Parameter for quality control and/or process optimization

Basic Concept for Rheology

❑Rheological properties often measured from simple shear experiments

Define

τ Shear stress

γ Shear strain

$\dot{\gamma}$ Shear strain rate or shear velocity

η Viscosity

We have $$\tau = \eta\dot{\gamma}$$

$$\dot{\gamma} = \frac{\tau}{\eta}$$

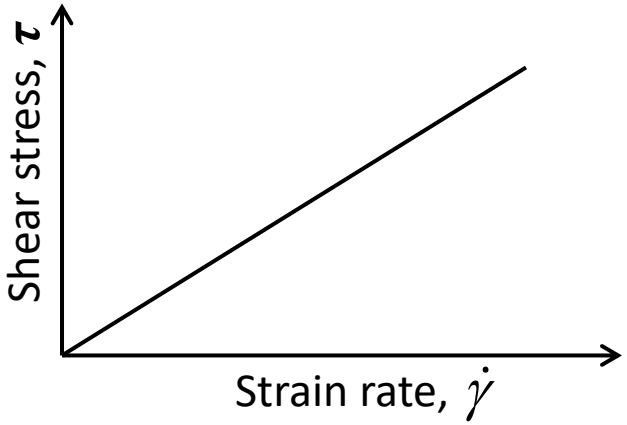
❑Classification of fluid

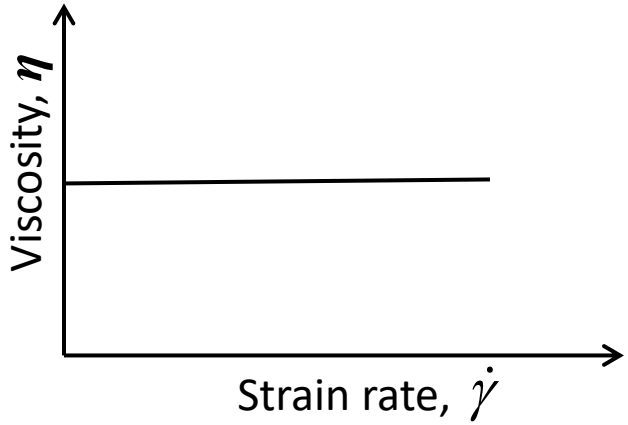
- Newtownian - viscosity of fluid η is a constant
- Non-Newtownian – viscosity of fluid η changes with shear strain rate

Newtonian Behavior

❑Newtownian fluid

- Linear relationship between shear stress and shear strain rate
- Viscosity does not change with shear strain rate (under normal condition)





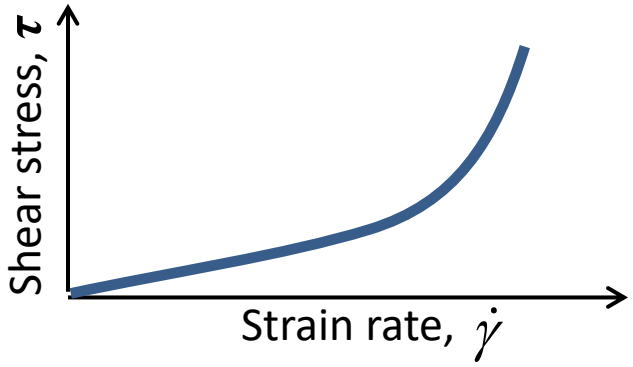
- Examples:
  - Water
  - Alcohol
  - Some molten oxides
  - Well dispersed colloidal suspension

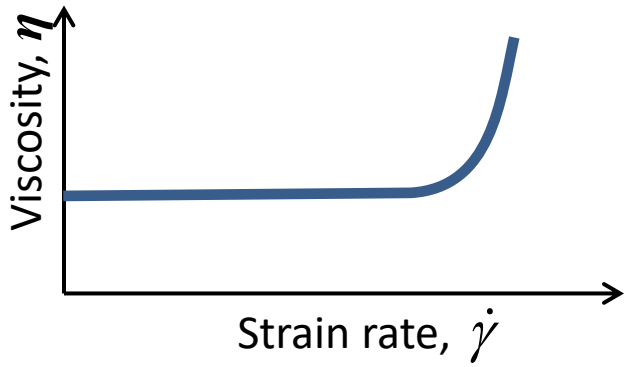
Non-Newtonian Behaviors (1)

❑Shear thickening or dilatant

Viscosity increases with increasing shear strain rate

Examples: High concentration suspension of small equiaxial particles

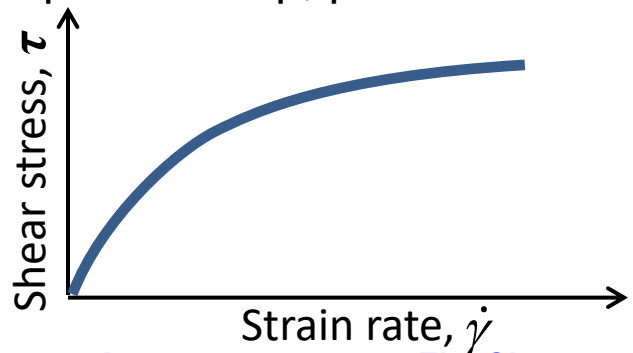


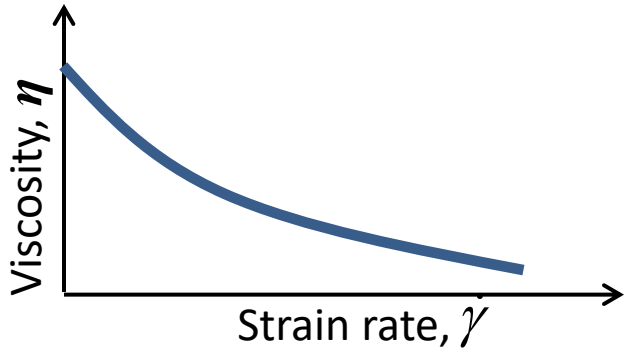


❑Shear thinning or pseudoplastic

Viscosity decreases with increasing shear strain rate

Example: ketchup, paint

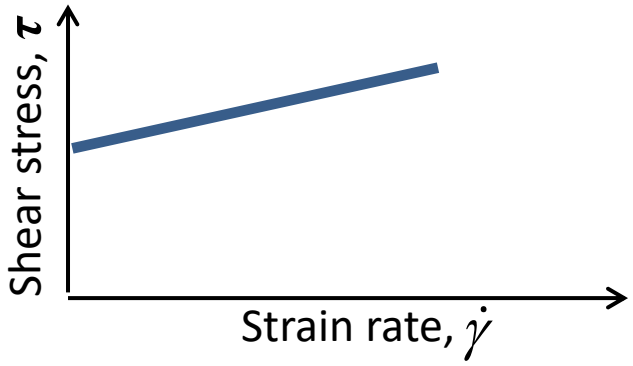


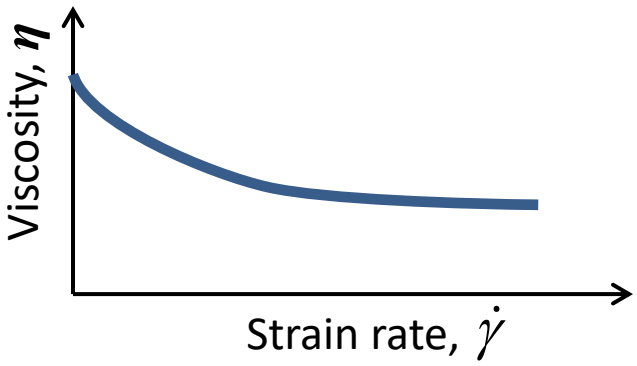


Non-Newtonian Behaviors (2)

❑Plastic or Bingham

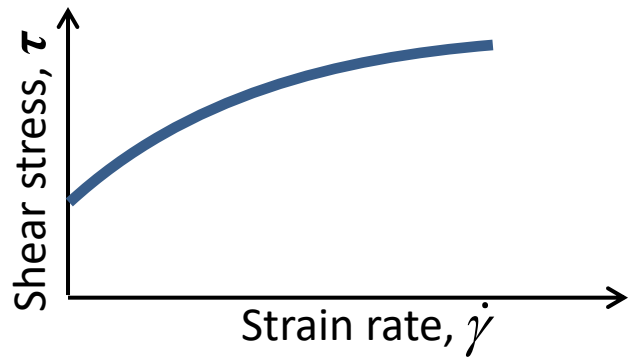
Elastic solid at low stress but flows as a viscous liquid beyond certain yield stress

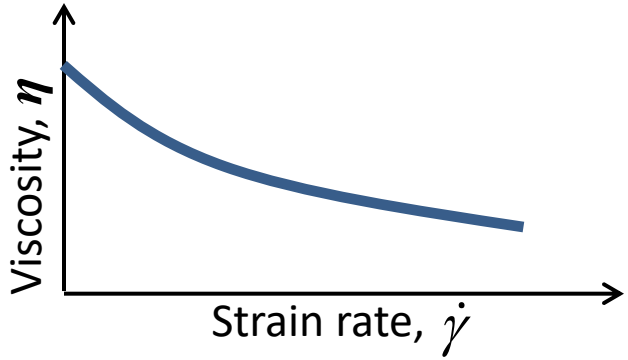




❑Pseudoplastic with a yield stress

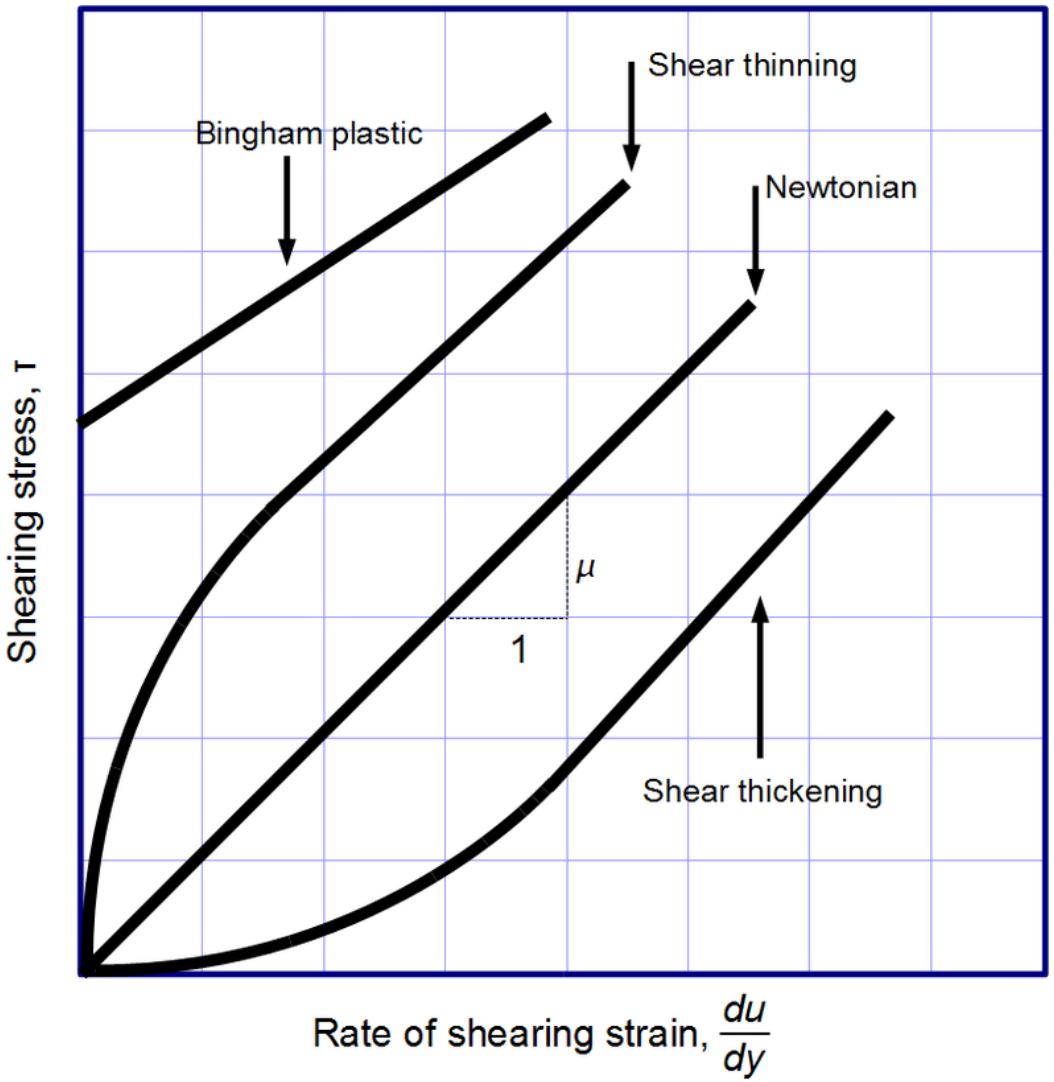
Viscosity decreases with increasing shear strain rate but with yield stress





Summary of Rheological Behaviors

- **Different behaviors:**
  - Newtonian – Simplified
  - Bingham plastic – Desirable
  - Shear thinning (Pseudo plastic) – Acceptable
  - Shear thickening (dilatant) – Often undesirable for slurry/paste used in ceramic processing



https://en.wikipedia.org/wiki/Viscosity

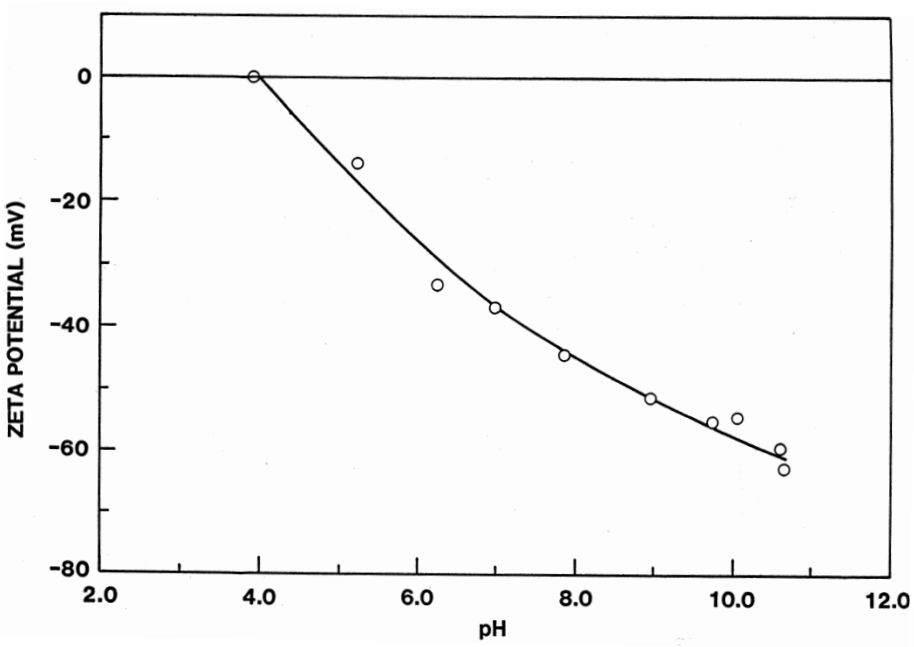
Surface Charge/Zeta Potential Effect on Colloidal Suspension Rheology (1)

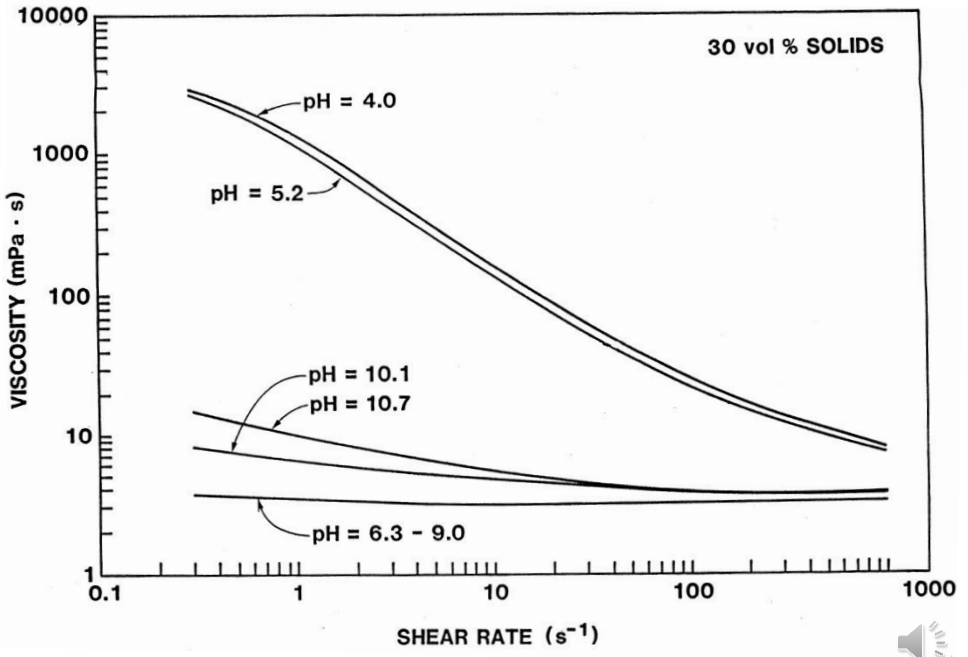
MD Sacks, (2001), Classnotes, *Fine Particle Technology*

- **For SiO_2, IEP = ~3.7**

Viscosity behavior changes with pH

- pH=4.0, very little charge on particle surface, particles tend to agglomerate and show high viscosity and shear thinning (plastic) behavior
- pH of ~6.3-9.0, OH^- adsorb on particle surface leading to electrostatic stabilization, and suspension viscosity decreases and gradually transform to (near) Newtonian behavior
- pH > 10, too high ionic strength leads to reduction in Debye length and suspension starts to agglomerate again with viscosity increase

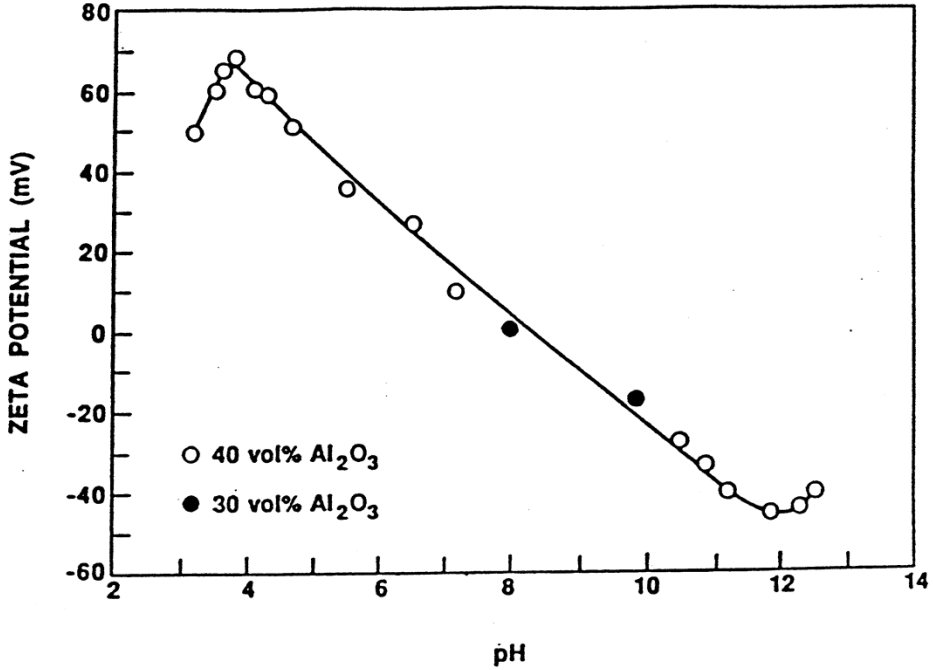


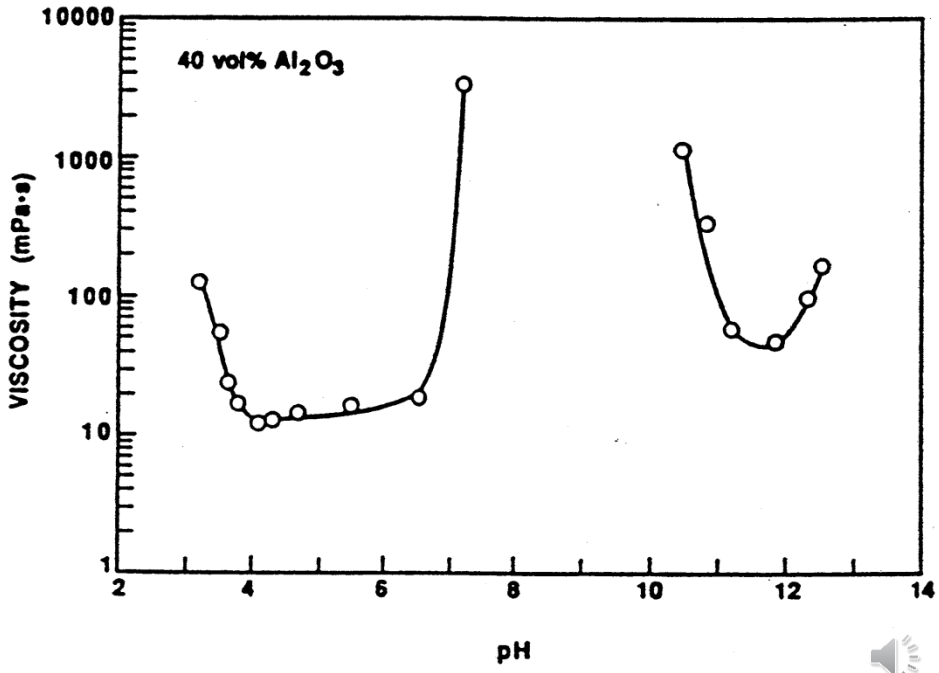


Surface Charge/Zeta Potential Effect on Colloidal Suspension Rheology (2)

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

- **For Al_2O_3, IEP ≈ 8-9**
  - When pH is in range of ~7-10, suspension has severe agglomeration and viscosity is high (and also shear thinning)
  - As pH decreases further from ~7 or increases further from ~10, suspension viscosity decreases due to stable dispersion
  - As pH decrease further from ~4 or increase further from ~12, viscosity increases due to too high ionic strength and aggolomeration

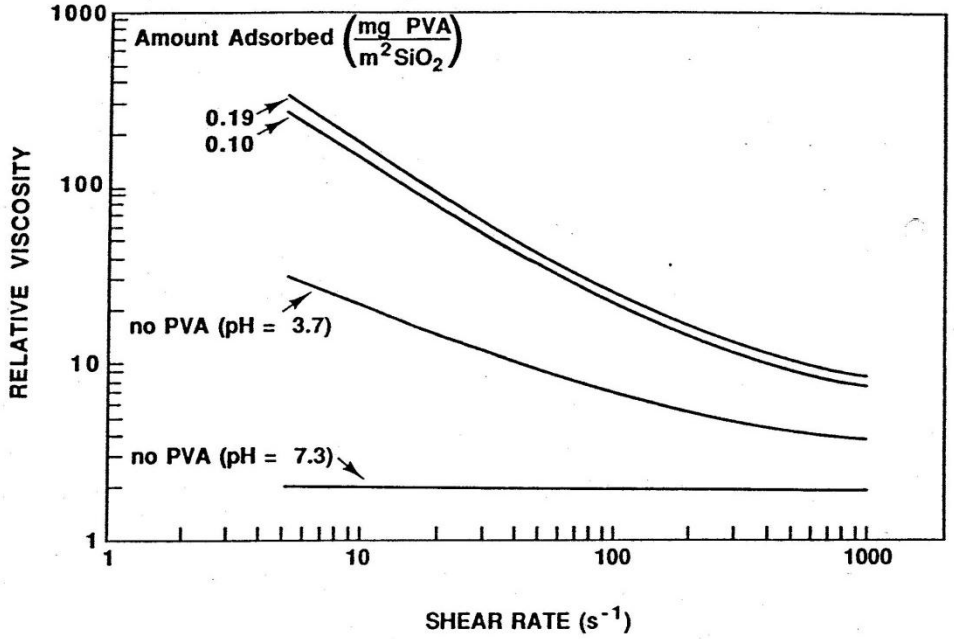


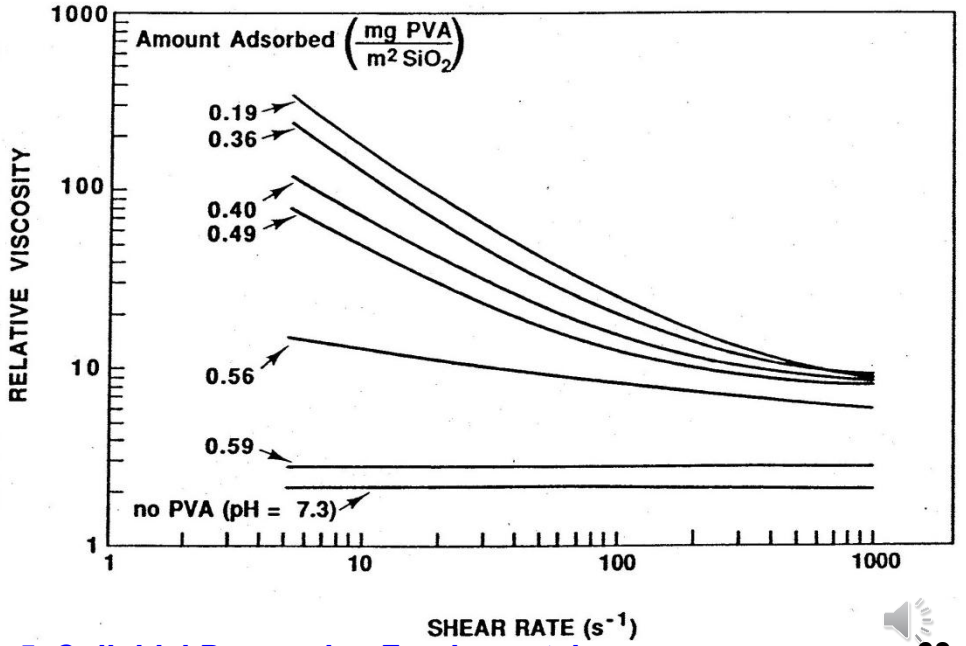


Adsorbed Polymer on Colloidal Suspension Rheology – Adsorption Amount Effect

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

- **For SiO_2, IEP = ~3-4**
  - At pH=7.3, high negative charge develop on particle surface, and suspension is stable and show Newtonian behavior
  - At pH=3.7, very little charge on particle surface, particles tend to agglomerate
    - With no dispersant, and show plastic or shear thinning behavior
    - With low PVA addition, bridging happen leading to agglomeration and shear thinning.
    - When more PVA is added to achieve "monolayer coverage", particles become well dispersed due to Steric stabilization and behave like Newtonian fluid

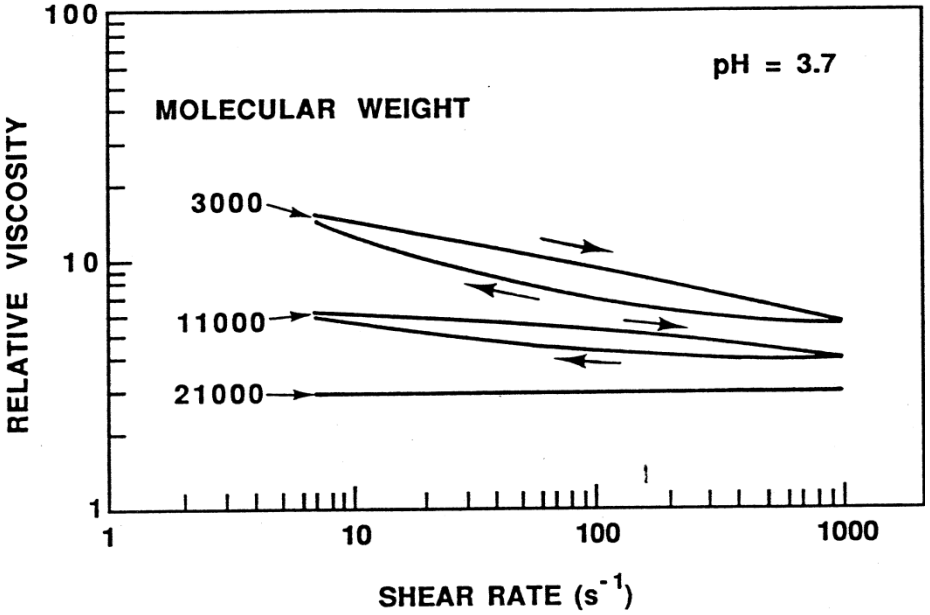


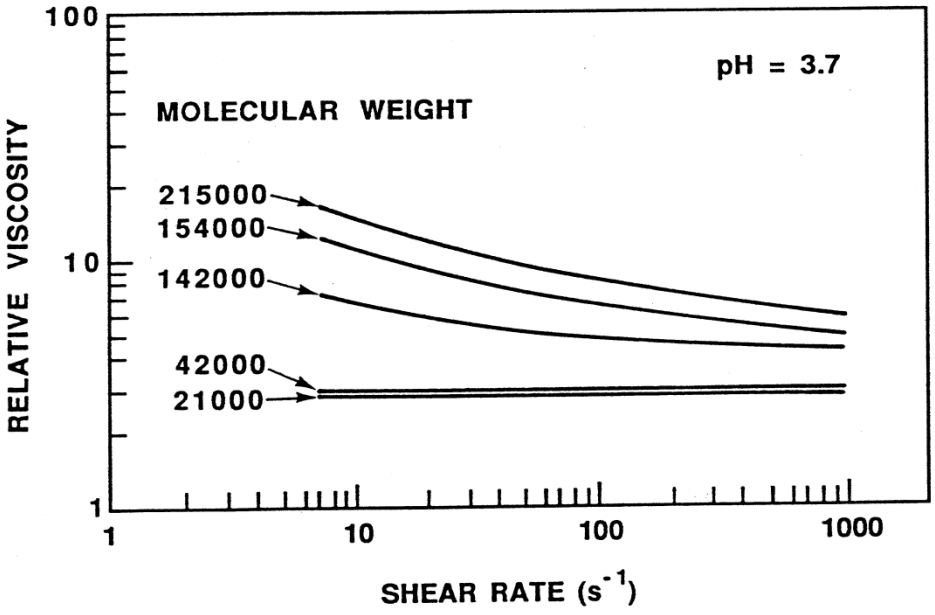


Adsorbed Polymer on Colloidal Suspension Rheology – Molecular Weight Effect

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

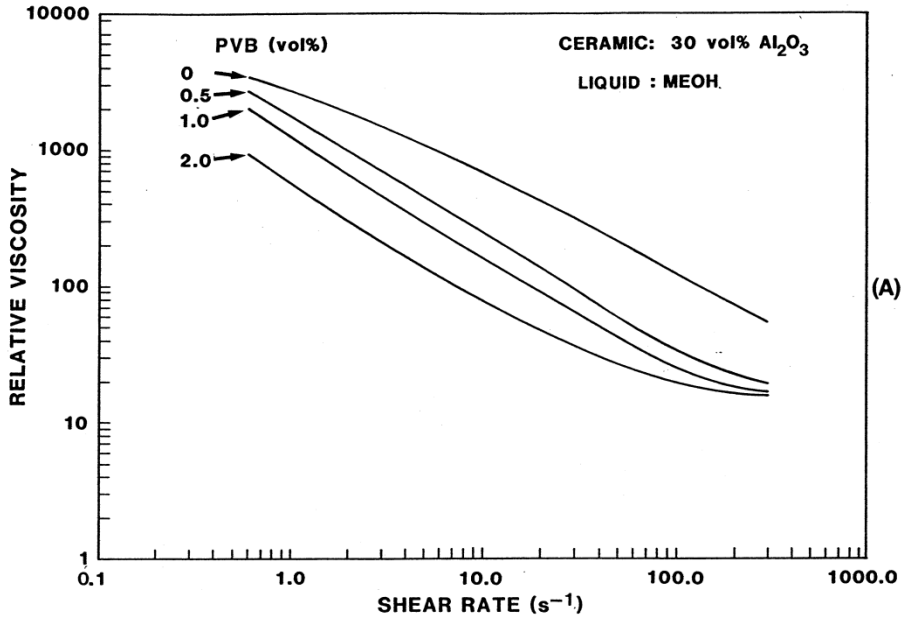
- **For SiO_2, IEP = ~3-4**
  - At pH=3.7, very little charge on particle surface, particles tend to agglomerate
    - With increasing PVA molecular weight, particles become better dispersed and viscosity decreases and display Newtonian behavior
    - As PVA molecular weight increases to too high, viscosity increases again and display shear thinning behavior again

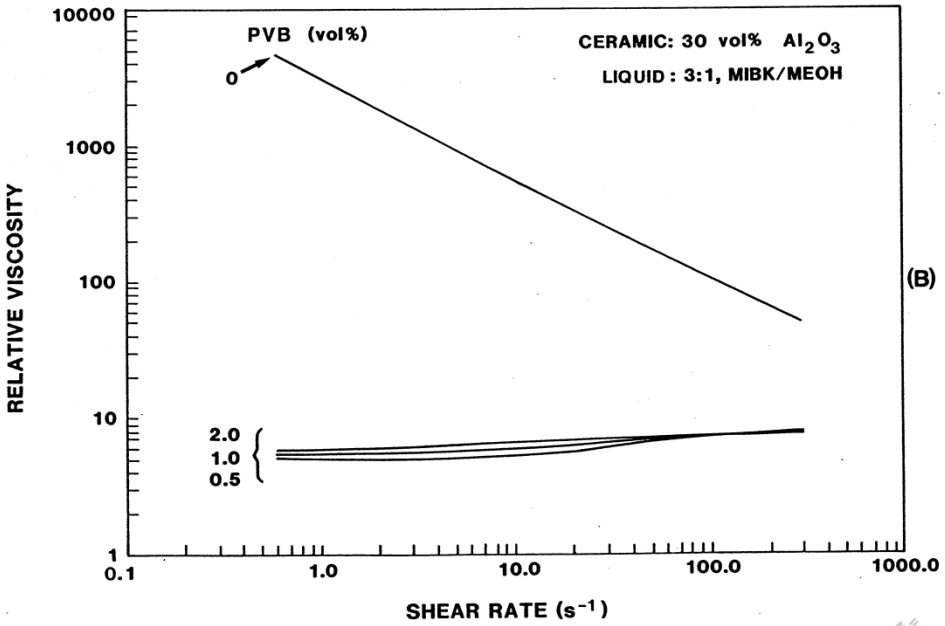




Adsorbed Polymer on Colloidal Suspension Rheology – Solvent Effect

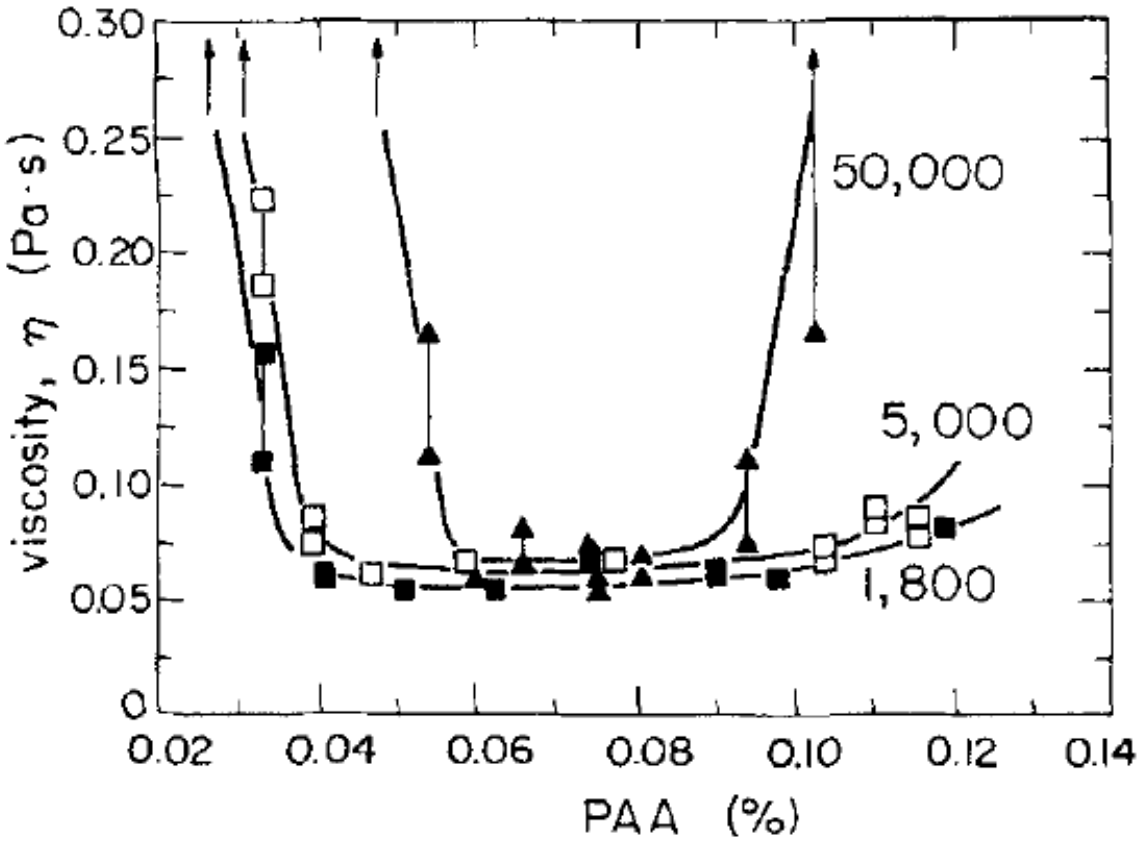
- **For Al_2O_3 in organic solvents with PVB dispersant**
  - When using methanol as solvent, solvent quality low and Al_2O_3 selectively covered by solvent and not polymer, leading to poor dispersion and high viscosity even up to high polymer loading
  - When using methanol-methyl-isobutyl ketone mixed solvent, Al_2O_3 surface become selectively covered by PVB polymer and suspension is stable and show Newtonian behavior even at very little polymer loading





Adsorbed Polyelectrolyte Effect on Colloidal Suspension Rheology

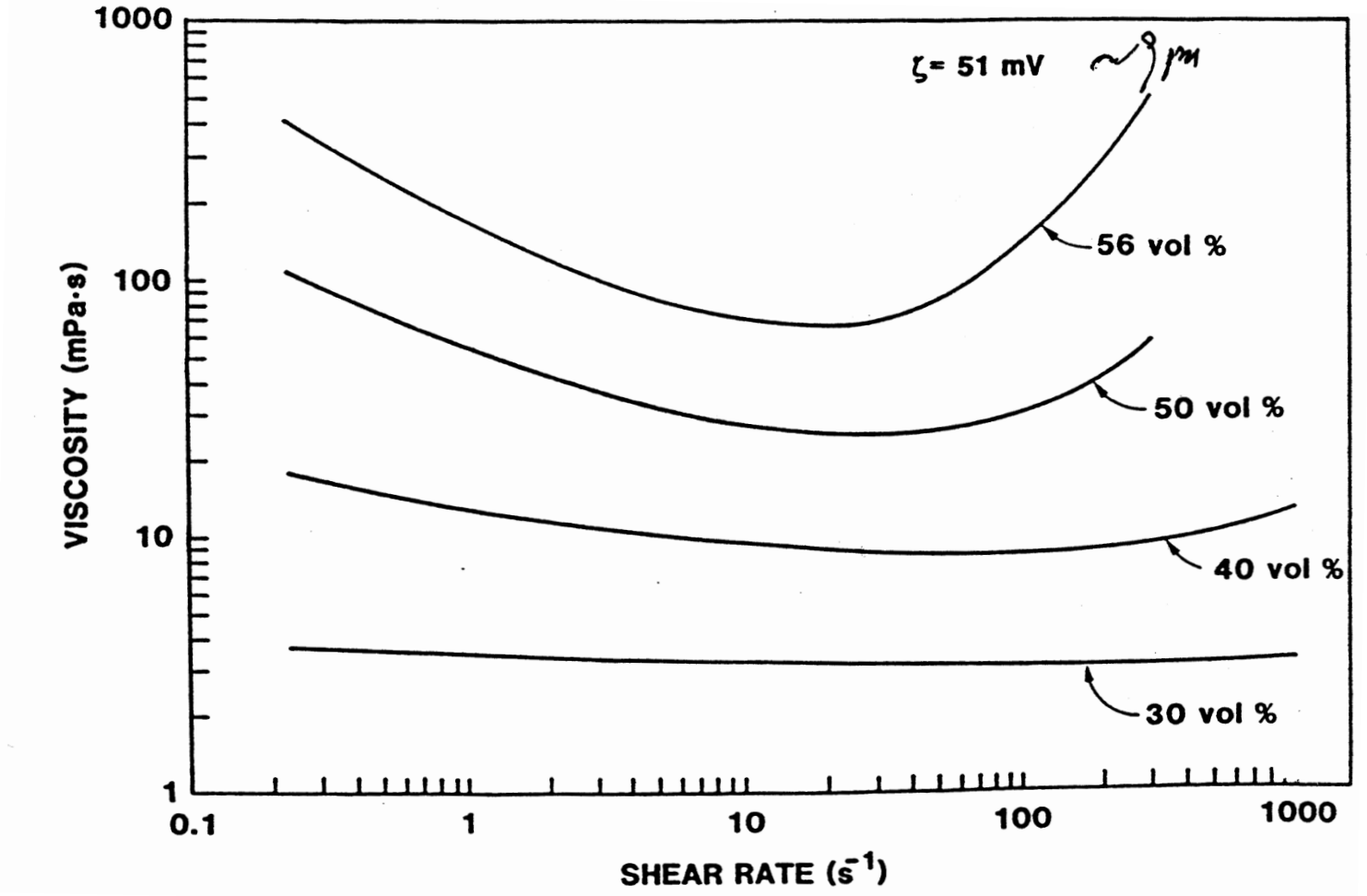
- As particle become better dispersed via adding more polyelectrolytes, the viscosity decreases
- Too much polyelectrolyte leads to viscosity increase



Solid Loading Effect on Colloidal Suspension Rheology

- **As solid loading increases, viscosity increases**

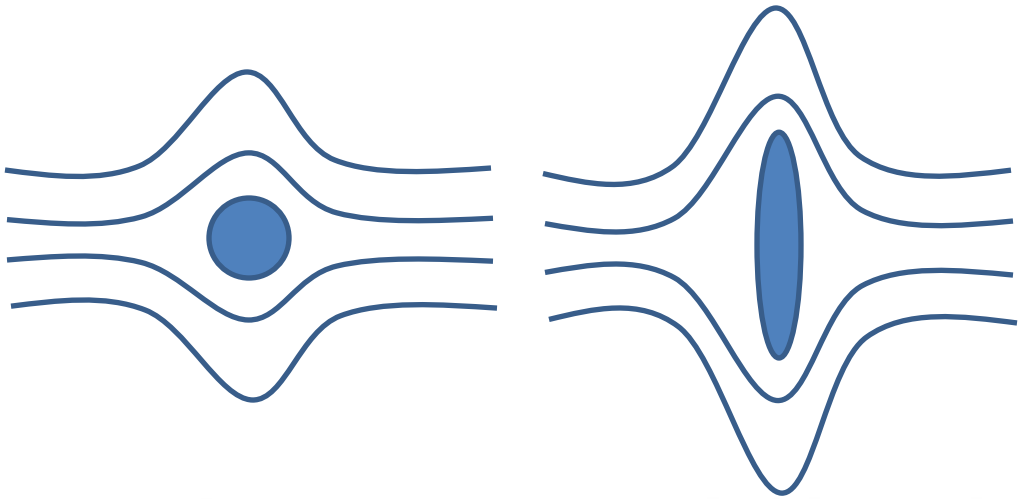
  Example: SiO_2 colloidal suspension in water



Particle Shape Effect on Colloidal Suspension Rheology

❑Particle shape

"A suspension of anisotropic particles usually has a higher viscosity compared to suspension of spherical particles at the same solids volume"

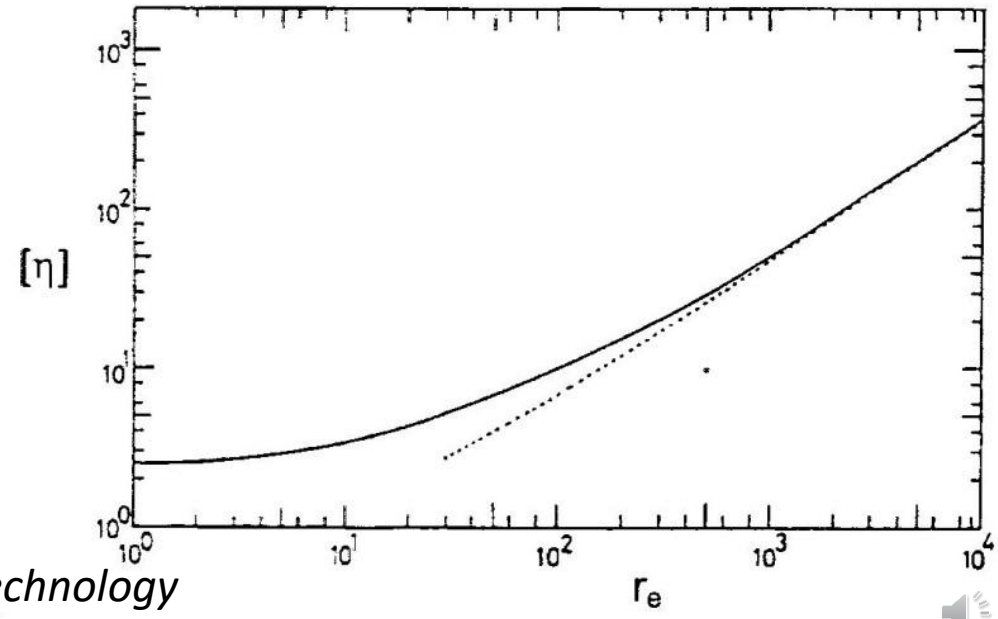


Reason

"Rotation of anisotropic particles produces greater perturbations… and, hence, enhanced energy dissipation"

Example

Compared with spherical particles, whiskers with axial ratio of ~20, the viscosity almost double and the effect is even more significant as aspect ratio increases further

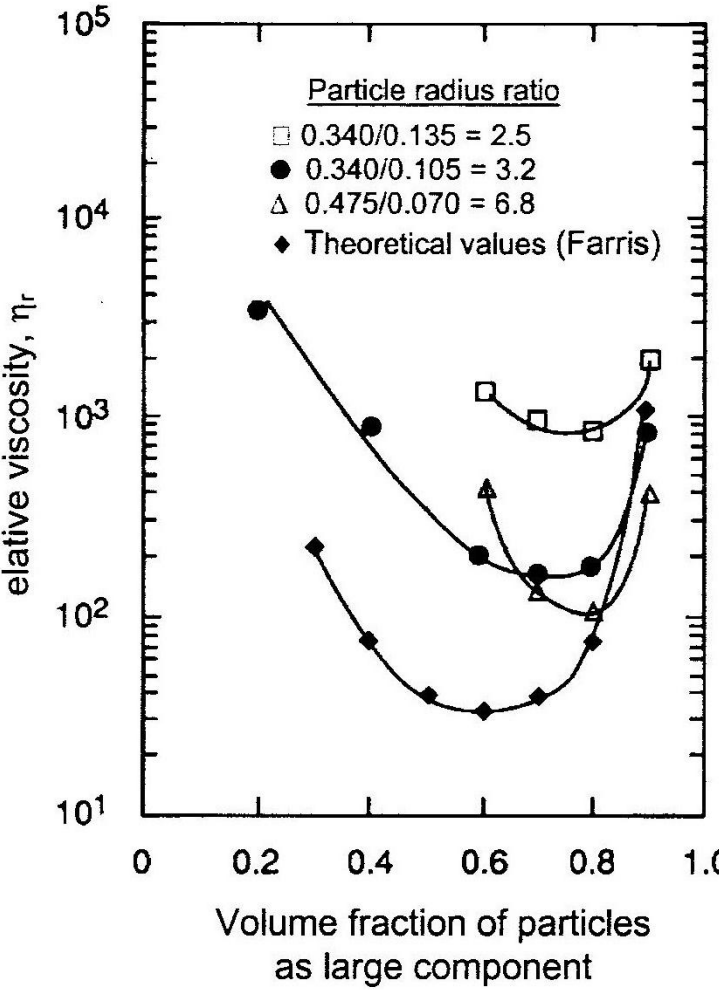


Rahaman (2003), 241-243

MD Sacks, (2001), Classnotes, *Fine Particle Technology*

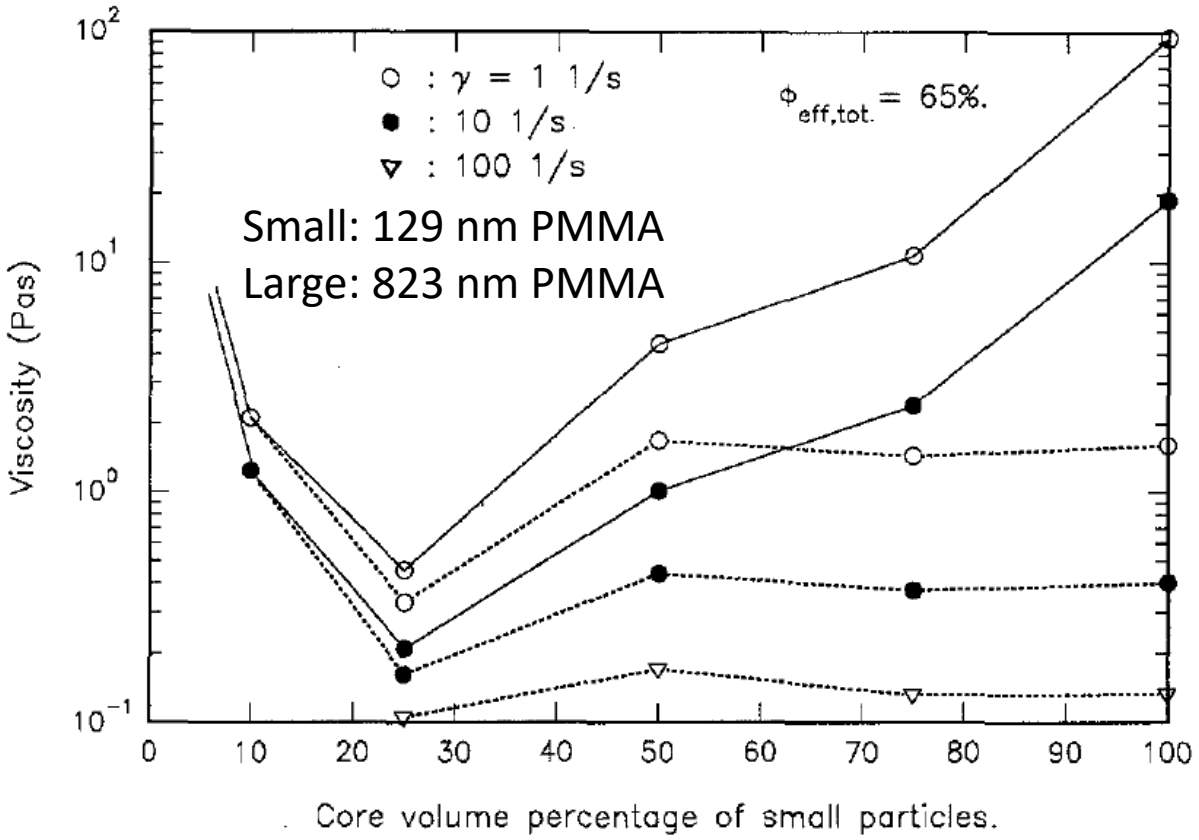
Particle Size Distribution Effect on Colloidal Suspension Rheology

- **Comparing of single mode, bi-modal or continuous particle size distribution leads to reduced viscosity at the same solid loading**



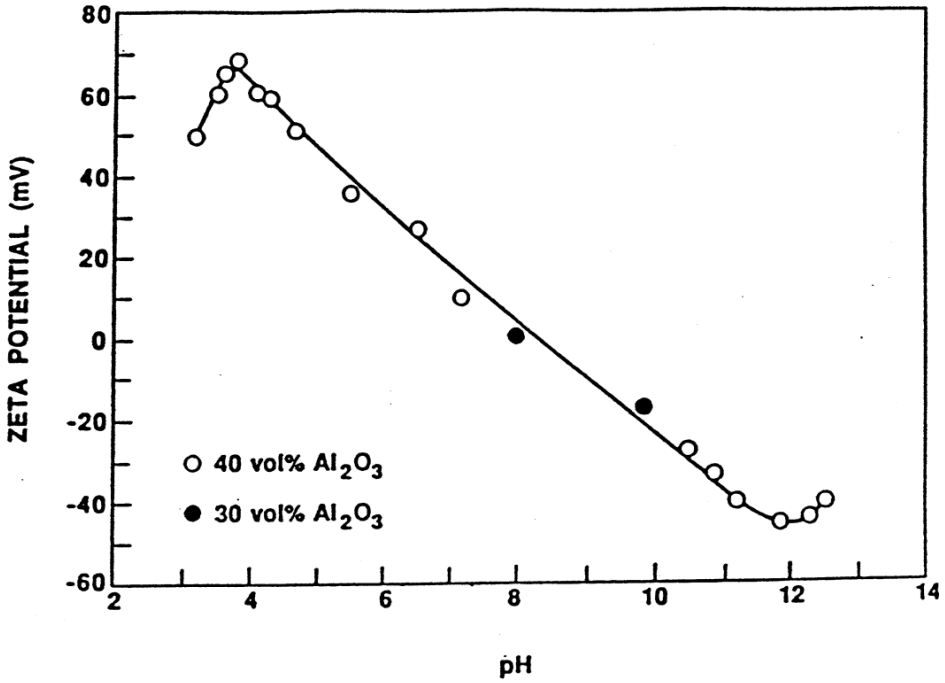
Rahaman (2003), 241-242

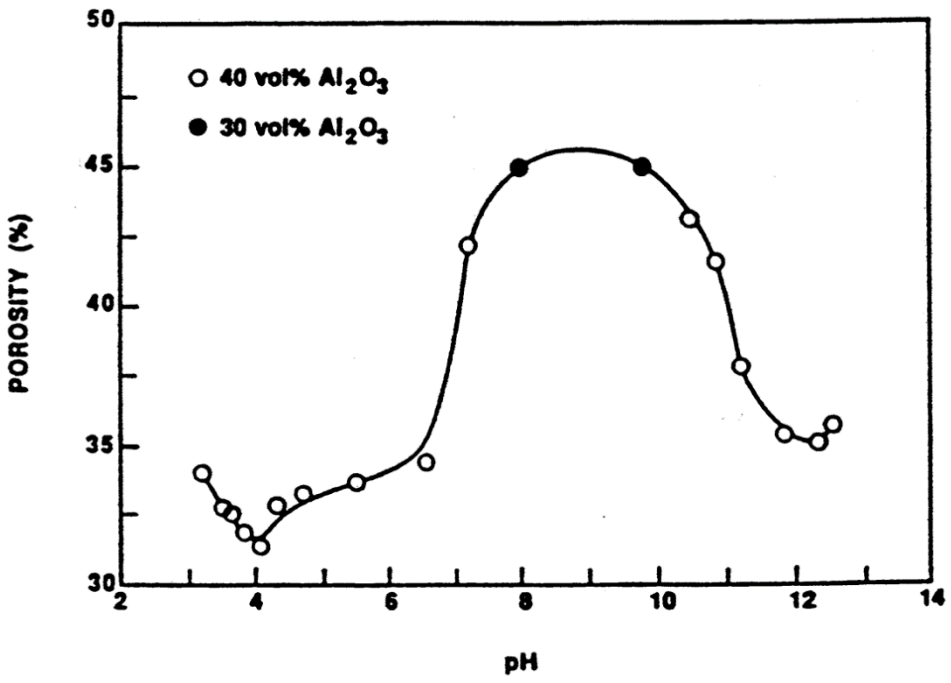
Haene (1994), Rheology Acta, vol. 33, p165



Homework

- Explain in your own words all the features in the following plots for Al_2O_3 colloidal in water





Homework

- Explain in your own words all the features in the following plots for SiO_2 colloidal in water with PVA dispersant