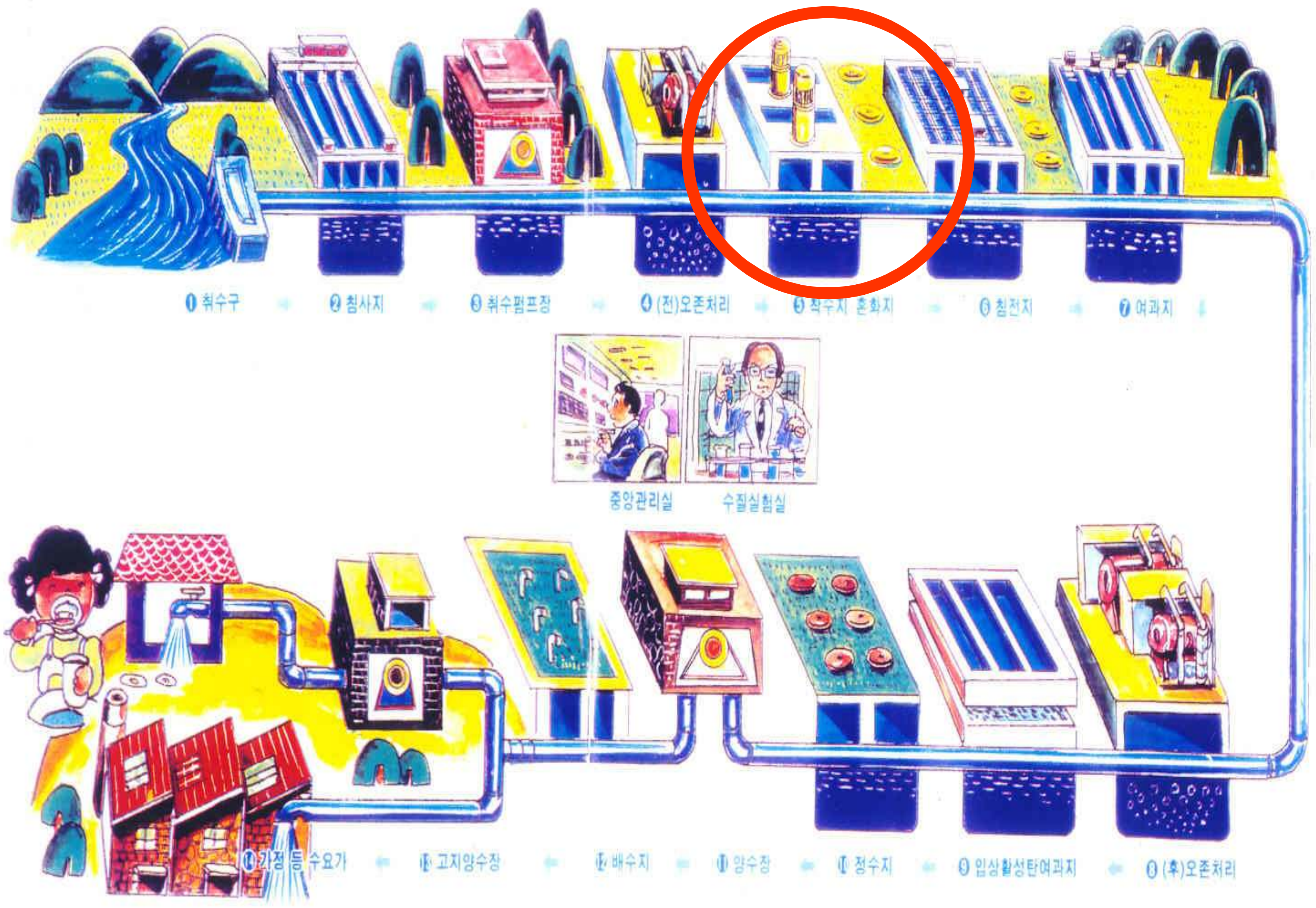
Coagulation/Flocculation/ Sedimentation /Filtration/Disinfection in Water Treatment Process?

Water Quality & Treatment, A Handbook of Community Water Supplies, 5th ed, 1999, AWWA

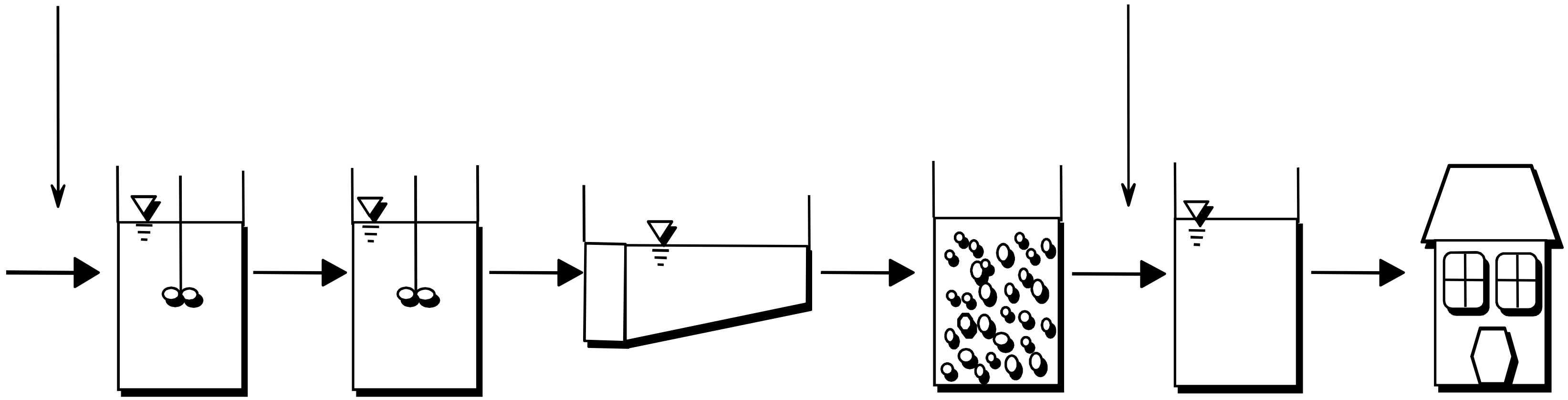
수돗물 생산과정

WATERWORKS IN PUSAN

Water Treatment Process?



Conventional water treatment process?



prechlorination

postchlorination

Raw water

Rapid mixing
coagulation

flocculation

Sedimentation

filtration

disinfection

Coagulation - destabilize the colloidal particles & to overcome the negative charge of particles with chemical addition

Flocculation - gently mix the destabilized particles to promote interparticle collisions in order to achieve particle growth

How can we achieve good coagulation?
➔ Initial Mixing (very fast!)

~ intend to provide good encounters between molecules and colloidal particles in the source water and the coagulent species

~ stability of particles – Electrical double layer, Zeta potential

Initial Mixing and Mechanism of Coagulation

$Al_2(SO_4)_3(H_2O)_n$

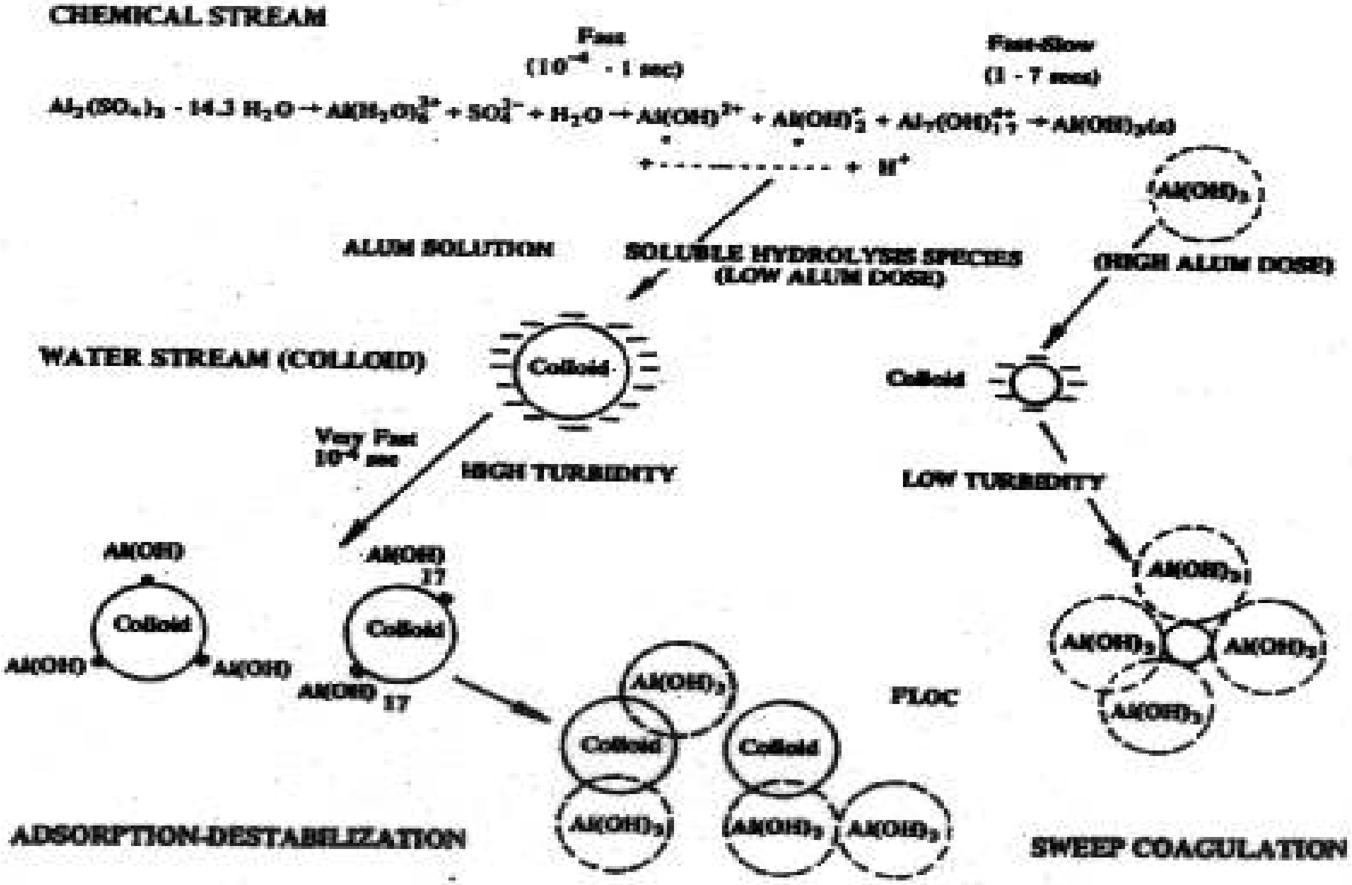
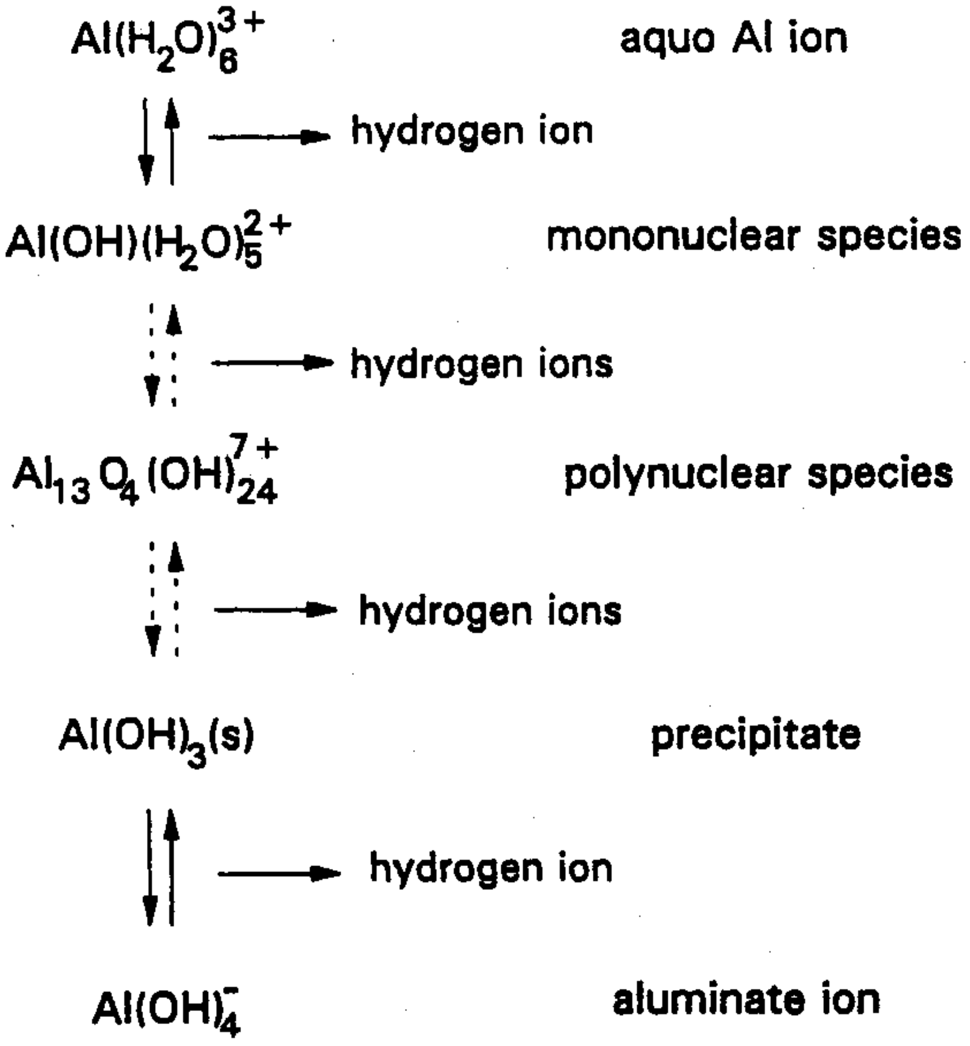


Figure 1. Reaction schematics of coagulation

Aluminum coagulation chemistry



$Al(H_2O)_6^{3+}$ aquo Al ion

→ hydrogen ion

$Al(OH)(H_2O)_5^{2+}$ mononuclear species

→ hydrogen ions

$Al_{13}O_4(OH)_{24}^{7+}$ polynuclear species

→ hydrogen ions

$Al(OH)_3(s)$ precipitate

→ hydrogen ion

$Al(OH)_4^-$ aluminate ion

FIGURE 6.8 Aluminum hydrolysis products (from Letterman, 1991).

Particles in water

Representative particles in water

~ Clay, Silt (진흙보다 굵은 침적토, 개흙)

~ Algae

~ Bacteria (~0.5μ), Virus (~0.03μ), Giardia Cysts (Protozoan, 3~10μ), NOM (Natural organic matter), Humic substances

~ Abestos fibers

How about Nanoparticles?

Reference : O'melia " Aquasols : The Behavior of small particles in Aquatic System " ES & T 14(9) 1052 (1980)

Nanoparticle

- **Nanoparticle ?**

  1) nano-sized particles at dimensions of usually 1 to 100 nanometers (nm) (nano = 10^{-9})

  2) - higher reactivity with the large surface area
     - used as excellent adsorbents, catalysts, and sensors

- **Properties of nanoparticles**

  1) optical
  2) electromagnetic
  3) mechanical
  4) photonic
  5) antimicrobial

Toxicity of nanoparticles

- **Toxicity of various engineered nanomaterials**

Type of nanomaterial	Effects observed
C_{60} water suspension	antibacterial; cytotoxic to human cell lines; taken up by human keratinocytes; stabilizes proteins
C_{60} fullerene derivatives (e.g., adducts of carboxylate and multihydroxide)	oxidative eukaryotic cell damage; bactericidal for Gram-positive bacteria; cytotoxic to human cell lines
Carbon nanotubes	antibacterial; cell membrane damage; mitochondrial DNA damage; inhibitory effect on respiratory function
Quantum dots (CdSe)	antibacterial; toxicity toward human cell due to metal release; oxidative DNA damage
Metal nanoparticle (Cu)	acute toxicity to liver and kidney
Metal oxides (TiO_2, Fe_2O_3, Co_3O_4, Mn_3O_4)	oxydative stress to human lung epithelial cell

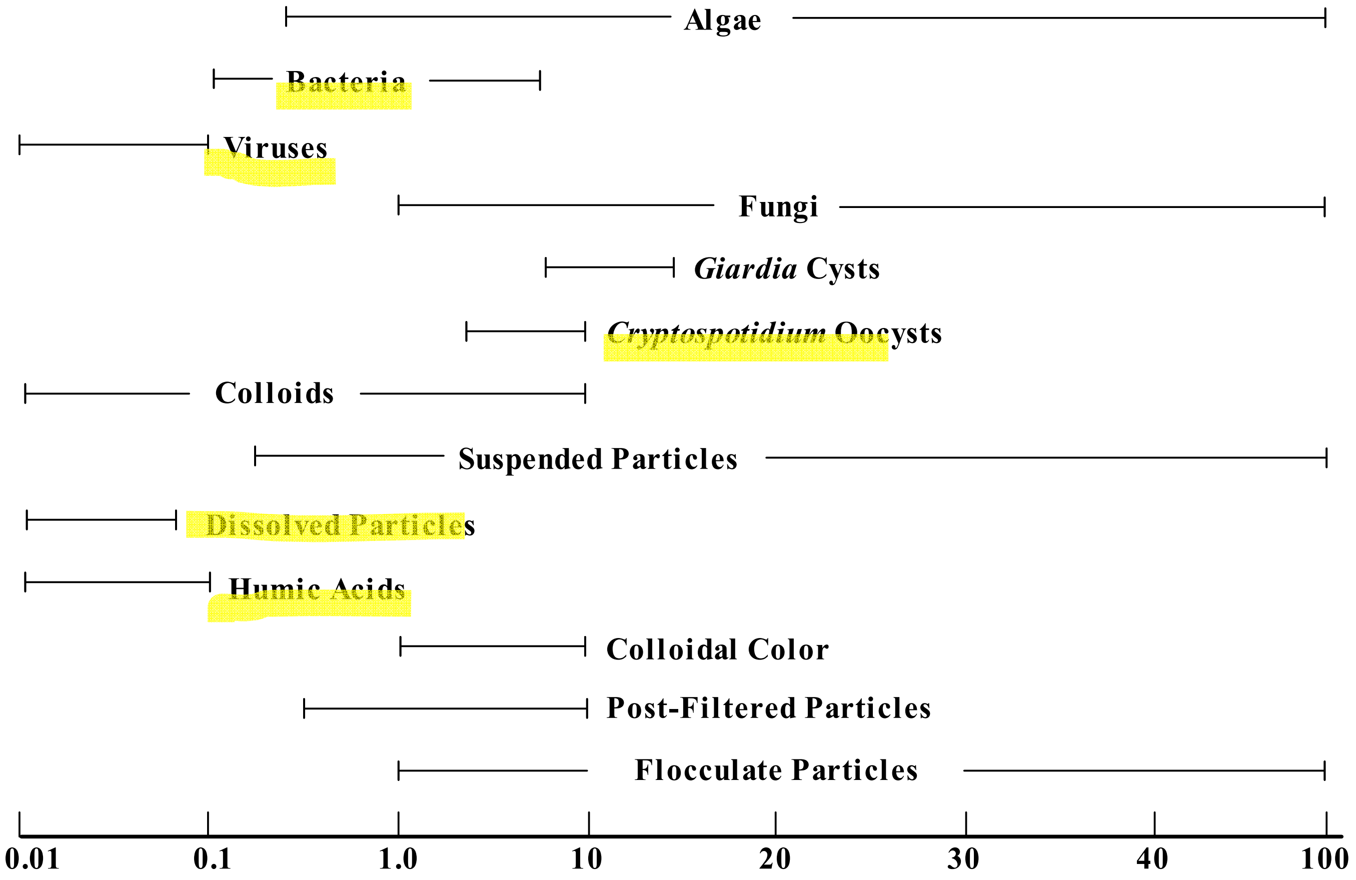
Colloidal impurity in drinking water

(1) **Particles**
  - **Clay**
  - **Silt**

(2) **Macromolecules**
  - **Fulvic acid**
  - **Humic acid**
  - **Proteins**
  - **Polysacchrides**
  - **Bacteria**
  - **Viruses**

(3) **Nanomaterials**

Size distribution of representative particles in water



Source : McTigue and Cornmell (1988).

Figure 3-1 Particulates present in raw and finished water

Size distribution of representative particles in water

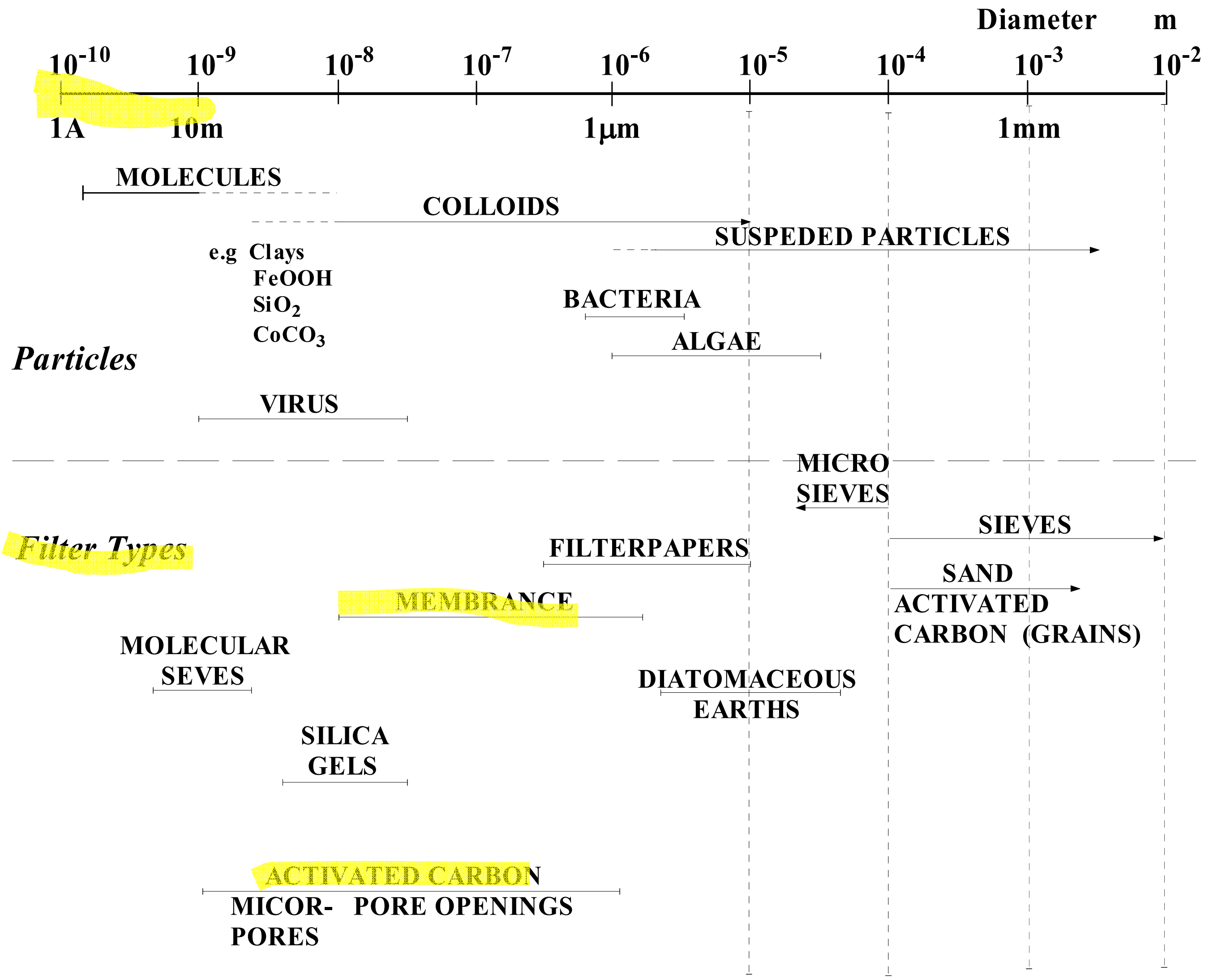


Figure 6.1 Size spectrum of waterborne particles and filer pores.

(From Stumm and Morgan.)

Why are particles important in water treatment?

➔ High specific surface area (m^2/g)

Clay and silt tend to be adsorbed by impurities such as :

~ Natural organic material (Humic substance)
~ Trace metals (such as Hg, Ni, Cd) associated with organics
~ Trace organic Contaminants, ex) Pesticides, SOCs

Clay and silt - high specific surface area/settle slowly

Colloidal size particles 5 nm ~ 10 μm, (10^{-5} m ~10^{-9} m)

These colloidal particles tend to be charged in water

" Negatively charged" ➔ electrical double layer

➔ They do not come together to form aggregate.
Thus, they stay as small stable particles

Several models of Humic substances
Humic Substance (1)

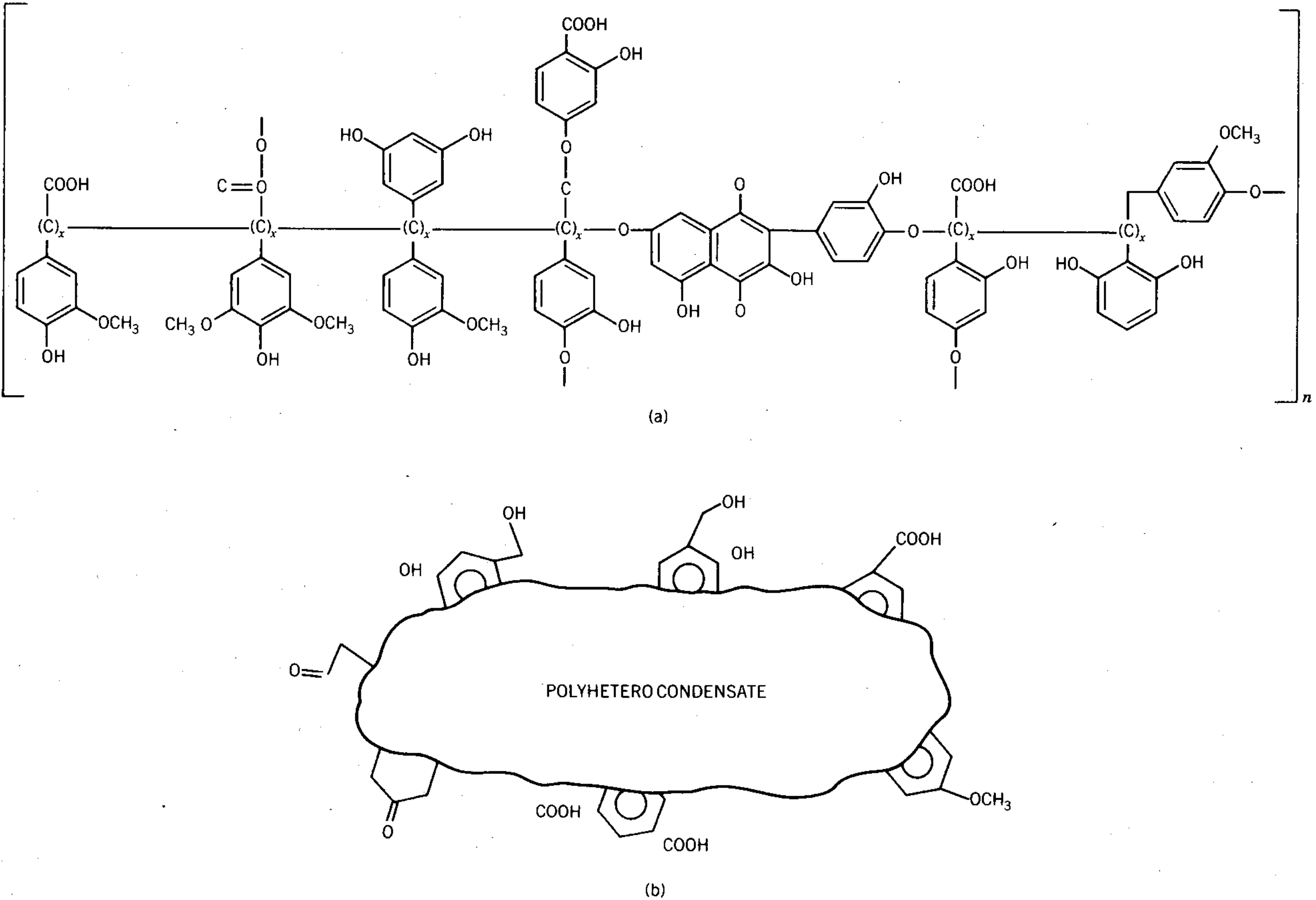


FIGURE 16-7. Proposed models for humic acid structure: (a) from Christman and Ghassemi (1966); (b) from Perdue (1978).

Humic Substances (2)

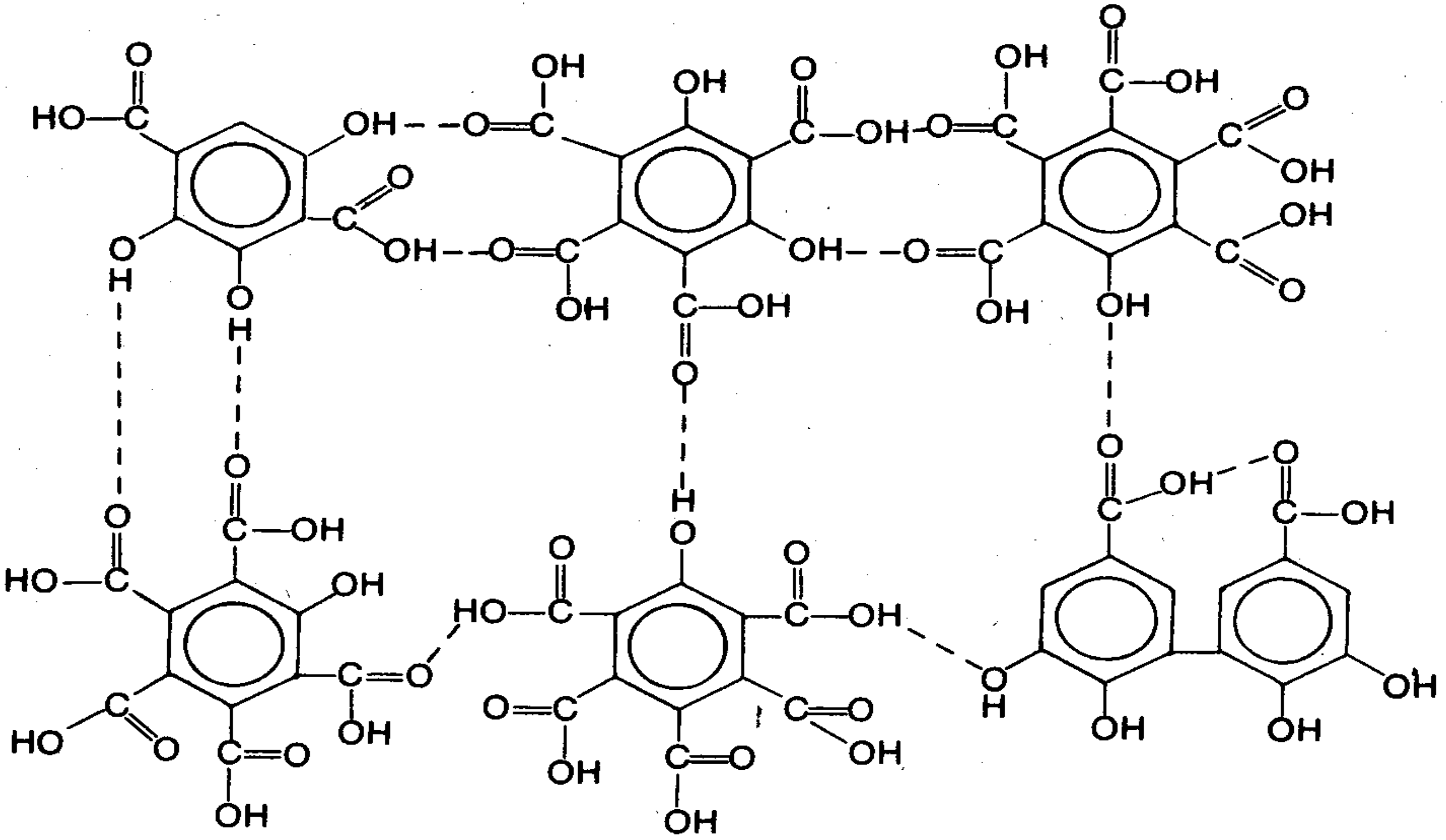
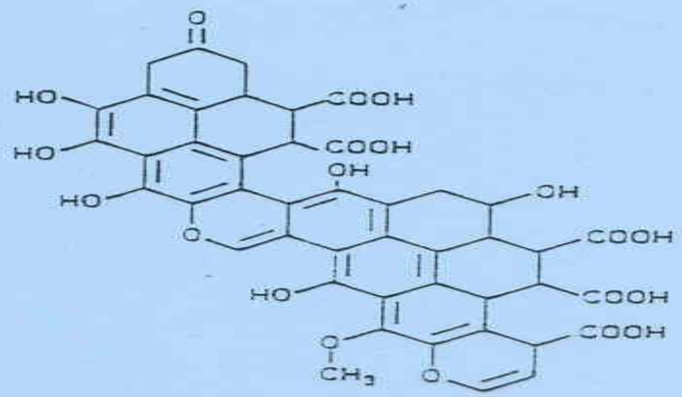
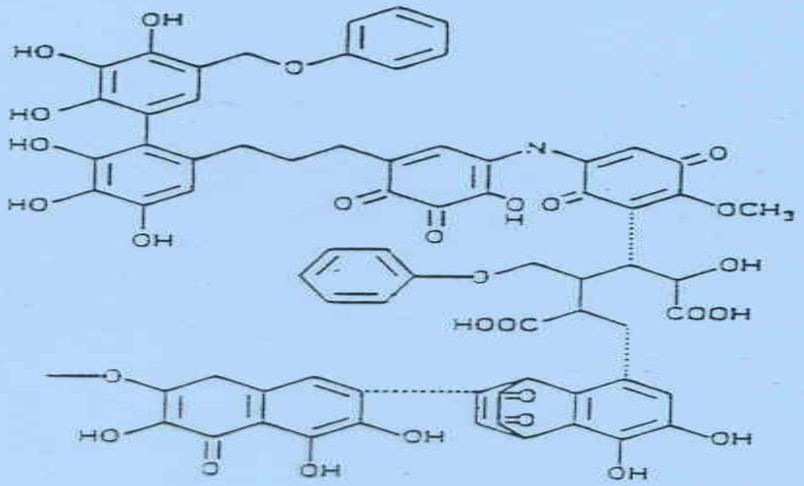


Fig. 5-9. Suggested chemical structure of fulvic acid. Reprinted from M. Schnitzer and S. U. Khan, Humic Substances in the Environment, p. 196, Marcel Dekker, New York, 1972, by courtesy of Marcel Dekker, Inc.

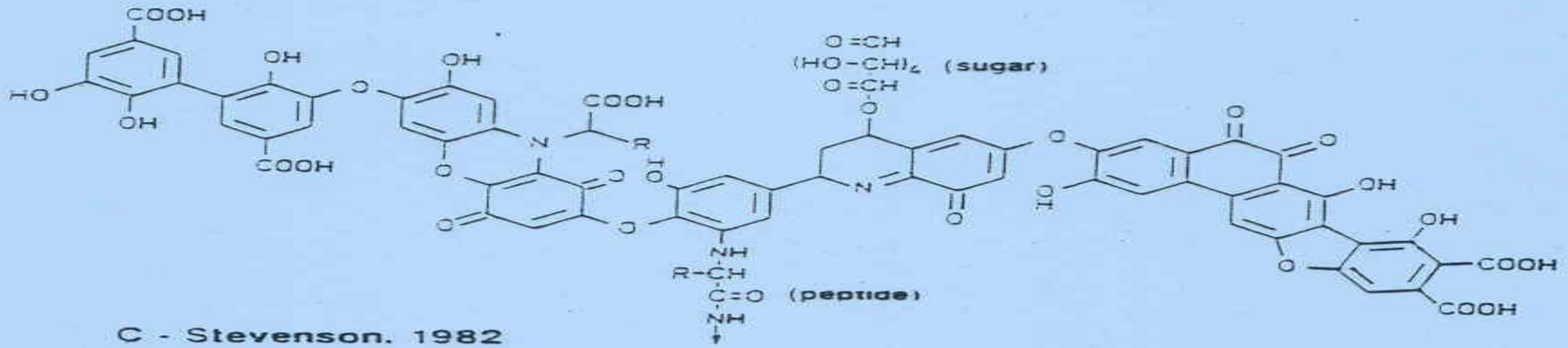
STRUCTURE OF HUMIC SUBSTANCES AS PROPOSED BY VARIOUS AUTHORS



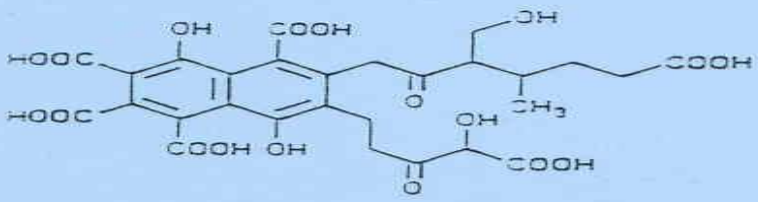
A - Fuchs. 1930



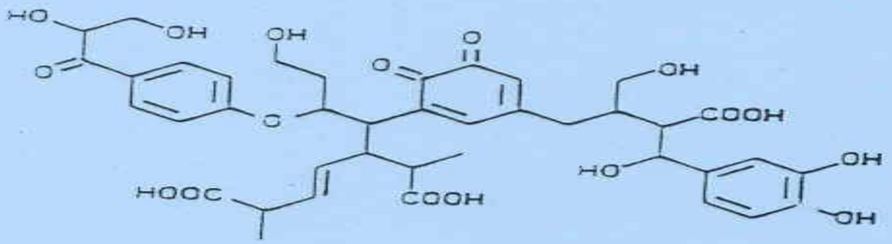
B - Flaig, 1960



C - Stevenson. 1982



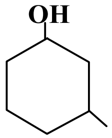
D - Buffle. 1977



E - Steelink. 1985

Particles and their Structure

~ negatively charged (-) at natural water

R-COOH and  dissociate as pH increases

fulvic acid : soluble in strong acid, MW 200 ~10,000
humic acid : insoluble in strong acid, MW 100 ~ several millions

Composition by weight for fulvic acid:
(Carbon content :40~50%)/(Hydrogen: 4~6%)/(Oxygen: 44~50%)

Stoke's law (Sedimentation)

$$V_s = \frac{g(\rho_1 - \rho)d^2}{18\mu}$$

$$V_s \propto d^2$$

V_s : settling velocity (cm/sec)
g: gravity constant (cm/sec2)
ρ: density of water (g/cm3)
ρ_1: mass density of particles (g/cm3)
d : particle diameter (cm)
~ discrete particle (independent settling)
~ small particle (& less dense) settles very slowly
u: Pa sec = 1 (N/m_2) sec = 1 kg /(sec m)

Stocks' Law

- Independent settling, terminal velocity exists

settling force (F_I) = drag force (F_D)

$$F_I = (\rho_s - \rho) g$$

$$F_D = C_D A \rho \left(\frac{v_s^2}{2} \right.$$

$$(\rho_S - \rho)\cdot g \cdot V = C_D A_C \rho \left(\frac{V_S^{2}}{2}\right)$$

$$V_S = \sqrt{\frac{2g}{C_D}\left(\frac{\rho_S - \rho}{\rho}\right)\frac{V}{A_C}} \qquad -(1)$$

직경 d 인 원형 입자의 부피 V, 단면적 A_C 는

$$V = \left(\frac{\pi}{6}\right)d^3, \quad A_C = \left(\frac{\pi}{4}\right)d^2$$

$$\therefore \frac{V}{A_C} = \left(\frac{\pi}{6}\right)d^3\left(\frac{4}{\pi}\right)\frac{1}{d^2} = \frac{2}{3}d \qquad -(2)$$

(2)를 (1)에 대입하면,

$$V_S = \sqrt{\frac{4g}{3C_D}\left(\frac{\rho_S - \rho}{\rho}\right)d}$$

$$C_D = \frac{24}{N_R} + \frac{3}{\sqrt{N_R}} + 0.34$$

If $N_R < 0.3$, $C_D = 24/N_R$
$N_R = (\text{rho})g\ V/u$

$$V_S = \frac{g(\rho_S - \rho)d^2}{18\mu}$$

Stokes' Law

C_D drag coefficient
u: viscosity

Stokes' law example

$$Vs = \frac{g(\rho_1 - \rho)d^2}{18\mu}$$

- ρ_1 = 2g/cm^3, (At 20℃ μ_{water} = 1.003×10^{-3} Pa·sec = 1 kg /(sec m), ρ_{water}=0.998 g/cm^3)

(1) d = 0.1 μm (100 nm) Vs = 5×10^{-9} m/s = 0.0018 cm/h = 0.0432 cm/day = 0.3024 cm/week

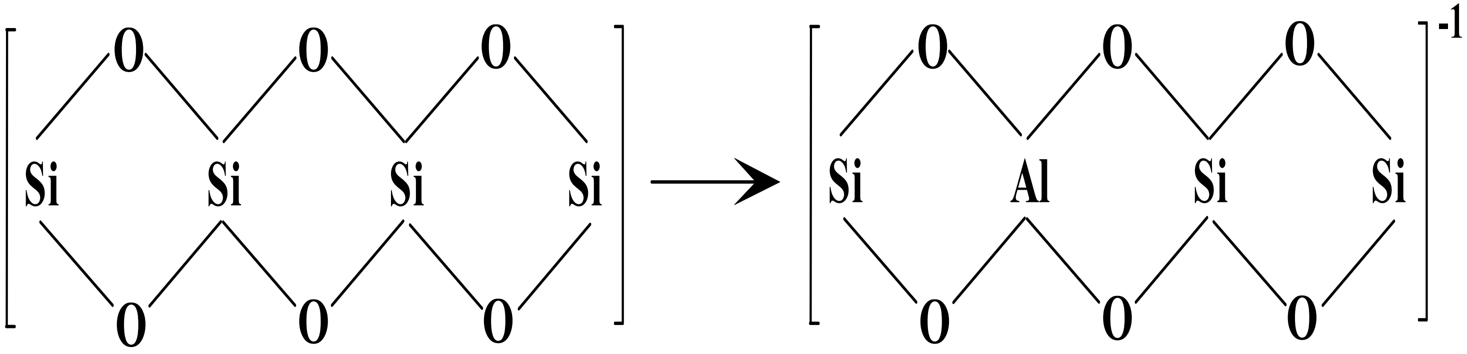
(2) d = 1 μm, Vs = 5×10^{-7} m/s = 0.18 cm/h = 4.32 cm/day = 30.24 cm/week

(3) d = 10 μm, Vs = 5×10^{-5} m/s = 18 cm/h = 4.32 m/day = 30.24 m/week

Origin of Charge Property ?

1. Crystal Imperfection (Clays : 1~ 2 μm)

The silica tetrahedra have an average composition of SiO_2.
If an Al atom is substituted for an Si atom, ➔ negatively charged



Origin of Charge Property ?

2. Ionization of surface functional group

~ surface groups on the solid may accept or donate protons

(humic subatances)

-COOH, Ar-OH

- charge is pH dependent
- Net surface charge is zero at the isoelectric point (IEP)

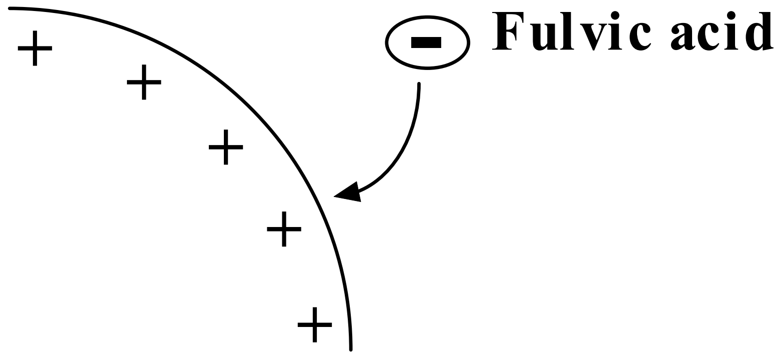
in case of humic acid pHzpc ~ 3.0 (zero point of charge)

(cf: pHI_{IEP} is more comprehensive)

Origin of Charge Property ?

3. Preferential Adsorption

~ if the adsorption of NOM (negatively charged) onto particles occurs,



pHzpc & pHiep

pHzpc : pH where σ_o = zero i.e, ($\Gamma H = \Gamma OH$)
zpc : zero point of charge

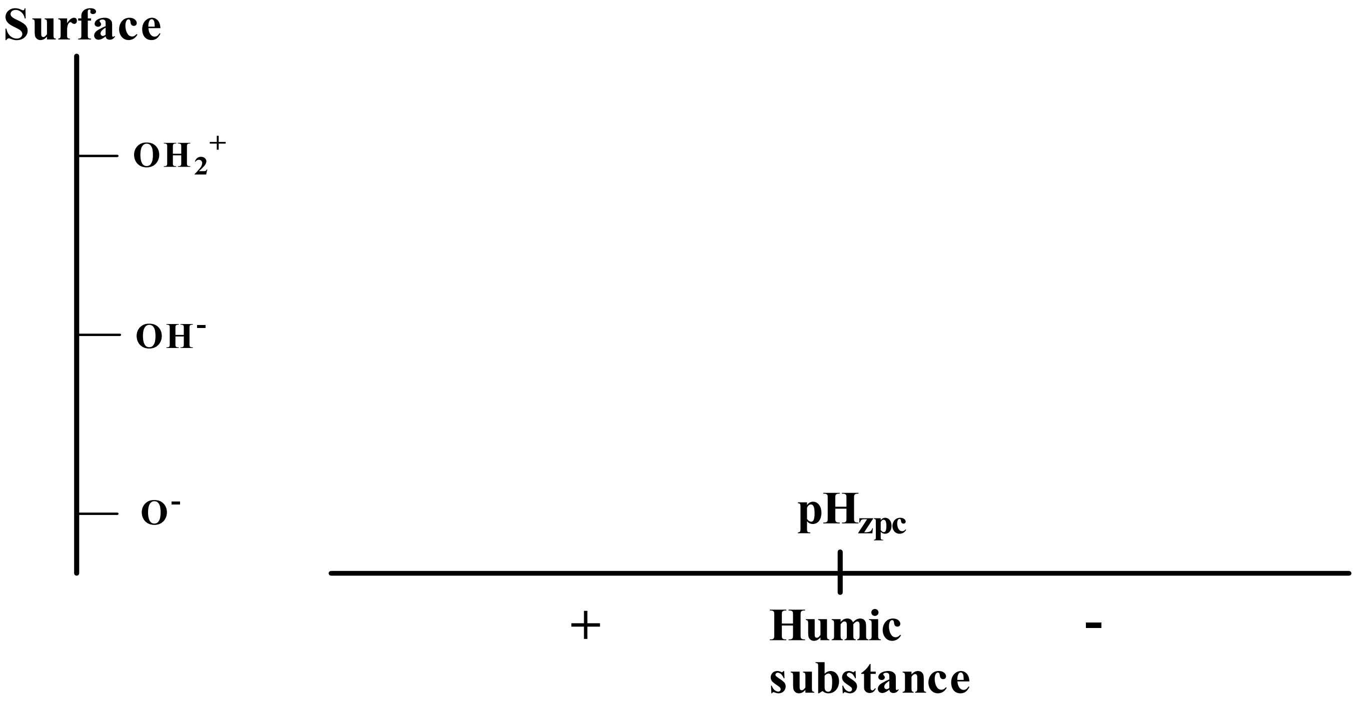
pHiep : in the presence of specifically adsorbable ion other than H^+ and OH^-

IEP : isoelectric point

Net surface charge

$$\sigma_o = F(\Gamma H - \Gamma OH)$$

σ_o = surface charge density (coulombs/cm^2)
ΓH, ΓOH ; quantities of bound H^+, or OH^- (mole/cm$_2$)
F = Faraday constant (coulombs/mole)
1 F = 96500 C (1 C = 6.25×10^{18} e)



Surface

OH_2^+

OH^-

O^-

pH_{zpc}

+

Humic substance

-

Change of surface charge property of humic substances

Principle Mechanisms of Stability

Electrical Double Layer - uneven distribution of charge (Net charge in solution is zero

➔ principle of electroneutrality

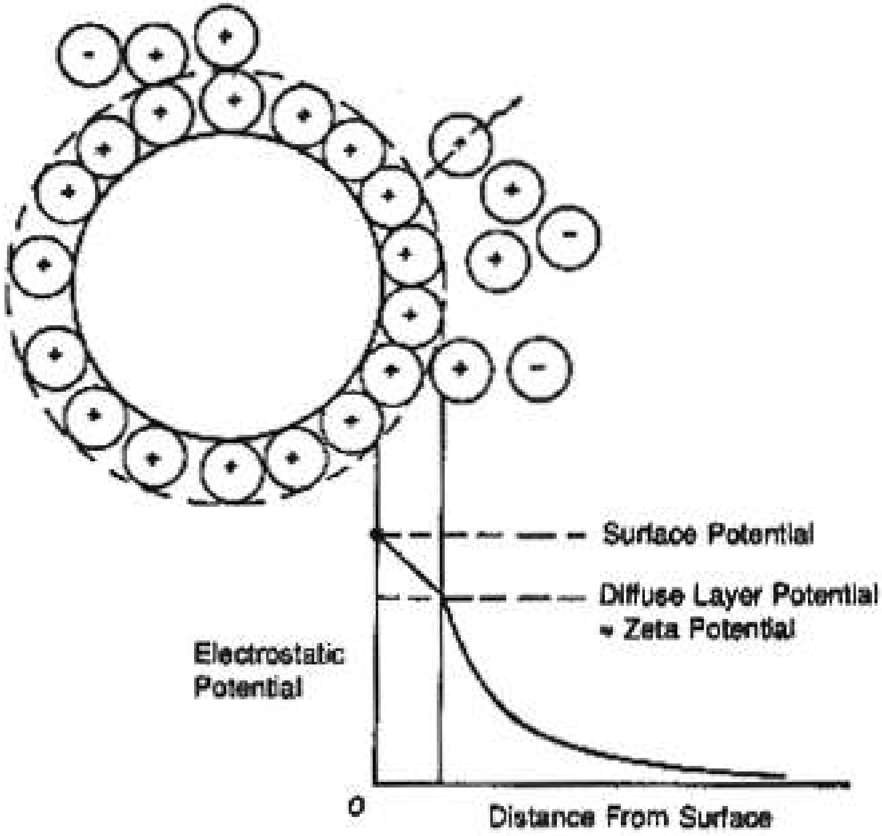
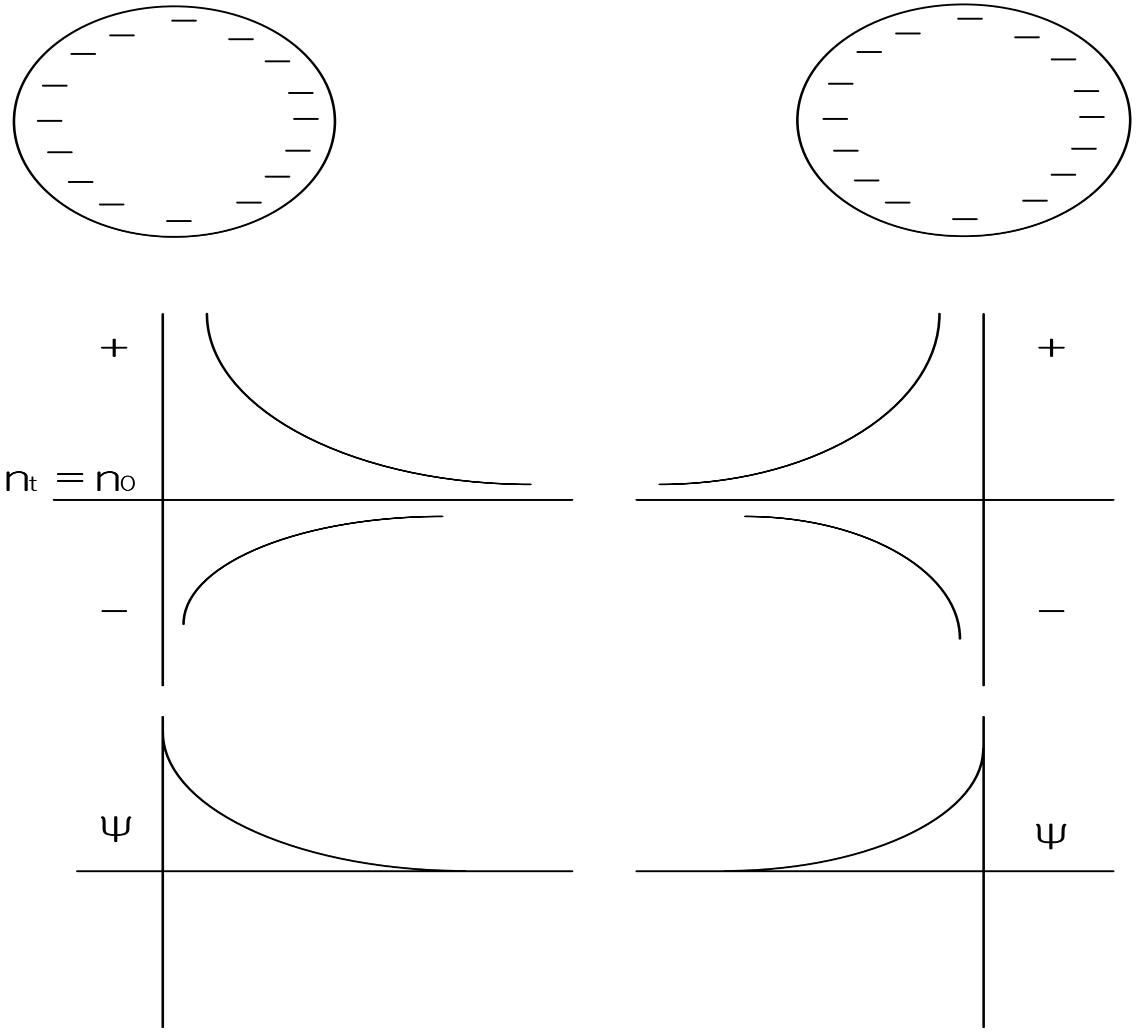


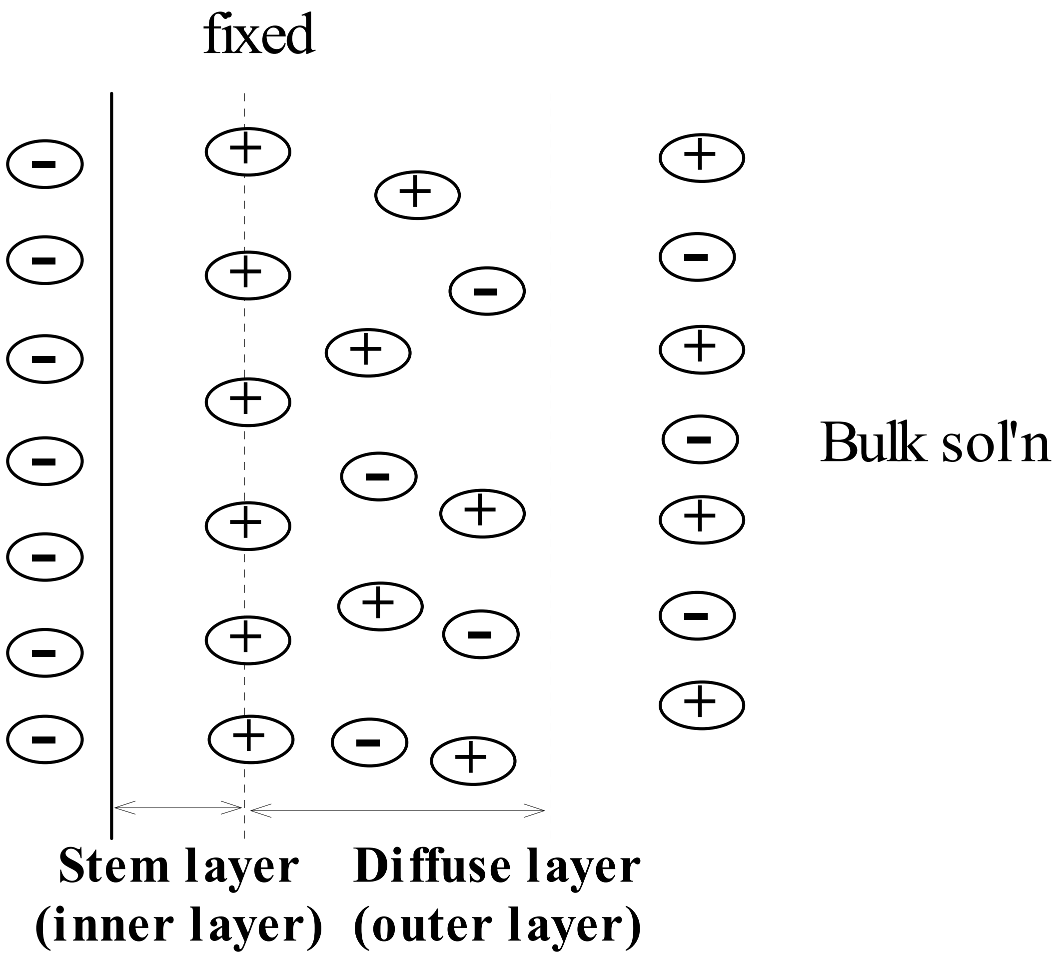
Figure 4-1. Schematic diagram showing the distribution of charge and potential **near a negatively charged particles**

The potential ; The force required to move a unit charge through the field

Interactions between Particles



Electric double layer



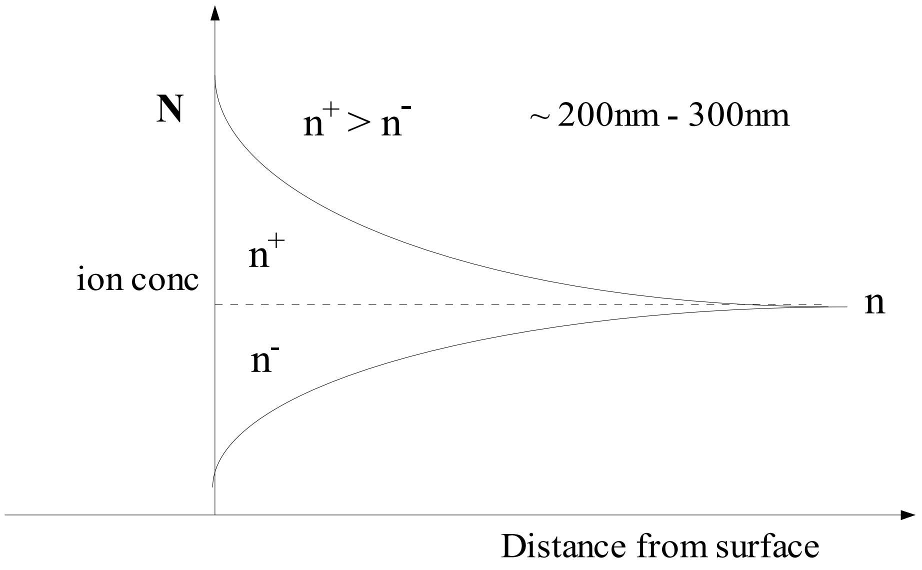
fixed

Bulk sol'n

Stem layer (inner layer)

Diffuse layer (outer layer)

Electric double layer



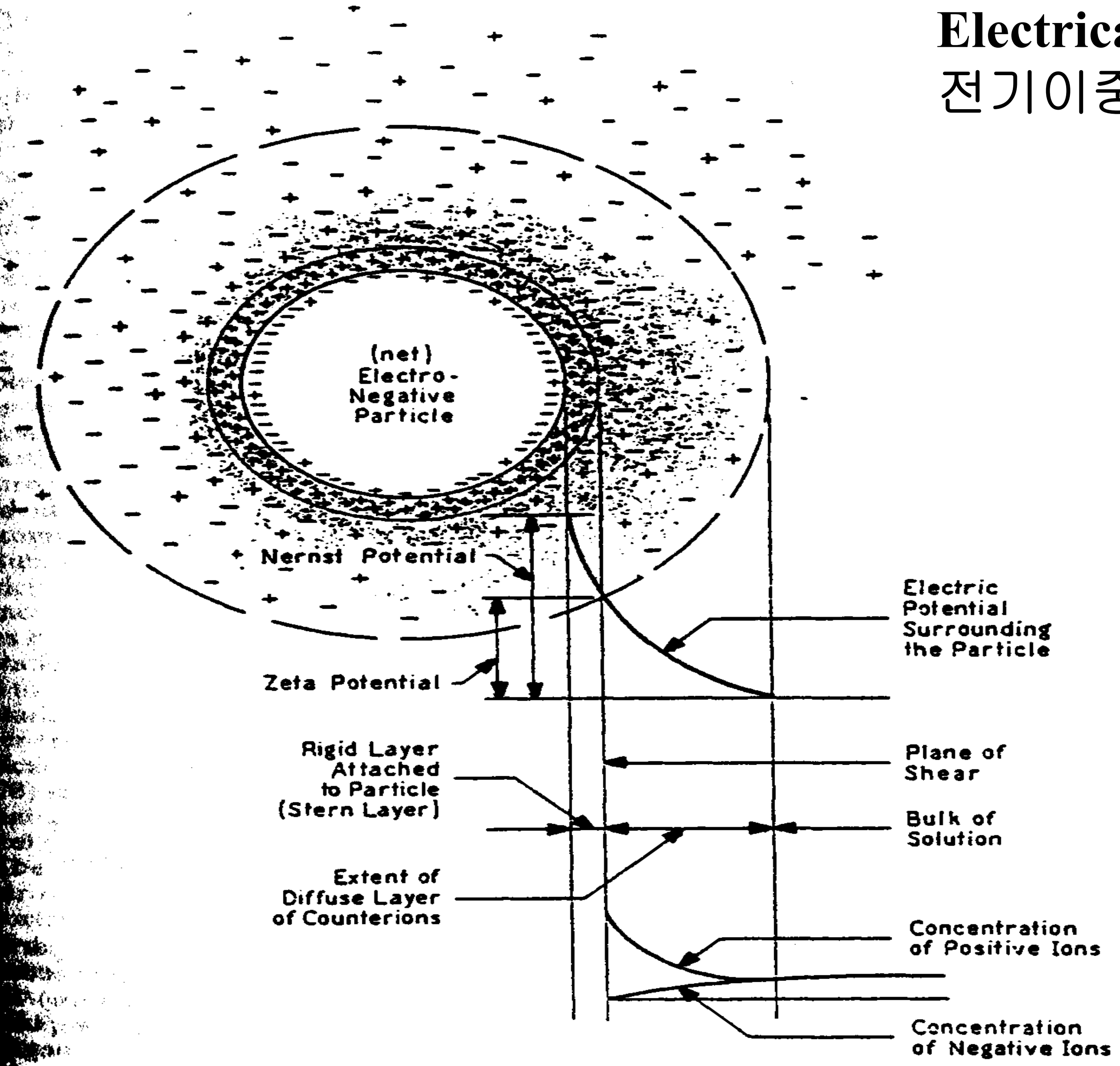
pH 9 Electrical double layer at solid-liquid interface
(Gouy-Chapman Model)

Interfacial electroneutrality

$$\sigma o + \sigma s + \sigma d = 0$$

σo = fixed surface charge (-)
σs = stern layer charge (+)
σd = diffusive layer charge (+)

Electrical double layer
전기이중층



RE 6.3 Negatively charged particle, the diffuse double layer, and the location of the zeta
ial.

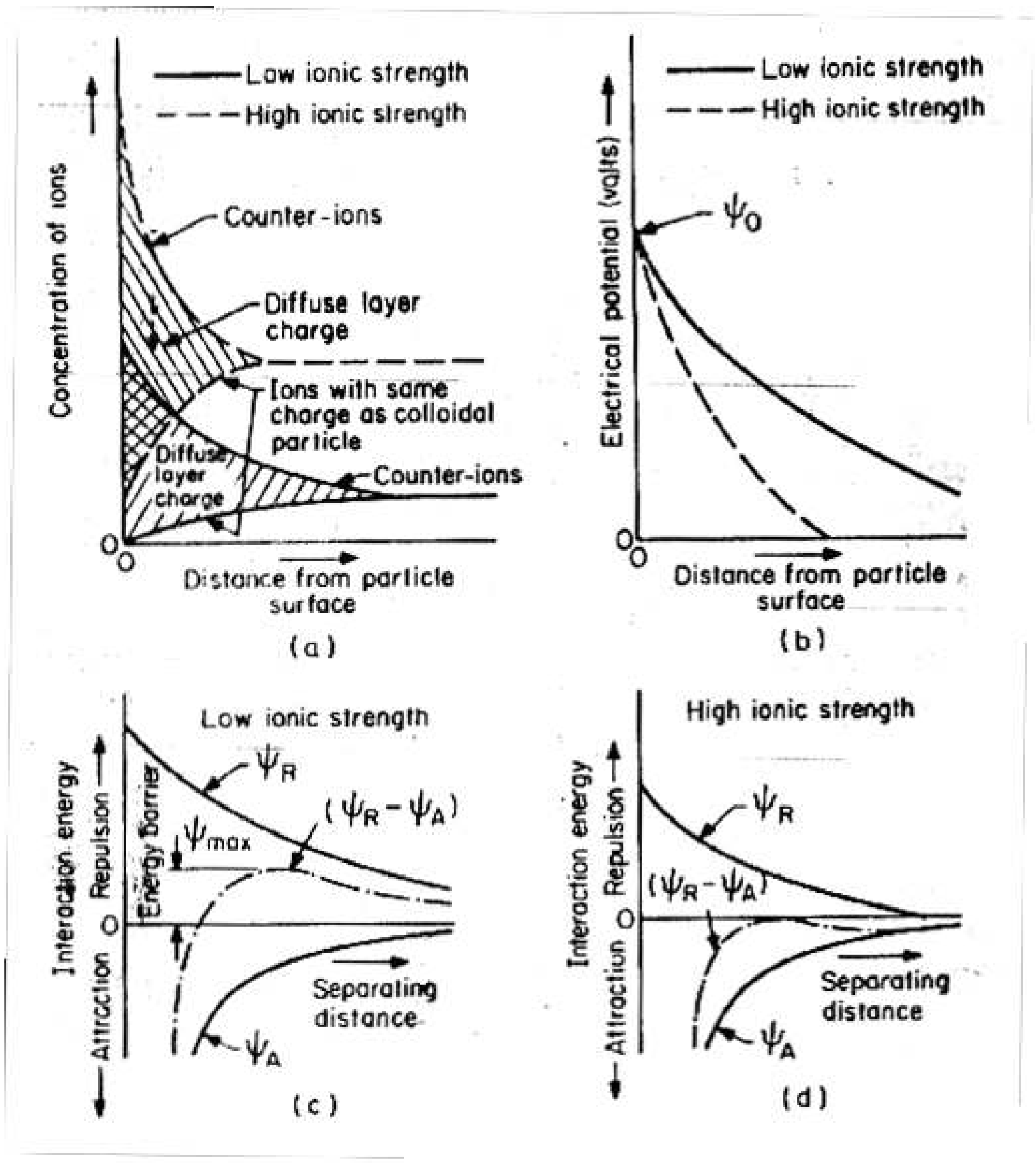
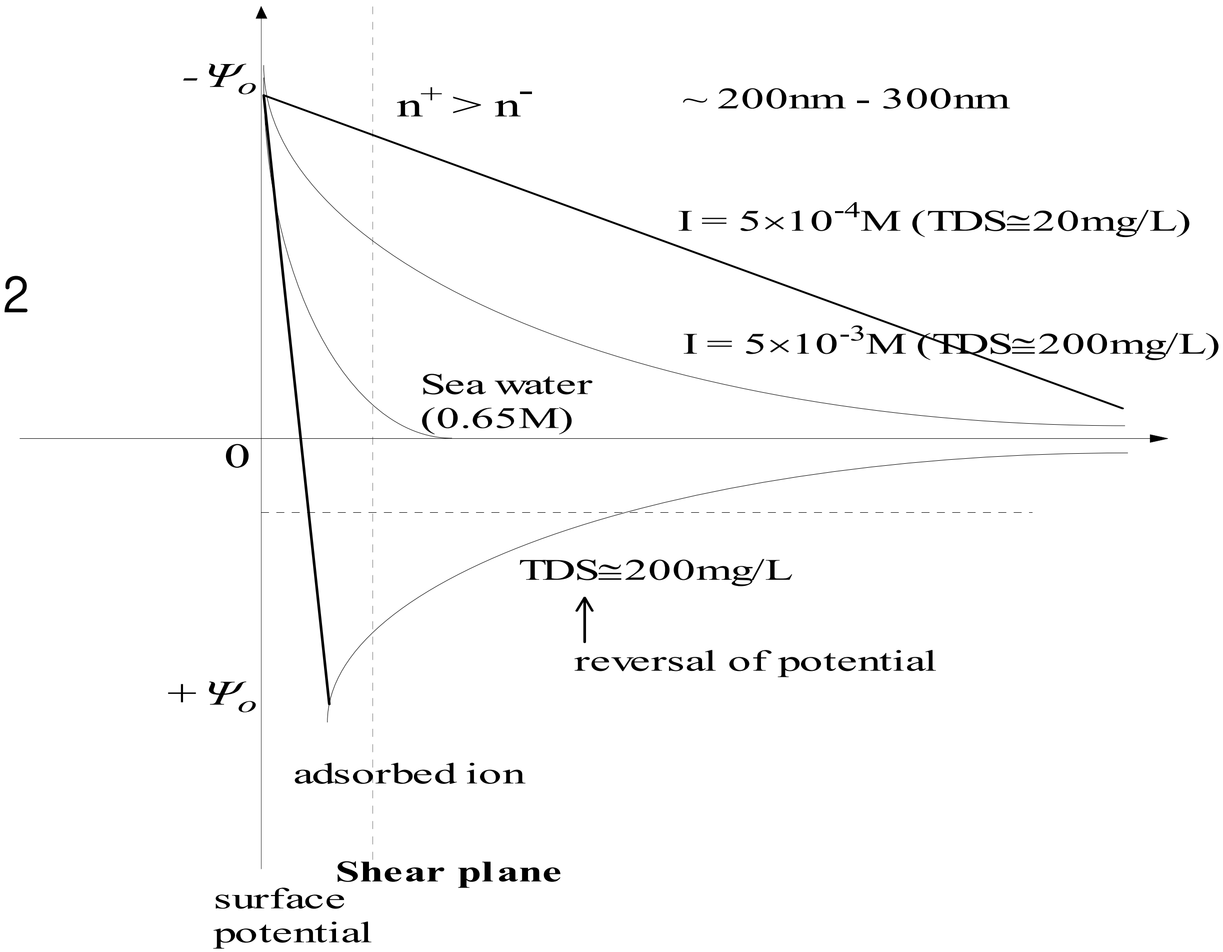


Figure 6.3 Schematic representations of (a) the diffuse double layer; (b) the diffuse layer potential; and (c and d) two cases of particle-particle interaction energies in electrostatically stabilized colloidal systems The result termed as the Guoy-Chapman Model is well presented by Verwey Overbeek

Charge Gradient – Electrical Field

Fig 6-2



Measurement of Zeta Potential

Zeta potential (ζ)): the potential at shear plane (mV)

Electrophoresis (전기영동) : the movement of charged particles relative to a stationary fluid due to applied potential

Electrophoretic mobility (EPM)
$\mathrm{EPM} = \zeta\varepsilon\varepsilon_o/\eta$
ε: relative dielectric permittivity
ε_0 : permittivity in a vaccum
η : fluid viscosity
$\mathrm{EPM} \propto \zeta$

Effective coagulation : at EPM = 0

➔ The classical approach
How do we measure zeta potential in our laboratory?

pH_{zpc}
Zero Point Charge

$Al_4(Si_4O_{10})(OH)_8$,고령석

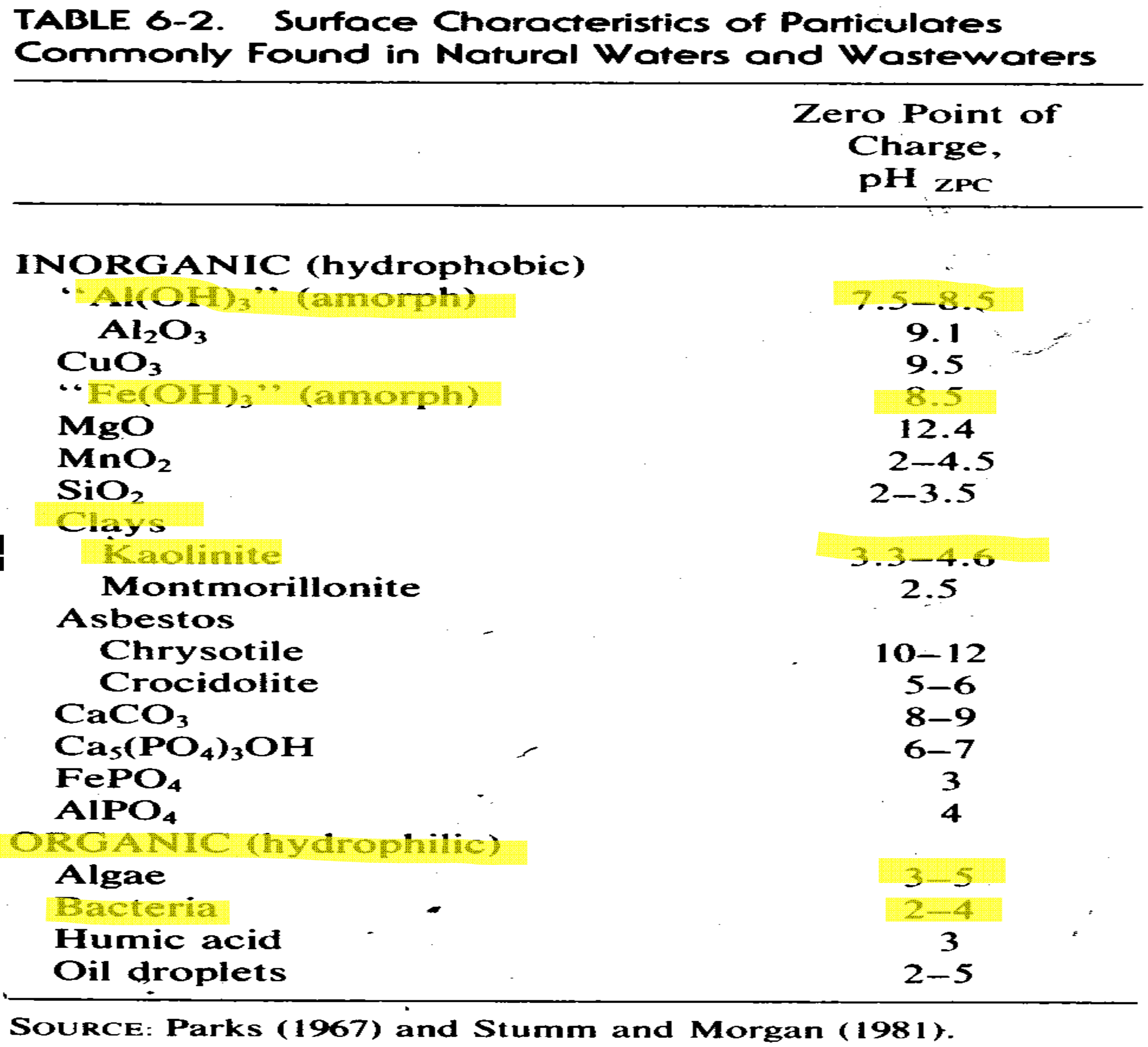


TABLE 6-2. Surface Characteristics of Particulates Commonly Found in Natural Waters and Wastewaters

	Zero Point of Charge, pH_{ZPC}
INORGANIC (hydrophobic)	
"$Al(OH)_3$" (amorph)	7.5–8.5
Al_2O_3	9.1
CuO_3	9.5
"$Fe(OH)_3$" (amorph)	8.5
MgO	12.4
MnO_2	2–4.5
SiO_2	2–3.5
Clays	
Kaolinite	3.3–4.6
Montmorillonite	2.5
Asbestos	
Chrysotile	10–12
Crocidolite	5–6
$CaCO_3$	8–9
$Ca_5(PO_4)_3OH$	6–7
$FePO_4$	3
$AlPO_4$	4
ORGANIC (hydrophilic)	
Algae	3–5
Bacteria	2–4
Humic acid	3
Oil droplets	2–5

SOURCE: Parks (1967) and Stumm and Morgan (1981).

How to measure particle concentration ?

(1) by turbidity

~ A measure of light scattering characteristics of a particle at 90◦

-~" Hach Device" → measure nepheolometric turbidity unit (NTU)
Maximum Concentration Level for turbidity " 0.5 NTU"

~ Turbidity does not correlate to the number of particles

~ Low turbidity does not guarantee the absence of particles

(2) by particle counter

~ count the number of particles

~ size distribution of particles

-

Classification		Water Quality Inspection Item	Tap Water	Spring Water	Deep Ocean Drinking Water	Drinking water from Community facility(mountain pond, etc.)	Remarks
Hazardous Inorganic Substances	Pesticide	Diazinon	0.02㎎/L	0.02㎎/L	0.02㎎/L	0.02㎎/L	
		Parathion	0.06㎎/L	0.06㎎/L	0.06㎎/L	0.06㎎/L	
		Fenitrothion	0.04㎎/L	0.04㎎/L	0.04㎎/L	0.04㎎/L	
		Carbaryl	0.07㎎/L	0.07㎎/L	0.07㎎/L	0.07㎎/L	
		1,2-Dibromo-3-Chloropropan	0.003㎎/L	0.003㎎/L	0.003㎎/L	0.003㎎/L	
	Disinfection Residues	Free Residual Chlorine	4.0㎎/L	-	-	-	
		THMs; Trihalomethanes	0.1㎎/L	-	-	-	
		Bromodichloromethane	0.03㎎/L	-	-	-	Applied starting from 2009
		Dibromochloromethane	0.1㎎/L	-	-	-	Applied starting from 2009
		Chloroform	0.08㎎/L	-	-	-	
		Chloralhydrate	0.03㎎/L	-	-	-	
		Dibromoacetonitrile	0.1㎎/L	-	-	-	
		Dichloroacetonitrile	0.09㎎/L	-	-	-	
		Trichloroacetonitrile	0.004㎎/L	-	-	-	
		HAA; Haloacetic acid	0.1㎎/L	-	-	-	
Materials that are Offensive to Human Sensory System		Hardness	300㎎/L	500㎎/L	500㎎/L	1,200㎎/L	
		Consumption of $KMnO_4$	10㎎/L	10㎎/L	10㎎/L	10㎎/L	
		Odor (except disinfection)	ND	ND	ND	ND	
		Taste (except disinfection)	ND	ND	ND	ND	
		Cu; Copper	1㎎/L	1㎎/L	1㎎/L	1㎎/L	
		Color	5 PCU	5 PCU	5 PCU	5 PCU	
		ABS; Alkyl Benzene Sulfate	0.5㎎/L	ND	ND	0.5㎎/L	
		pH	5.8～8.5	5.8～8.5	5.8～8.5	5.8～8.5	
		Zn; Zinc	3㎎/L	3㎎/L	3㎎/L	3㎎/L	
		Cl^-; Chloride	250㎎/L	250㎎/L	250㎎/L	250㎎/L	
		Total Solids	500㎎/L	500㎎/L	500㎎/L	500㎎/L	
		Fe; Iron	0.3㎎/L	0.3㎎/L	0.3㎎/L	0.3㎎/L	
		Mn; Manganese	0.3 ㎎/L	0.3㎎/L	0.3㎎/L	0.3㎎/L	2011: 0.05㎎/L (only for tap water)
		Turbidity	0.5 NTU	1 NTU	1 NTU	1 NTU	
		SO_4^{2-}; Sulfate	200㎎/L	200㎎/L	200㎎/L	200㎎/L	
		Al; Aluminum	0.2㎎/L	0.2㎎/L	0.2㎎/L	0.2㎎/L	
Water Purification Standard		Viruses	99.99% removed	-	-	-	
		Giardia lambia	99.9% removed	-	-	-	

Mechanism of Destabilization (Four Coagulation theory)

(1) Electrical Double Layer Compression

(2) Adsorption-Charge Neutralization

(3) Sweep Precipitation (or sweel floc)

(4) Interparticle Bridging

4가지 응집이론

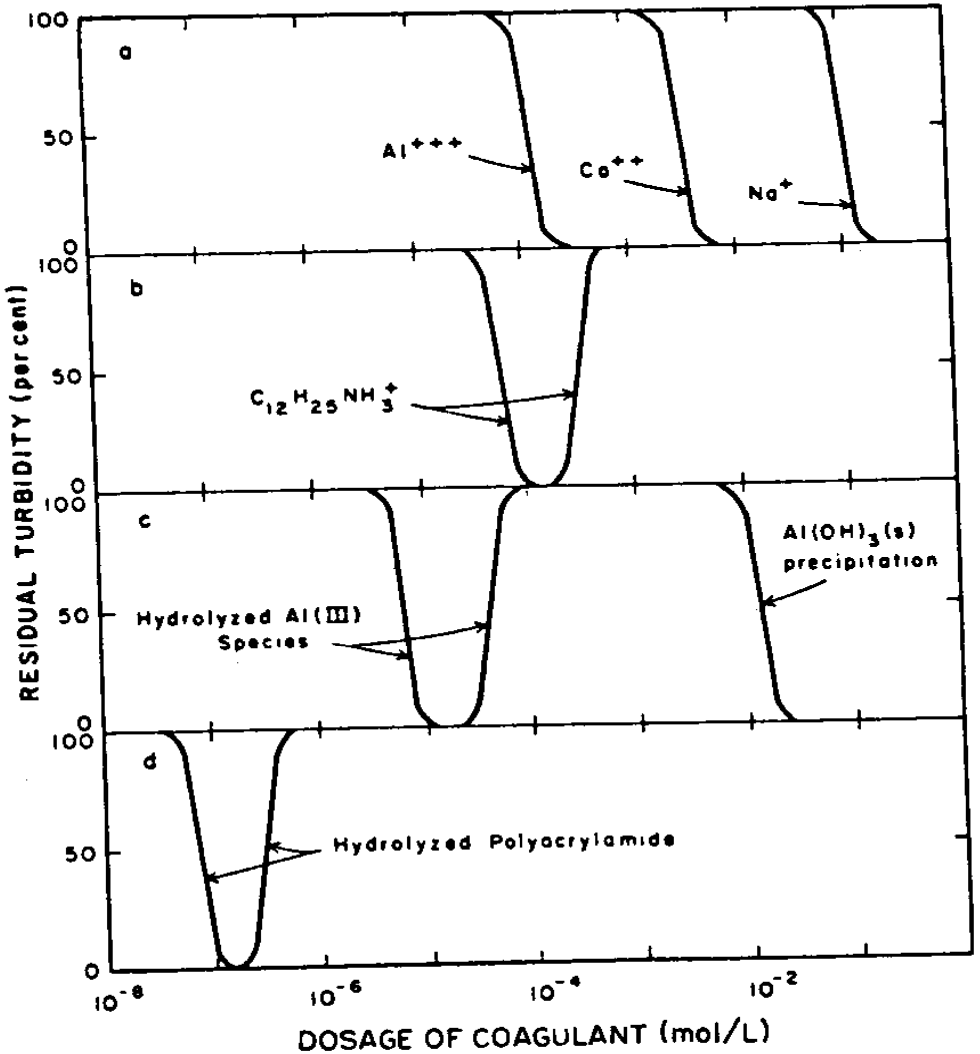


Figure 6.6 Schematic coagulation curves (jar test results) for four types of coagulants.

(1) Double Layer Compression

~ the interactions of some coagulent species with a colloidal particle are purely electrostatic - " indifferent" electrolyte

~ the destabilization of a colloid is brought by ions of opposite charges to that of a colloid, and the effectiveness of these ions increases markedly with charge.

➔ Schultz-Hardy rule

~ Verway and Overbeek (1948)

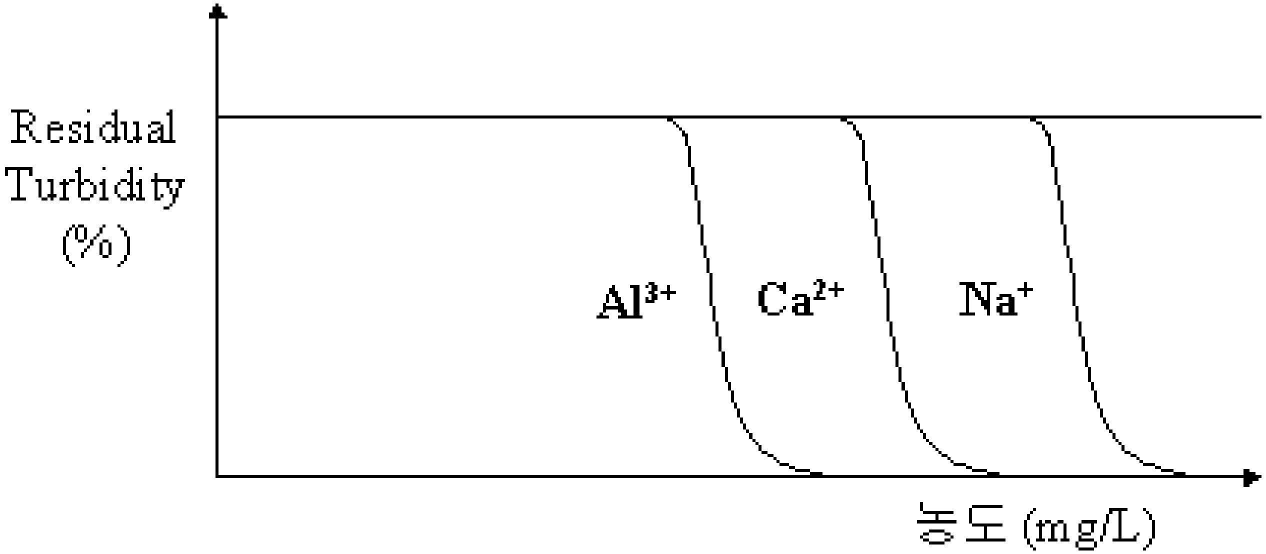
~ Increasing the ionic strength compresses the double layer

$\zeta < \pm 20$ mV → rapid coagulation

~ VODL theory (Verwey-Overbeek, Derjaguin-Landau) or DOVL theory (Schultz-Hardy Rule) was proposed

~ not important water/waste water treatment (overdosing not possible)

(1) Double Layer Compression



Effectiveness $Al^{3+} > Ca^{2+} > Na^{+}$

(1) Double Layer Compression

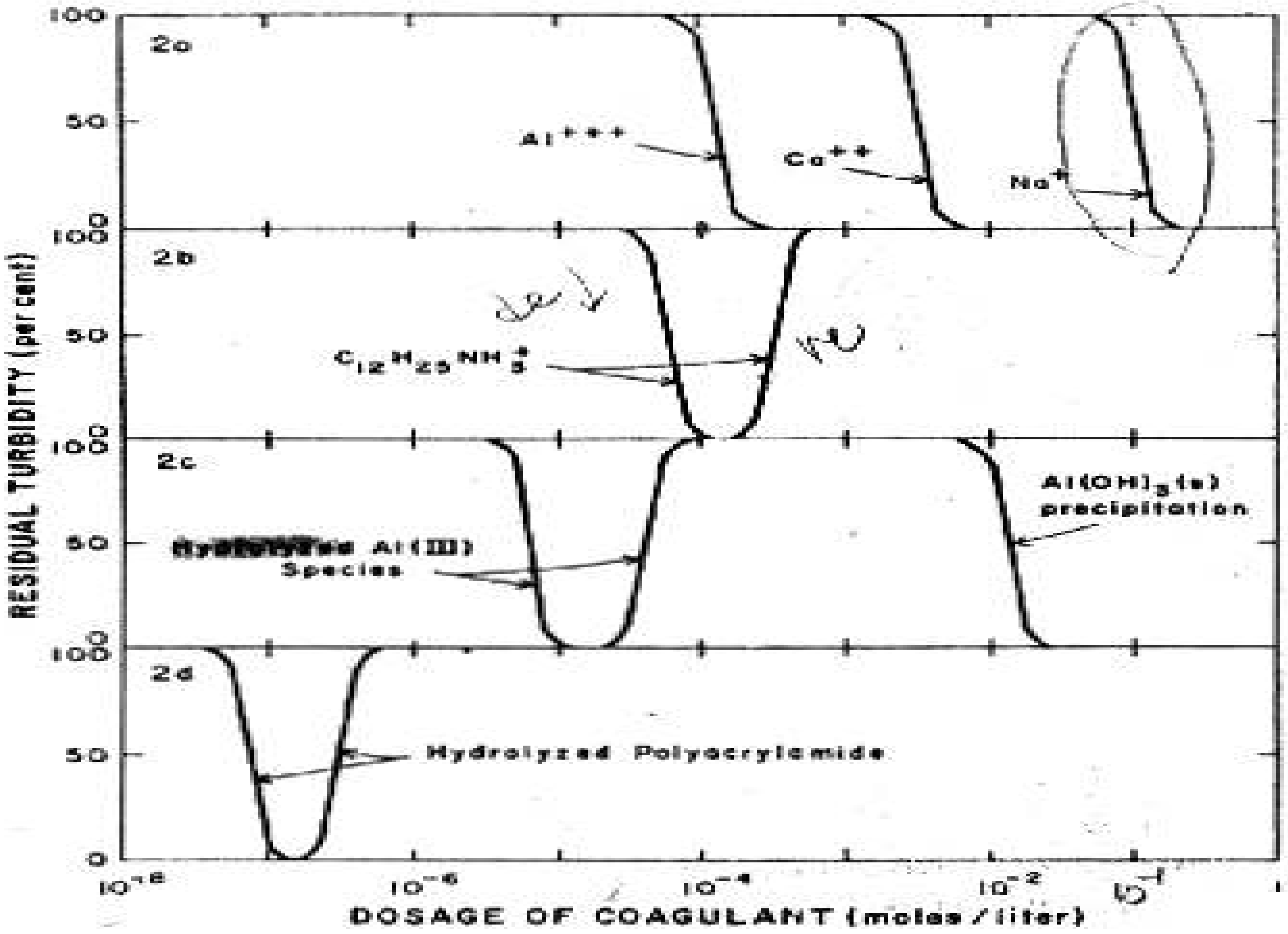


Figure 2-2 Schematic coagulation curves for several different coagulants.

(2) Adsorption—Charge neutralization

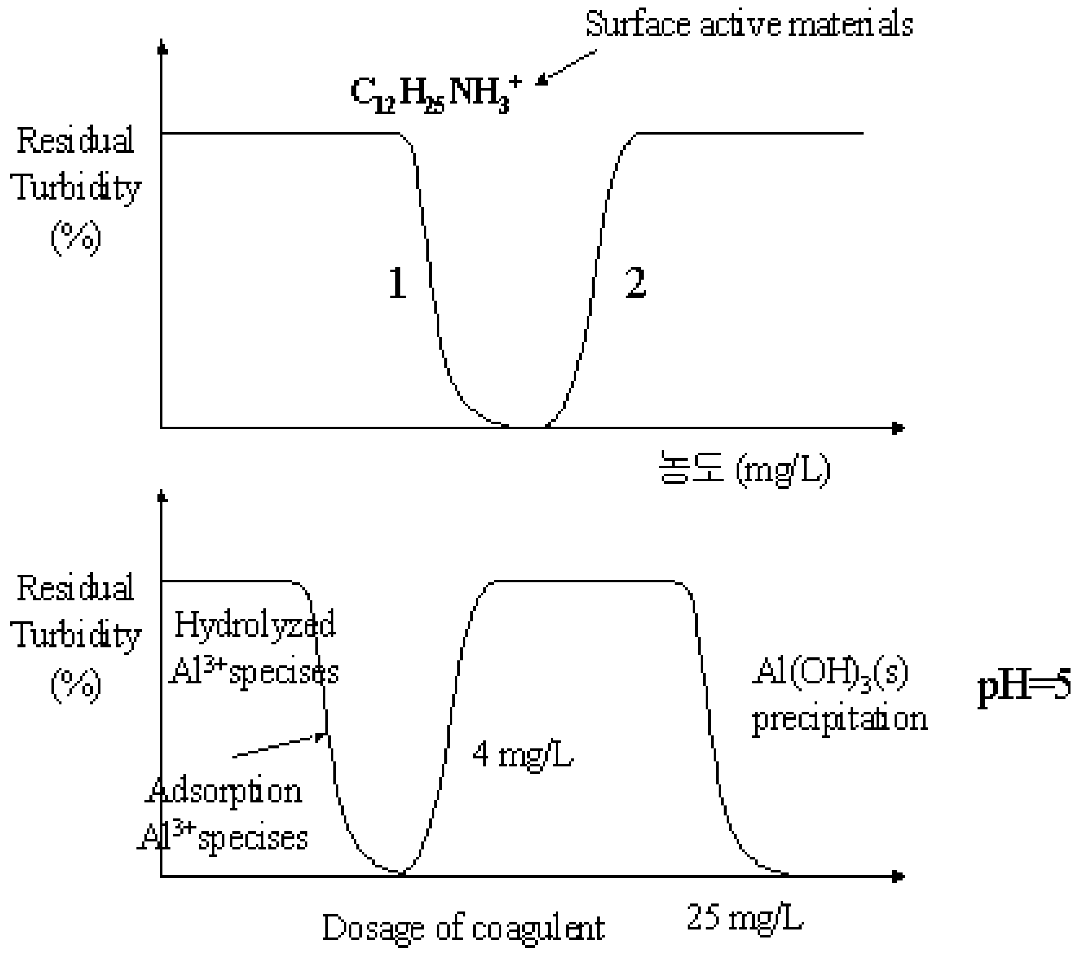
$C_{12}H_{25}NH_3^+$

~ Many possible colloid-coagulent interactions can overshadow **the coulombic effect** in the destabilization of colloids

① At the lower concentration in comparison with Na+, stabilization occurs

② Restabilization with charge reversal; the net charge on the colloidal particle is reversed from negative to positive by the adsorption of an excess of counter-ions

(2) Adsorption—Charge neutralization



by emeshment of colloidal particles in a precipitate of aluminum hydroxide

(2) Adsorption—Charge neutralization

~ clay silica, most organic particulates ➔
at pH 7.0, negatively charged

~ zero point of charge (ZPC)

~ The ability of a coagulent to destabilize a colloidal dispersion is actually a composite of coagulent -colloid, coagulent-solvent, and colloid-solvent interactions

Restabilization of Particles

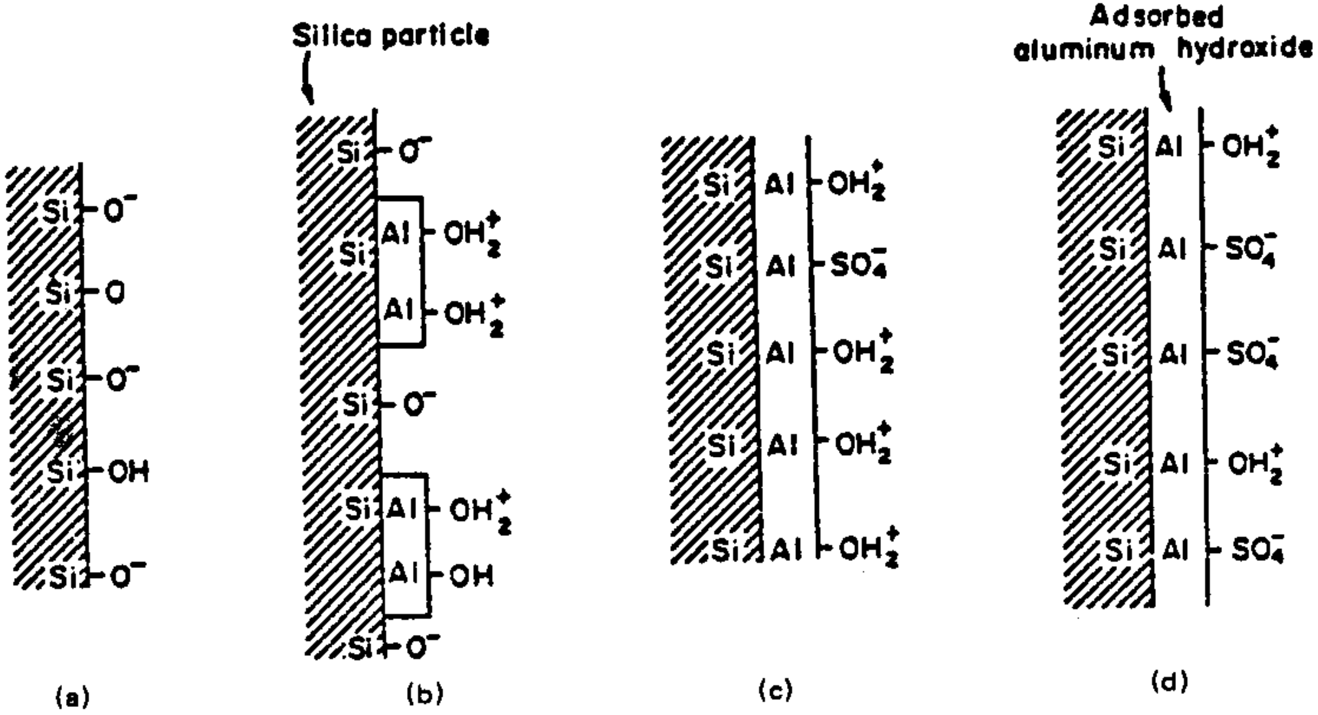


Figure 6.13 Schematic diagram of alum-treated particles. (*a*) Negatively charged particle; (*b*) particle destabilized by charge neutralization; (*c*) particle restabilized by excess alum hydrolyses species; (*d*) destabilization by adsorption of sulfite ions. (*After Letterman and Vanderbrook.*[38])

(3) Enmeshment in a precipitate, Sweep Floc

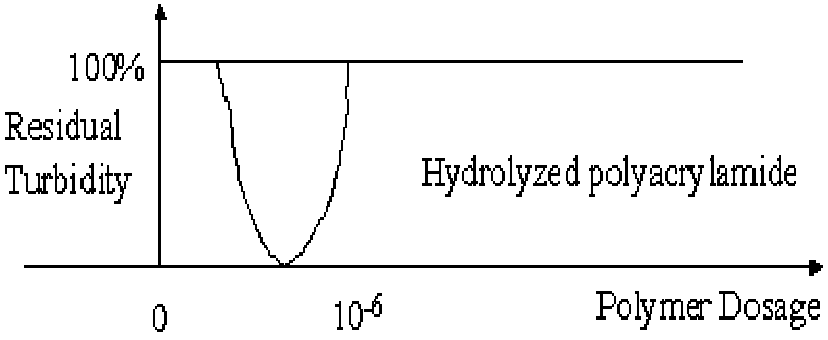
~ When high concentration of a metal salt such as $Al_2(SO_4)_3$ or $FeCl_3$ is used as a coagulent to cause rapid precipitation of a metal hydroxide(ex, Al(OH)3(s), Fe(OH)3(s), colloidal particles can be enmeshed in these precipitate as they are formed.

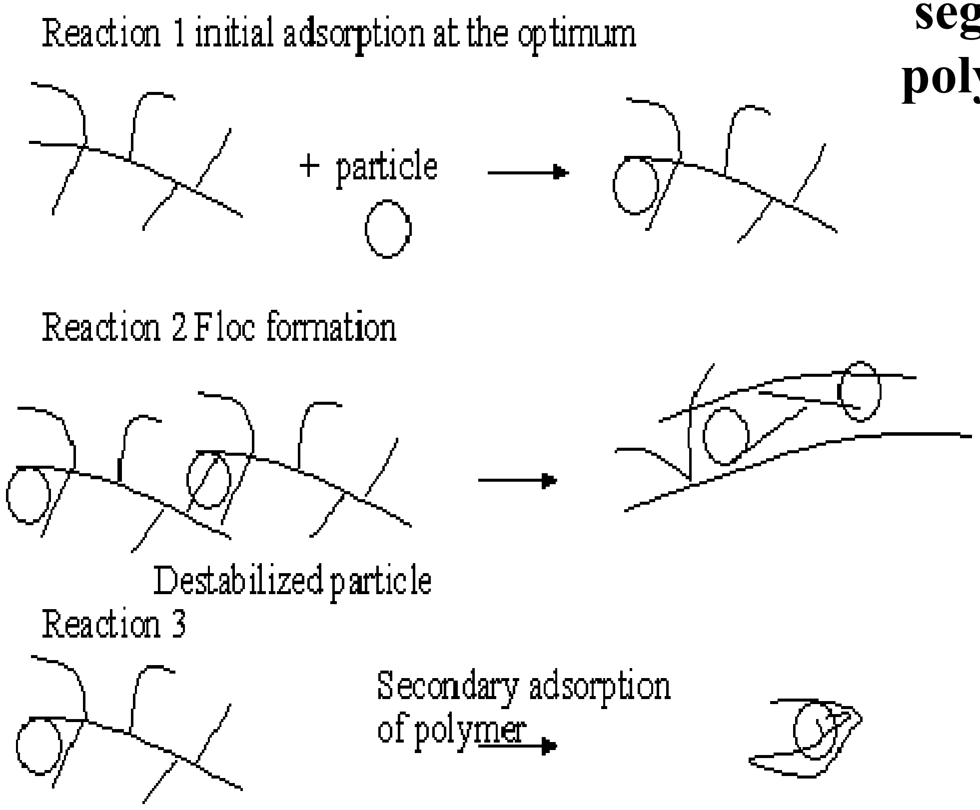
~ The colloidal particle can serve as nuclei for the formation of the precipitate, so that the rate of precipitation increases with increasing concentration of colloidal particles to be removed.

~ overdose is not possible

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+$$

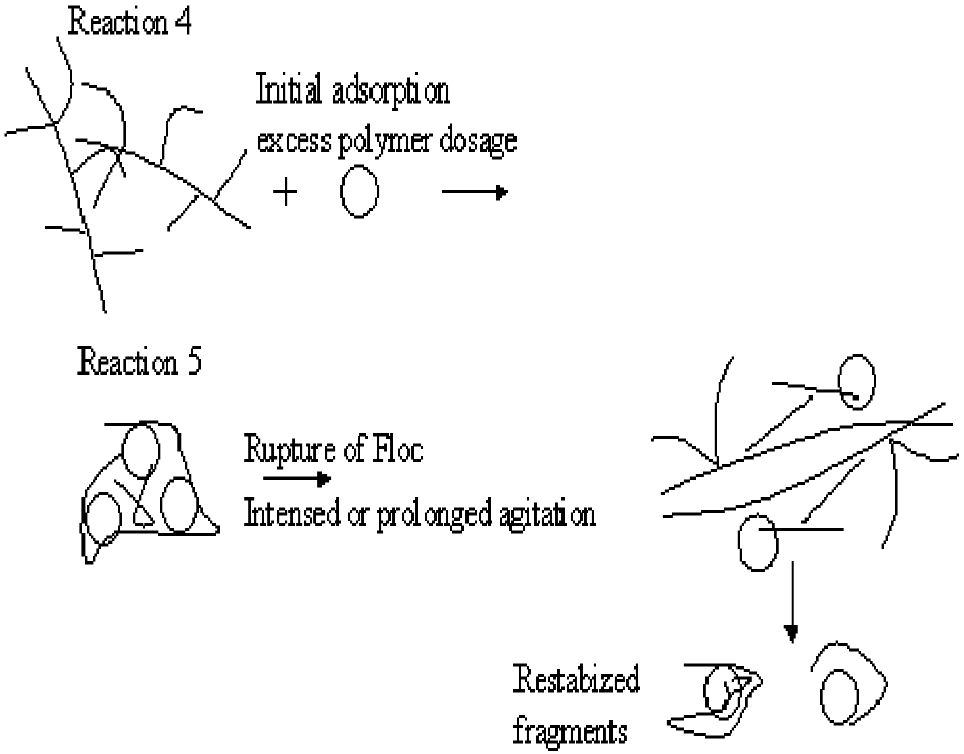
4. Polymer Bridging





Destabilization by bridging occurs when segment of a high molecular weight polymer adsorb on more than one particle

4. Polymer Bridging



Reaction 4

Initial adsorption

excess polymer dosage

Reaction 5

Rupture of Floc

Intensed or prolonged agitation

Restabized fragments

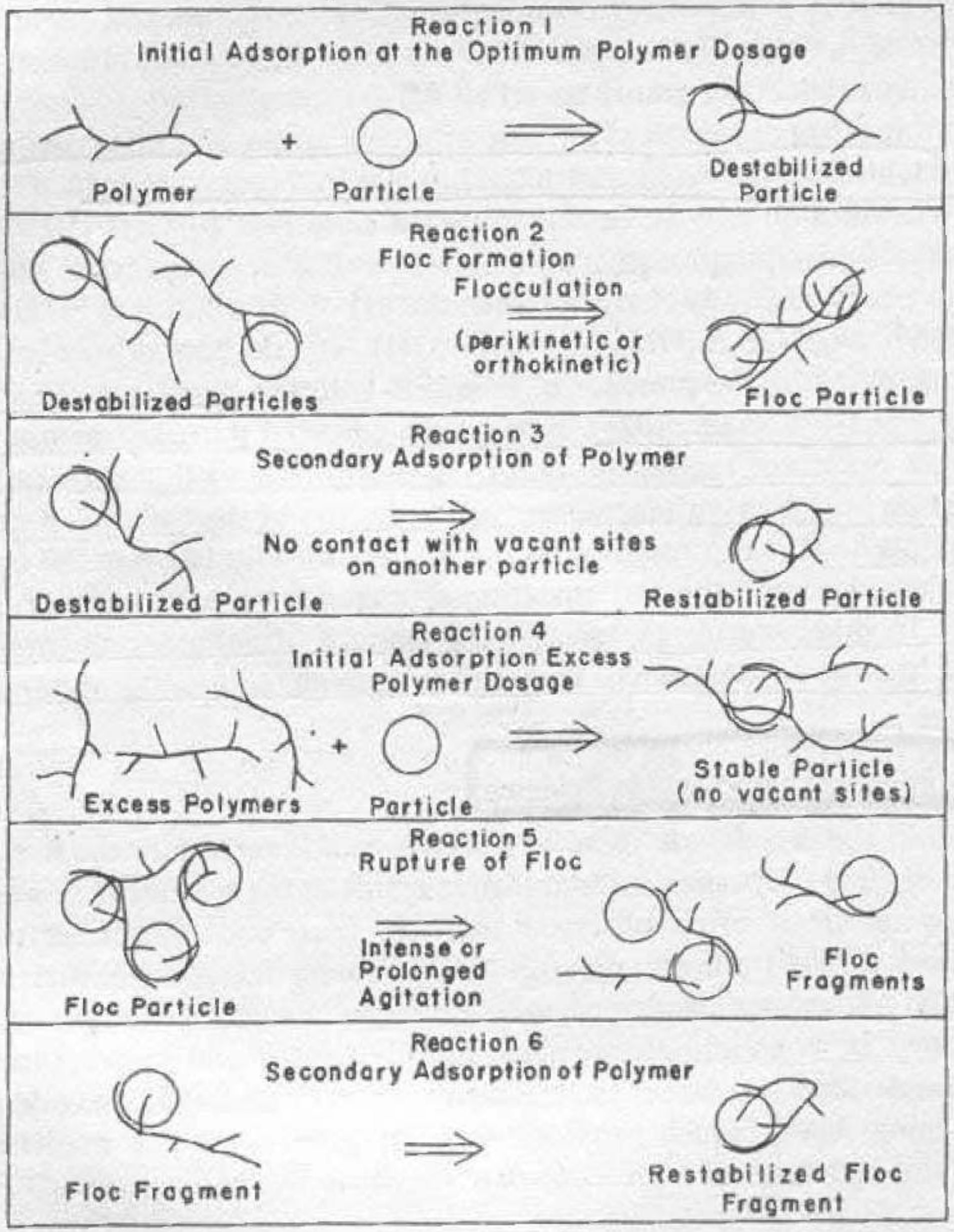
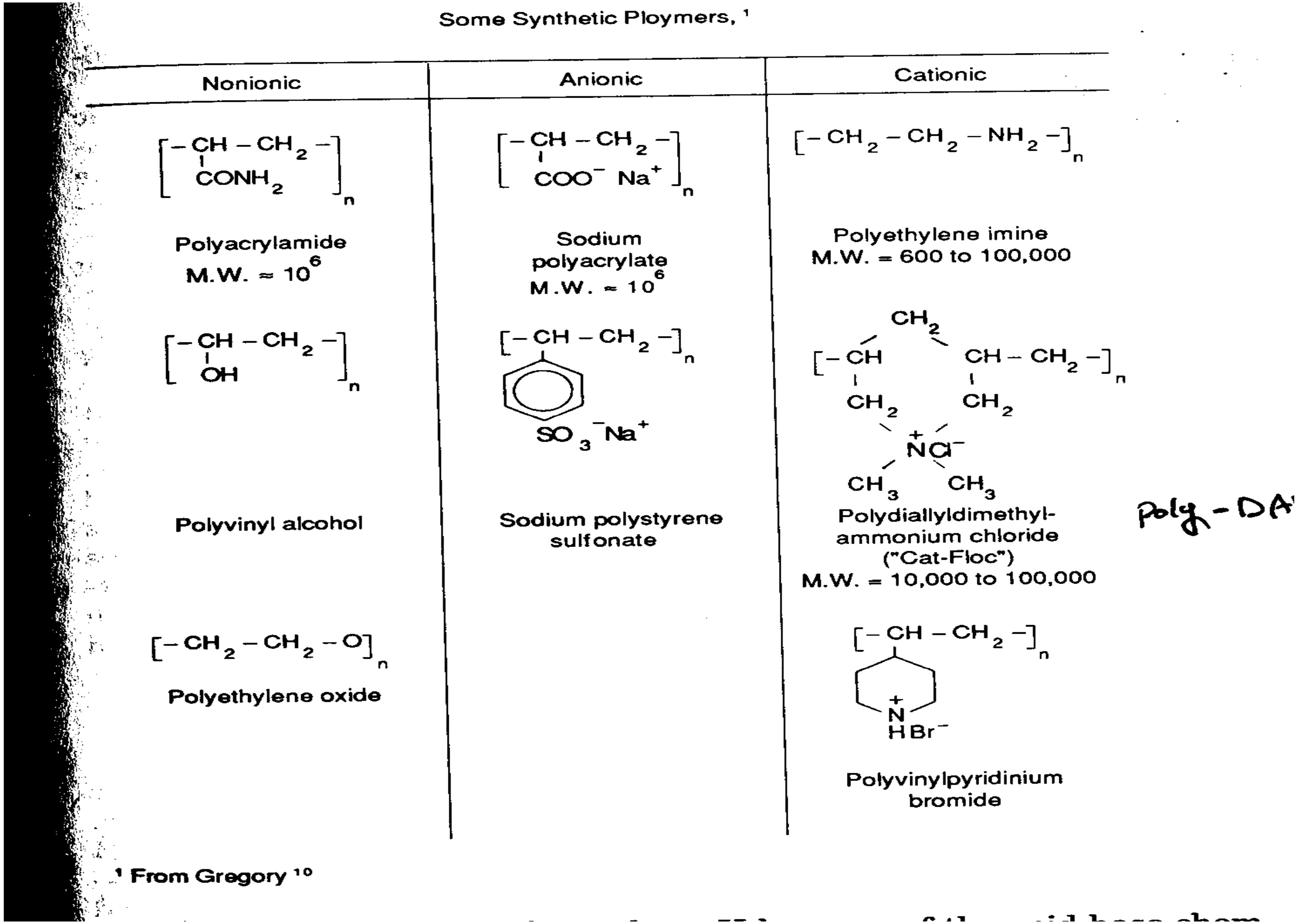


Figure 2-3 Schematic representation of the bridging model for the destabilization of colloids by polymers.

Organic coagulents



Some Synthetic Ploymers, [1]

Nonionic	Anionic	Cationic
$\left[-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\mathrm{CH_2}-\right]_n$ Polyacrylamide M.W. ≈ 10^6	$\left[-\underset{\mathrm{COO^-\ Na^+}}{\mathrm{CH}}-\mathrm{CH_2}-\right]_n$ Sodium polyacrylate M.W. ≈ 10^6	$[-CH_2-CH_2-NH_2-]_n$ Polyethylene imine M.W. = 600 to 100,000
$\left[-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-\right]_n$ Polyvinyl alcohol	$[-CH-CH_2-]_n$ $SO_3^-Na^+$ Sodium polystyrene sulfonate	CH_2 $[-CH$ $CH-CH_2-]_n$ CH_2 CH_2 $\overset{+}{N}Cl^-$ CH_3 CH_3 Polydiallyldimethylammonium chloride ("Cat-Floc") M.W. = 10,000 to 100,000
$[-CH_2-CH_2-O]_n$ Polyethylene oxide		$[-CH-CH_2-]_n$ $\overset{+}{N}$ HBr^- Polyvinylpyridinium bromide

Poly-DA

[1] From Gregory [10]

Interactions Between Particles

Inorganic Coagulents

- Salts of Aluminum and Ferric Ions
- Aluminum Sulfate (or Alum) ~ very popular
- $Al_2(SO_4)_3 \cdot x\ H_2O$ $x \sim 14$

Interactions between Particles

Interaction with particulates

pH < 6 ~ charge neutralization for alum
pH < 4 for ferric ion

Stoichiometry
pH > 6 ~ sweep floc for alum
pH > 4 for ferric
require a greater quantity of coagulant than charge neutralization
➔ larger quantities of solids (sludges)

No Stoichiometry
larger nymber of clay particulates ➔ accelerate the aggregation of the coagulent-clay floc particles

example) Fig 6-6 p125
(sweep floc is not influenced by the types of particulates)

Aluminum Chemistry

$Al(H2O)_6^{3+} + H_2O \rightleftarrows [Al(H_2O)_5OH]^{2+} + H_3O^+$ ………… (1)

Equilibrium constant Ku

$Al^{3+} + 4H_2O \rightleftarrows Al(OH)^{4-} + 4H^+$ ………… (2)

Equilibrium constant KH

$Al^{3+} + 3H_2O \rightleftarrows Al(OH)_3(s)\downarrow + 3H^+$ ………… (3)

Equilibrium constant Ks

$[Al^{3+}]\ [OH^-]^3 = Ks = 10^{-15}$ ………… (4)

$$[Al^{3+}]\left[\frac{10^{-14}}{H^+}\right]^3 = 10^{-15} \qquad \left[Al^{3+}\right] = \frac{10^{-15}}{\left(\frac{10^{-14}}{\left[H^+\right]}\right)^3}$$

Aluminum Chemistry

$$\mathrm{pAl} = \log \frac{Ks}{10^{-42}} + 3pH$$

$$K_H = \frac{\left[\mathrm{Al(OH)_4^-}\right]^- \left[H^+\right]^4}{\left[\mathrm{Al^{3+}}\right]} = 10^{-23}$$

$$P_{\mathrm{Al(OH)_4^-}} = -\log \frac{K_H K_S}{10^{-42}} - pH$$

$$[\mathrm{Al}]_{T1} = [\mathrm{Al^{3+}}] + [\mathrm{Al(OH)}]^{2+} + \cdots\cdots + [\mathrm{Al(OH)_4}]^-$$

$[\mathrm{Al_{13}(OH)_{34}}^{5+}]$
$[\mathrm{Al_7(OH)_{17}}^{4+}]$ charge neutralization mechanism에 중요

pH
aluminum concentration
a coagulent demand의 존재

Aluminum Chemistry

황산알루미늄 $Al_2(SO_4)^3 . 14H_2O$ M.W : 594
1ppm(1mg/L)를 가하였을 때 알칼리도의 감소분은?

$$C_B - C_A = [HCO_3^-] + 2[CO_3^{2-}] + [H^+] - [OH^-]$$

$$Al_2(SO_4)^3 \rightleftarrows 2Al^{3+} + 3SO_4^{2-}$$

1ppm $\qquad$ C_A'

$$\frac{1}{594 \times 1000} = 1.68 \times 10^{-6} M$$

$$Alk - C_A' = Alk - 6 \times (1.68 \times 10^{-6}) \times 50 \text{ eq/L}$$

C_A' = 0.5 mg/L as $CaCO_3$

$6 \times (1.68 \times 10^{-6}) M \times 50 mg/eq$

Aluminum Chemistry

황산알루미늄(M.W 594, 15% Al_2O_3) 1ppm을 가하였을 때 알칼리도의 감소분은?

Al_2O_3 → 0.15mg

이중 Al의 양 $0.15 \times \frac{27 \times 2}{102} = 0.079mg$

황산알루미늄 양으로 역환산

$0.079 \times \frac{594}{27 \times 2} = 0.873mg$ as $Al_2(SO_4)_3 14H_2O$

$Al_2(SO_4)^3 . 14H_2O$ Alk
1ppm : 0.5mg/L
0.873ppm : x
x = 0.44 ppm
mg/L as $CaCO_3$

Coagulation and Zeta potential

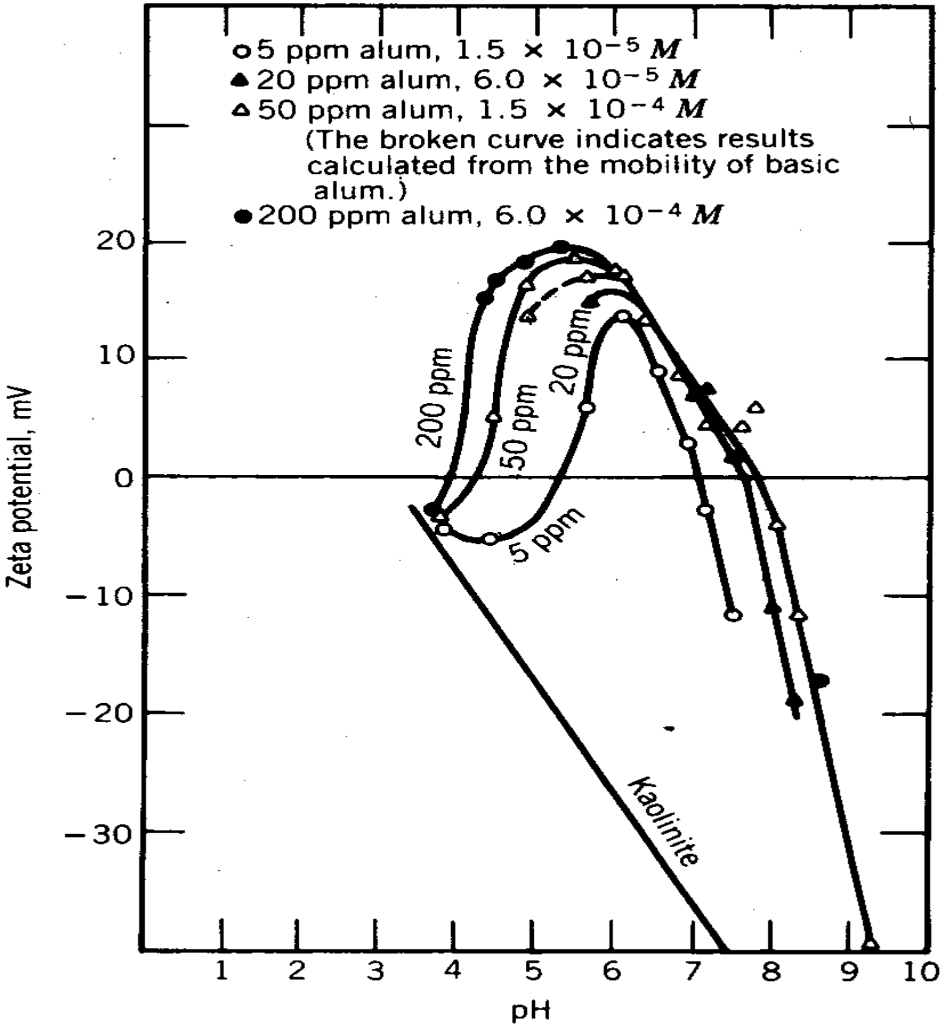
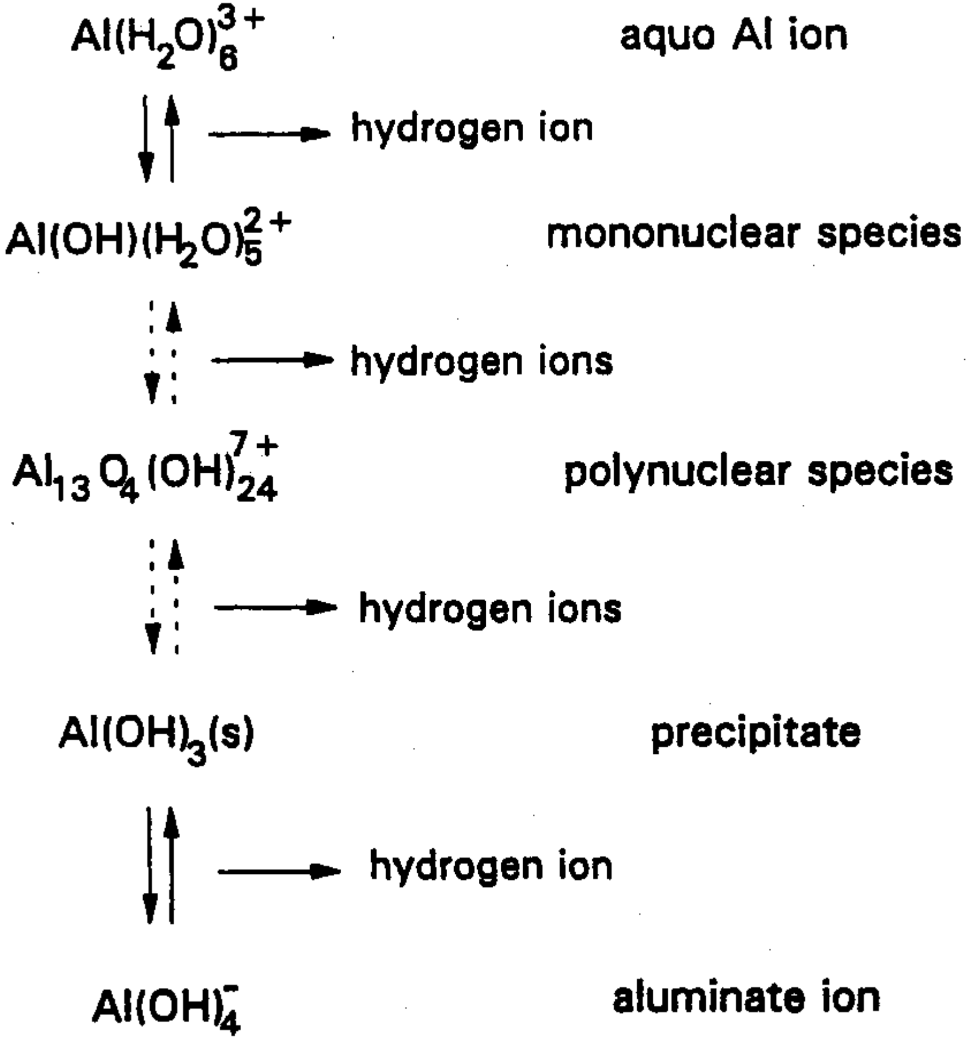


FIGURE 6-3. Effect of pH and alum dose on zeta potential of kaolin (after Packham, 1965).

Aluminum coagulation chemistry



$Al(H_2O)_6^{3+}$ aquo Al ion

hydrogen ion

$Al(OH)(H_2O)_5^{2+}$ mononuclear species

hydrogen ions

$Al_{13}O_4(OH)_{24}^{7+}$ polynuclear species

hydrogen ions

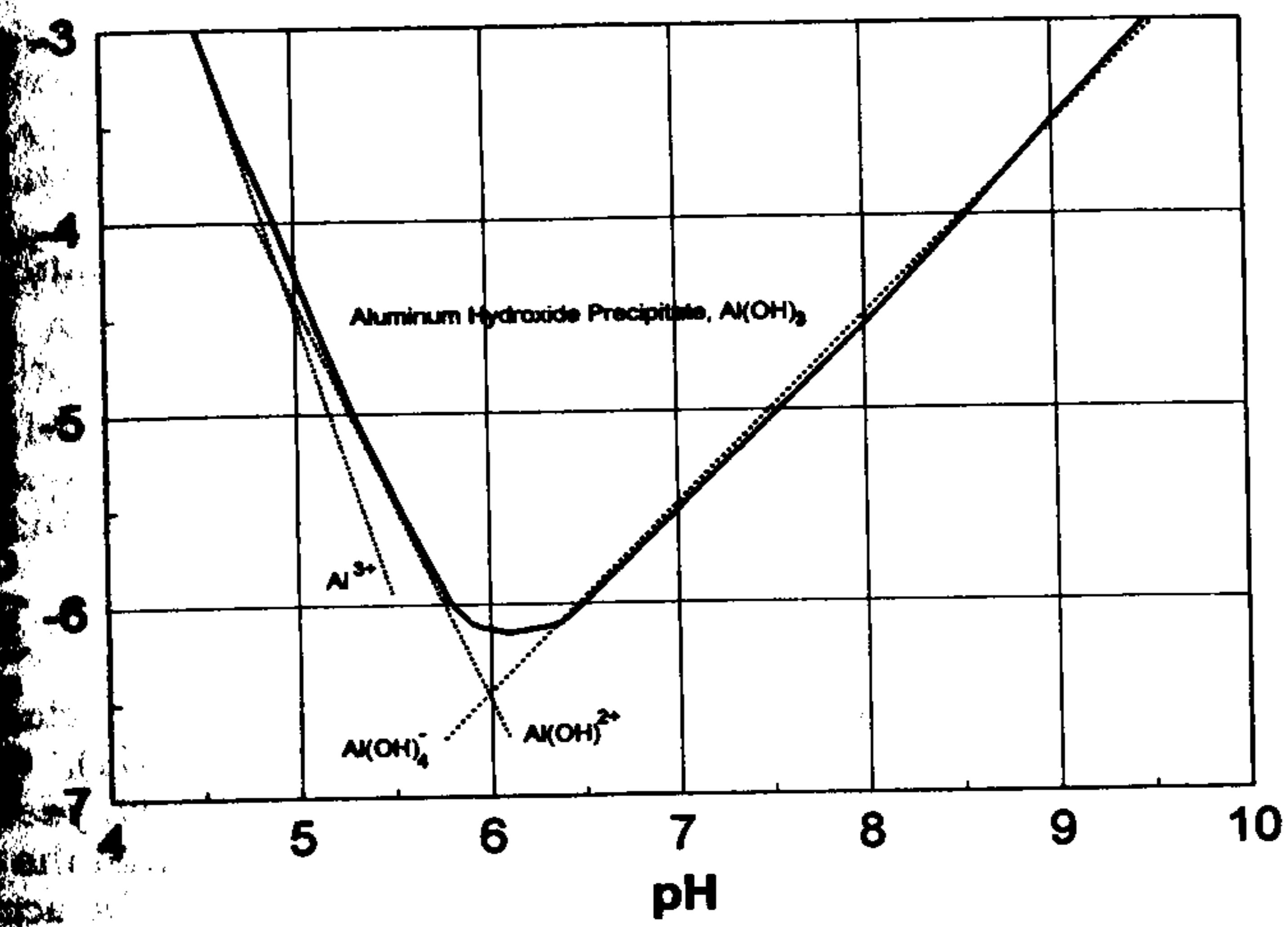
$Al(OH)_3(s)$ precipitate

hydrogen ion

$Al(OH)_4^-$ aluminate ion

FIGURE 6.8 Aluminum hydrolysis products (from Letterman, 1991).

Solubilty of Aluminum Coagulent



RE 6.9 Solubility diagram for amorphous, freshly precipitated alu-
hydroxide. Water molecules are omitted in species notation.

ALUMINIUM CHEMISTRY

1) $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$ $K_{11}=10^{-5.02}$

2) $Al^{3+} + 2H_2O = Al(OH)_2^{+} + 2H^+$ $K_{12}=10^{-8.71}$

3) $2Al^{3+} + 2H_2O = Al_2(OH)_2^{4+} + 2H^+$ $K_{22}=10^{-6.27}$

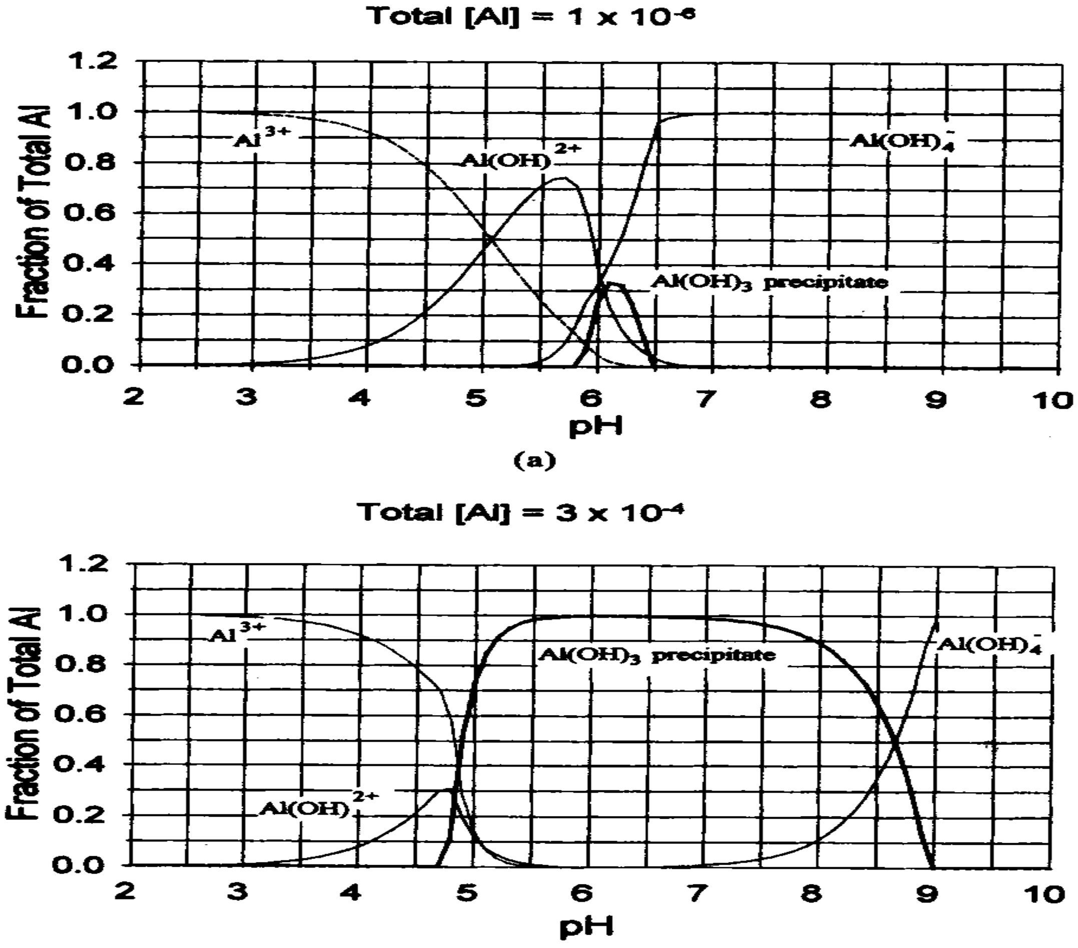
4) $Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$ $K_{13}=10^{-10.4}$

. Precipitate form: $Al(OH)_{2.5}(SO_4)_{0.25}$ over a wide range of alum neutralization.

. Active types of alum: at about 1/3 to 1/2 neutralization.

. Al^{3+} will be more precipitated in the form of $Al(OH)_3$ with a longer residence time.

pH dependant Aluminum species



(a)

(b)

FIGURE 6.11 Effect of pH and total aluminum concentration on the speciation of Al(III): (*a*) $Al_T = 1 \times 10^{-6}$ M, and (*b*) $Al_T = 3 \times 10^{-4}$ M.

Alum coagulation diagram

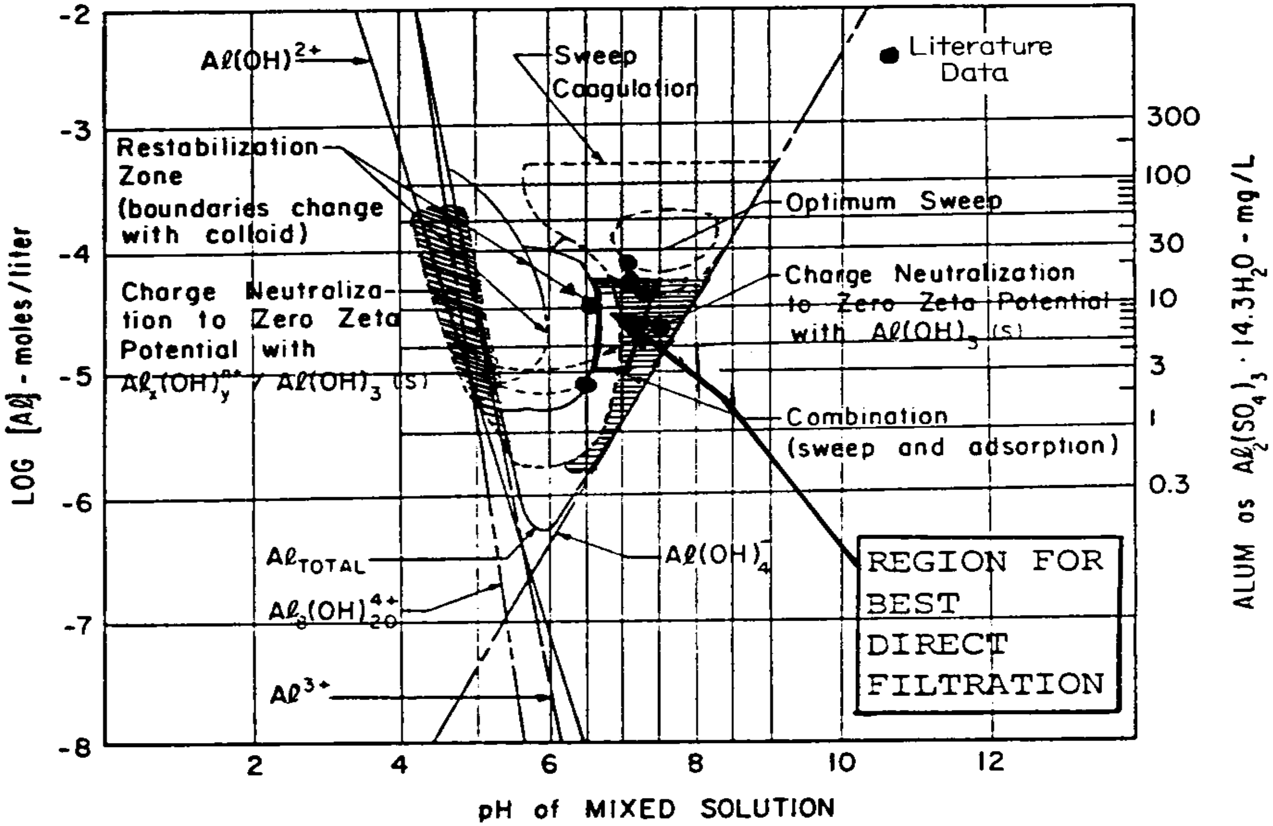


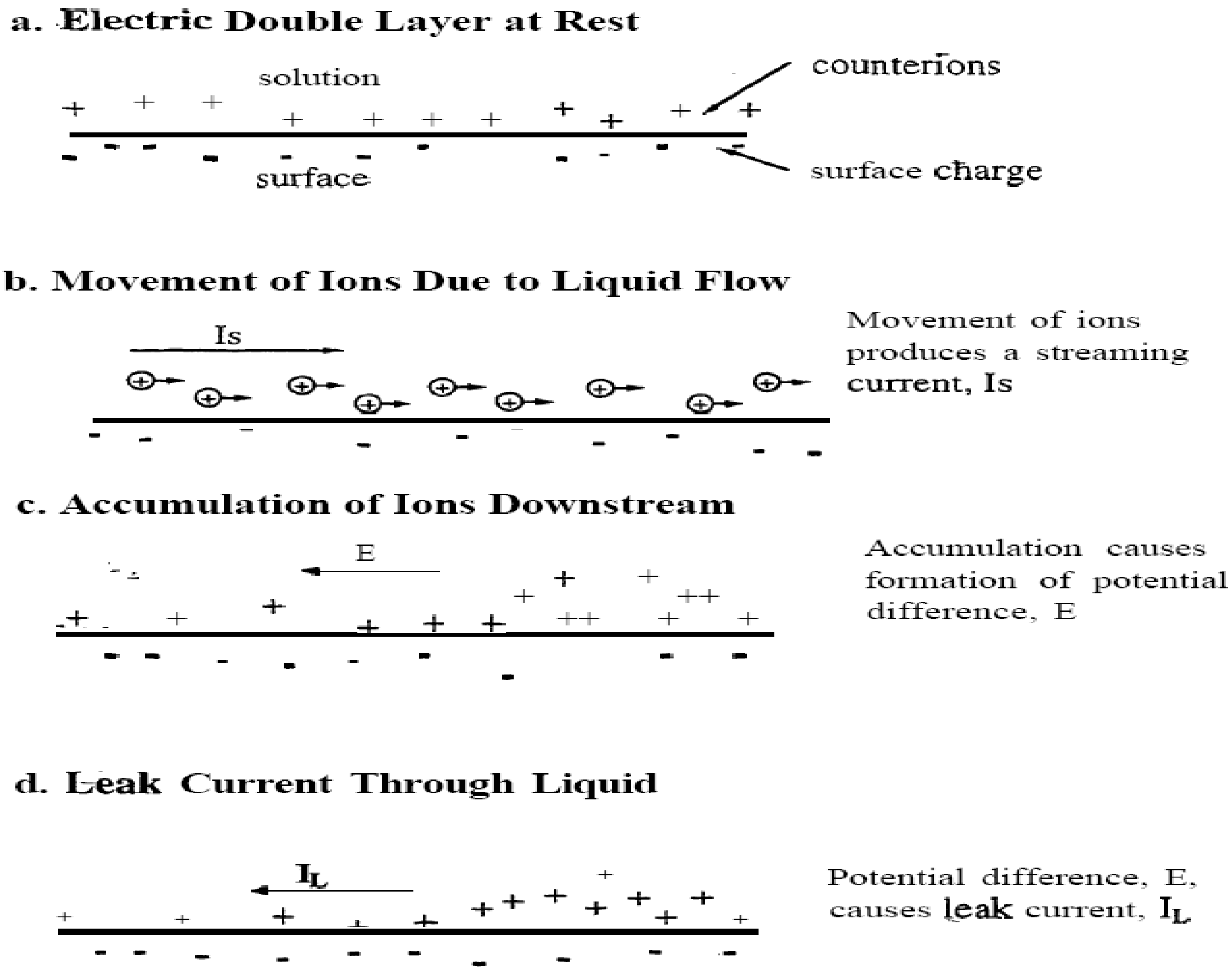
Figure 6.16 The domain for "best" direct filtration on the alum coagulation diagram. Other studies from the literature are also shown.

How to determine the charge of particles ?

(1) Create an Electrical Field
(2) Negative Particles move toward positive pole
(3) Electrophoresis : Zeta Potential

Zeta-potential Measurement

(1) Streaming potential; the electrolye existing in compressed flow inside a shallow channel creating streaming potential



a. Electric Double Layer at Rest

b. Movement of Ions Due to Liquid Flow

Movement of ions produces a streaming current, Is

c. Accumulation of Ions Downstream

Accumulation causes formation of potential difference, E

d. Leak Current Through Liquid

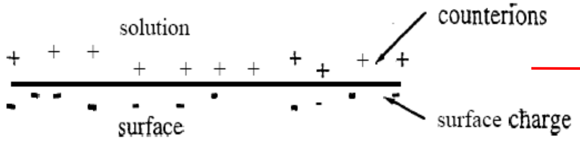
Potential difference, E, causes leak current, I_L

Zeta-potential of RO membrane (2)

(1) Streaming potential

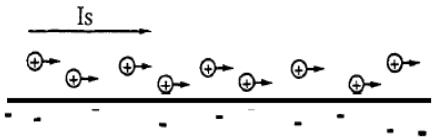
Electrolyte가 압력을 갖고 얇은채널에 흐를 때 streaming potential이 발생한다.

a. Electric Double Layer at Rest



→ 압이 없는 조건에서는 elctrolyte에 의해 멤브레인 표면에 electric double layer가 발생.

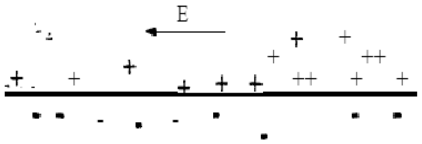
b. Movement of Ions Due to Liquid Flow



Movement of ions produces a streaming current, Is

→ 압을 갖고 흐르는 유체는 streaming current를 증가시켜 potential 차이를 발생시킨다.

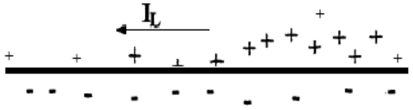
c. Accumulation of Ions Downstream



Accumulation causes formation of potential difference, E

→ 순간적으로 전자의 밀도가 달라지게 되어 potential 차이가 생기고 가해준 current방향에 대해 역흐름이 생긴다 (leak current).

d. Leak Current Through Liquid

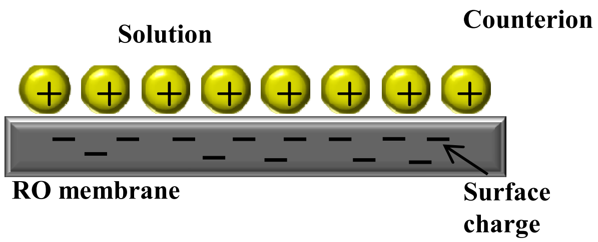


Potential difference, E, causes leak current, I_L

→ 평형에 도달했을때 측정된 potential이 streaming potential이다.

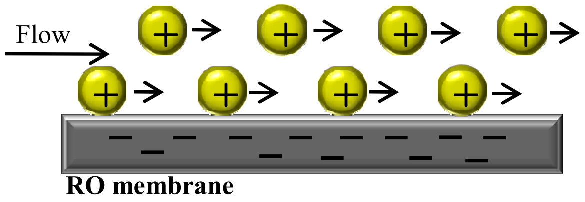
Zeta-potential of RO membrane (streaming potential)

1. Electric double layer at rest



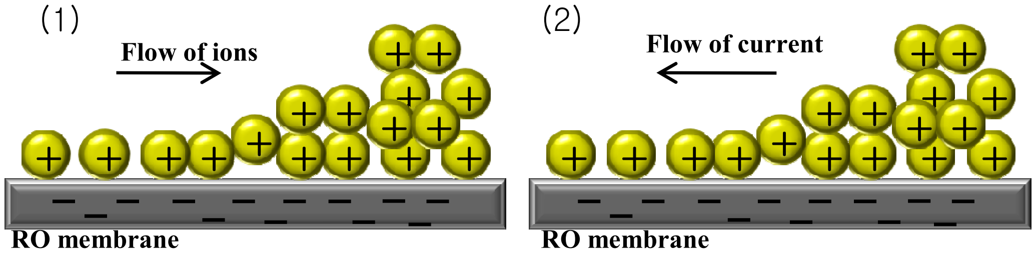
압력이 없는 조건에서는 electrolyte에 의해 멤브레인 표면에 전기이중층이 발생한다.

2. Movement of ions due to liquid flow



압력을 가하면서 흐름을 주면 이온들은 움직이기 시작하고 전자들의 밀도가 변하기 시작한다.

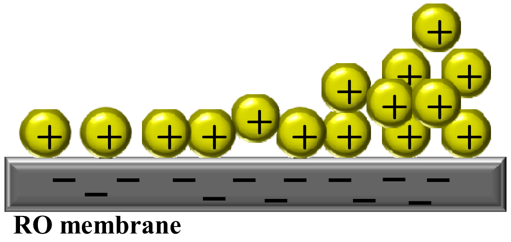
3. Accumulation of ions downstream


(1)

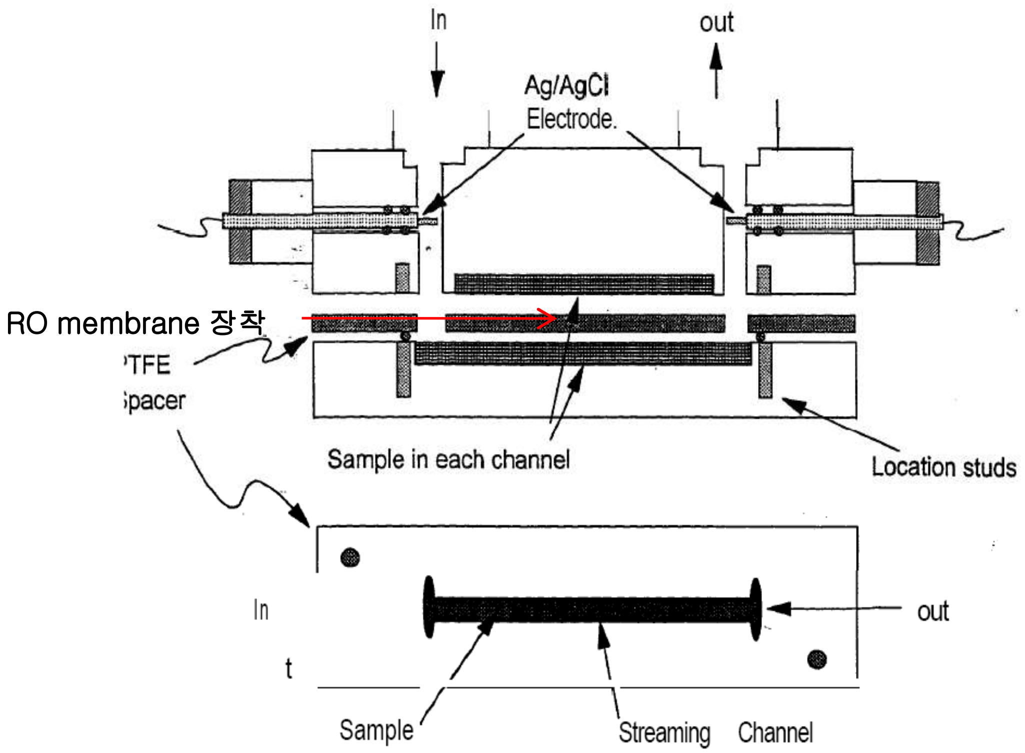
(2)

흐름에 의한 전자의 밀도는 오른쪽이 상대적으로 +, 왼쪽이 상대적으로 –를 띄게 된다. 따라서 전자는 왼쪽에서 오른쪽으로 흐르고 전류는 반대로 흐르게 된다. 이때의 전류를 leak current라고 한다.

4. Streaming potential



전자들의 이동이 평형상태에 도달하게 되었을 때의 potential의 차이를 streaming potential이라고 한다.



Schematic of stream current measuring cell

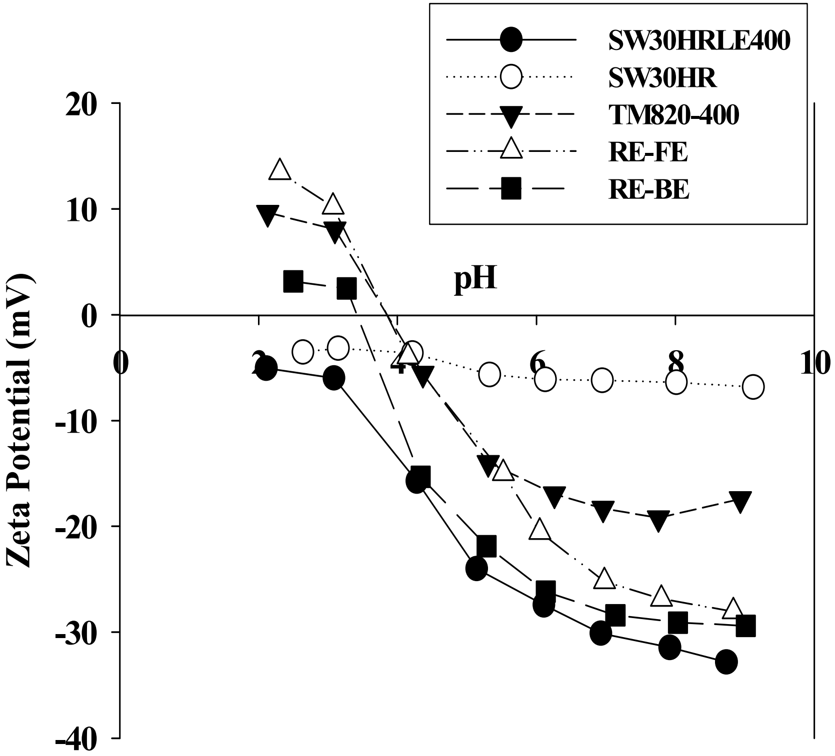
Helmholtz-Smoluhowski equation

Find zeta-potential with streaming potential

$$\zeta = \frac{U_s}{\Delta P}\frac{\mu}{\epsilon\epsilon_0}\frac{L}{A}\frac{1}{R}$$

ξ : zeta-potential
U_S : induced streaming potential
ΔP : hydraulic pressure
μ : liquid viscosity
ϵ : liquid permittivity
ϵ_o : permittivity in vacuum
R : electric resistance
L : length of channel
A : cross-sectional area of channel

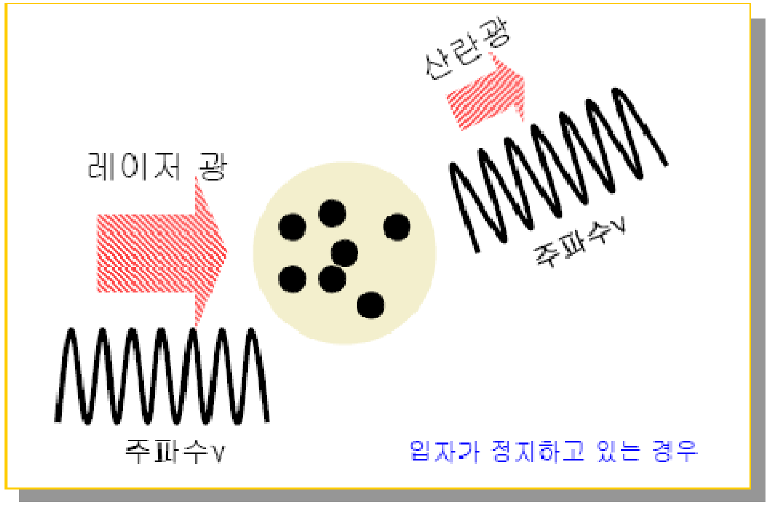
Zeta-potential measurements by streaming current measurement



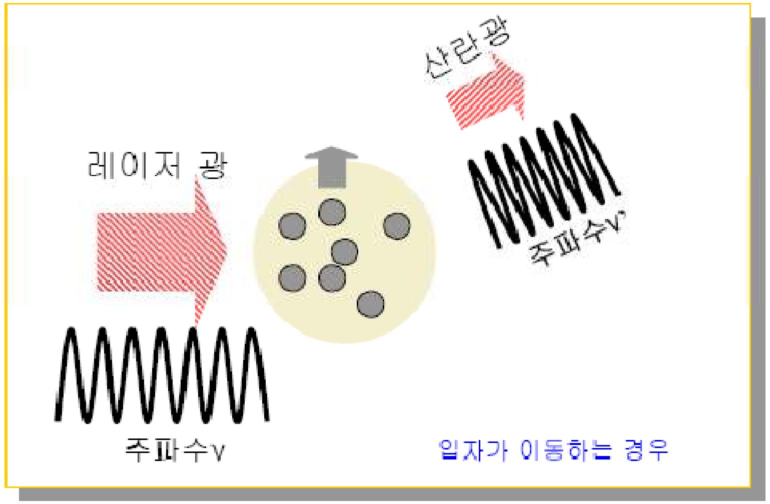
zeta-potential measurements
of several types of membrane

Measurement of zeta potential
(2) Principle of electrophoretic light scattering method

< Doppler Shift >



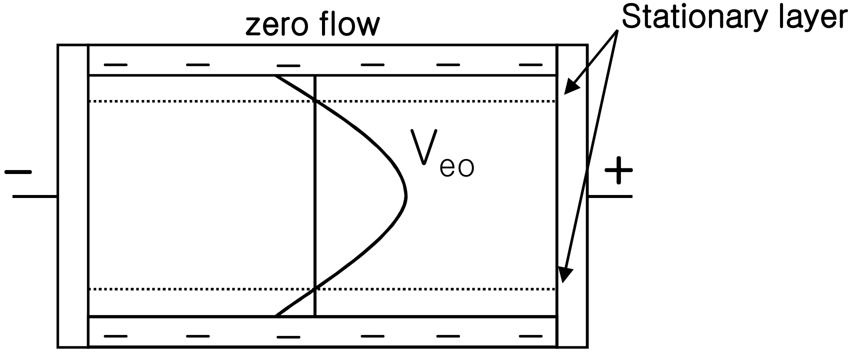
입자가 정지하고 있는 경우 산란광의 주파수는 레이저 광 주파수 ν와 같다.



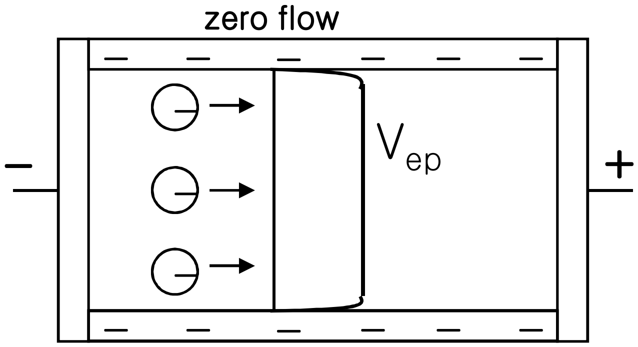
입자가 이동하고 있는 경우 산란광의 주파수는 레이저 광 주파수$\nu' = \nu + \Delta\nu$로 변화한다.

Measurement of the surface zeta-potential

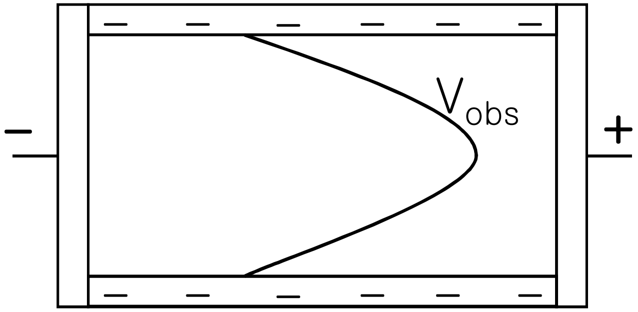
< Electroosmotic flow >



< Electrophoretic movement >



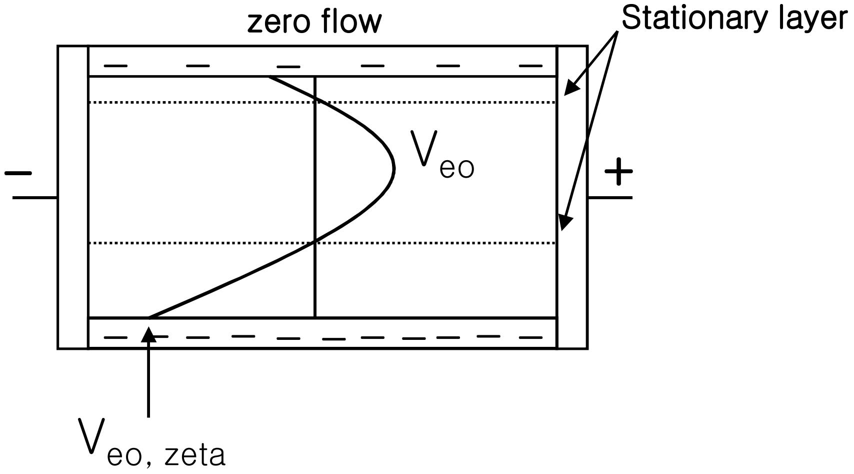
< Electroosmotic flow + Electrophoretic movement >



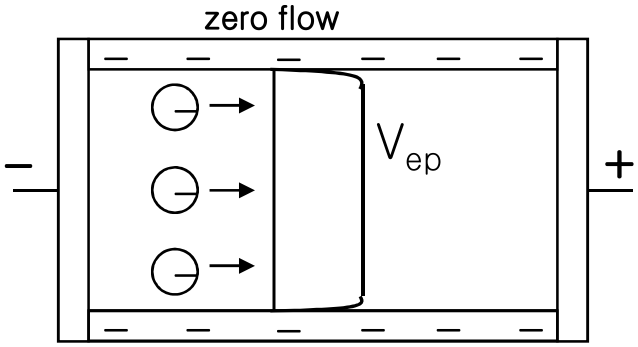
$$V_{obs} = V_{eo} + V_{ep}$$

Analysis of the surface zeta-potential

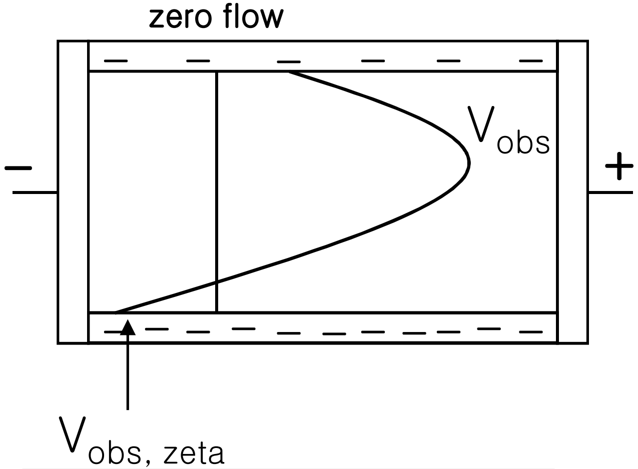
< Electroosmotic flow >



< Electrophoretic movement >



< Electroosmotic flow + Electrophoretic movement >



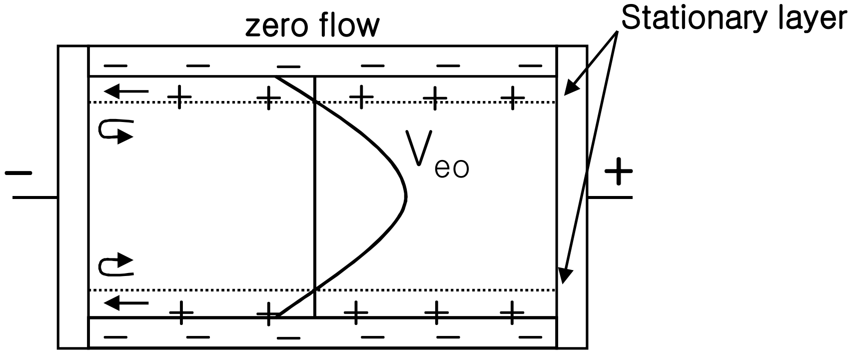
$$V_{obs} = V_{eo} + V_{ep}$$

$$V_{eo} = V_{obs} - V_{ep}$$

$$\boxed{V_{eo,\ zeta} = V_{obs,\ zeta} - V_{ep,zeta}} \quad \zeta = -\frac{V_{eo} \cdot \eta}{\varepsilon \cdot E}$$

Analysis of the surface zeta-potential using electrophoresis – light scattering method

< Electroosmotic flow >

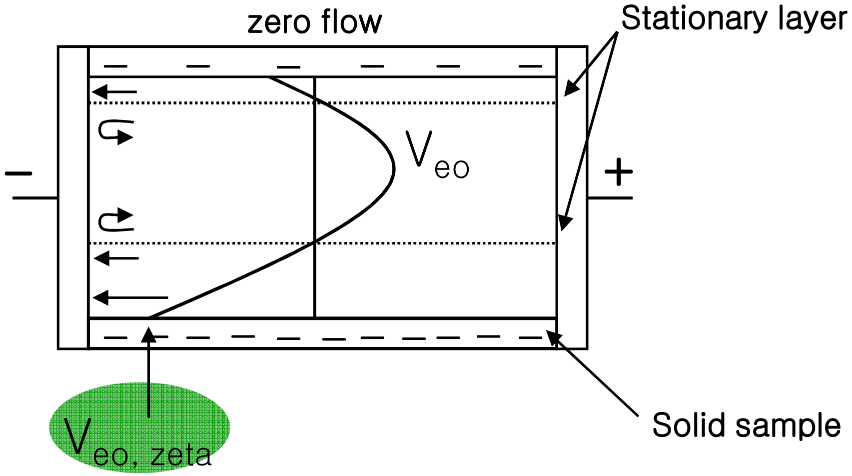


- 전하를 가지고 있는 표면에는 표면전하의 counter ion들이 전기이중층 (electrical double layer)를 형성하게 됨
- 이때 두 표면 사이에 존재하는 유체(염을 포함)에 전기장을 가하면 전기이중층에 유체의 흐름이 발생하게 되며 이에 따라 관 내부에 전체적인 유체의 흐름이 형성됨. 이를 electroosmitoc flow라 함.
- 특히, 양쪽 면이 막혀있는 경우 유체의 흐름이 제한되어 마치 pressure-driven flow와 유사한 유체의 속도 profile (V_{eo})을 가지게 됨.
- 표면에서의 $V_{eo,zeta}$ (엄밀히 말하면 표면자체의 속도가 아니라 전기이중층 내부 제타포텐셜을 측정하는 위치에서의 속도)는 아래와 같이 표면의 제타포텐셜과 직접적인 관계가 있으며 이를 측정함으로써 표면의 제타포텐셜을 알 수 있다.

$$\zeta = -\frac{V_{eo} \cdot \eta}{\varepsilon \cdot E}$$

- 한편, 양쪽 표면이 같은 제타포텐셜을 가지는 것이 아니라 서로 상이할 경우 아래 그림과 같이비대칭성의 속도 profile을 가지게 되는데, 이 경우에도 $V_{eo,zeta}$를 구할 수 있으면 원하는 고체표면의 제타포텐셜을 구할 수 있게 된다.

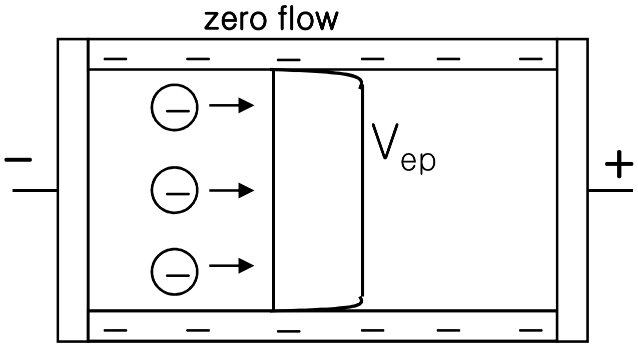
< Electroosmotic flow >



- 하지만 이러한 속도 profile은 가시적으로 알 수 없기 때문에 유체의 흐름에 따라 유동하는전하를 가진 입자를 유체에 인위적으로 첨가하여 이 입자의 속도를 광산란법으로 분석하는 방법으로 실제 V_{eo}를 계산해 내게 된다.

- 한편, 이 입자는 electroosmotic flow가 없는(DI water) 유체에서 전기장이 존재할 경우 아래 그림과 같은 속도 profile(V_{ep})을 가지게 된다. 입자의 제타포텐셜과 크기를 알고 있는 상황에서 주어진 전기장에서의 이러한 V_{ep}의 분포는 직접 계산을 통해 도출해 낼 수 있다.

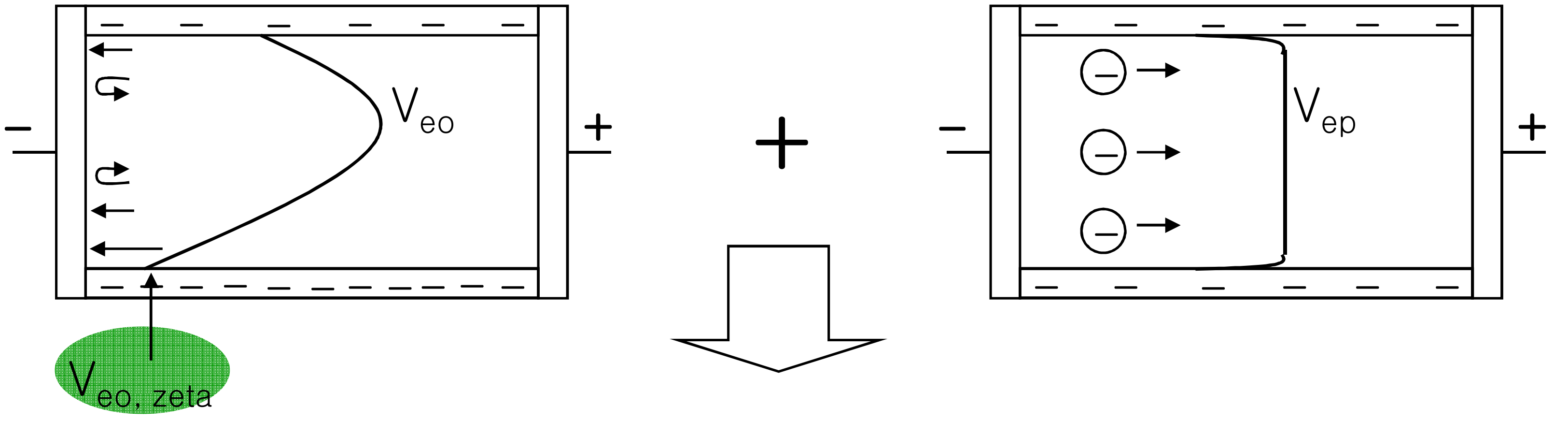
< Electrophoretic movement >



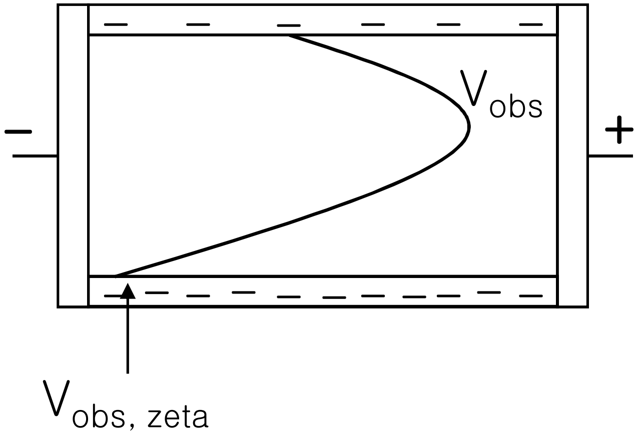
- 따라서, 실제로 염이 존재하여 electroosmotic flow와 입자의 electrophoretic move가 동시에 일어날 경우 광산란법을 통해 '실제로 관측되는' 입자의 속도 (V_{obs})는 다음과 같이 표현된다.

- 따라서, 실제로 염이 존재하여 electroosmotic flow와 입자의 electrophoretic move가 동시에 일어날 경우 광산란법을 통해 '실제로 관측되는' 입자의 속도 (V_{obs})는 다음과 같이 표현된다.

< Electroosmotic flow > < Electrophoretic movement >



< Electroosmotic flow + Electrophoretic movement >



$$V_{obs} = V_{eo} + V_{ep}$$

$$V_{eo} = V_{obs} - V_{ep}$$

$$\zeta = -\frac{V_{eo} \cdot \eta}{\varepsilon \cdot E}$$

- V_{ep}를 이미 알고 있으므로 V_{eo}를 계산해 낼 수 있으며 이 그래프의 피팅을 통해 고체 시료 표면의Veo를 계산해 내고 마지막으로 위 식을 통해 실제 고체 시료 표면의 제타포텐셜을 구해내게 된다.

Example I: zeta-potential of particle

Smoluchowski equation

$$\zeta = \frac{\eta \cdot \mu}{\varepsilon} = \frac{\eta \cdot \mu}{\varepsilon_r \varepsilon_0}$$

$$\zeta = \frac{\eta \cdot \mu}{\varepsilon_r \varepsilon_0} = \frac{0.8878 \times (-2.349 \times 10^{-4})}{78.3 \times 8.855 \times 10^{-12}} \times \frac{cP \times \dfrac{\frac{0.001 C \cdot V \cdot s}{m^3}}{cP} \times \dfrac{cm^2}{V \cdot s} \times \dfrac{10^{-4} m^2}{cm^2}}{\dfrac{C}{V \cdot m}}$$

$$= -0.03007\ (V) = -30.07\ (mV)$$

E : Electric field: −16.01 (V/cm)
η : Viscosity: 0.8878 (cP)
ε_r : Dielectric const.: 78.3
ε_0 : Permittivity in free space: 8.855 x 10^{-12} (C/Vm)
μ : Mobility: −2.349 x 10^{-4} (cm^2/Vs)

Example II: zeta-potential of solid surface

$$\zeta = -\frac{V_{eo} \cdot \eta}{\varepsilon \cdot E} = -\frac{V_{eo} \cdot \eta}{\varepsilon_r \varepsilon_0 \cdot E}$$

$$\zeta = -\frac{V_{eo} \cdot \eta}{\varepsilon_r \varepsilon_0 \cdot E} = -\frac{0.01 \times 0.8878}{78.3 \times 8.855 \times 10^{-12} \times (-25.63)} \times \frac{\frac{cm}{s} \times \frac{m}{100cm} \times cP \times \frac{\frac{0.001 C \cdot V \cdot s}{m^3}}{cP}}{\frac{C}{V \cdot m} \times \frac{V}{cm} \times \frac{100cm}{m}}$$

$$= -0.0499\ (V) = -49.99\ (mV)$$

E : Electric field: −25.63 (V/cm)
V_{eo} : Velocity at the surface: 0.01 (cm/s)
η : Viscosity: 0.8878 (cP)
ε_r : Dielectric const.: 78.3
ε_0 : Permittivity in free space: 8.855 x 10^{-12} (C/Vm)