

Soles:

Estabilidad de Dispersiones Coloidales

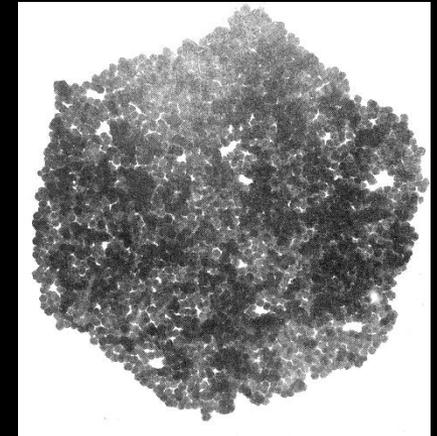
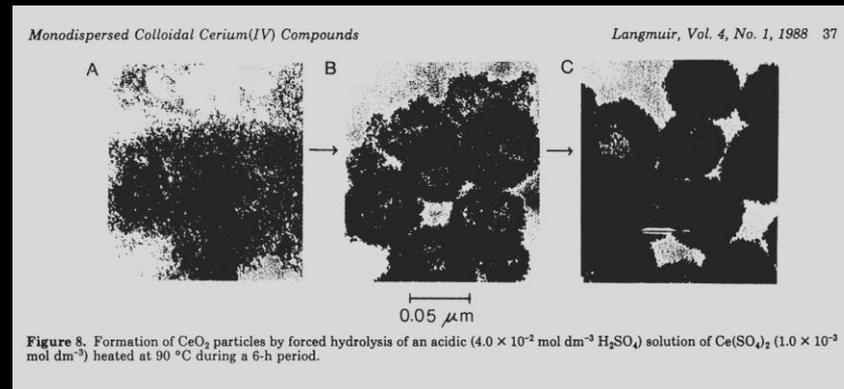
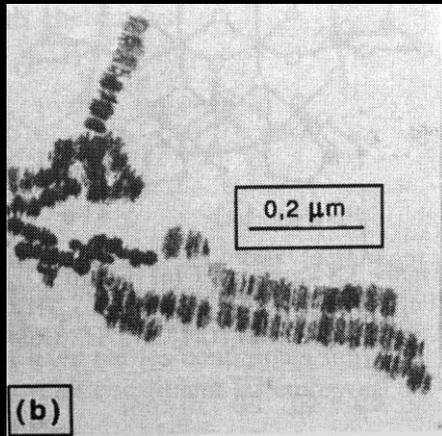
Alberto E. Regazzoni

Gerencia Química
Centro Atómico Constituyentes
Comisión Nacional de Energía Atómica

e-mail: regazzon@cnea.gov.ar

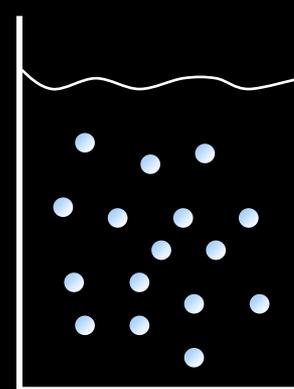
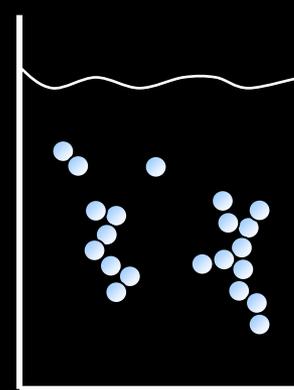
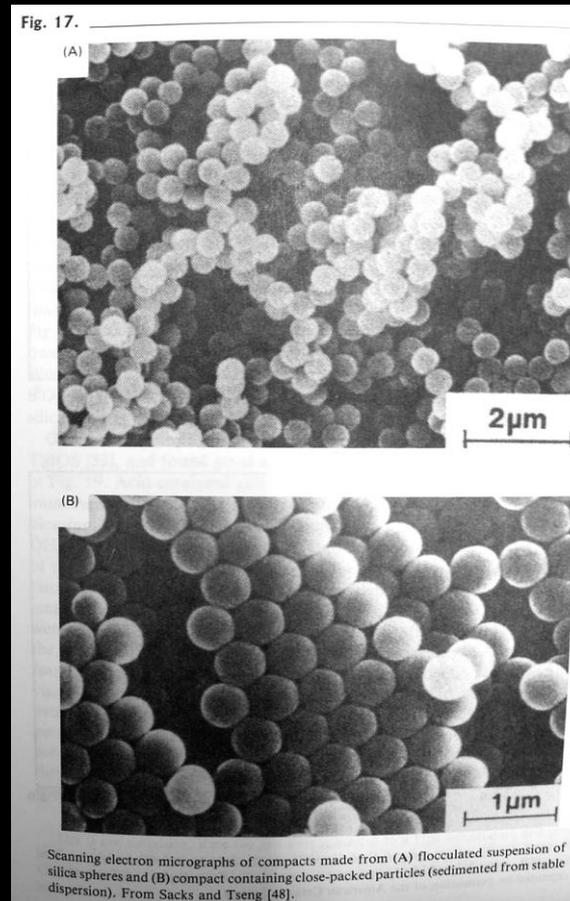
Interacciones Partícula-Partícula

Porqué controlarlas?



Interacciones Partícula-Partícula

Porqué controlarlas?



Fuerzas de Interacción

Responsables de la estabilidad de los soles

1. Dispersivas (London - van der Waals)
2. Electrostáticas (repulsivas o atractivas)
3. Estéricas (repulsivas)
4. Magnéticas

Interacciones Intermoleculares

Dipolo permanente 1 – dipolo inducido 2
(Debye)

$$-\frac{(\alpha_1\mu_2^2 + \alpha_2\mu_1^2)}{x^6}$$

Dipolo permanente 1 – dipolo permanente 2
(Keesom)

$$-\frac{2}{3} \frac{\mu_1^2 \mu_2^2}{kT x^6}$$

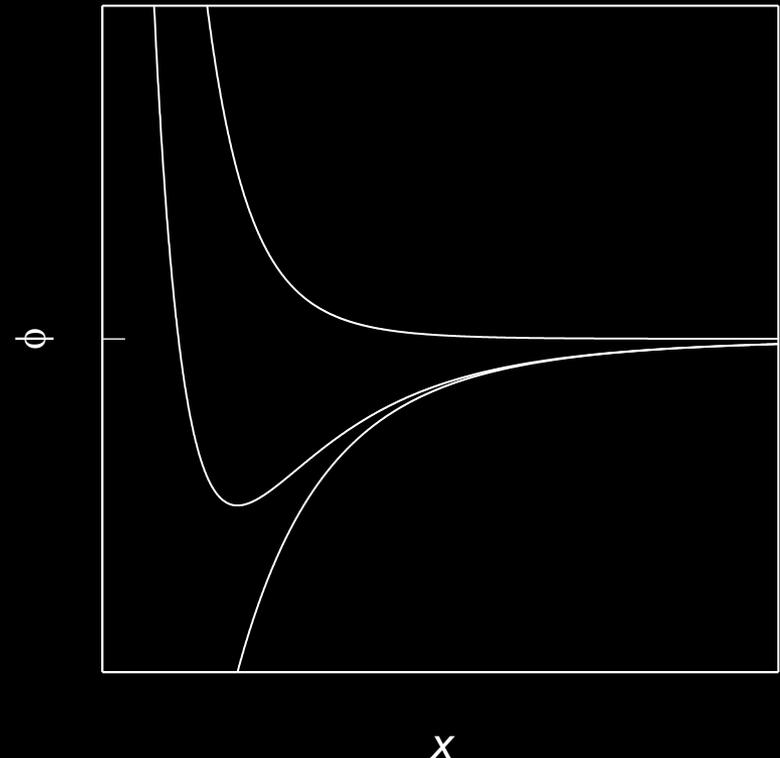
Dipolo inducido 1 – dipolo inducido 2
(London)

$$-\frac{2}{3} \frac{h}{x^6} \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} \alpha_1 \alpha_2$$

Repulsión

$$+\frac{\xi}{x^{12}}$$

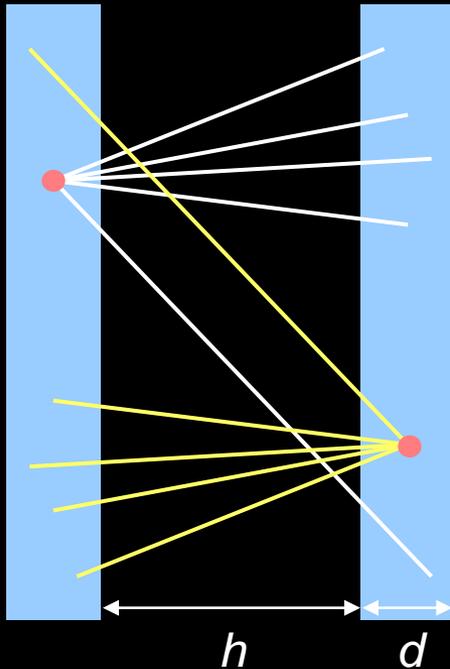
$$\phi(x) = +\frac{\xi}{x^{12}} - \frac{\beta}{x^6}$$



Interacción entre Cuerpos Macroscópicos

$$\phi = -\beta x^{-6}$$

$$\phi = -\frac{1}{2} \left(\frac{\rho N_A}{M} \right)^2 \beta \iint x^{-6} dV_1 dV_2$$



Bloques de igual espesor

$$\phi = -\frac{A}{12\pi} \left[\frac{1}{h^2} + \frac{1}{(h+2d)^2} - \frac{2}{(h+d)^2} \right]$$

Bloques espesor infinito

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

Esferas

$$\phi = -\frac{A}{6} \left[\frac{2r_1 r_2}{h^2 + 2r_1 h + 2r_2 h} + \frac{2r_1 r_2}{h^2 + 2r_1 h + 2r_2 h + 4r_1 r_2} \right] - \frac{A}{6} \ln \left(\frac{h^2 + 2r_1 h + 2r_2 h}{h^2 + 2r_1 h + 2r_2 h + 4r_1 r_2} \right)$$

Esferas igual radio

$$\phi = -\frac{A}{6} \left[\frac{2r^2}{h^2 + 4rh} + \frac{2r^2}{h^2 + 4rh + 4r^2} + \ln \left(\frac{h^2 + 4rh}{h^2 + 4rh + 4r^2} \right) \right]$$

Esferas igual radio ($r \gg h$)

$$\phi = -\frac{Ar}{12h}$$

La Constante de Hamaker



$$\Delta\phi = \phi_{11} + \phi_{22} - 2\phi_{12}$$

$$A = A_{11} + A_{22} - 2A_{12} \simeq (A_{11}^{1/2} - A_{22}^{1/2})^2$$

$$A_{12} \simeq \sqrt{A_{11}A_{22}}$$

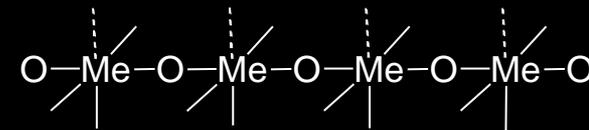
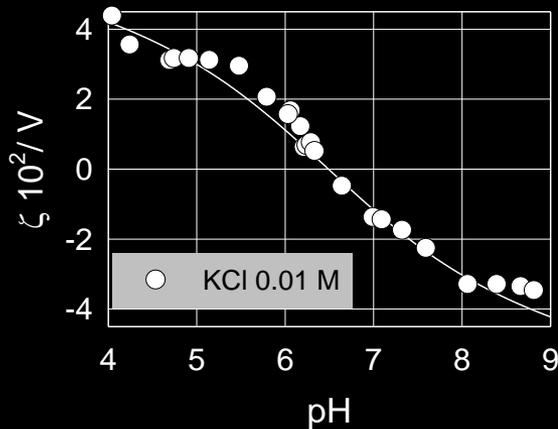
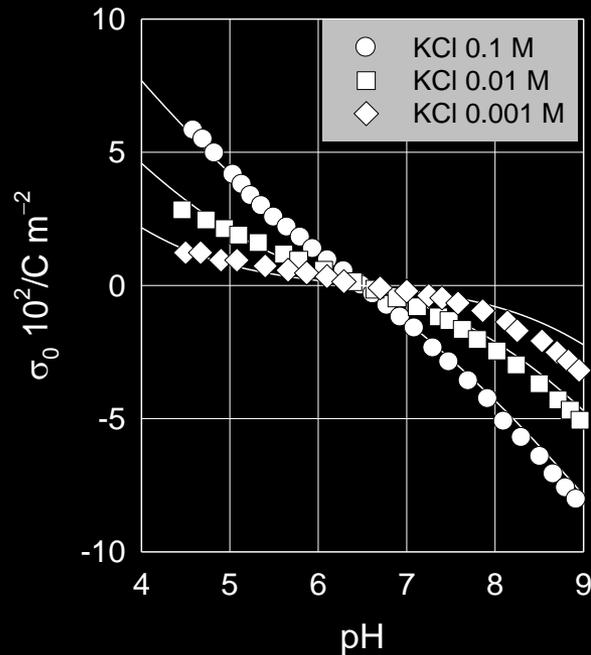
$$A \simeq 1 - 15kT \simeq 4 - 60 \times 10^{-21} \text{ J}$$

Fuerzas de Interacción

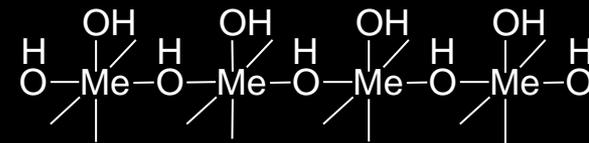
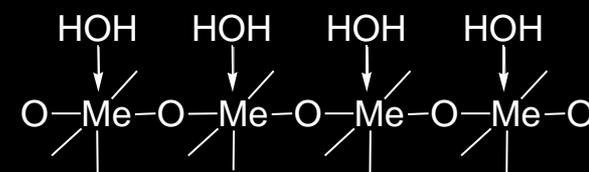
Responsables de la estabilidad de los soles

1. Dispersivas (London - van der Waals)
2. Electrostáticas (repulsivas o atractivas)
3. Estéricas (repulsivas)
4. Magnéticas

Interacción Electrostática: La Carga Superficial



H₂O

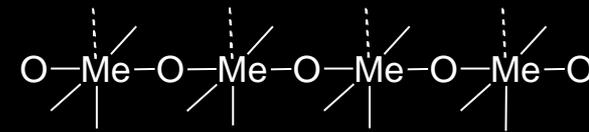
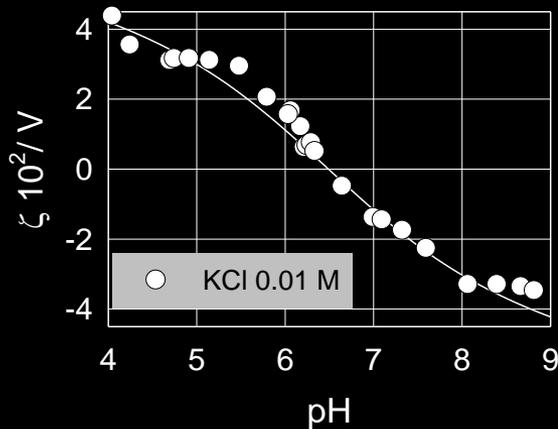
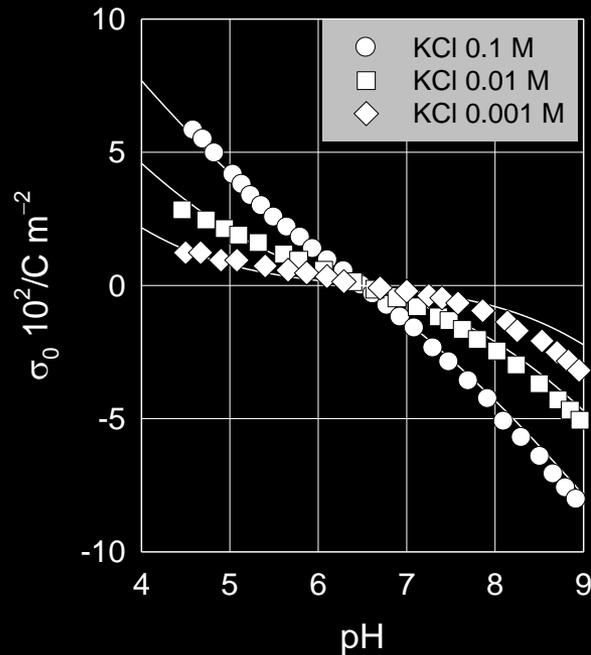


Puntos de carga cero óxidos metálicos

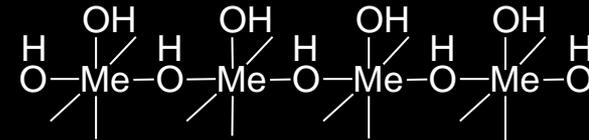
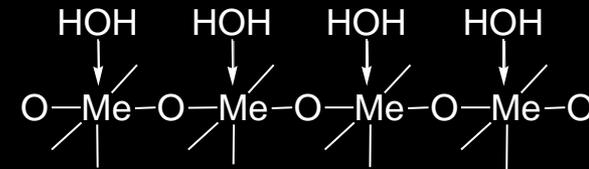
Oxido	pH ₀
MgO	~12.0
Al ₂ O ₃	9.0
α-Fe ₂ O ₃	8.6
ZnO	8.0
Cr ₂ O ₃	~8.0
β-MnOOH	7.3
γ-FeOOH	6.7
Fe ₃ O ₄	6.8
CoFe ₂ O ₄	~7.0
NiFe ₂ O ₄	6.6
TiO ₂ (a)	6.5
ZrO ₂	6.4
TiO ₂ (r)	5.8
SnO ₂	4.5
SiO ₂	~2.0
δ-MnOOH	1.5
V ₂ O ₅	1 - 2
WO ₃	< 1.0

El *Punto de Carga Cero* **NO** es necesariamente igual al *Punto isoeléctrico*

Interacción Electrostática: La Carga Superficial

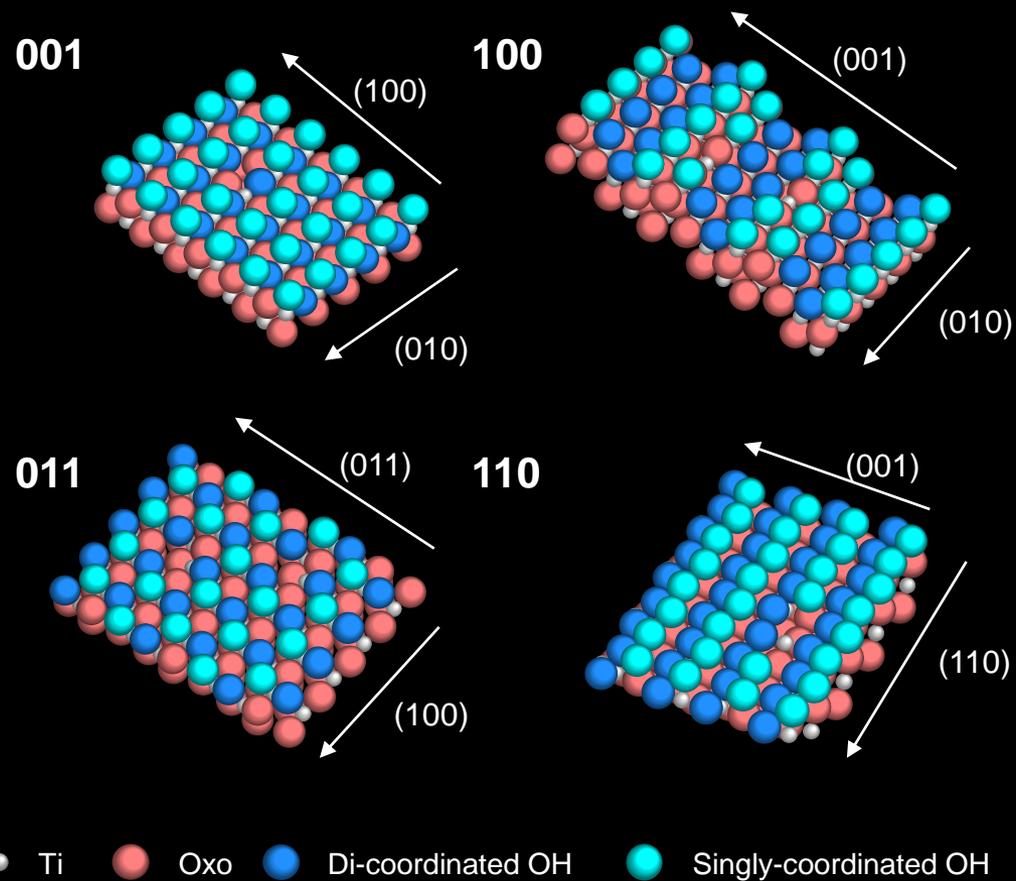


H_2O



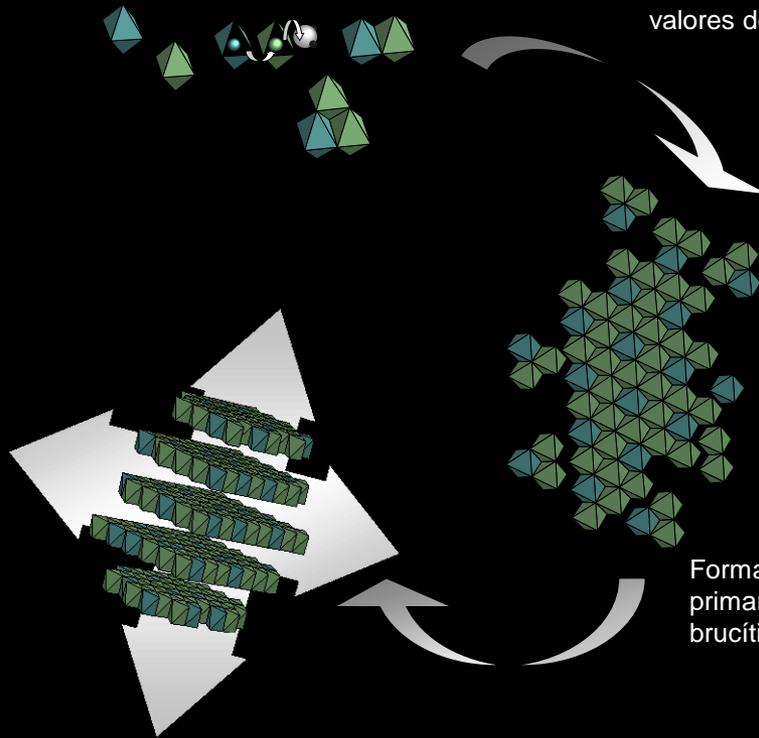
Interacción Electroestática: Los Sitios Superficiales

Superficies de Anatasa

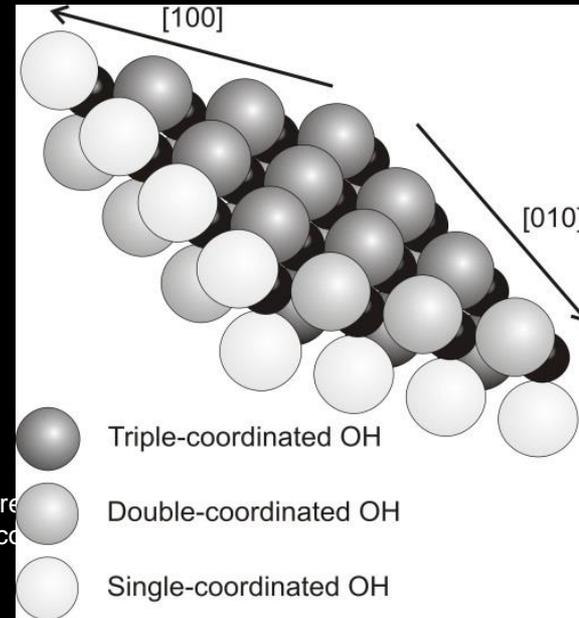


Mecanismo de Precipitación de HDLs de Ni(II)–Cr(III)

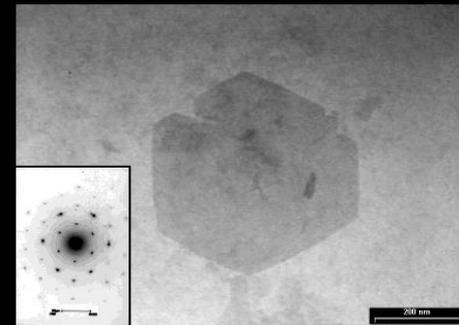
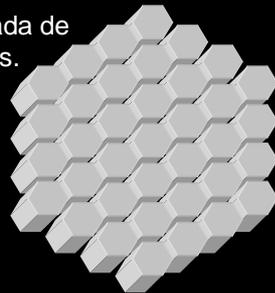
Hidrólisis. Formación de especies heteropolinucleares por ataque nucleofílico de $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$ sobre $\text{Ni}(\text{H}_2\text{O})_6^{2+}$; notar los diferentes valores de $k_{\text{H}_2\text{O}}$.



Formación y crecimiento de partículas primarias por co-precipitación de brucíticas.



Agregación orientada de partículas primarias.



La Carga Superficial



$$Q_{a1}^S = K_{a1}^S \exp(e\psi_0/kT) = \frac{\{>\text{MeOH}\}}{\{>\text{MeOH}_2^+\}} a_{\text{H}^+}$$

$$Q_{a2}^S = K_{a2}^S \exp(e\psi_0/kT) = \frac{\{>\text{MeO}^-\}}{\{>\text{MeOH}\}} a_{\text{H}^+}$$

$$\sigma_0 = F \left(\{>\text{MeOH}_2^+\} - \{>\text{MeO}^-\} \right)$$

$$\psi_0 = \frac{2.3RT}{F} (\text{pH}_0 - \text{pH}) + \frac{2.3RT}{2F} \log \frac{\{>\text{MeO}^-\}}{\{>\text{MeOH}_2^+\}}$$

$$\text{pH}_0 = \frac{1}{2} (\text{p}K_{a1}^S + \text{p}K_{a2}^S)$$

Equilibrios de Complejación Superficial

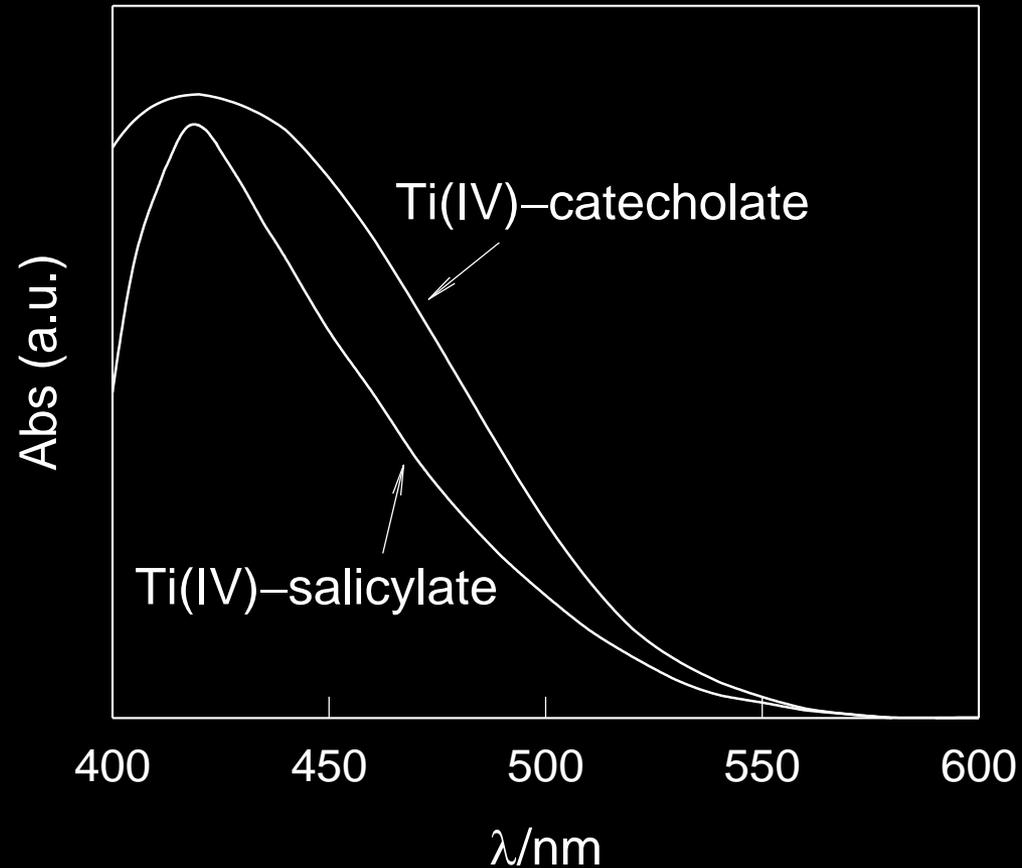


$$K_L^{\text{S,os}} = \frac{\{>\text{MeOH}_2^+ \dots \text{L}^{n-}\}}{\{>\text{MeOH}\} a_{\text{H}^+} a_{\text{L}^{n-}}} \exp[-e(n\psi_\beta - \psi_0)/kT]$$

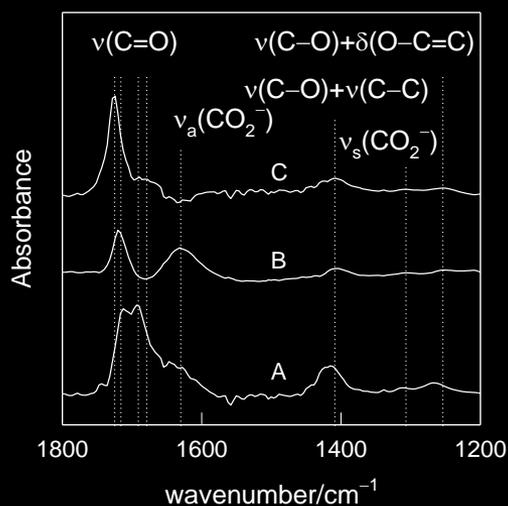
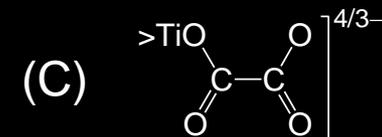
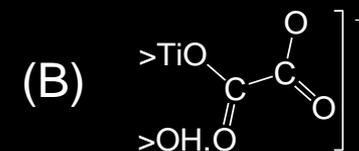
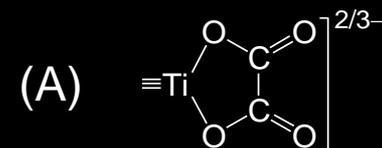
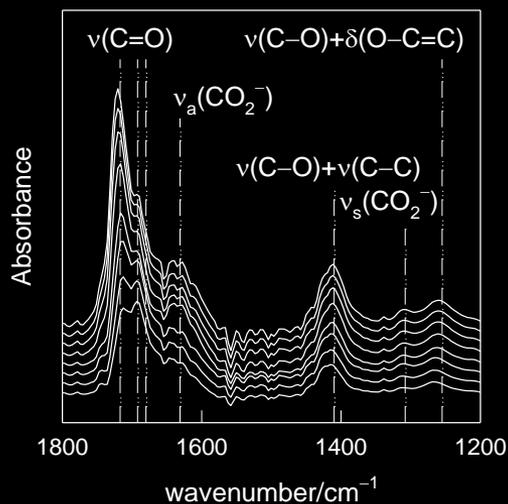
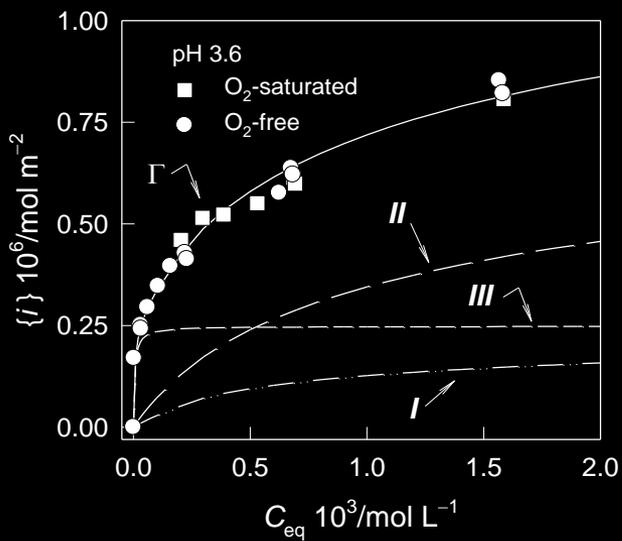
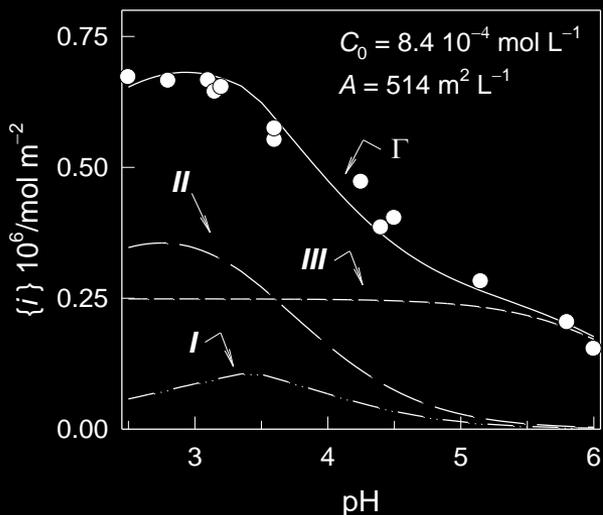
$$K_L^{\text{S,is}} = K_L^{\text{S,w}} K_L^{\text{S,os}} = \frac{\{>\text{MeL}^{(n-1)-}\}}{\{>\text{MeOH}\} a_{\text{H}^+} a_{\text{L}^{n-}}} \exp[-e(n-1)\psi_0/kT]$$

$$K_L^{\text{S,is}} = \exp[-(\mu_{\text{H}^+}^0 + \mu_{\text{L}^{n-}}^0 + \mu_{>\text{MeOH}}^0 - \mu_{>\text{MeL}^{(n-1)-}}^0)/kT]$$

Complejación en la Interfaz TiO_2 /Solución



Complejación en la Interfaz TiO_2 /Solución



La Carga Superficial



$$Q_{a1}^S = K_{a1}^S \exp(e\psi_0/kT) = \frac{\{>\text{MeOH}\}}{\{>\text{MeOH}_2^+\}} a_{\text{H}^+}$$

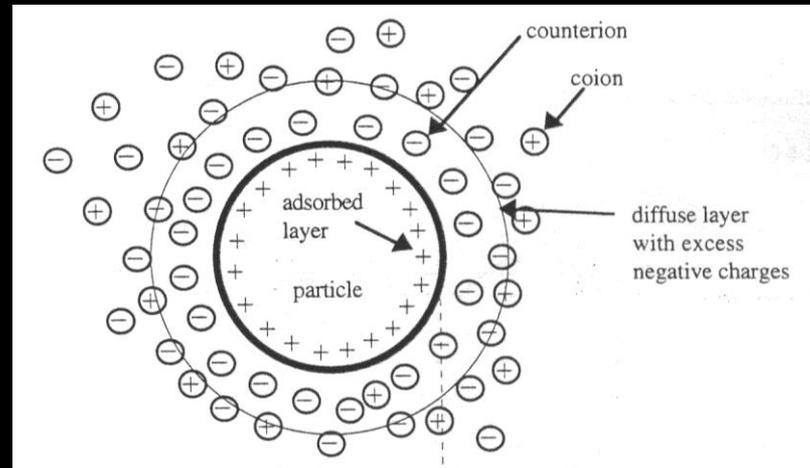
$$Q_{a2}^S = K_{a2}^S \exp(e\psi_0/kT) = \frac{\{>\text{MeO}^-\}}{\{>\text{MeOH}\}} a_{\text{H}^+}$$

$$\sigma_0 = F \left(\{>\text{MeOH}_2^+\} - \{>\text{MeO}^-\} \right)$$

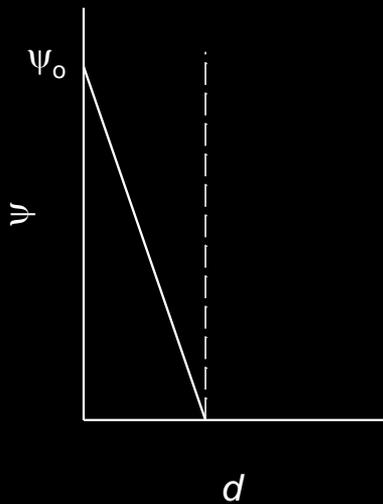
$$\psi_0 = \frac{2.3RT}{F} (\text{pH}_0 - \text{pH}) + \frac{2.3RT}{2F} \log \frac{\{>\text{MeO}^-\}}{\{>\text{MeOH}_2^+\}}$$

$$\text{pH}_0 = \frac{1}{2} (\text{p}K_{a1}^S + \text{p}K_{a2}^S)$$

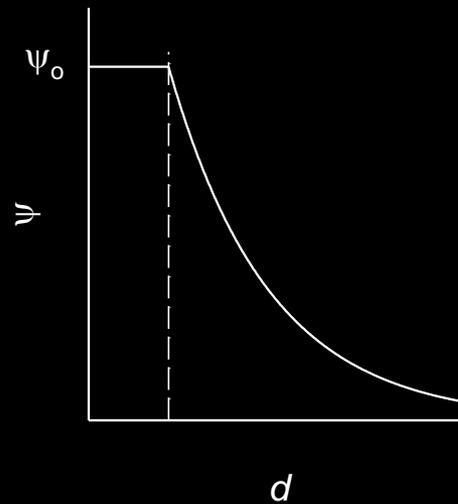
La Doble Capa Eléctrica



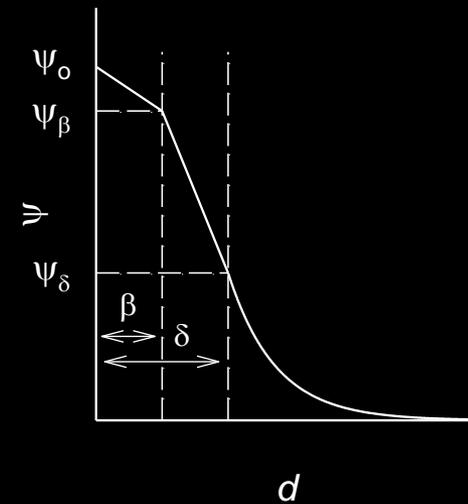
Capacidad Constante



Capa Difusa

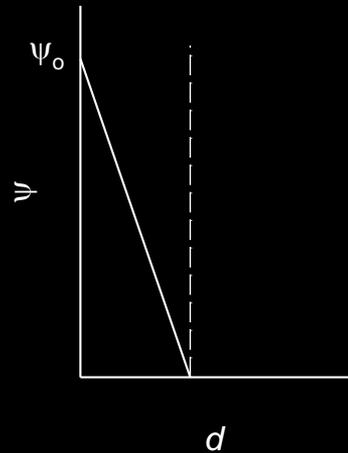


Triple Capa

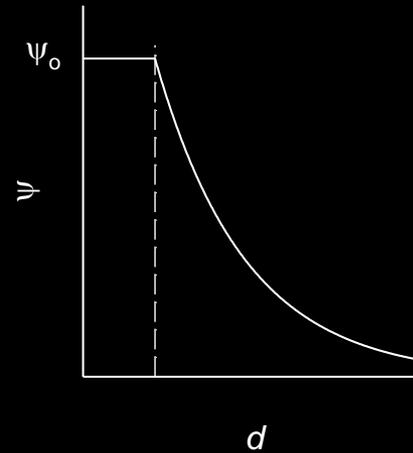


La Doble Capa Eléctrica

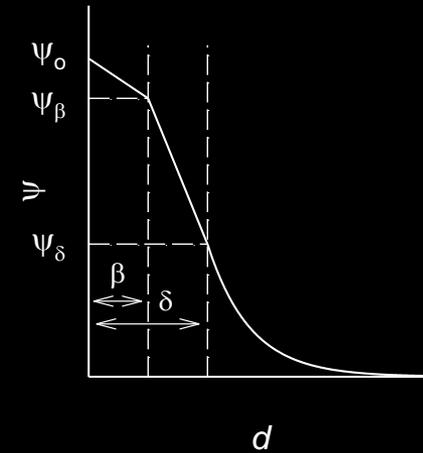
Capacidad Constante



Capa Difusa



Triple Capa



	CC	CD	GCSG (TC)
Electroneutralidad	$\sigma_0 = -\sigma_\beta$	$\sigma_0 = -\sigma_\delta$	$\sigma_0 = -(\sigma_\beta + \sigma_\delta)$
Relaciones carga-potencial	$\psi_0 = \sigma_0/C_1$		$\psi_0 - \psi_\beta = \sigma_0/C_1$ $\psi_\beta - \psi_\delta = -\sigma_\delta/C_2$ $\sigma_\beta = \sum \frac{z_i \sigma_{0,i} K_i c_i \exp(-z_i e \psi_\beta / kT)}{1 + K_i c_i \exp(-z_i e \psi_\beta / kT)}$ $\sigma_\beta = e[\{>MeOH_2^+ \dots Cl^-\} - \{>MeO^- \dots Na^+\}]$
		$\sigma_\delta = 11.74 I^{0.5} \sinh(-e\psi_\delta/kT)$	

La aproximación de Debye-Hückel: $z_i e \psi < kT$

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \rho(x) = \frac{d^2 \psi}{dx^2}$$

$$\rho = \sum z_i e n_i(x) = \sum z_i e n_{i0} \exp\left(-\frac{z_i e \psi}{kT}\right)$$

$$\rho = \sum z_i e n_{i0} \left(1 - \frac{z_i e \psi}{kT}\right) = -\sum \frac{z_i^2 e^2 n_{i0} \psi}{kT}$$

$$\frac{d^2 \psi}{dx^2} = \frac{4\pi e^2 \psi}{\epsilon kT} \sum z_i^2 n_{i0}$$

$$\kappa^2 = \frac{4\pi e^2 \sum z_i^2 n_{i0}}{\epsilon kT} = \frac{8\pi e^2 N_A I}{1000 \epsilon kT}$$

$$\frac{d^2 \psi}{dx^2} = \kappa^2 \psi$$

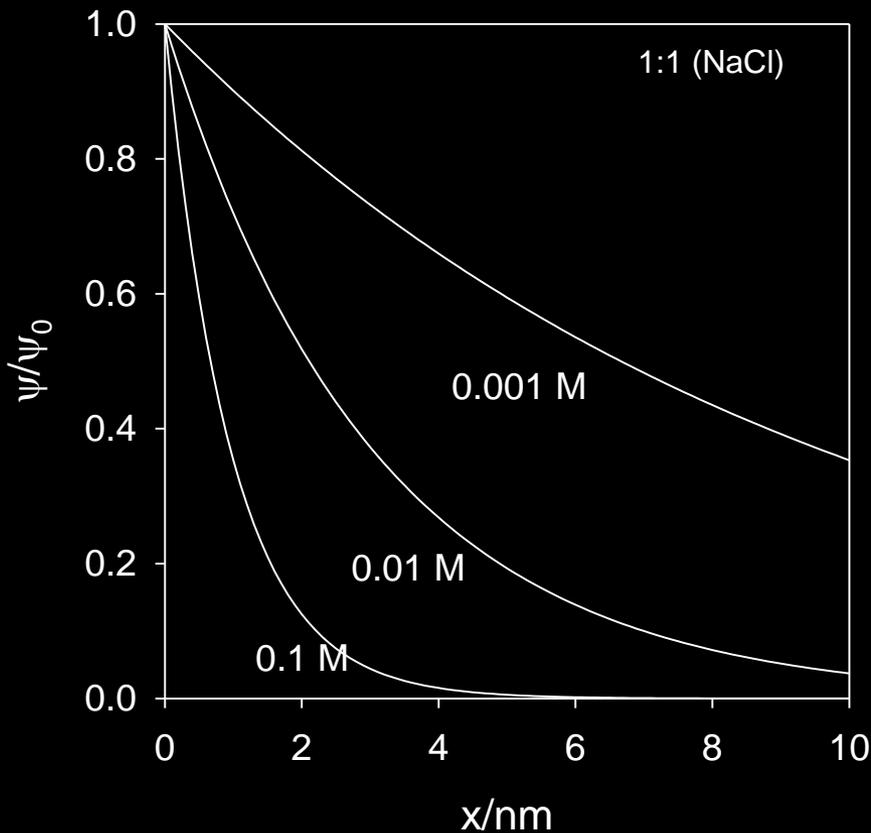
$$(d\psi/dx)_{x \rightarrow \infty} = 0$$

$$\psi_{x \rightarrow 0} = \psi_0 \quad \psi_{x \rightarrow \infty} = 0$$

$$\psi = \psi_0 \exp(-\kappa x)$$

La aproximación de Debye-Hückel: $z_i e \psi < kT$

$$\psi = \psi_0 \exp(-\kappa x) \quad \kappa = \left(\frac{8\pi e^2 N_A I}{1000 \epsilon kT} \right)^{1/2}$$



La carga:

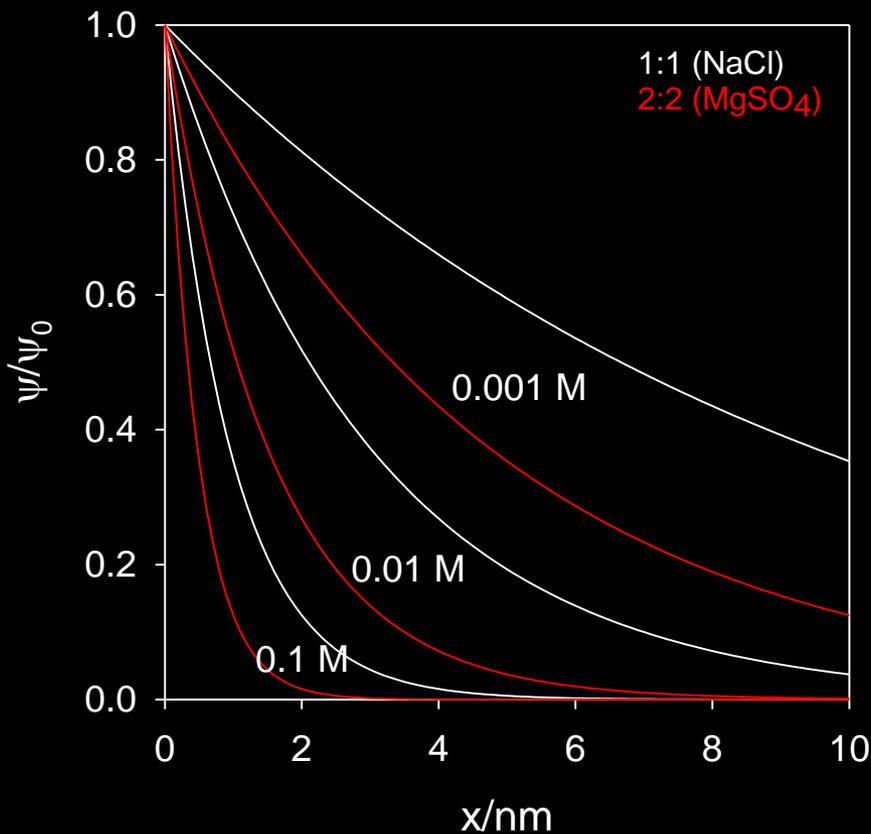
$$\sigma = \frac{\epsilon}{4\pi} \int_0^{\infty} (d^2\psi/dx^2) dx$$

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_0$$

$$\sigma = \frac{\epsilon}{4\pi} \kappa \psi_0$$

La aproximación de Debye-Hückel: $z_i e \psi < kT$

$$\psi = \psi_0 \exp(-\kappa x) \quad \kappa = \left(\frac{8\pi e^2 N_A I}{1000 \epsilon kT} \right)^{1/2}$$



La carga:

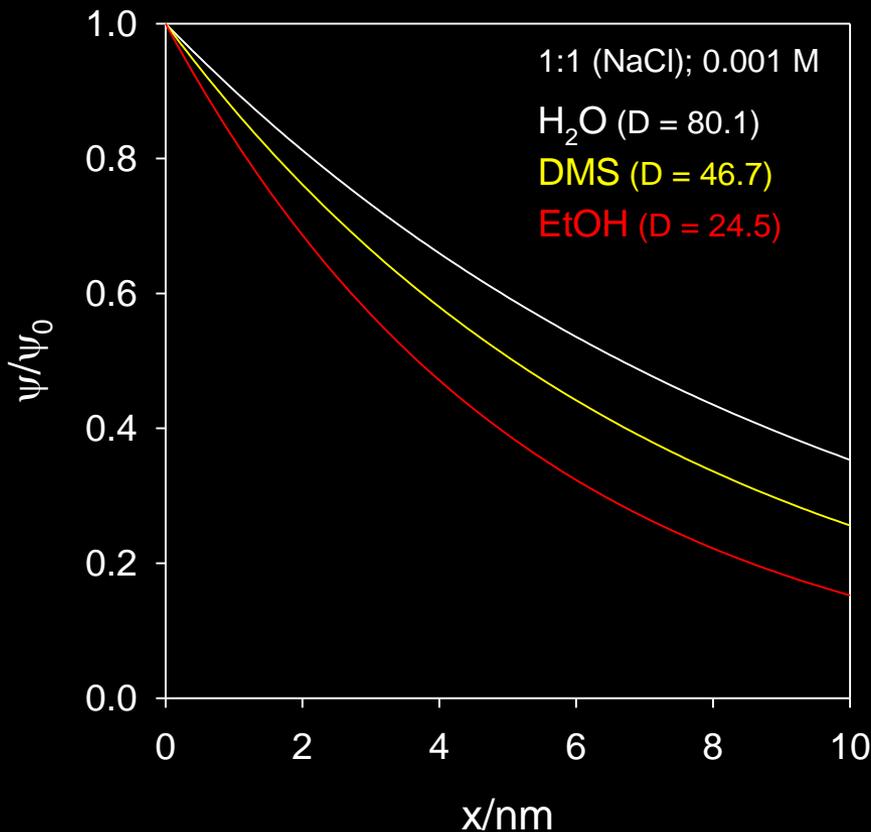
$$\sigma = \frac{\epsilon}{4\pi} \int_0^\infty (d^2\psi/dx^2) dx$$

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_0$$

$$\sigma = \frac{\epsilon}{4\pi} \kappa \psi_0$$

La aproximación de Debye-Hückel: $z_i e \psi < kT$

$$\psi = \psi_0 \exp(-\kappa x) \quad \kappa = \left(\frac{8\pi e^2 N_A I}{1000 \epsilon kT} \right)^{1/2}$$



La carga:

$$\sigma = \frac{\epsilon}{4\pi} \int_0^\infty (d^2\psi/dx^2) dx$$

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_0$$

$$\sigma = \frac{\epsilon}{4\pi} \kappa \psi_0$$

La aproximación de Gouy-Chapman

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \rho = \frac{d^2 \psi}{dx^2}$$

$$\rho = \sum z_i e n_i = \sum z_i e n_{i0} \exp\left(-\frac{z_i e \psi}{kT}\right)$$

La carga:

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx}\right)_0$$

$$\sigma = \frac{\epsilon}{4\pi} \left(\frac{8\pi kT n_0}{\epsilon}\right)^{1/2} \left[\exp\left(\frac{ze\psi_0}{2kT}\right) - \exp\left(-\frac{ze\psi_0}{2kT}\right) \right]$$

$$\gamma = \gamma_0 \exp(-\kappa x)$$

$$\gamma = \frac{\exp(ze\psi / 2kT) - 1}{\exp(ze\psi / 2kT) + 1}$$

si $\psi_0 \gg \psi$

$$\psi = \frac{4kT\gamma_0}{ze} \exp(-\kappa x)$$

si ψ_0 es grande, $\gamma_0 \rightarrow 1$

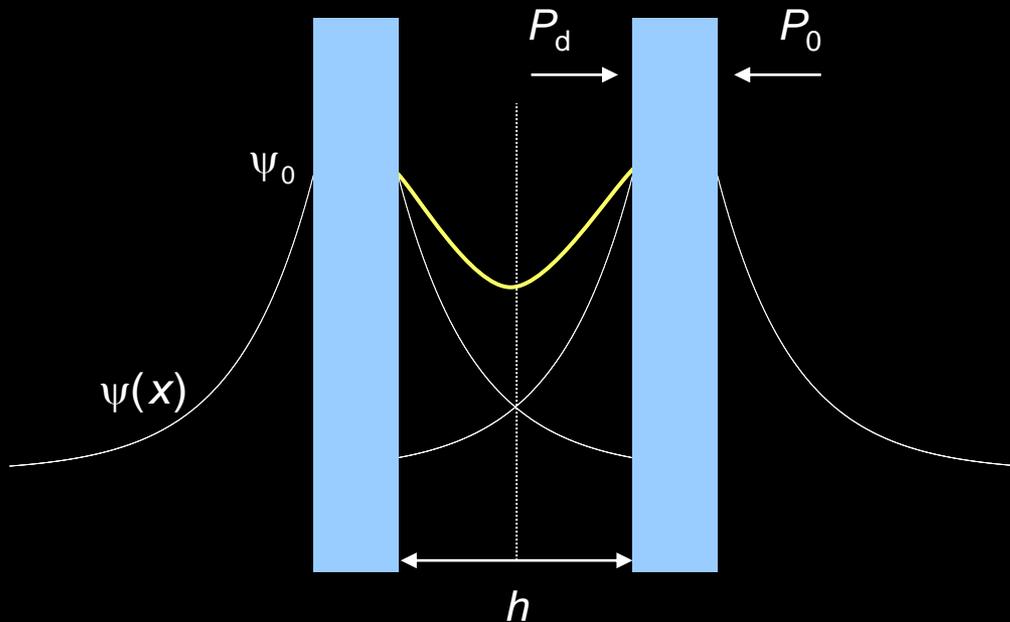
$$\psi = \frac{4kT}{ze} \exp(-\kappa x)$$

Interacciones Electroestáticas Partícula-Partícula

Solapamiento de las Doble Capas

$$F_x = \frac{dP}{dx} \quad F_{el} = \rho \frac{d\psi}{dx}$$

$$\frac{dP}{dx} + \rho \frac{d\psi}{dx} = 0$$



$$dP = -\rho d\psi$$

$$\rho = \sum z_i e n_{i0} \exp\left(-\frac{z_i e \psi}{kT}\right)$$

Para un electrolito z:z

$$dP = 2ze n_0 \sinh\left(\frac{ze\psi}{kT}\right) d\psi$$

$$F_R = P_d - P_0 = 2kTn_0 \left[\cosh\left(\frac{ze\psi_d}{kT}\right) - 1 \right]$$

Para h grande

$$F_R \approx 64kTn_0 \gamma_0^2 \exp(-h\kappa)$$

$$\phi_R = \frac{64kTn_0 \gamma_0^2}{\kappa} \exp(-h\kappa)$$

Fuerzas de Interacción

Responsables de la estabilidad de los soles

1. Dispersivas (London - van der Waals)
2. Electrostáticas (repulsivas o atractivas)
3. Estéricas (repulsivas)
4. Magnéticas

Interacción Partícula-Partícula

$$\phi = \phi_A + \phi_E$$

Interacción Partícula-Partícula

$$\phi = \phi_A + \phi_E$$

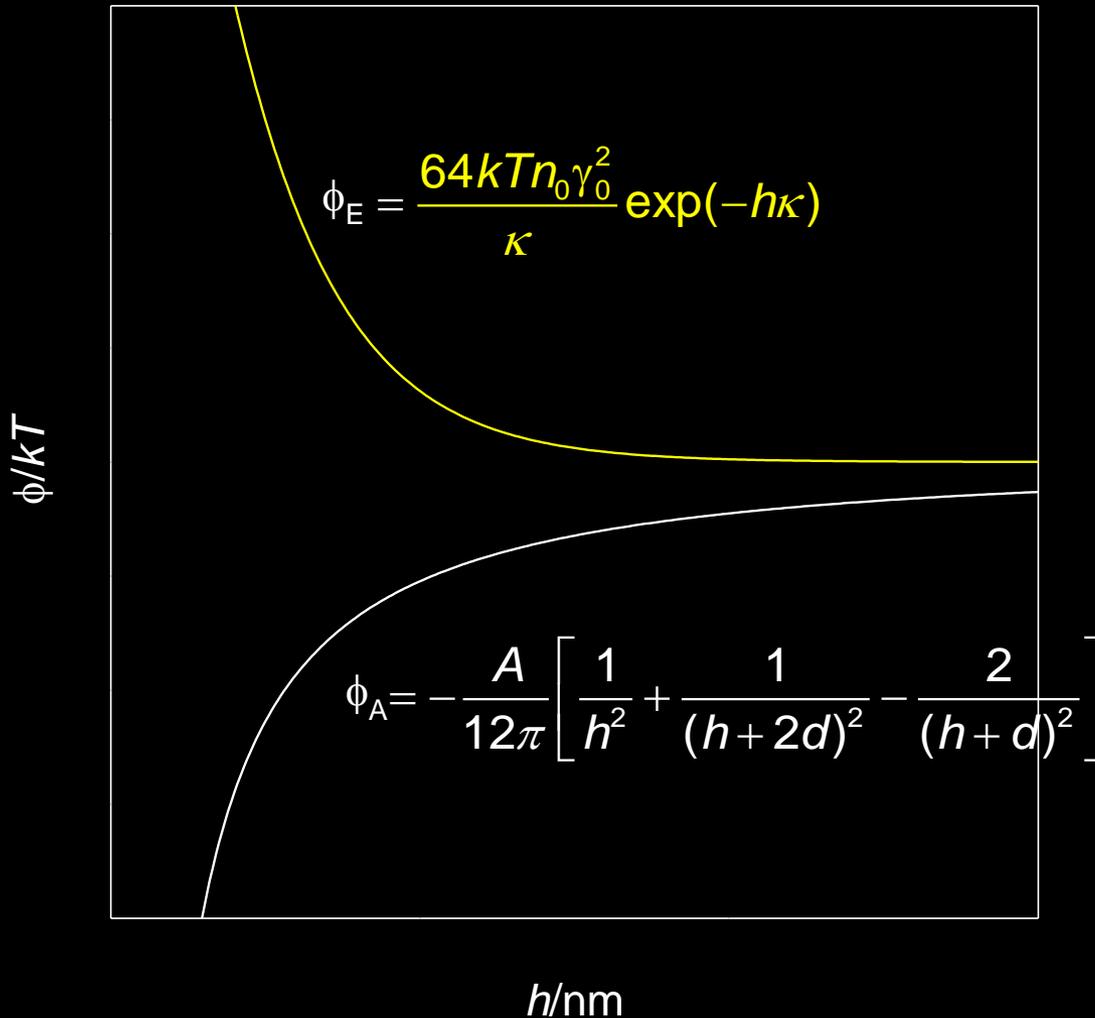
Para bloques de igual espesor

$$\phi = -\frac{A}{12\pi} \left[\frac{1}{h^2} + \frac{1}{(h+2d)^2} - \frac{2}{(h+d)^2} \right] + \frac{64kTn_0\gamma_0^2}{\kappa} \exp(-h\kappa)$$

Para esferas de igual radio

$$\phi = -\frac{A}{6} \left[\frac{2r^2}{h^2 + 4rh} + \frac{2r^2}{h^2 + 4rh + 4r^2} + \ln \left(\frac{h^2 + 4rh}{h^2 + 4rh + 4r^2} \right) \right] + \frac{64n_0kTr\gamma_0^2}{\kappa^2} \exp(-\kappa h)$$

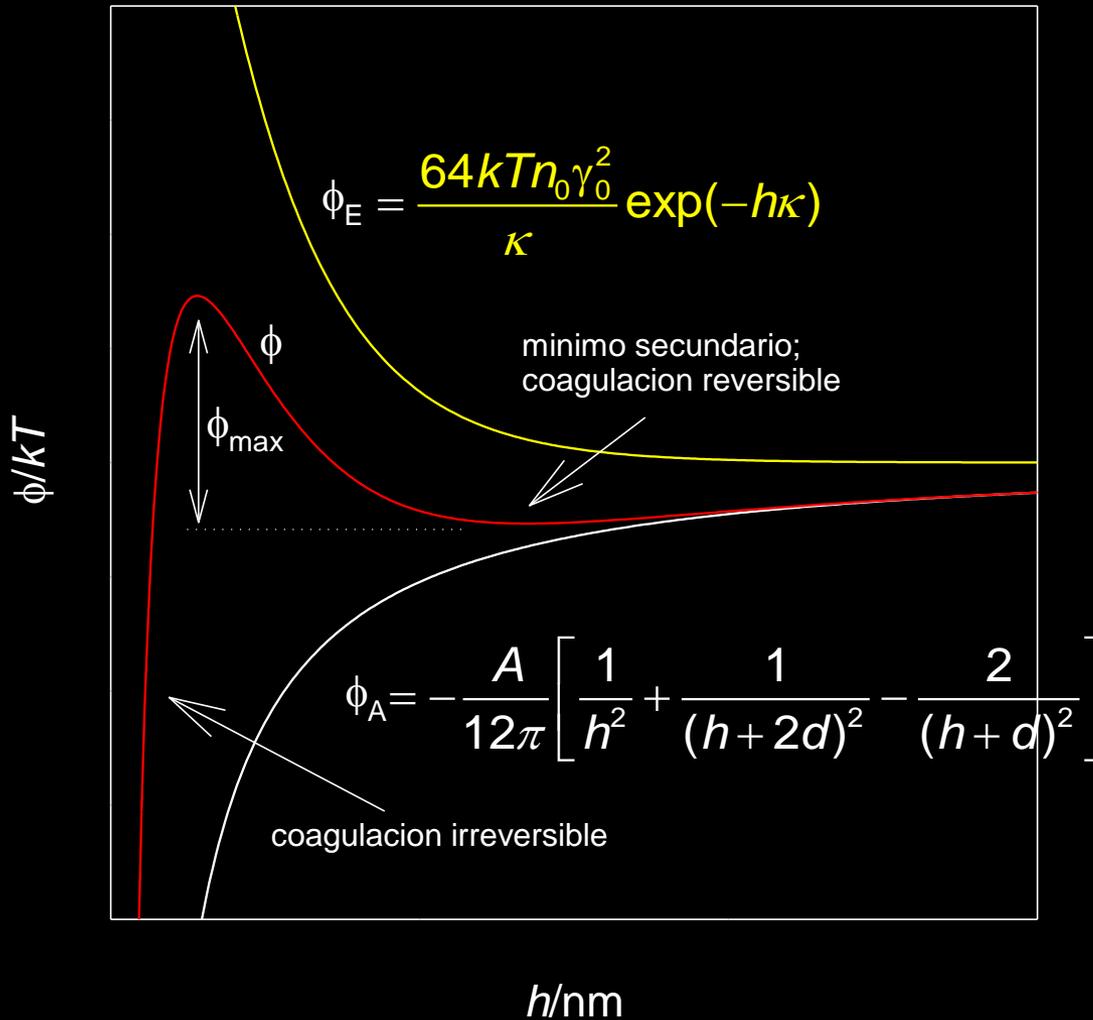
Interacción Partícula-Partícula: Cinética de coagulación



$$v = k_0 N^n \exp\left(-\frac{\phi_{\max}}{kT}\right)$$

$$k_0 \propto D(r, \eta)$$

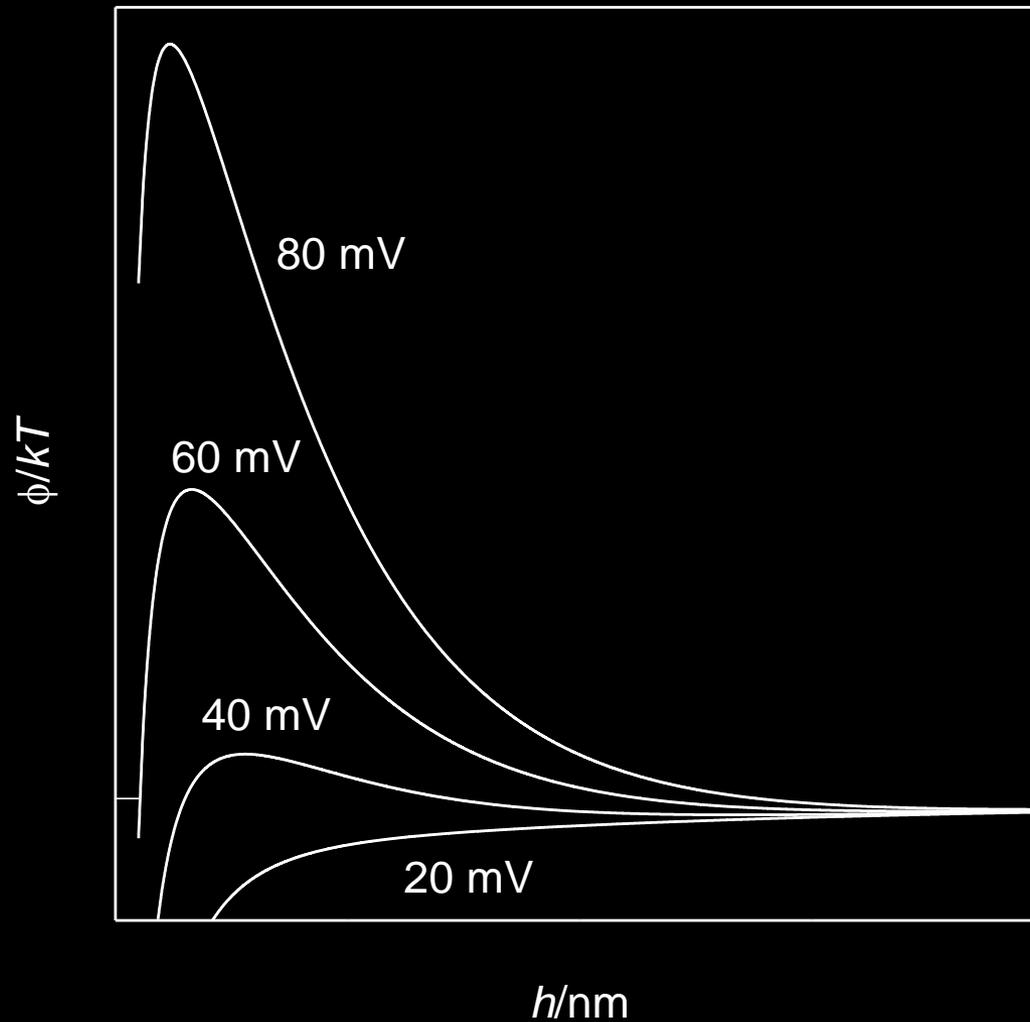
Interacción Partícula-Partícula: Cinética de coagulación



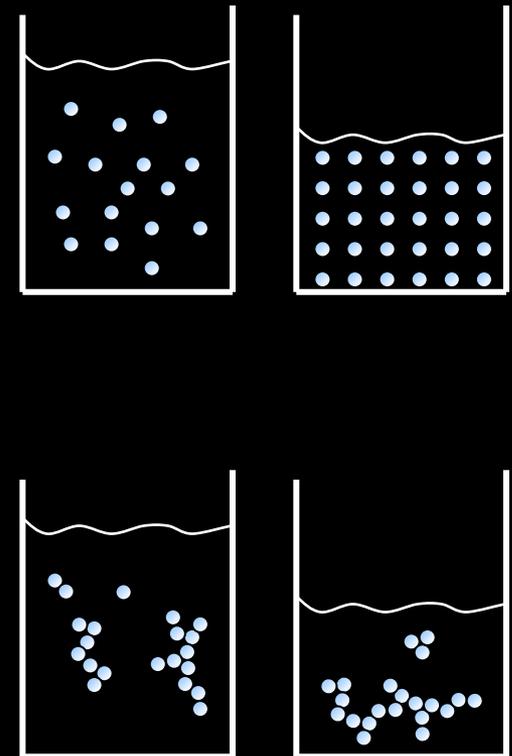
$$v = k_0 N^n \exp\left(-\frac{\Phi_{max}}{kT}\right)$$

$$k_0 \propto D(r, \eta)$$

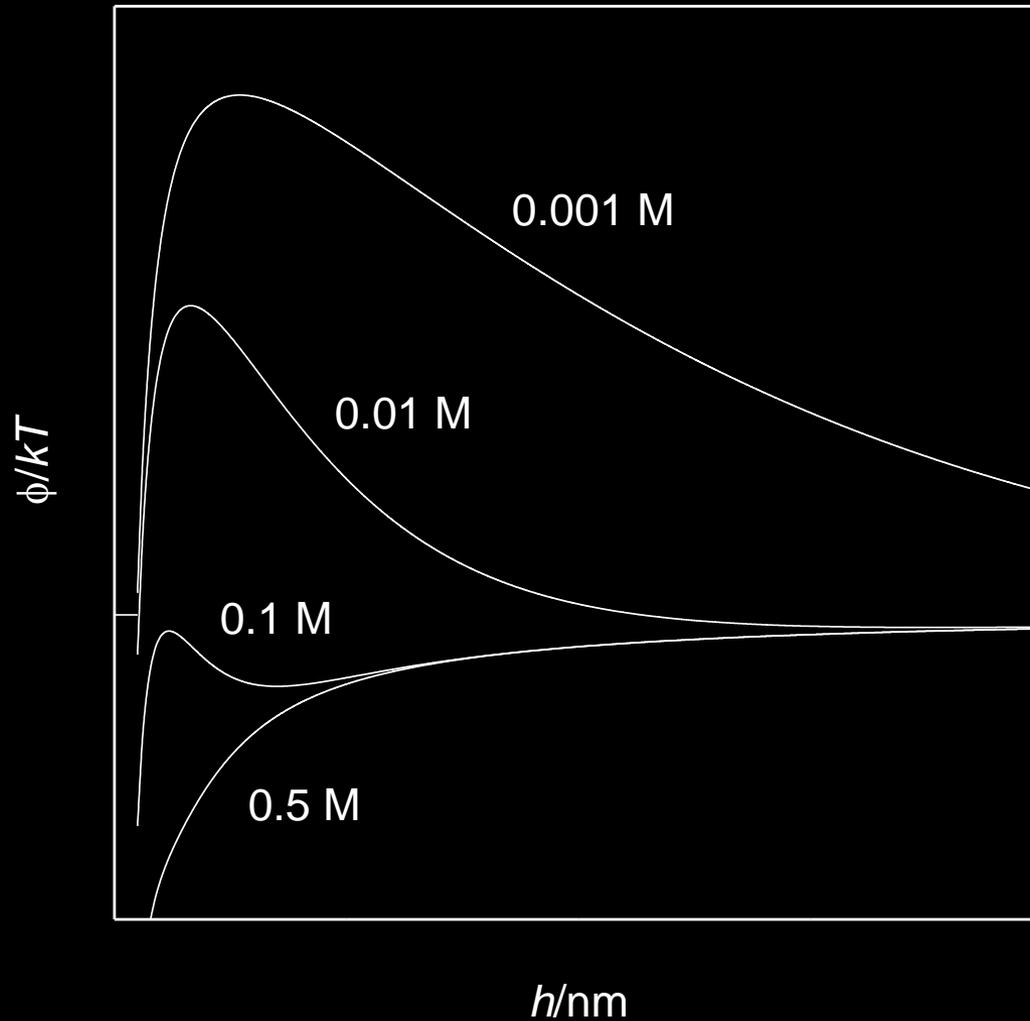
Interacción Partícula-Partícula: Efecto del Potencial Superficial



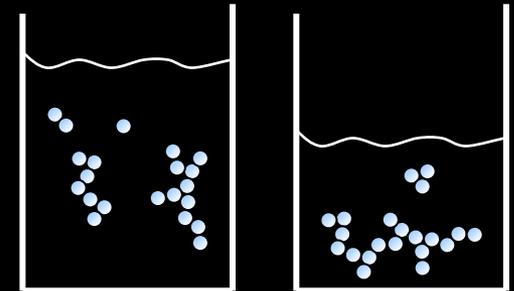
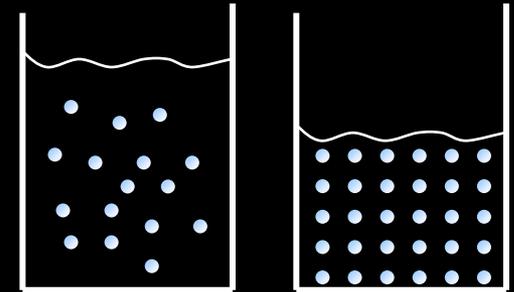
$$\phi_E = \frac{64kTn_0\gamma_0^2}{\kappa} \exp(-h\kappa)$$



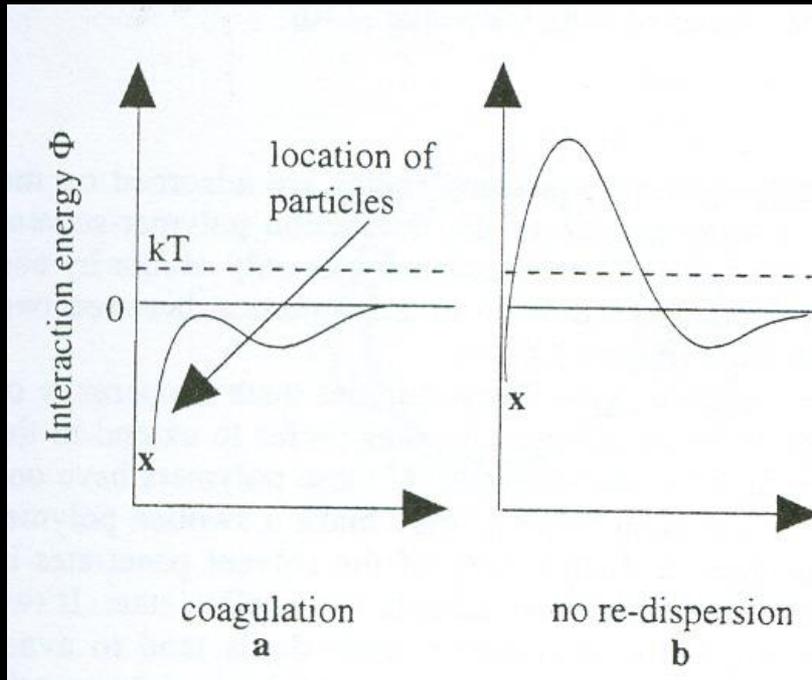
Interacción Partícula-Partícula: Efecto de la Fuerza Iónica



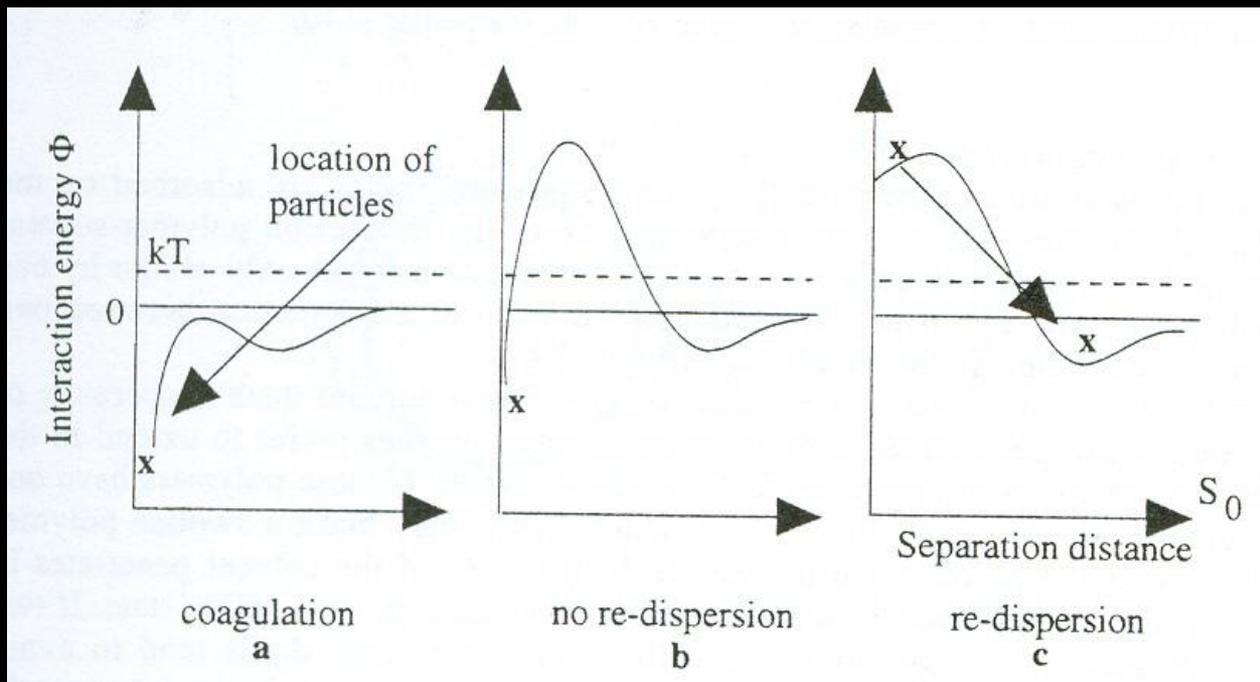
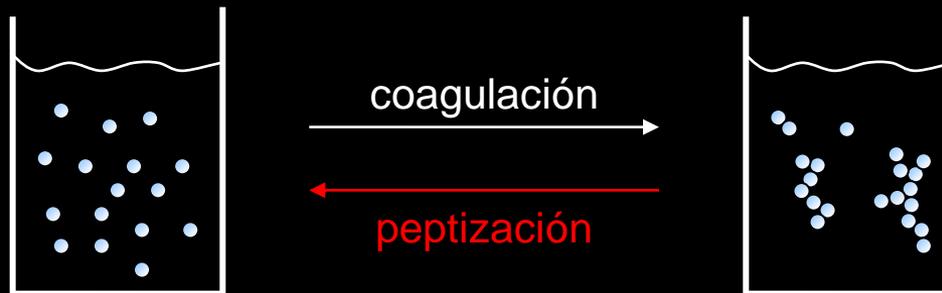
$$\phi_E = \frac{64kTn_0\gamma_0^2}{\kappa} \exp(-h\kappa)$$



Evitando las Interacciones: Peptización

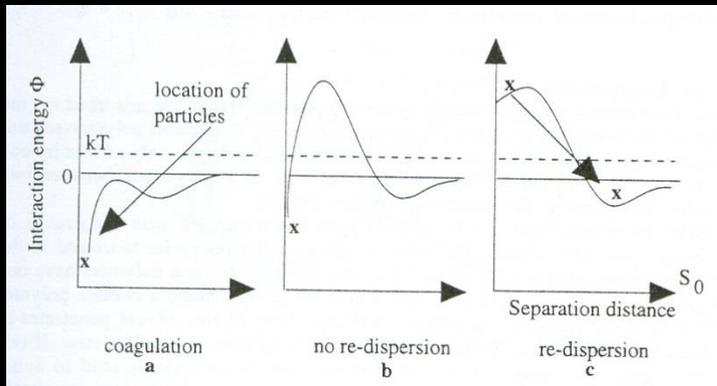
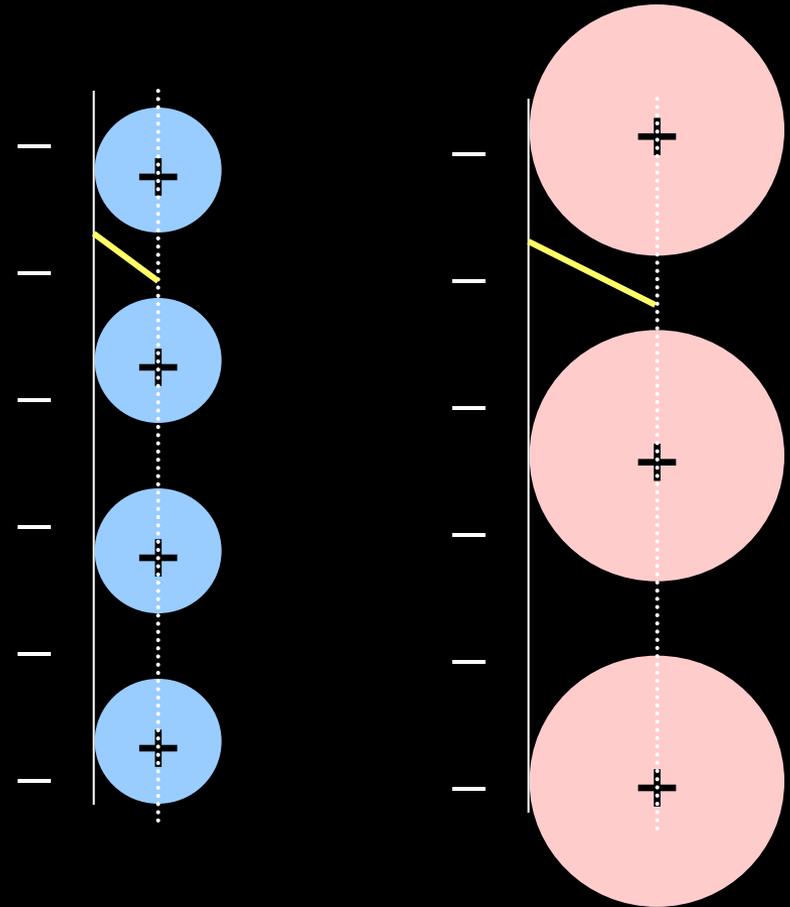
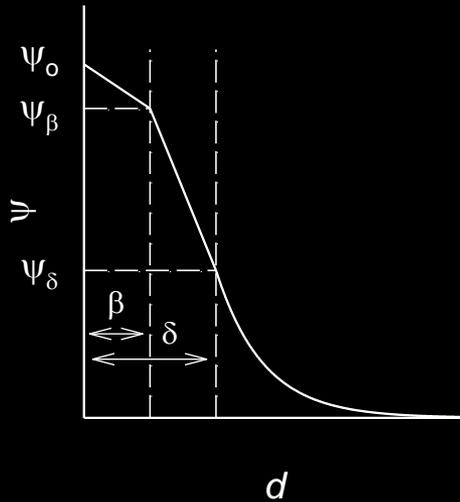


Evitando las Interacciones: Peptización



Peptización

Triple Capa

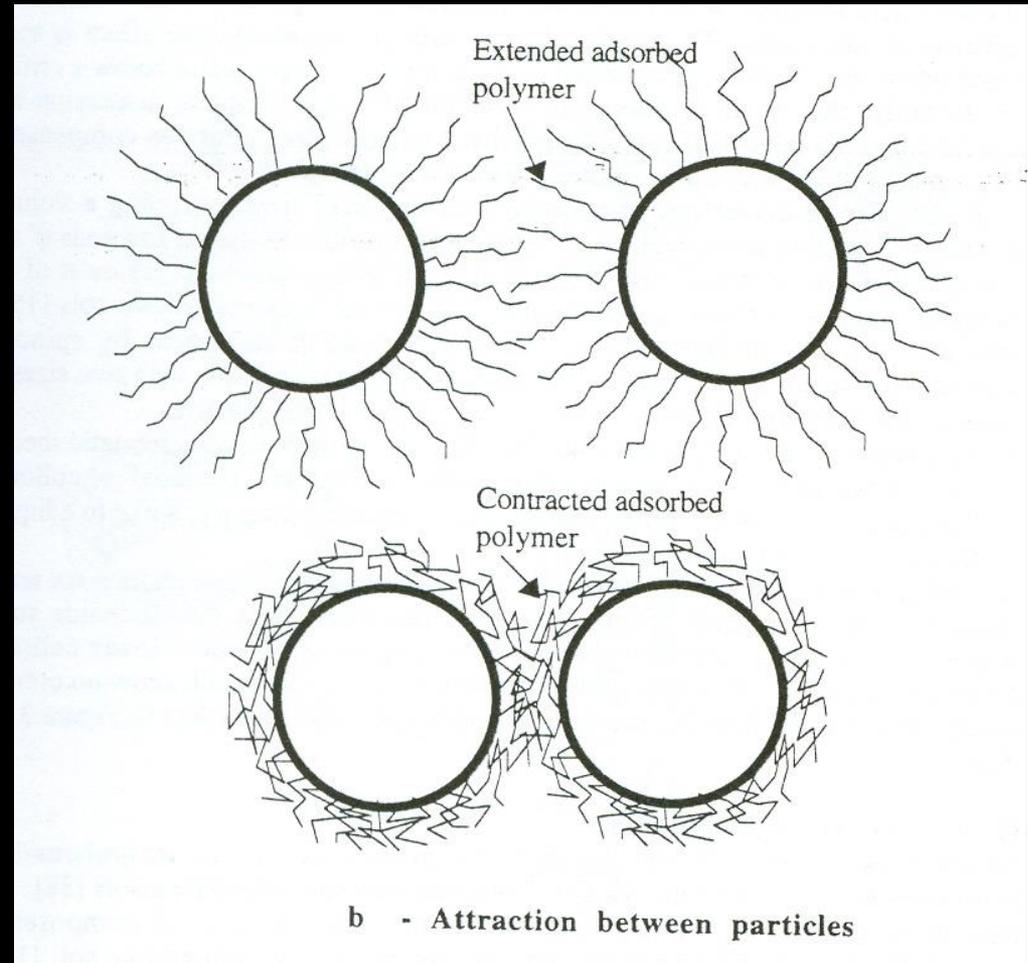
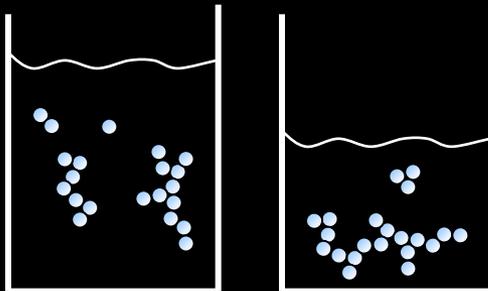
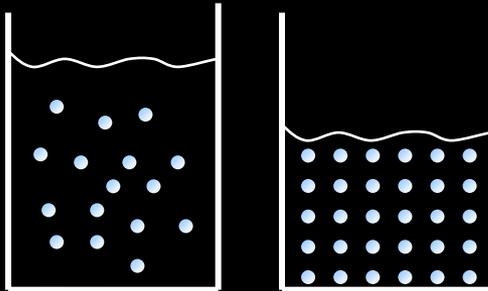


Fuerzas de Interacción

Responsables de la estabilidad de los soles

1. Dispersivas (London - van der Waals)
2. Electrostáticas (repulsivas o atractivas)
3. Estéricas (repulsivas)
4. Magnéticas

Estabilización Estérica: Adsorción de Polímeros



Teniendo en cuenta estas ideas...

