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Cours de chimie séparative



instn

2009-2010



*Pression osmotique de systèmes séparatifs
ou à reconnaissance ionique*

Ions libres, ions liés physiquement, ions liés « chimiquement »

La géométrie plane cristalline permet d'interpréter les pressions

Co-extraire de l'eau et sélectivement des sels chaotropes sans complexation

Les équations d'état permet de remonter à l'énergie libre associée à l'extraction

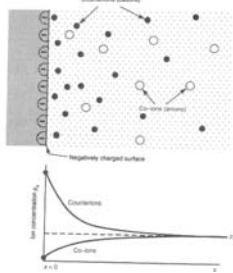
Cela fonctionne aussi avec des lipides chargés

Cours n°3



Ions près d'UNE surface

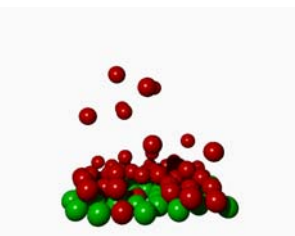
Modélisation
Poisson-Boltzmann



Cf. J. Israelachvili « Intermolecular forces » page 232



*« Reconnaissance » par complexation partielle :
interface active*



$$K_s = \frac{[COO^-]_s}{[COOH]_s} [H^+]_s$$

$$K_s = \frac{\sum_{eff}}{\sum_{ar} - \sum_{eff}} [H^+] e^{-U_s/kT}$$

$$2 \operatorname{sh} \left(\frac{U_s}{2kT} \right) = 4 \cdot \pi \cdot L_b \cdot \Sigma_{eff}$$

$$K_{app} = K_s \cdot e^{-U_s/kT} \quad K_s = \frac{\Sigma_0}{\delta} \cdot e^{-\Delta G_y/RT}$$

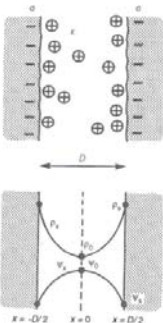
Régulation de charges Ninham-Parsegian 1973

Cf Cours de Jean-François Dufrêche et Ecoles d'été 2008 et 2010



En pratique, les ions sont entre DEUX interfaces

Modélisation
Poisson-Boltzmann

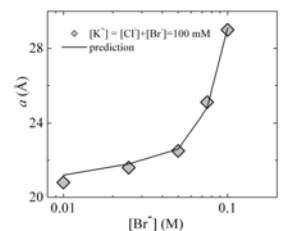
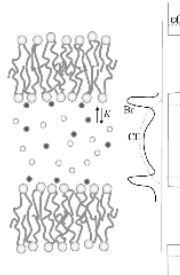


Extension au cas de deux surfaces: théorème du plan médian

$$\Pi = p_{median} kT$$



Mesure de $DG(Cl^-, Br^-) = 2kT$?



H. I. Petrache et al., PNAS (2006), 103(21), 7982-7987.

Micelles of dodecyl phosphocholine (DPC)

CCCCCCCCCCCCOP(=O)(O)N(C)C

7

gonflement de liposomes en présence de sels ?

E. Leontidis et al., Biophysical J. 2007

8

Gonflement de liposomes en équilibre avec de l'eau par du sel !

La manip
d'extraction
liquide-gel
la plus simple

Incompatible avec théorie des solutions régulières ou DLVO

9

Une extraction qui diminue avec la température ?

Et de plus, sélective chlore-brome sur 7 nm ?

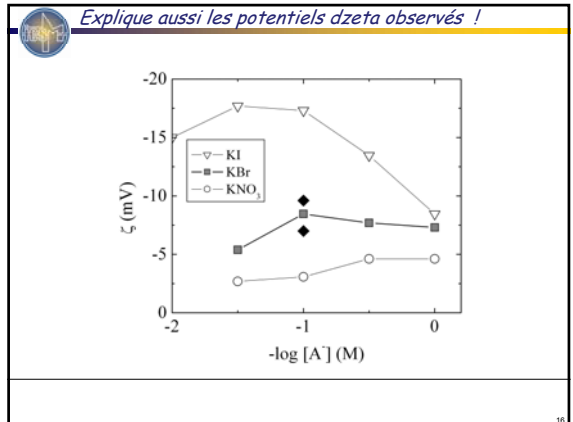
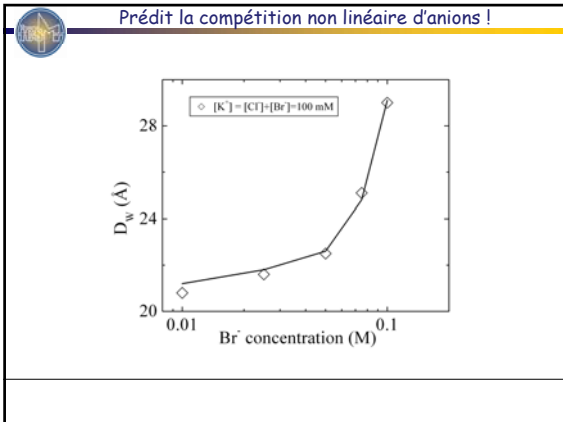
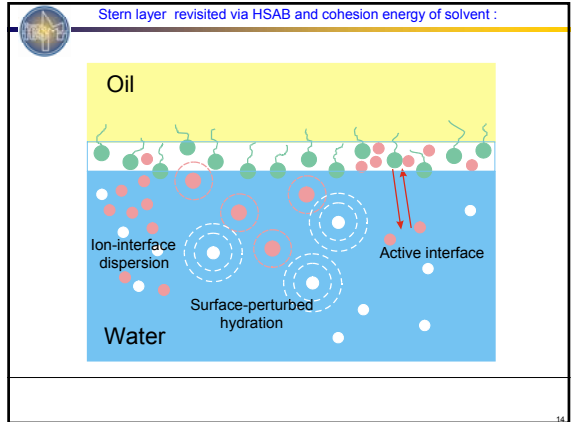
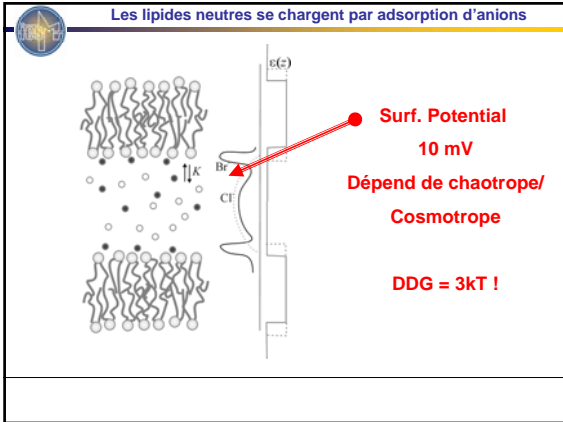
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L'équation d'état perpendiculaire est modifiée par le sel

11

L'interaction de van der Waals est écrantée par le sel

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Rappel : Hofmeister , lyotropic, ion-specific, chaotropes-cosmotropes, dispersion, « faibles »

CATIONS
Ca²⁺, Mg²⁺, Li⁺, Cs⁺, Na⁺, K⁺, NH₄⁺, (CH₃)₂NH₂⁺, (CH₃)₄N⁺

ANIONS
SO₄²⁻, HPO₄⁻, OH⁻, F⁻, HCOO⁻, CH₃COO⁻, Cl⁻, Br⁻, NO₃⁻, I⁻, SCN⁻, ClO₄⁻

<p>COSMOTROPIC ANIONS</p> <ul style="list-style-type: none"> Known as salting-out or water-structure makers Small - small polarizabilities Hydrophilic 	<p>CHAOTROPIC ANIONS</p> <ul style="list-style-type: none"> Known as salting-in or water-structure breakers Large - large polarizabilities Hydrophobic
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Stern layer revisited via HSAB and cohesion energy of solvent :

- Act indirectly through some modification of the water structure - Affect hydrogen bonds
 - Primary solvation shell
 - Secondary solvation
 - Disorder region
 - Bulk water

Collins and Washabaugh QRB, 18, 323, 1985
Chaplin Biophys. Chem., 83, 211, 1999
- Existence of a dispersion force between the anions and the interface
 - Air
 - Water

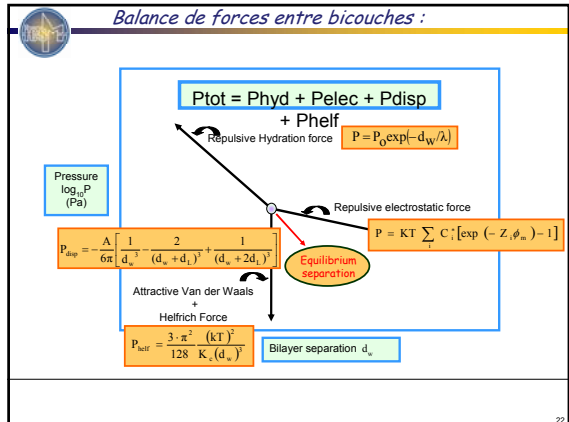
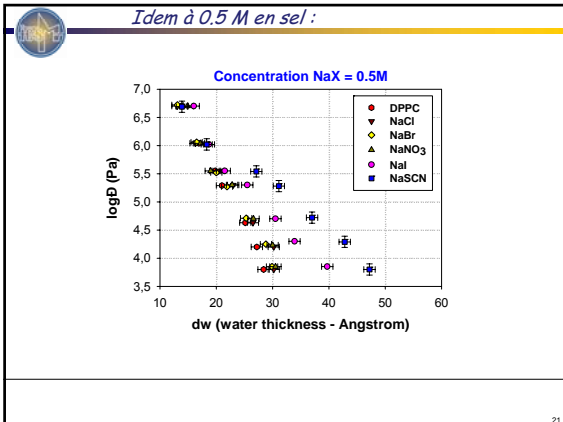
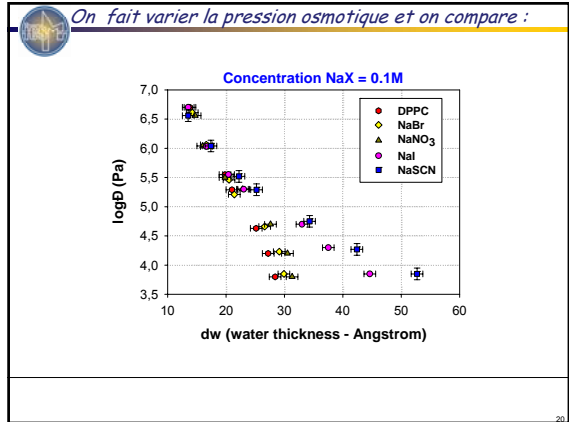
Ninham and Yaminsky Langmuir, 13, 2097, 1997
Boström et al., Langmuir, 17, 4475, 2001
- Expulsion of larger ions from bulk in the presence of a lipid interface by liberating water molecules
 - Air
 - Water

Karlström et al., J. Phys. Chem. 106, 11585, 2002
Hribar et al., JACS 124, 12302, 2002
Jungwirth, Leontidis, Netz

On fait l'expérience à pression osmotique imposée

Polymère stressant + Solution saline
Lipide en poudre

- ✓ POLYMER → PEG 20000
- ✓ LIPIDE → DPPC
- ✓ SELS → NaX, X = Cl⁻, Br⁻, NO₃⁻, I⁻, SCN⁻
- ✓ T = 50 ± 1 °C



Equation d'état perpendiculaire :

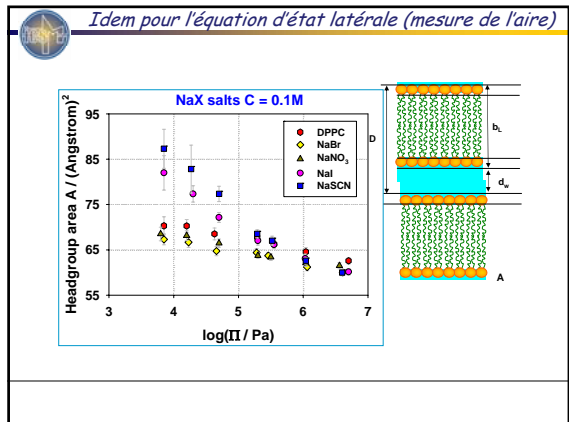
$$\Pi_{tot} = \Pi_{hydr} + \Pi_{und} + \Pi_{vdw} + \Pi_{ele}$$

- $\Pi_{hydr} = P_0 \exp(-d_w/\lambda)$

P_0 = hydration coefficient
 λ = characteristic decay length
- $\Pi_{und} = \frac{3\pi^2 (k_B T)^2}{128 \kappa_c} \frac{1}{(d_w)^3}$

κ_c = bending rigidity
- $\Pi_{vdw} = -\frac{H}{6\pi} \left[\frac{1}{(d_w)^3} + \frac{1}{(d_w+2b_l)^3} - \frac{2}{(d_w+b_l)^3} \right]$

H = Hamaker constant
D = lamellar repeat distance
 b_l = bilayer thickness
 d_w = water bilayer separation



Idem pour l'équation d'état latérale :

$$\Delta F(A) = \Delta F_{LW} + \Delta F_{\text{head-rep}} + \Delta F_{\text{vdw}} + \Delta F_{\text{elec}}$$

- $\Delta F_{LW} = \gamma(A - A_0)$
- $\Delta F_{LW} = \gamma[A - (A_0 - f_1 \Delta A)]$
- $\Delta F_{\text{head-rep}} = \frac{B(\mu_w)}{A - A_0}$
- $\Delta F_{\text{vdw}} = \frac{HN_{AV}\Delta}{12\pi} \left[\frac{1}{(d_w)^2} + \frac{1}{(d_w + 2b_c)^2} + \frac{2}{(d_w + b_c)^2} \right]$

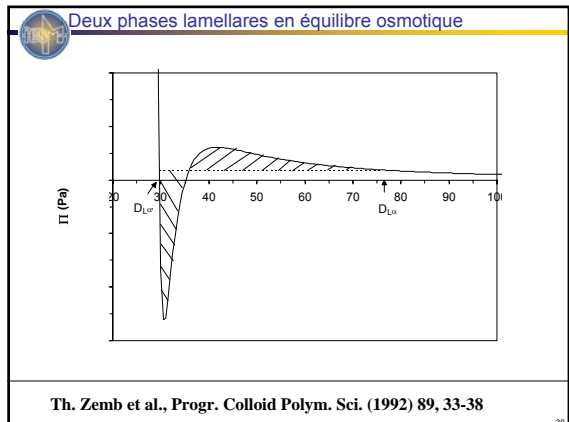
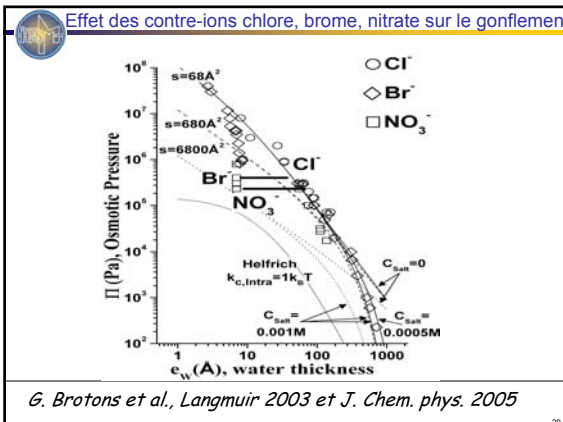
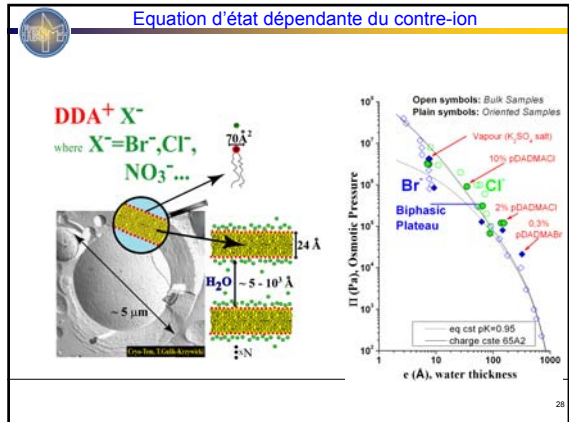
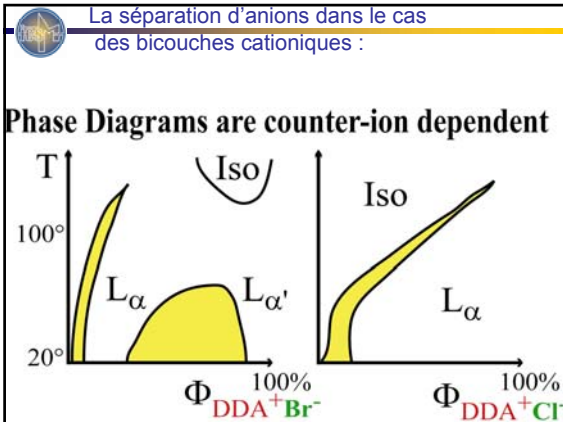
γ = interfacial tension of lipid/water interface
 A_0 = incompressible headgroup area of a lipid molecule
 f_1 = degree of counterion binding
 ΔA = ionic headgroup area of the lipid molecule
 $B(\mu_w)$ = constant
 H = Hamaker constant
 D = lamellar repeat distance
 b_c = bilayer thickness
 d_w = water bilayer separation

Calibration de la balance de forces :

Parameters	DPPC in water
H - Hamaker constant (kT)	1.0 ± 0.2
P ₀ - Hydration coefficient (Pa)	10 ^{9.95}
λ - hydration decay length (Å)	2.55 ± 0.05
K _c - bending rigidity (kT)	9 to 30

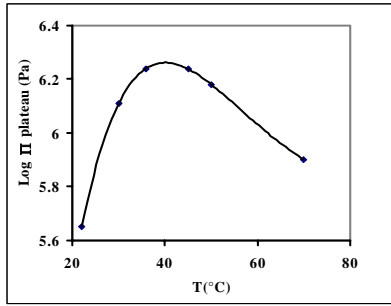
Energie libres associées à l'adsorption d'un anion (Cl⁻ = 0)

Concentration C / M	I. Potential U _B / kT	I. Potential U _{NO3} / kT	I. Potential U _i / kT	I. Potential U _{SKN} / kT
0.05	----	----	-1.70 ± 0.05	-3.00 ± 0.05
0.1	-0.26 ± 0.3	-0.8 ± 0.2	-2.2 ± 0.05	-3.20 ± 0.05
0.5	-0.93 ± 0.5	-1.5 ± 0.5	-6.00 ± 0.2	-7.00 ± 0.05





Plateau de pression : manifestation de la protrusion ?



M. Dubois, N. Fuller, R. P. Rand, Th. Zemb and V. A. Parsegian
« Equation of state of a charged bilayer system », J. Chem. Phys. (1998) 108, 7855