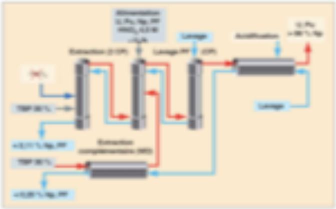
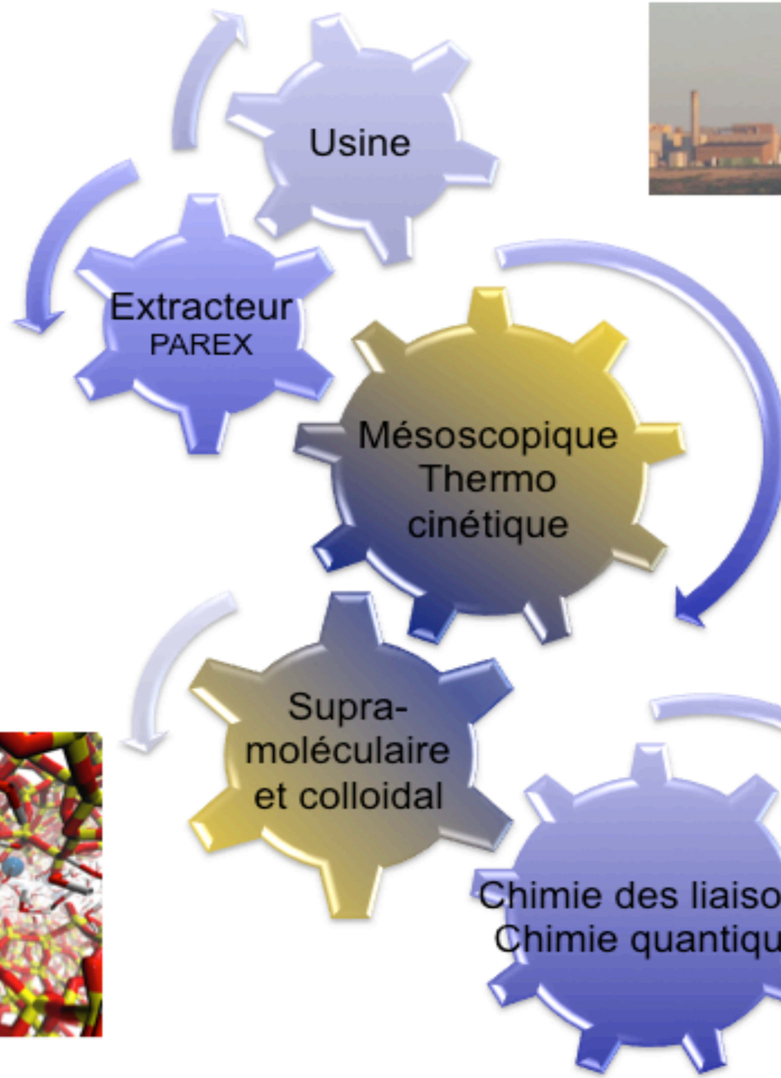
Thomas Zemb

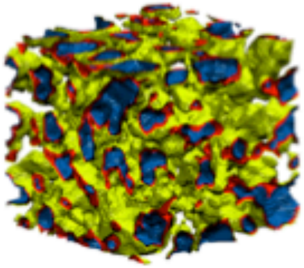
lecture n°10: The chemical potential step as molecular driving force - Thomas Zemb

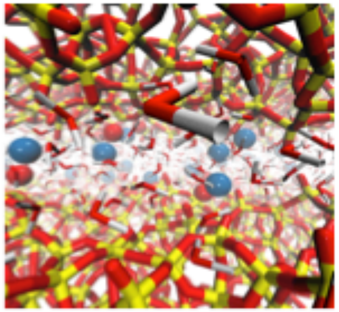
2014-2015

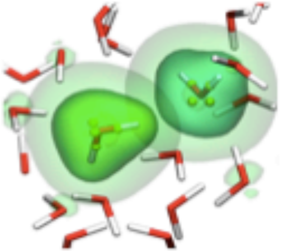
An intrinsic multi-scale approach :







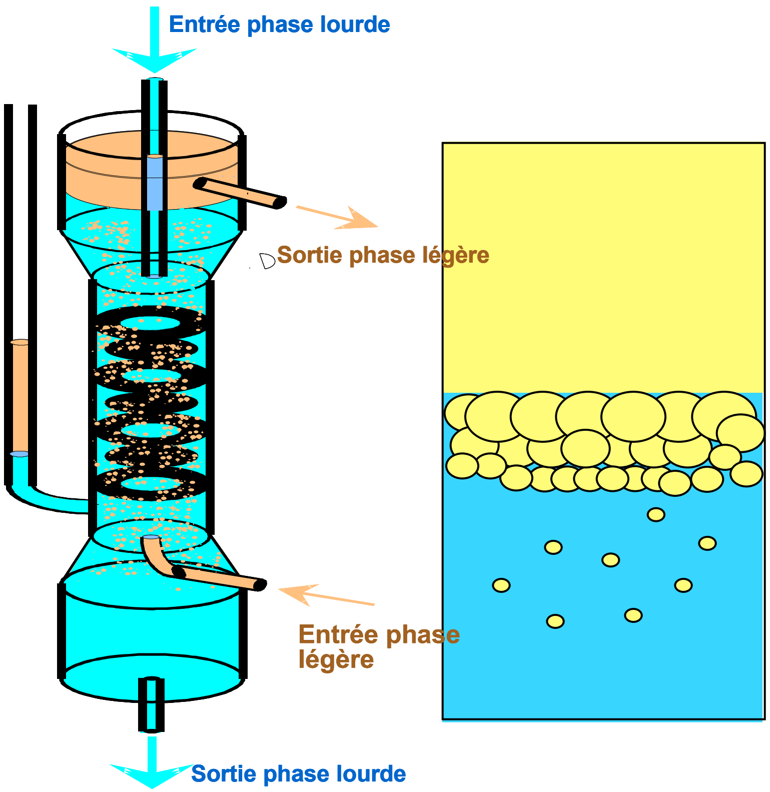


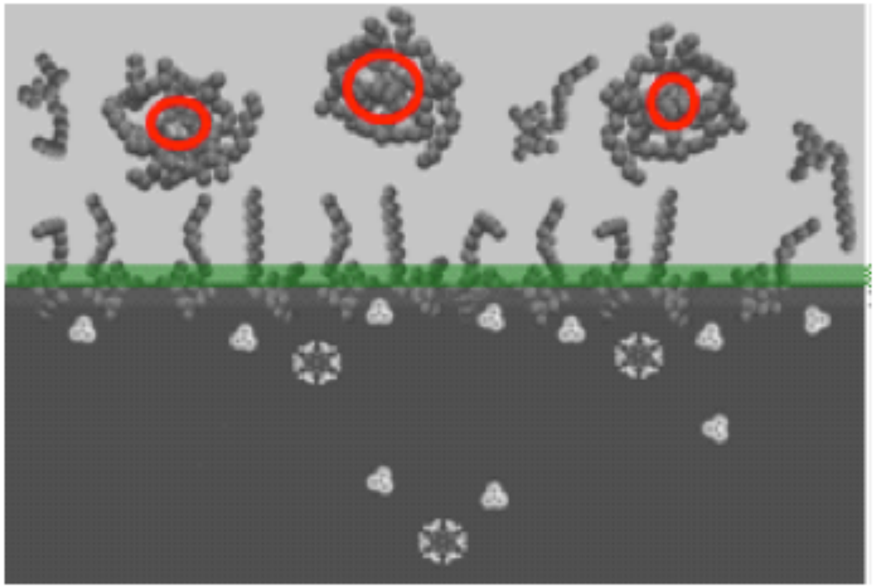


Content

- **Going down to meso-scale („nano“)**
- Locating w-rich and O-rich in the phase diagramm
- Mapping the three-phase accident
- The chemical potential level representation
- The driving force for phase transfer and selectivity
- Decomposing the chemical potential step in:
  - Complexation (frist neighbour)
  - „Bulk“ terms
  - Curvature, dispersion, entropic terms

go … Magnification * 10.000.000



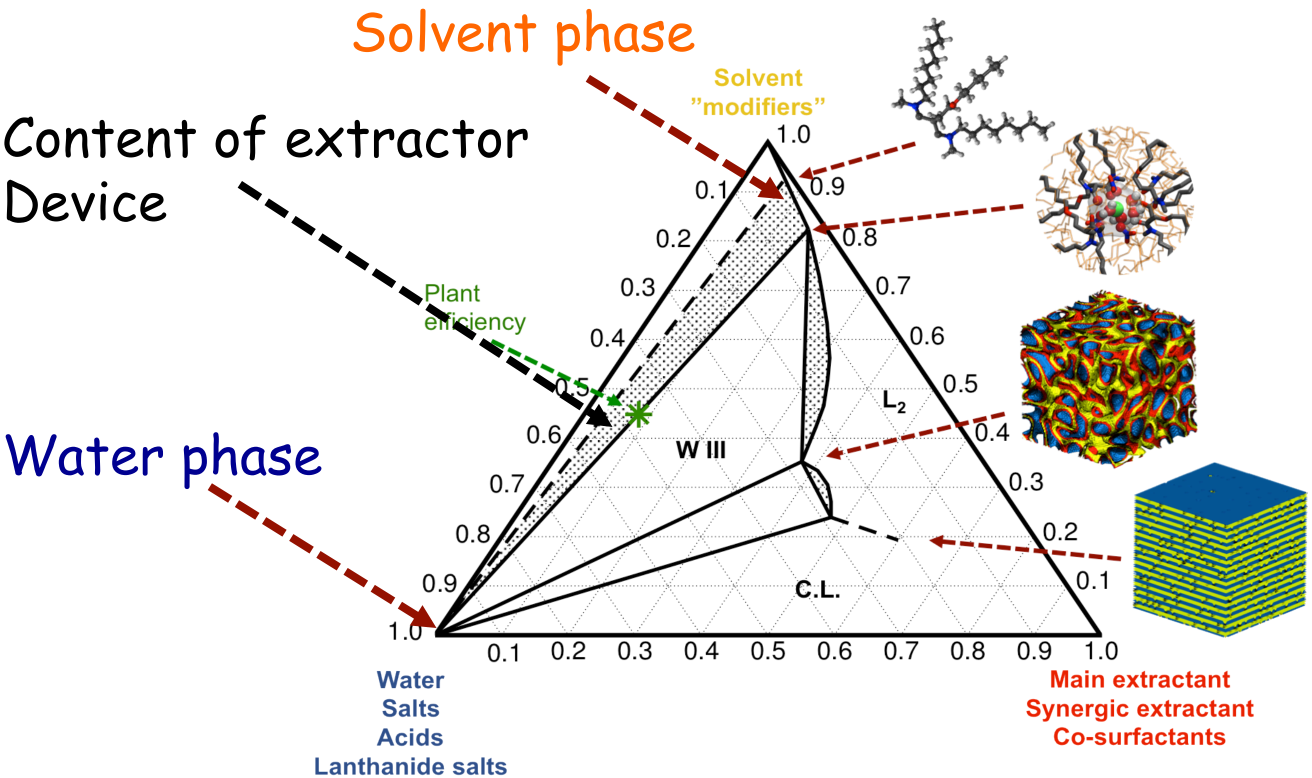


« Green » interface : Σ of macroscopic contact

« Red» interface in : extraction as an adsorption isotherm

Zemb T, Bauer C, Bauduin P, Belloni L, Déjugnat C, Diat O, et al. Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienaics." Colloid & Polymer Sci 2015:1–22.

Fluid in pulsed columns are at a given pint of phase duagram

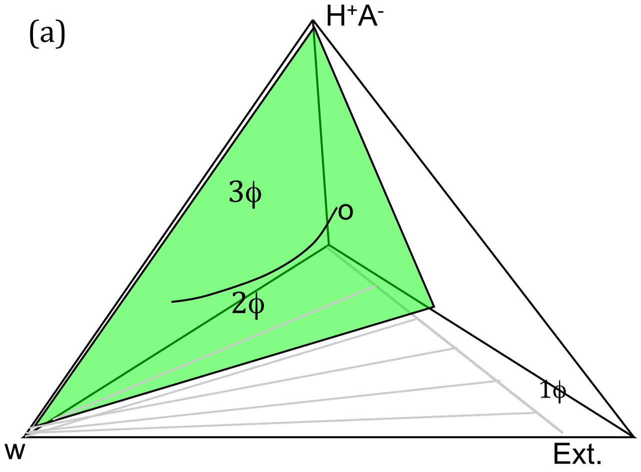


- *Y. Chevalier et Th. Z. Reports in Progress in Physics (1991)*

Distribution coeff.

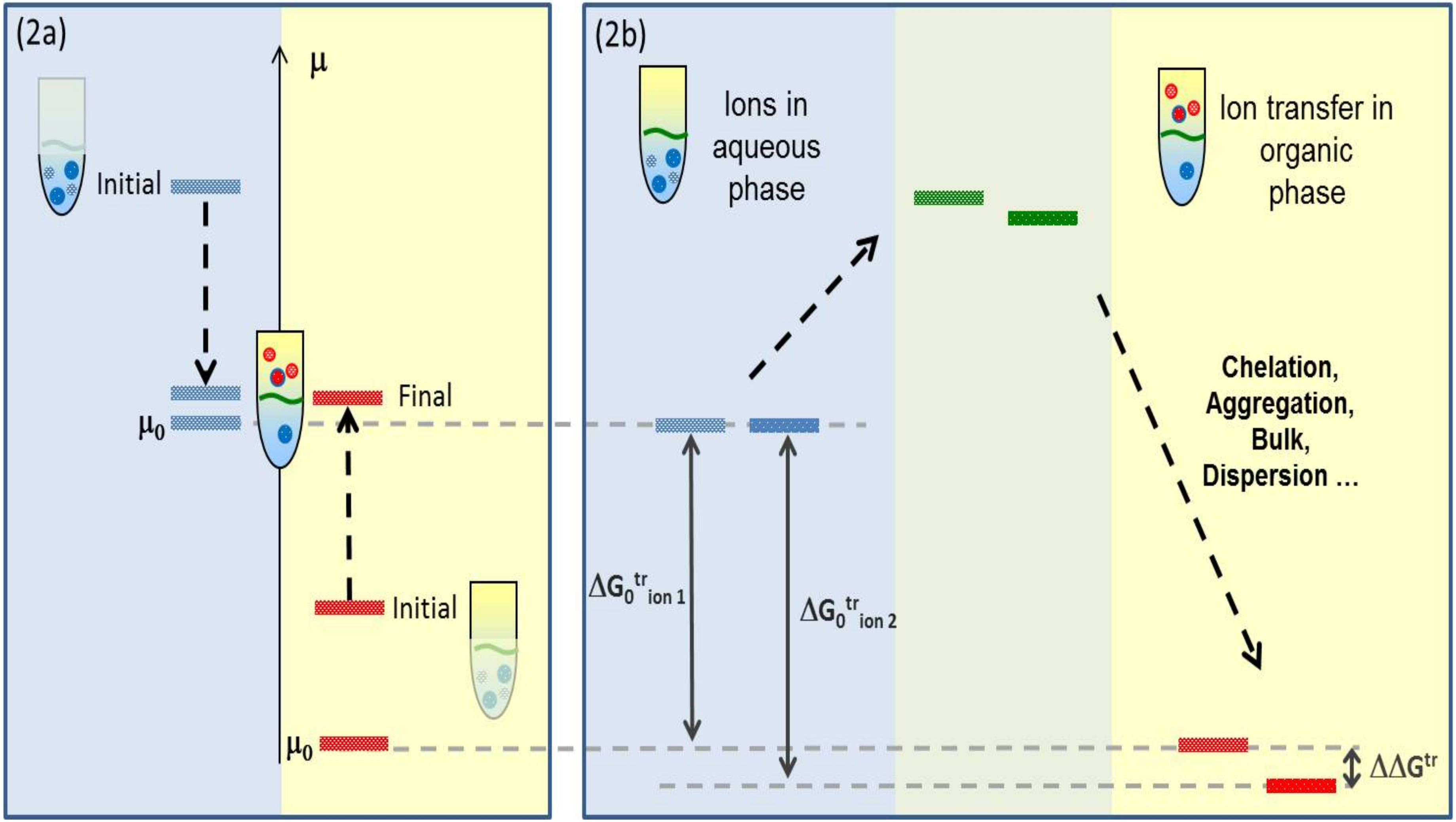
$$Y_f = D.X_f$$

$$D_{app} = \frac{\left(x_{C^+A^-}\right)^{O-rich}}{\left(x_{C^+A^-}\right)^{W-rich}}$$



Bauer C, Bauduin P et al. Liquid/liquid metal extraction: Phase diagram topology resulting from molecular interactions between extractant, ion, oil and water. Eur Phys J Spec Top 2012;213:225–41.

(2 and 3): the „ienaic“ : steps in chem. potentials



Zemb T, Bauer C, Bauduin P, Belloni L, Déjugnat C, Diat O, et al. Recycling metals by controlled transfer of ionic species between complex fluids: en route to “ienaics.” Colloid & Polymer Sci 2015:1–22.

The driving forces competing for extraction :

$$\delta\mu_0 = \left(\mu_0^{o-rich} - \mu_0^{w-rich}\right) = \delta\mu_{compl(O\_W)} + TdS_{conf} + \delta\mu_{Bulk} + \delta\mu_{D-I-FB}$$

$$n.\delta\mu_0 = dG_0 = kT.\ln K_{app}$$

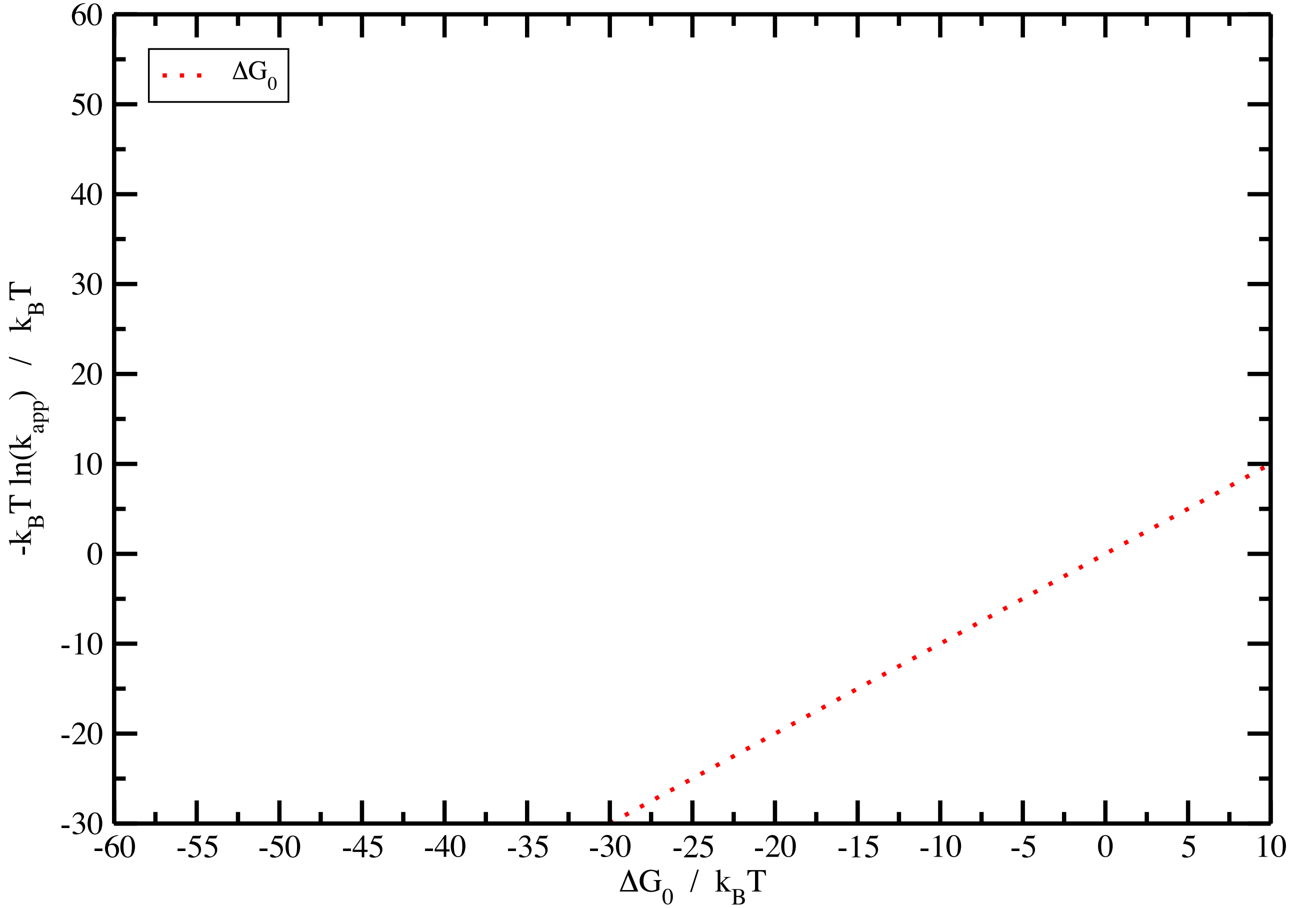
Link with parametric and activity " corrections" used for mass Conservation in design:

$$M^{m+} + b\,X^{-} + n\,\overline{L} \rightleftarrows \overline{MX_bL_n}$$

$$c_M^{org} = \left[\overline{MX_bL_n}\right] = K^{\circ}_{ext}\left[M^{m+}\right]\left[X^{-}\right]^{b}\left[\overline{L}\right]^{n}.\frac{\gamma_{\overline{L}}^{n}}{\gamma_{\overline{MX_bL_n}}}.\gamma_{M^{m+}}.\gamma_{X^{-}}^{b}$$

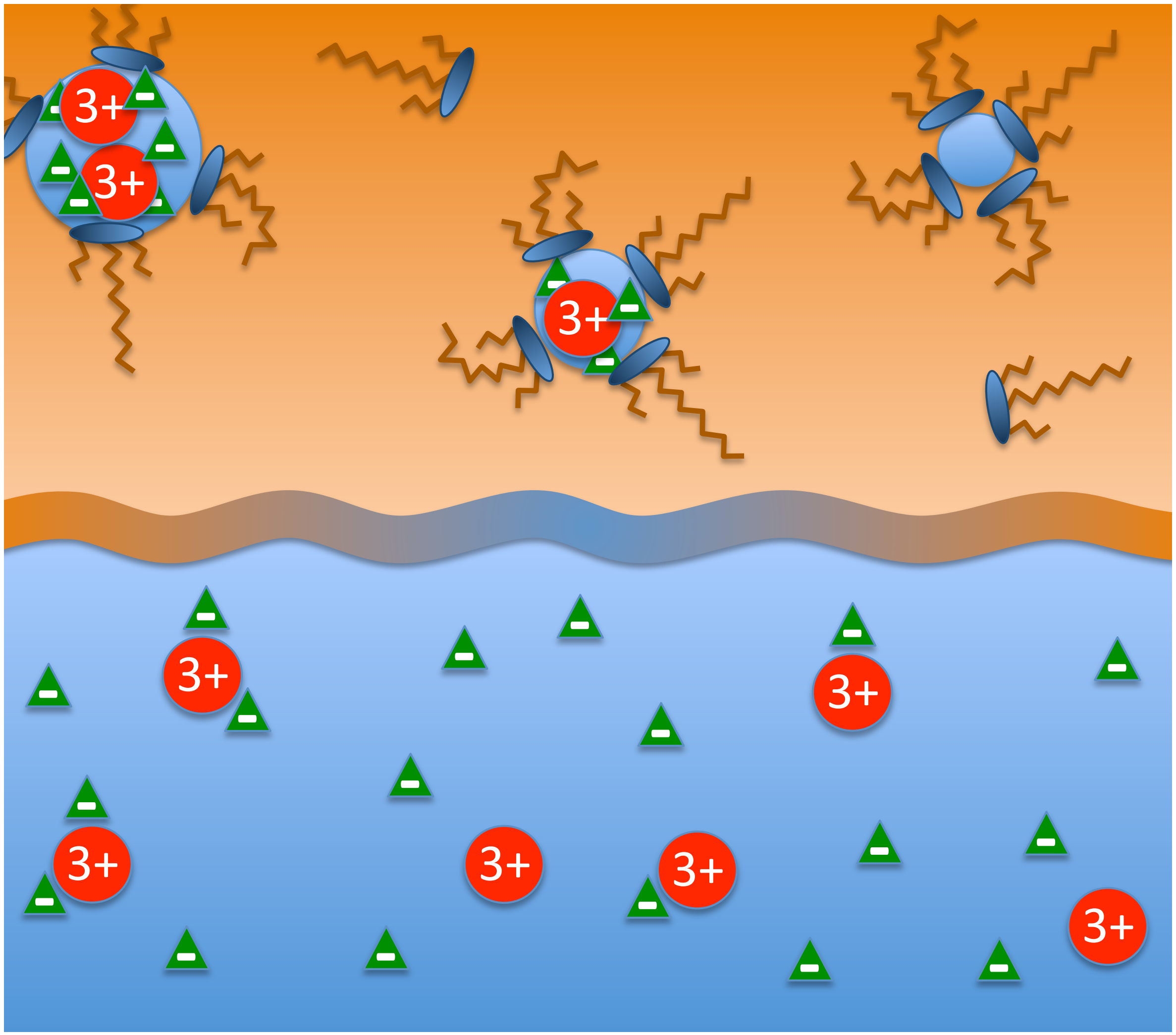
Zemb T, Bauer C, Bauduin P, Belloni L, Déjugnat C, Diat O, et al. Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienaics." Colloid & Polymer Sci 2015:1–22.

Representation : Y: ΔG extraction and X: ΔG complexation

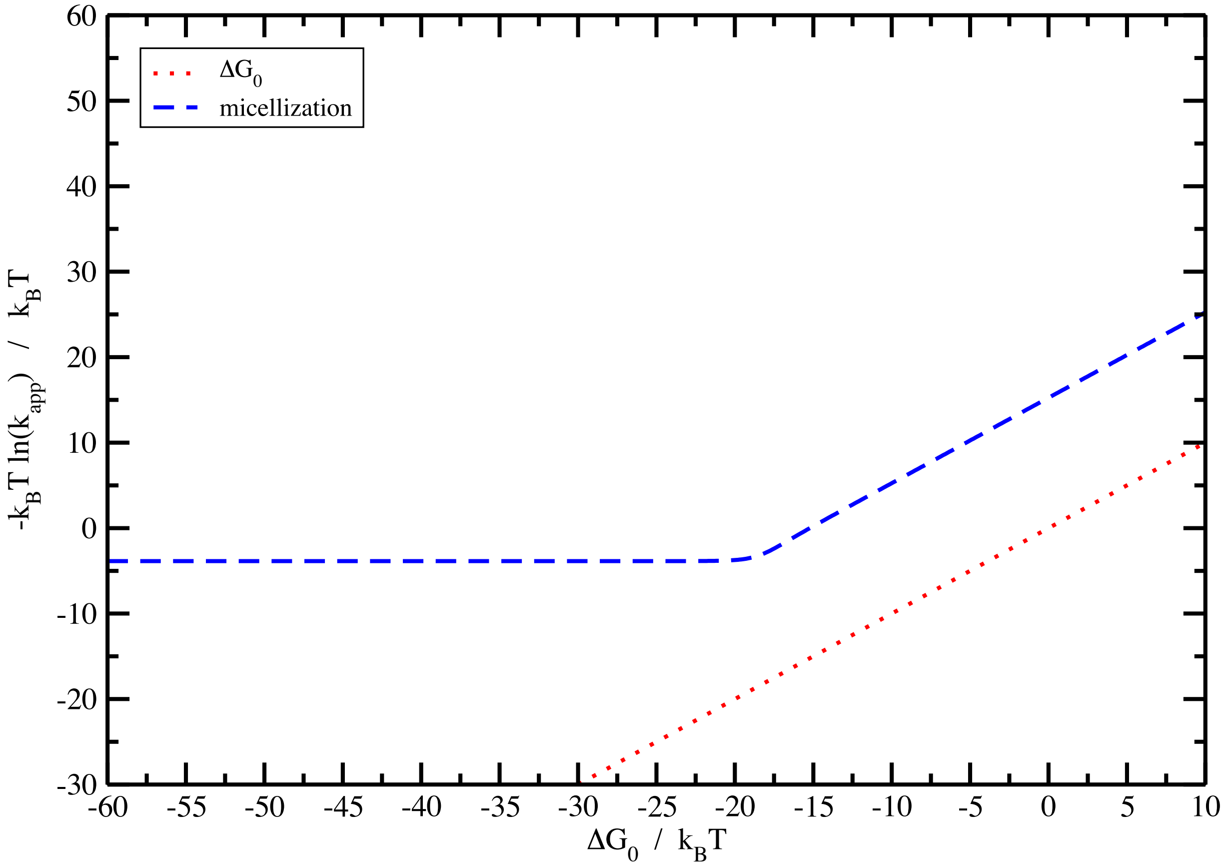


Hydrated ions and aggregates are chemical « complexes » but also « small » colloids

Extractants in oil aggregate :



The bulk term: cost in entropy of mixing forming aggregates



Hydrated ions and aggregates are chemical « complexes » but also « small » colloids

Extractant film stretches and bends ::

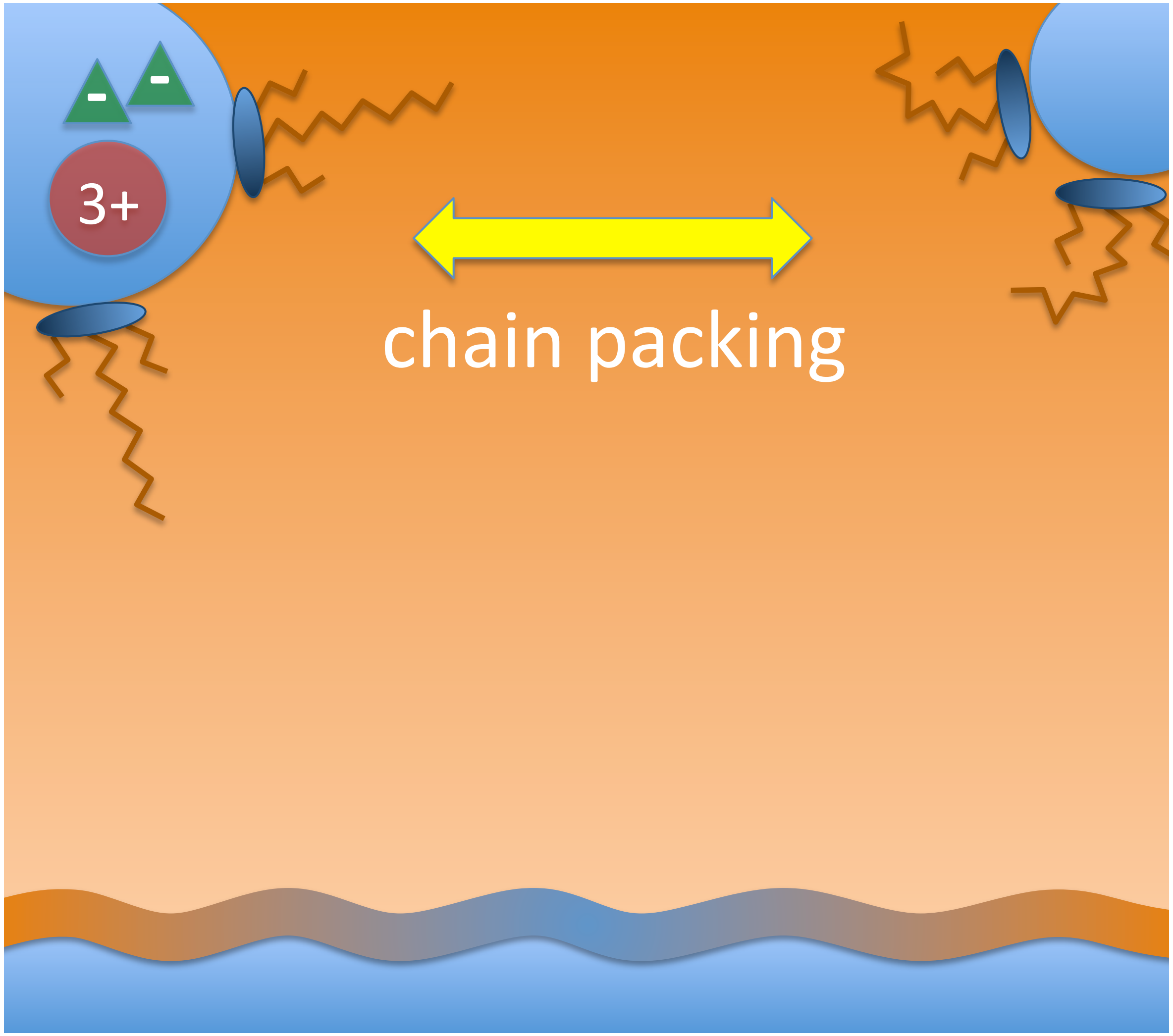
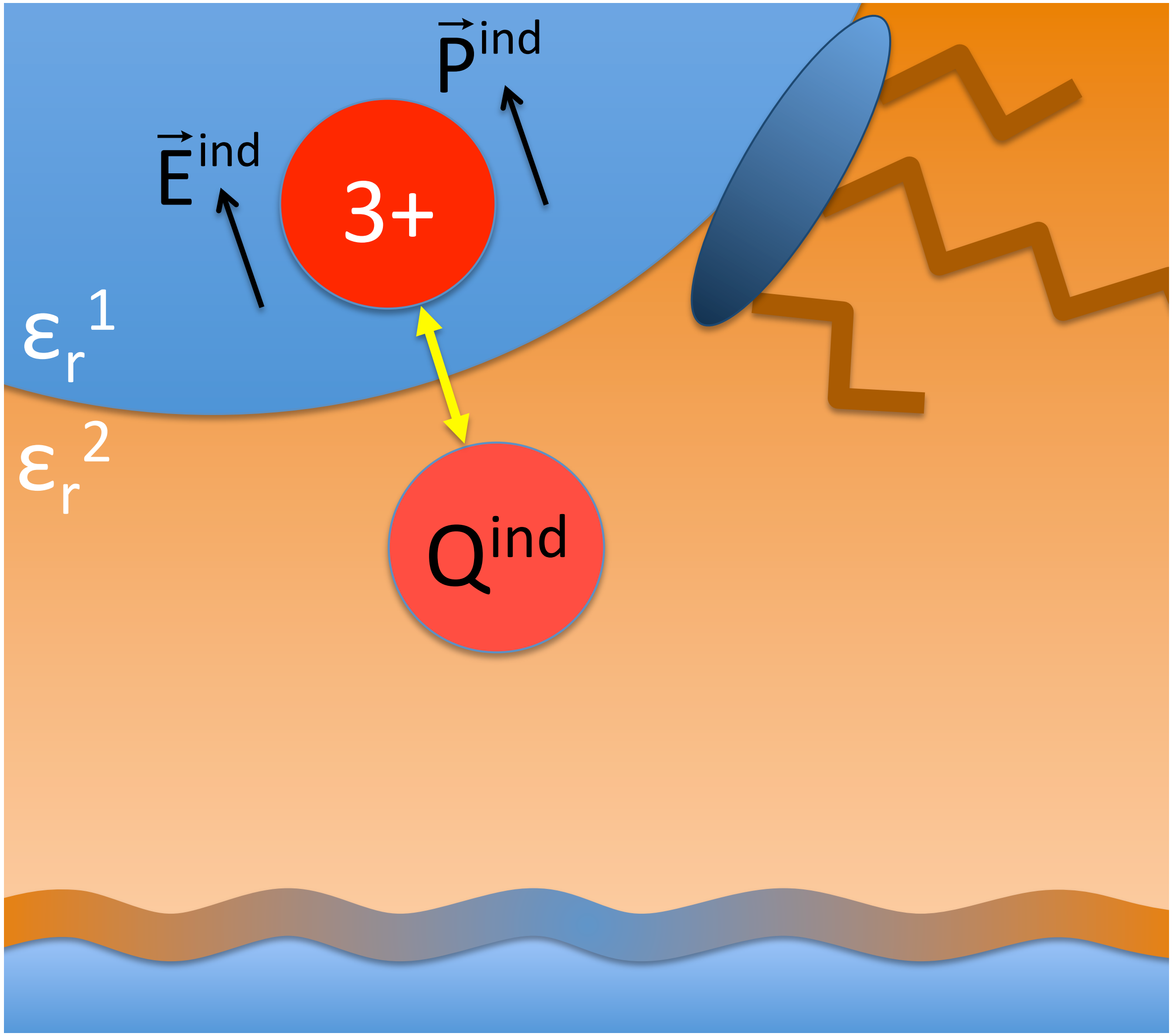
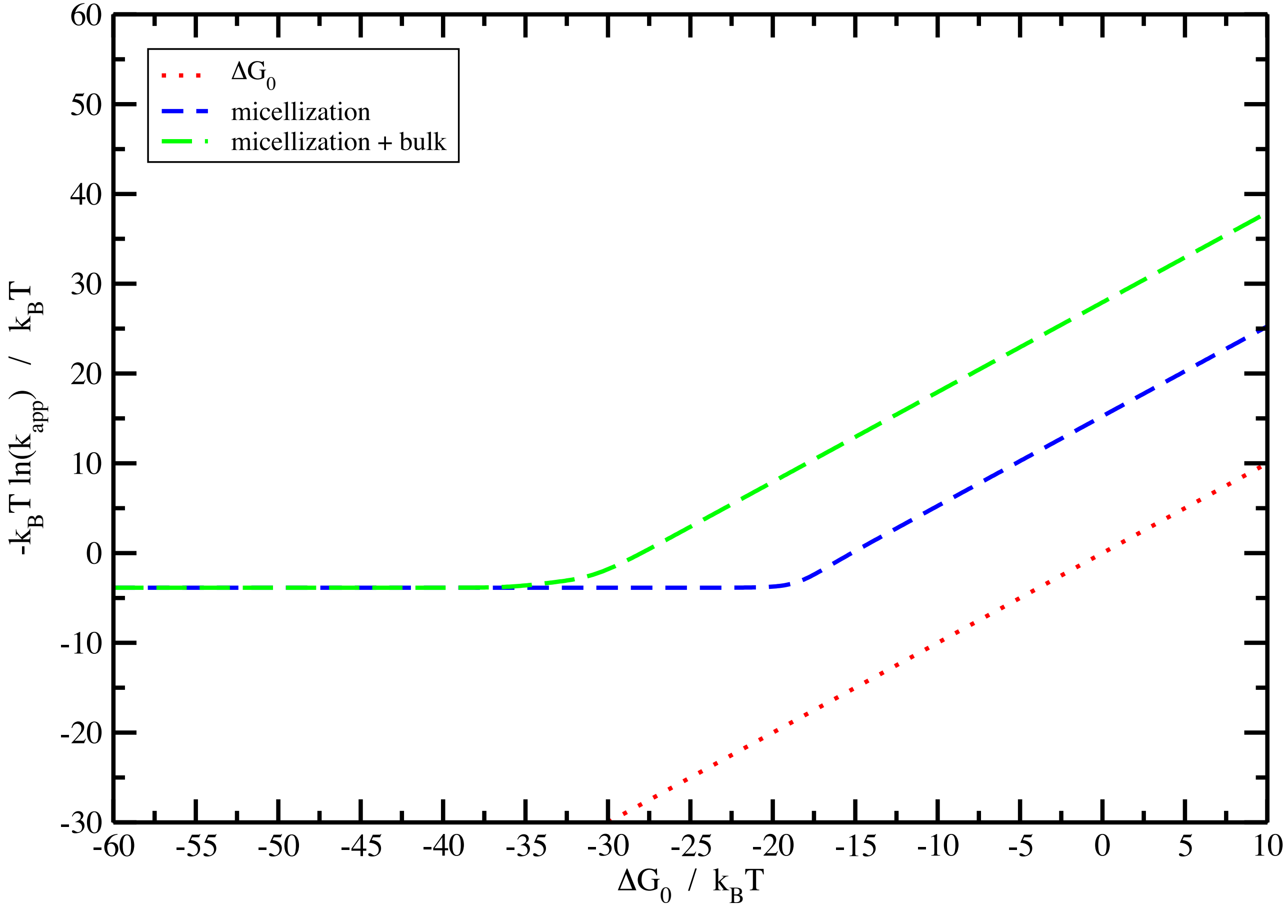


Image charges at o/w interface and polarisation

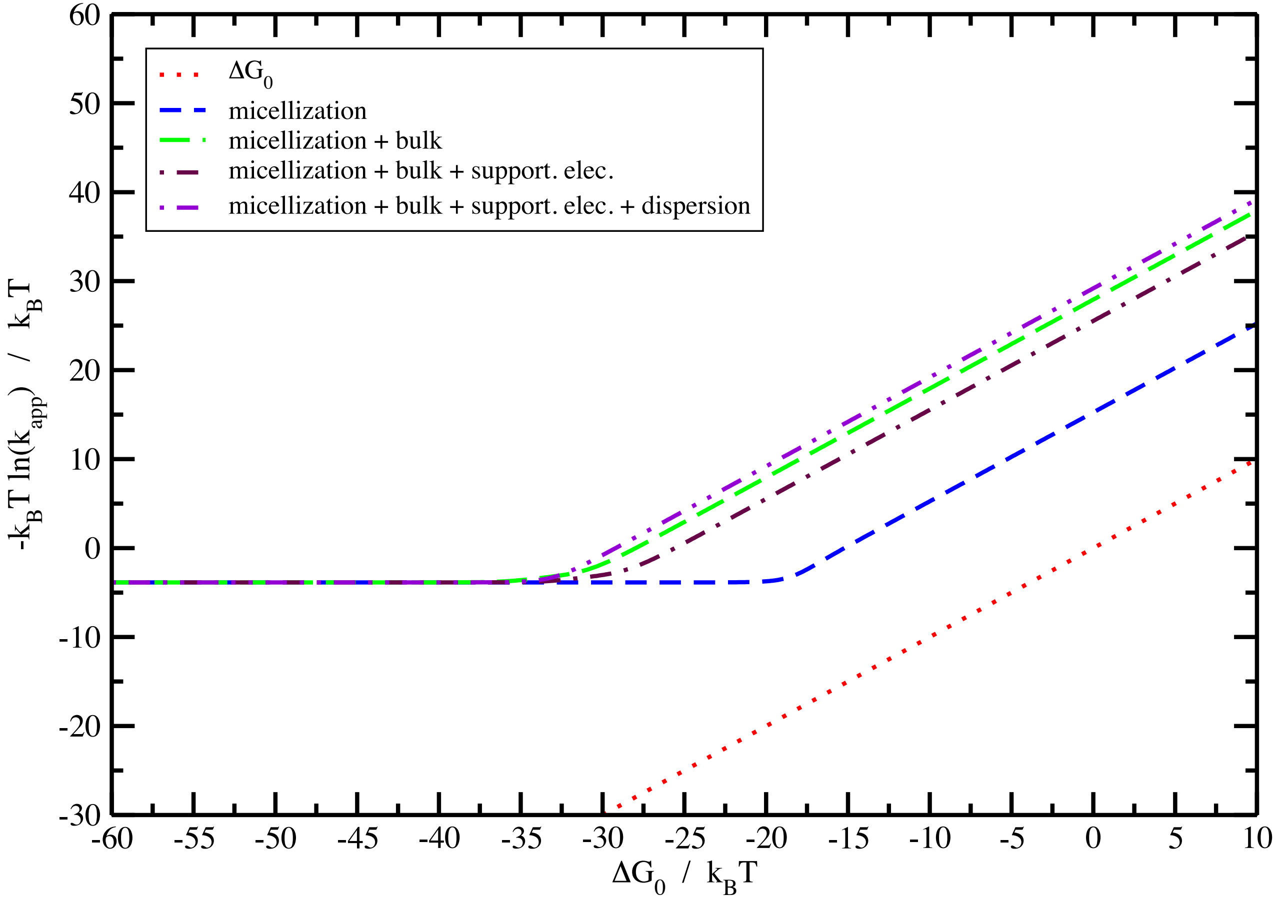


Ion pairs do not « like » oil !



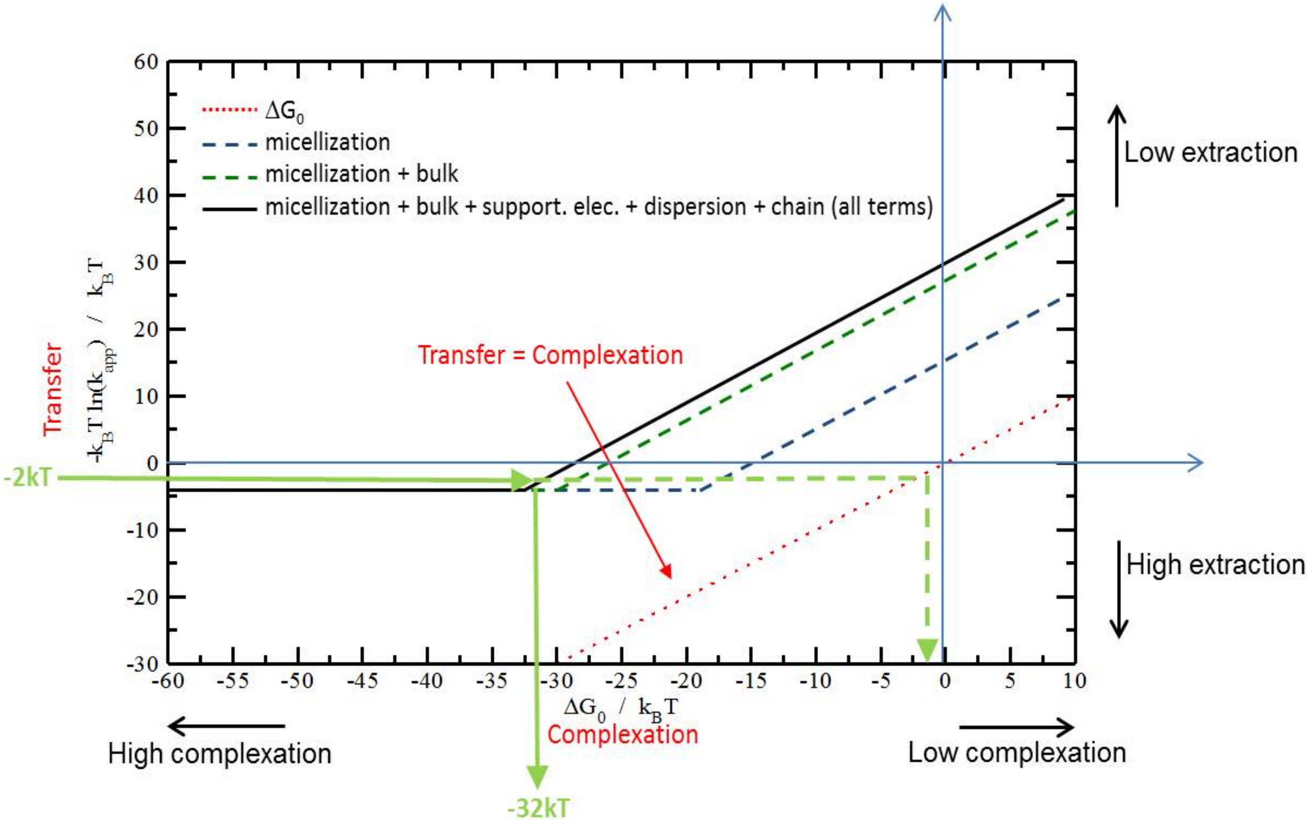
See W. Kunz in « Specific ion effects », 2010

Dispersion/polarisation influence also :



French RH, Parsegian VA et al. Long range interactions in nanoscale science. Rev Mod Phys 2010;82:1887–944.

full supra-molecular/complexation plus LRI picture :



..Explains how complexation 30 kT (70 kJ/mole) express in 2 kT, ie 5 kJ/Mole extraction free energy « motor » in common industrial processes…

Dufrêche J-F, Zemb TN. Effect of long-range interactions on ion equilibria in liquid–liquid extraction. Chem. Phys. Lett. 2015; 662: 45.