Fluctuations critiques dans un fluide ternaire s'opposant à la complexation dans l'extraction liquide-liquide de cations trivalents.

Thomas Zemb, Asmae el Maangar , Jean-François Dufrêche & Stéphane Pellet Rostaing (ICSM)

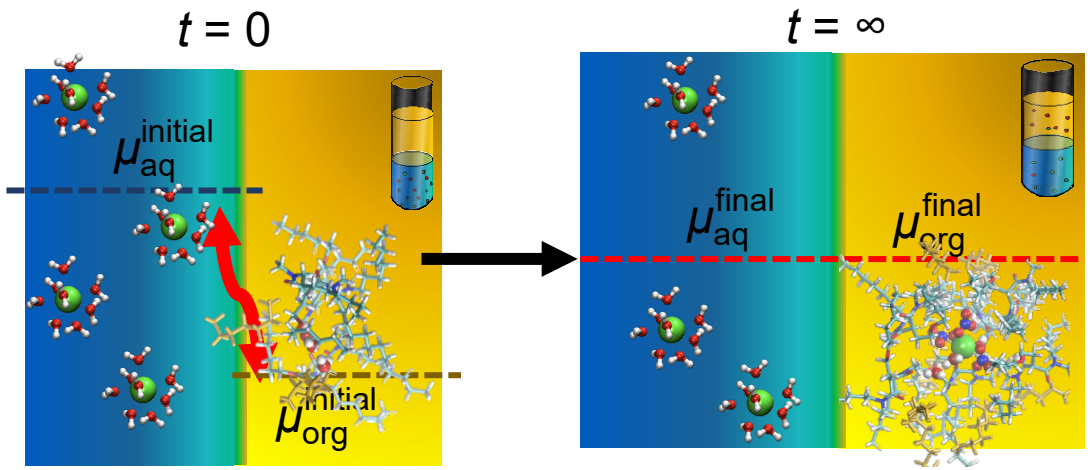
Werner Kunz (U Regensburg)

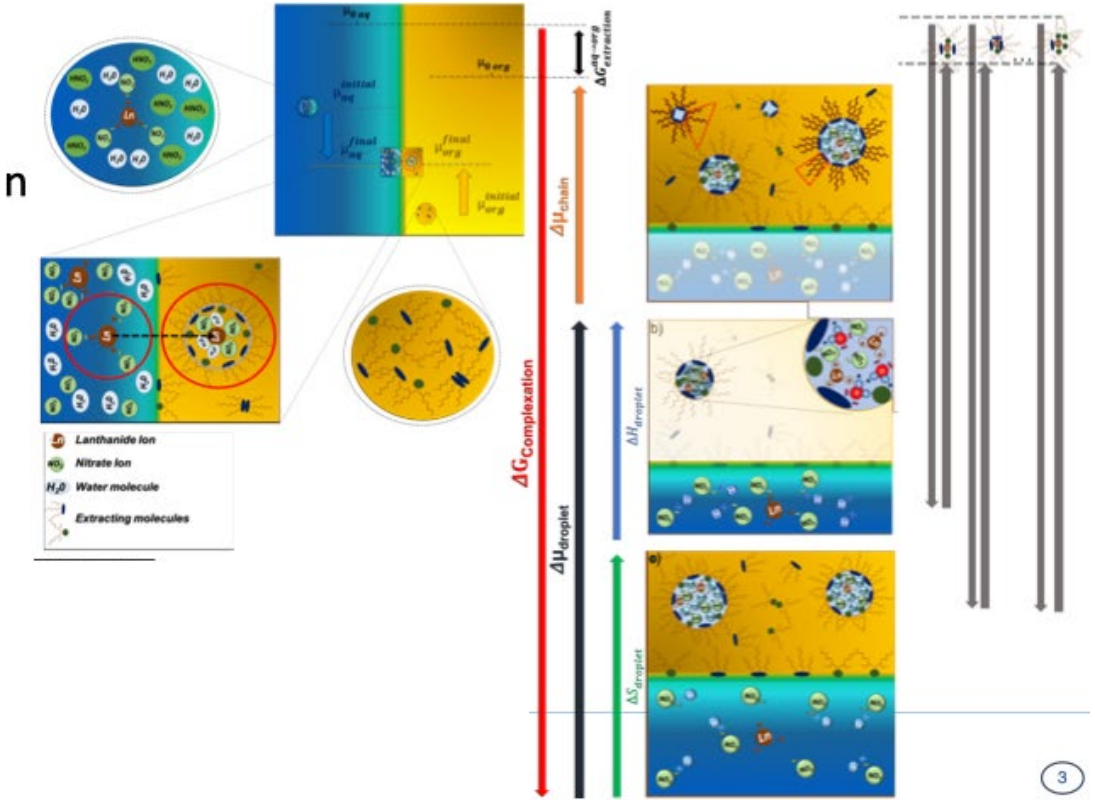
Critical fluctuations in a ternary fluid opposing complexation in the liquid-liquid extraction of trivalent cations.

Thomas Zemb, Asmae el Maangar , Jean-François Dufrêche & Stéphane Pellet Rostaing (ICSM)

Werner Kunz (U Regensburg)

Extraction/stripping view as a transfer between complex fluids





Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienaics. « ThZ et al Colloid Polym Sci (2015) 293:1–22

Gibbs energy of the transfer : fundamental equation of ienaics

$$-RT\ln D = \Delta_{\mathrm{tr}}G^{\circ} = \mu_{\alpha}^{\circ,\mathrm{org}} - \mu_{\alpha}^{\circ,\mathrm{aq}}$$

The approach last century (> 20.000 papers) : » supramolecular chemistry »& » supramolecular chemistry »

$$\underbrace{M^{n+} + n\,A^{-} + y\,\overline{L} \Leftrightarrow \overline{MA_nL_y}}$$

$\Delta G_{transfer} = \Delta G^{0}_{complex} + \Delta G^{0}_{solvent/complex\ mixing}$

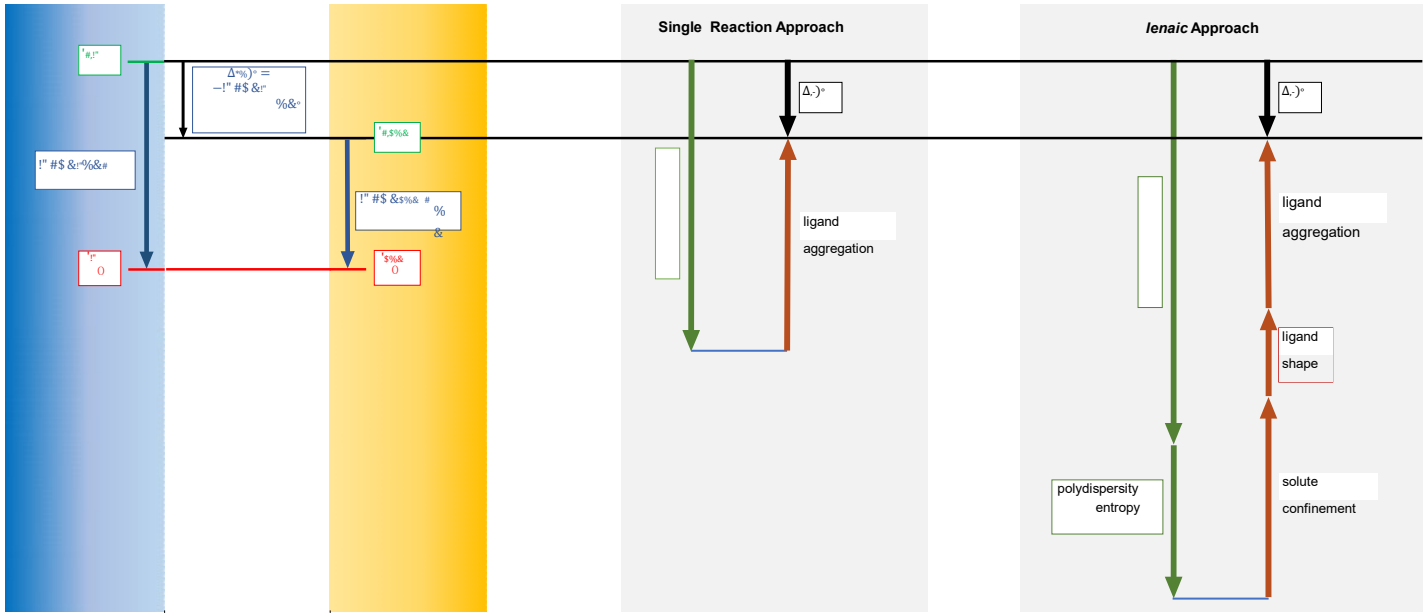
The « ienaics » approach (< 100 papers)) : take inot account beyond « nearest neighbour enthalpy (entropy)i.e. colloidal chemsit

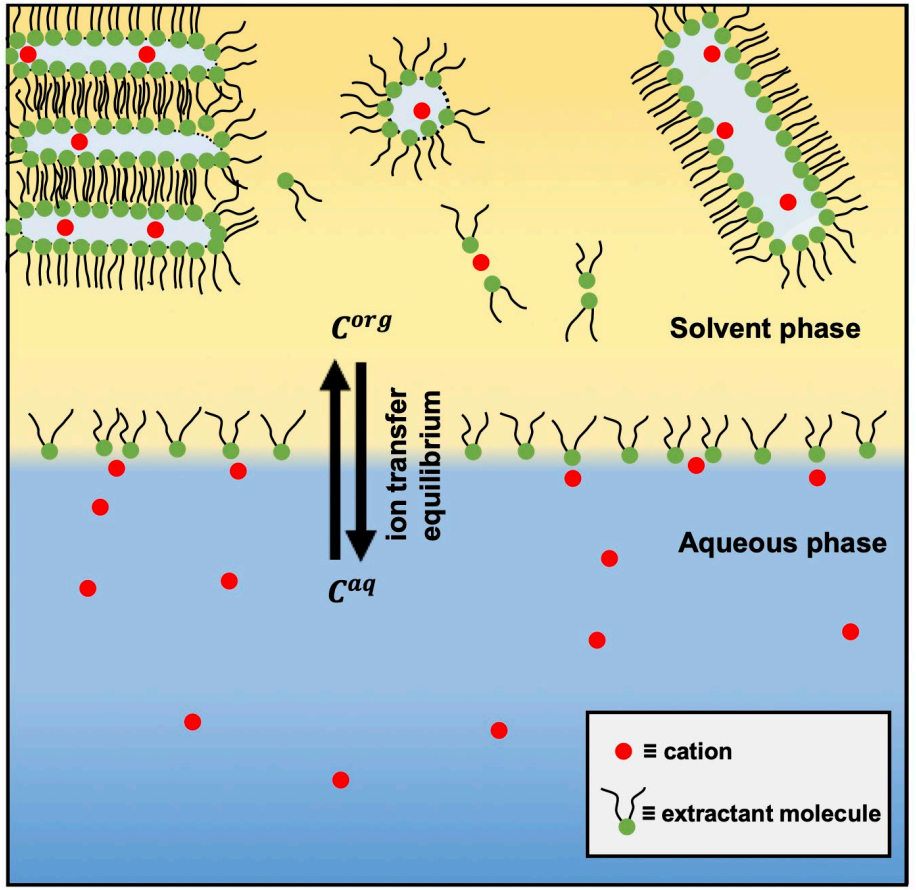
$$\Delta_{\mathrm{tr}}G^{\circ} = \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{complex}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{confin}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{apolar}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{lagg}} - T\Delta_{\mathrm{tr}}S^{\circ}_{\mathrm{pdisp}}$$

M. Spadina, JF Dufrêche et ThZ: « **Synergistic Solvent Extraction Is Driven by Entropy** »

ACS-nano (2019) 13,pp. 1375-13748

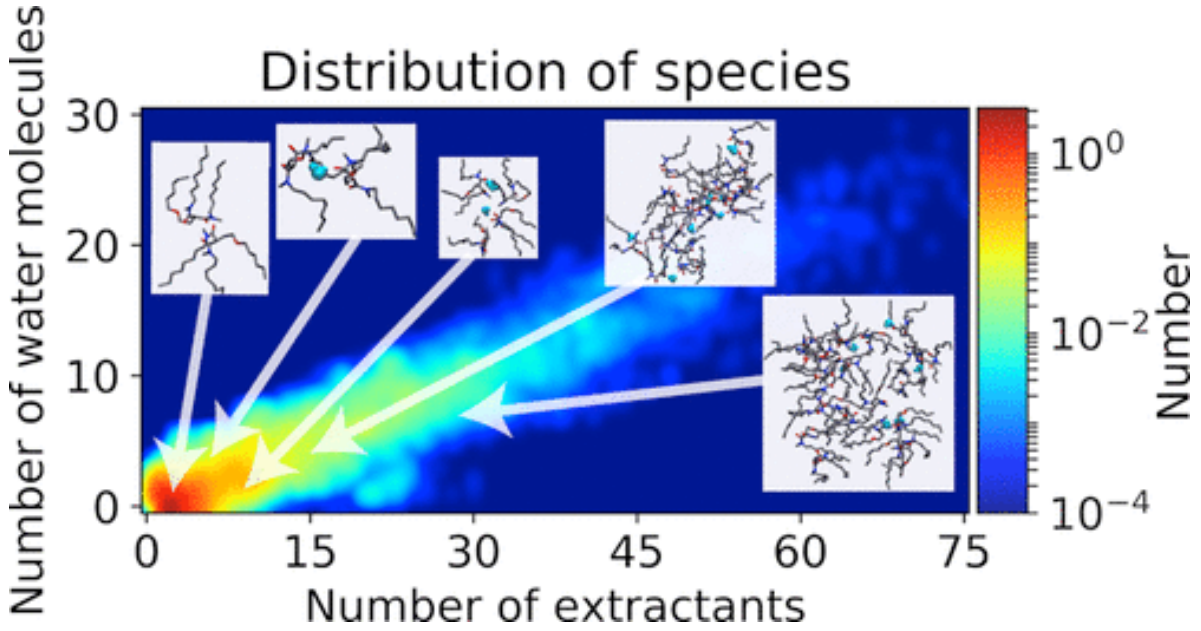
Extraction/stripping view as a transfer between complex fluids

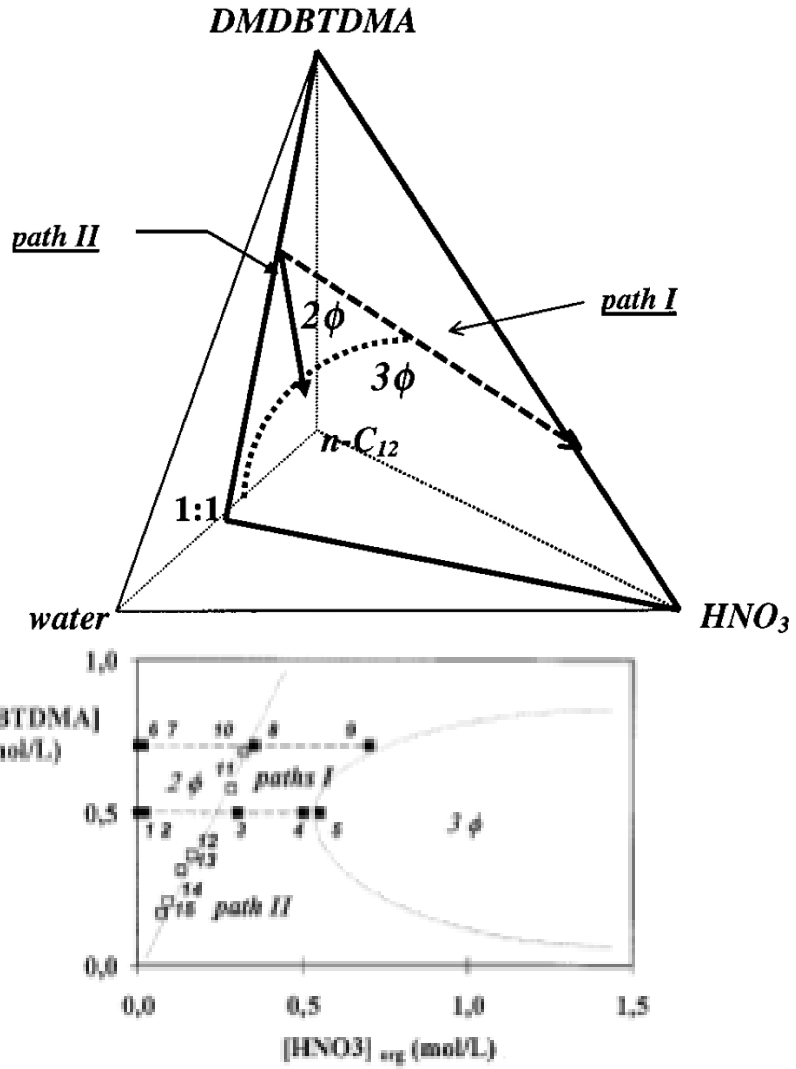




M. Spadina, JF Dufrêche, Stephane Pellet-Rostaing, S. Marcelja, Th. Zemb "Molecular forces in liq-liq Extraction" Langmuir 2020

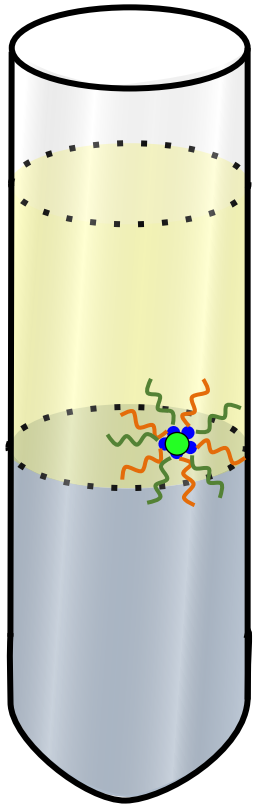
There are two general problems…

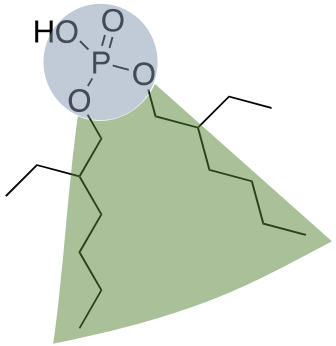




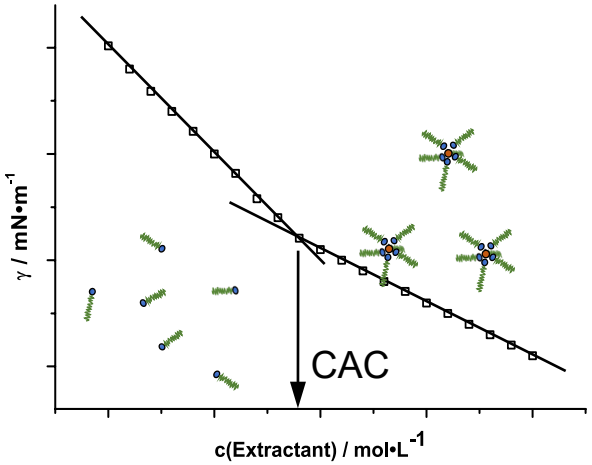
There is full distribution of aggregates f(Ne, Nw) in the solvent; with different extracting powers the yield and occurrence of spontaneous emulsification is influenced by proximity of critical points

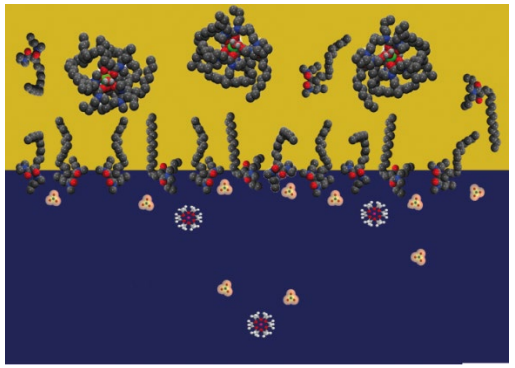
Classical extraction: water- solvent (extractant-diluent-modifier)

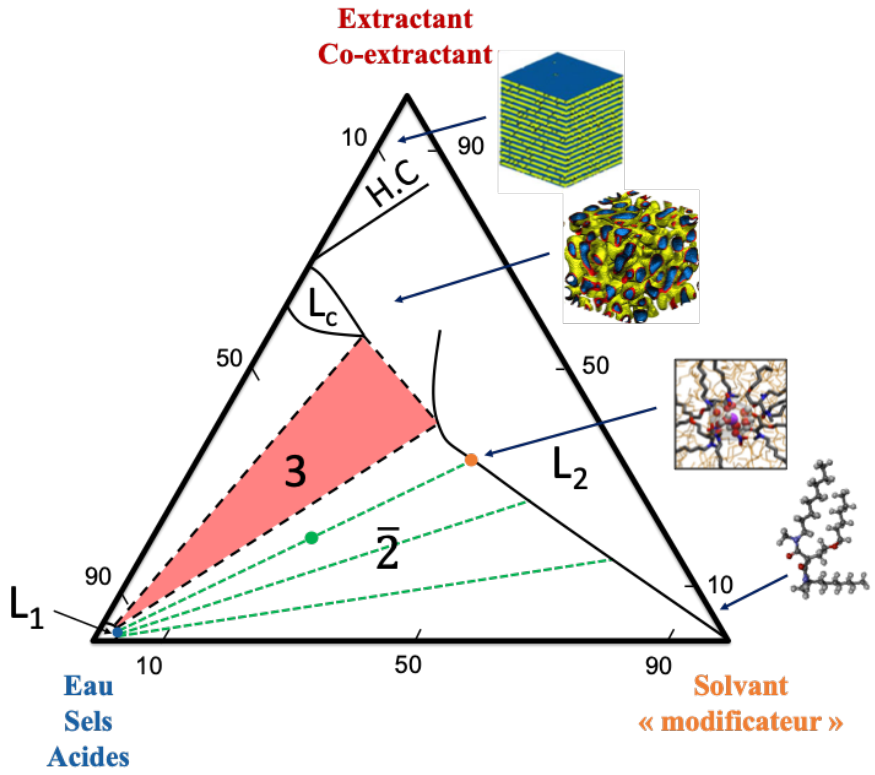




$$p_0 = \frac{v_{apolar}}{a_o \cdot l_c}$$

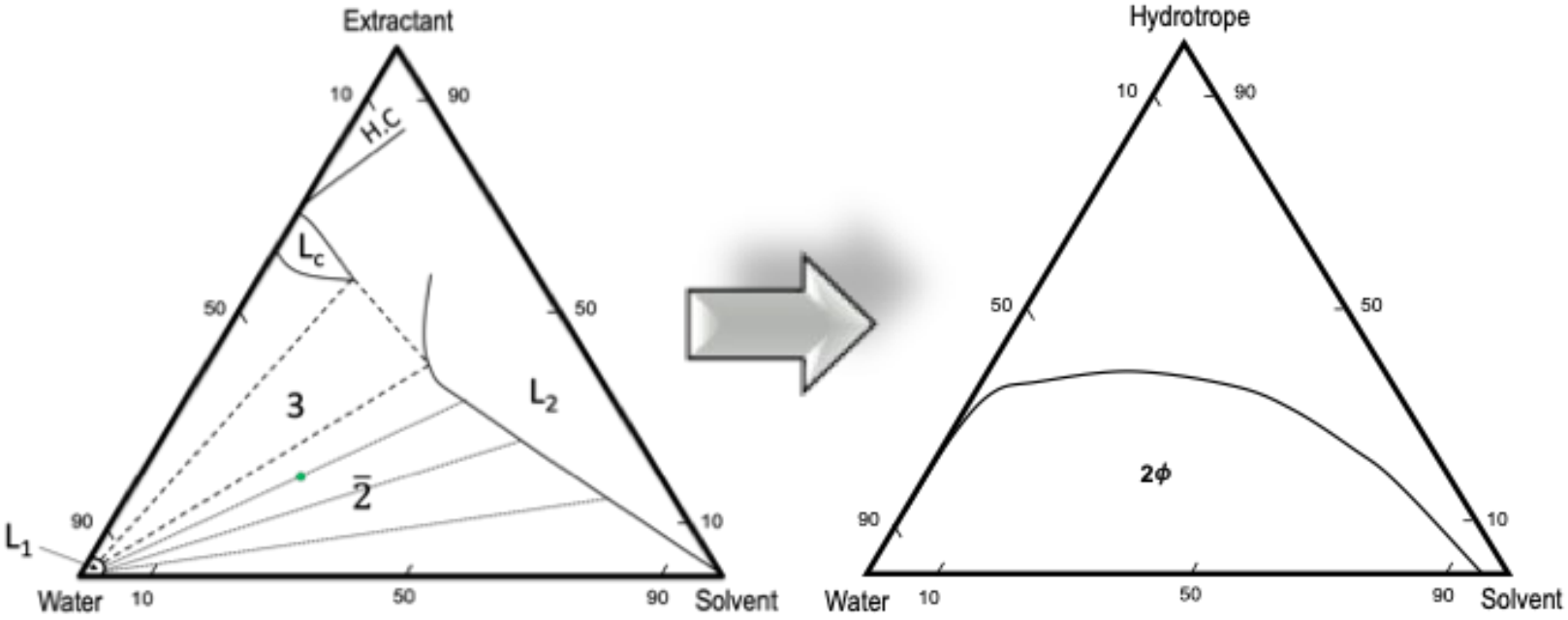


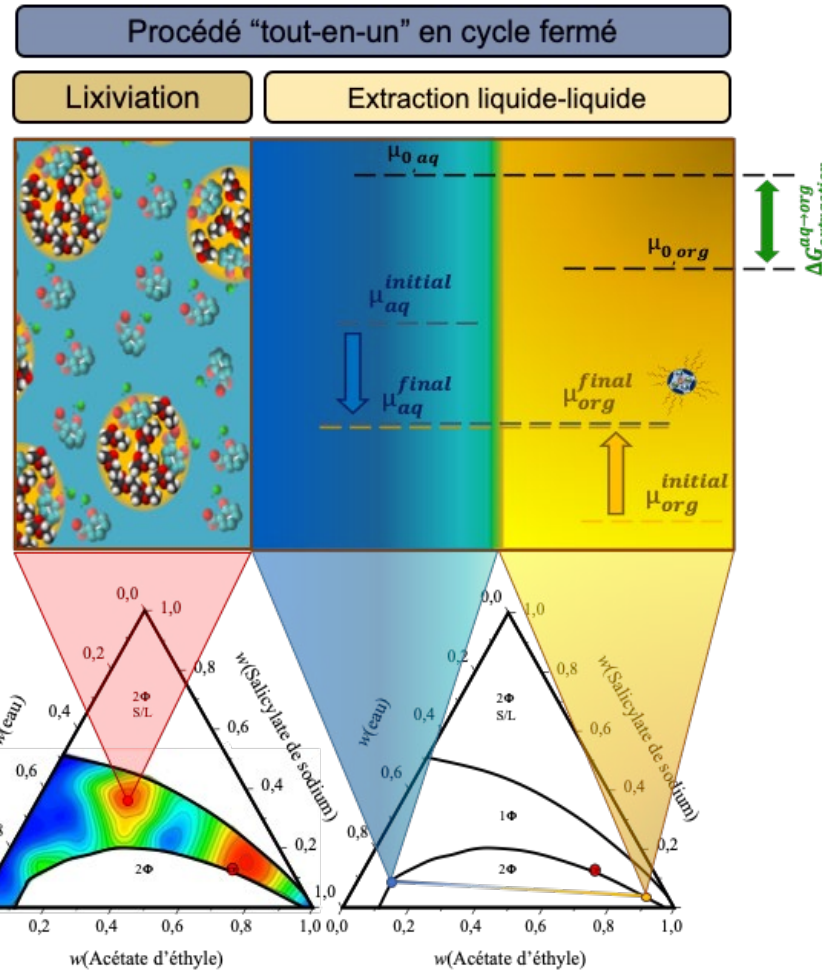




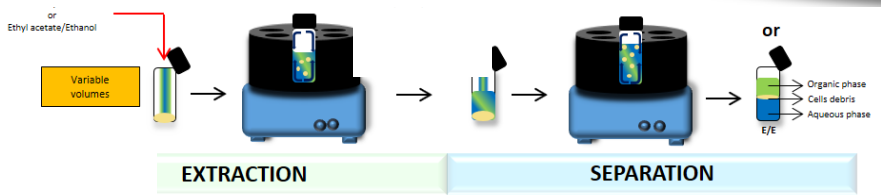
M. Spadina, JF Dufrêche, Stephane Pellet-Rostaing, S. Marcelja, Th. Zemb “Molecular forces in liq-liq Extraction” Langmuir 2020

Towards Hydrotrope assisted extraction ?





Using hydrotropes works well also for extraction: sepration of lipids versus via a green Bligh&Dyer (Folch) method

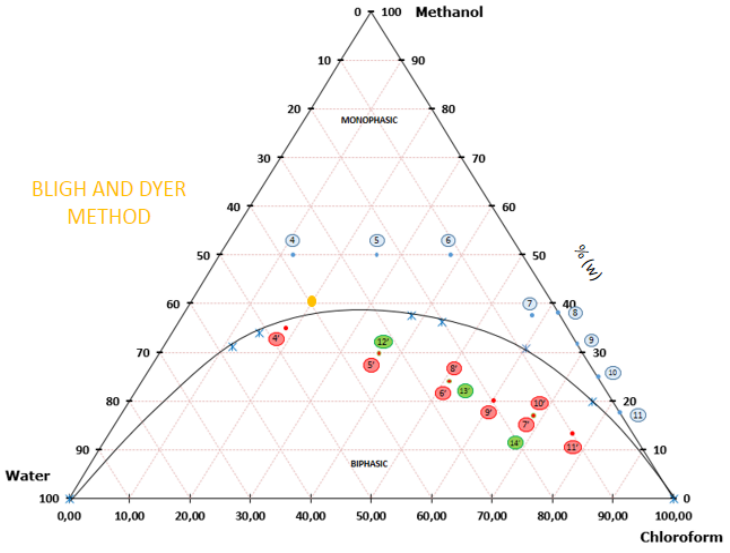


Aim is to extract all lipids (phospho- sphingo- glyco-) whatever their log p

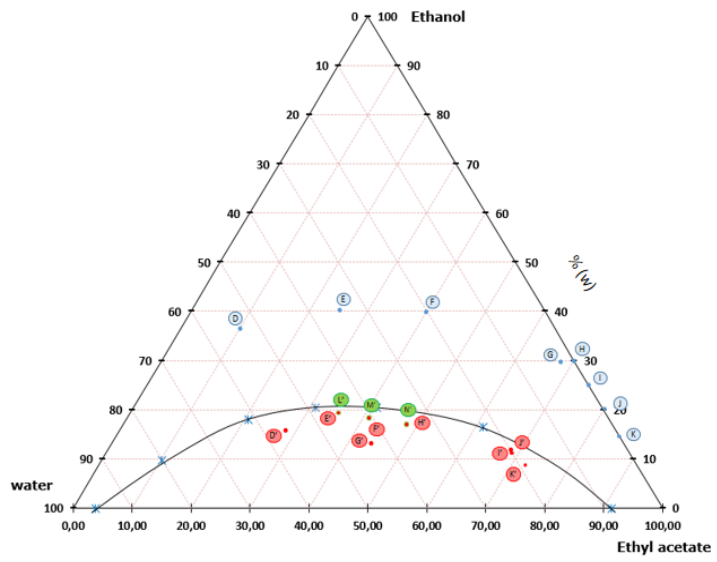
from glucids and proteins in cytoplasm of bacteria and other biomass

> 60.000 citations of « standard protocol » (no predictive theory before 2016)…

CLASSICAL BLIGH AND DYER

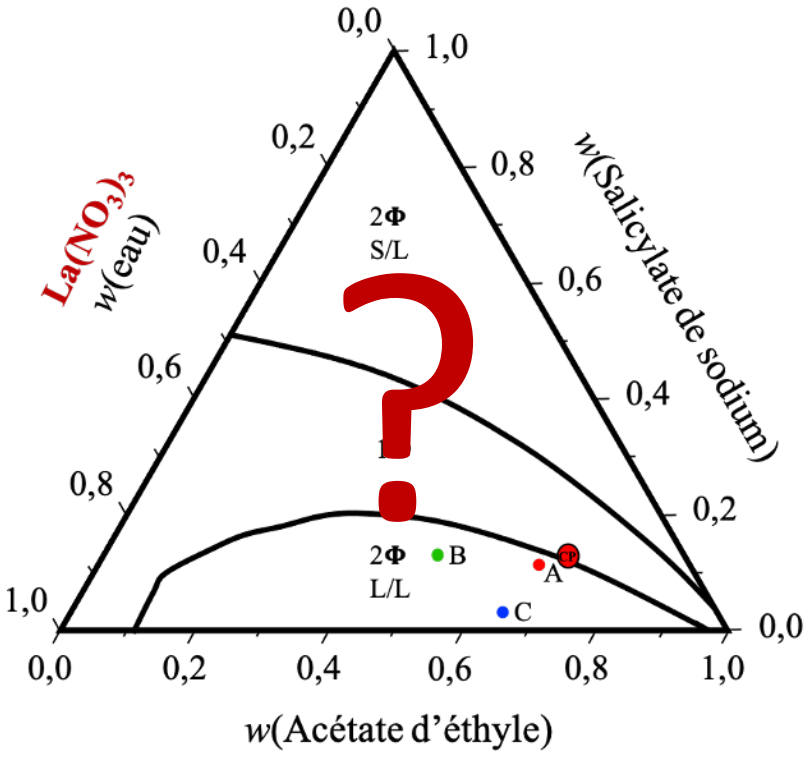


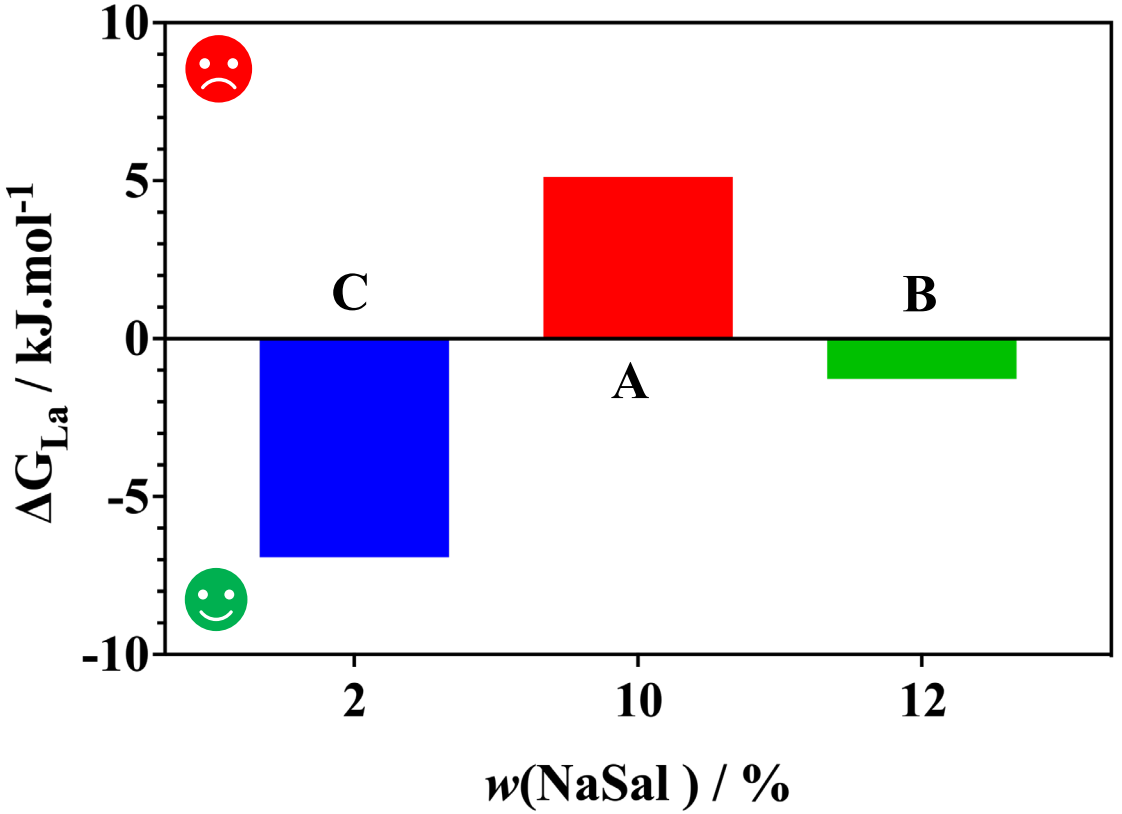
GREEN BLIGH AND DYER



C. Breil, Th Zemnb, W. kunz & F. Chemat :**A green "Bligh and Dyer" and Folch Method for Solid–Liquid–Liquid Extraction of Lipids from Microorganisms: Comprehension of Solvatation Mechanisms and towards Substitution with Alternative Solvents** *Int. J. Mol. Sci.* **2017**

Varying the complexing hydrotrope content in solvent (ethyl acetate)

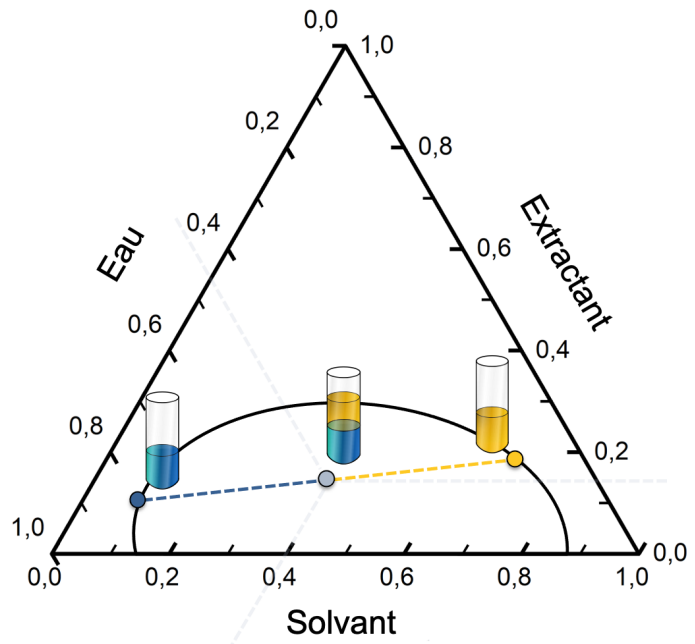


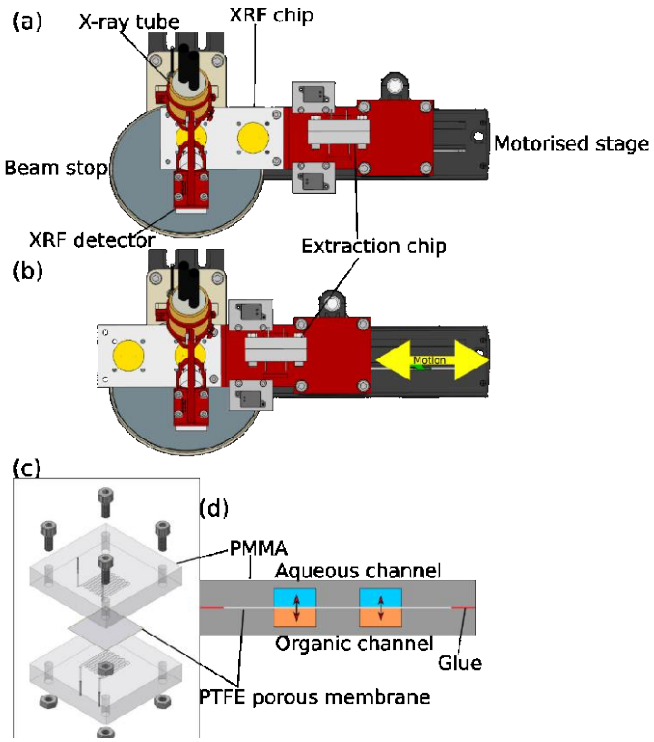


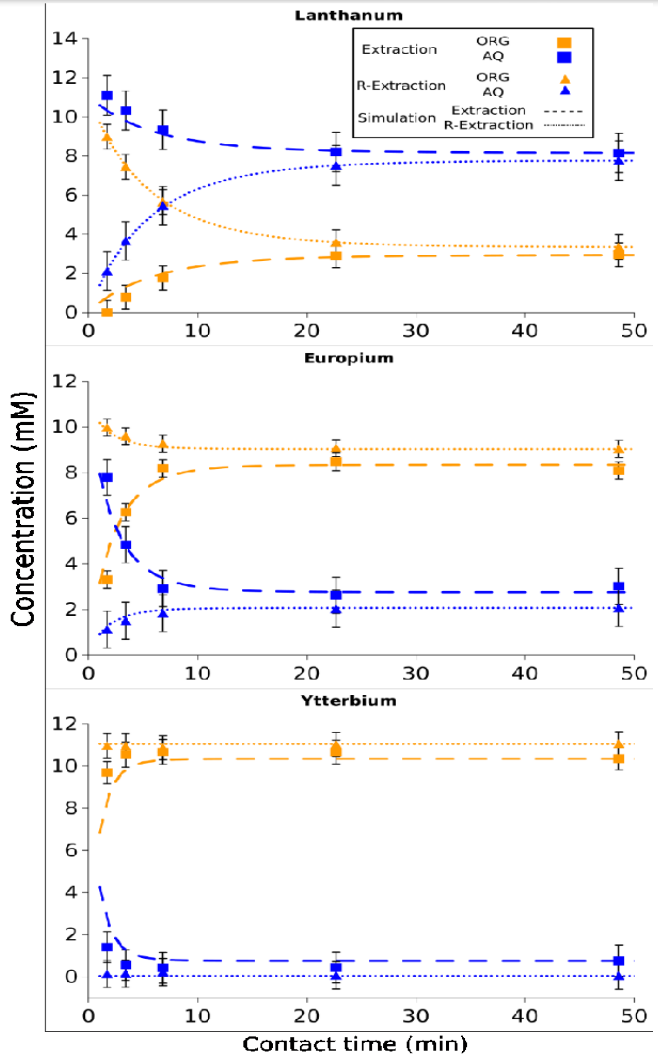
Replace « yield » % : $\Delta G_{tr} = RT \ln D = RT \ln ([w]/[o])$

Similarity the green Bligh and Dyer ?

First: necessity of XRF to have error bars of ln D < 0.5 (k_BT)



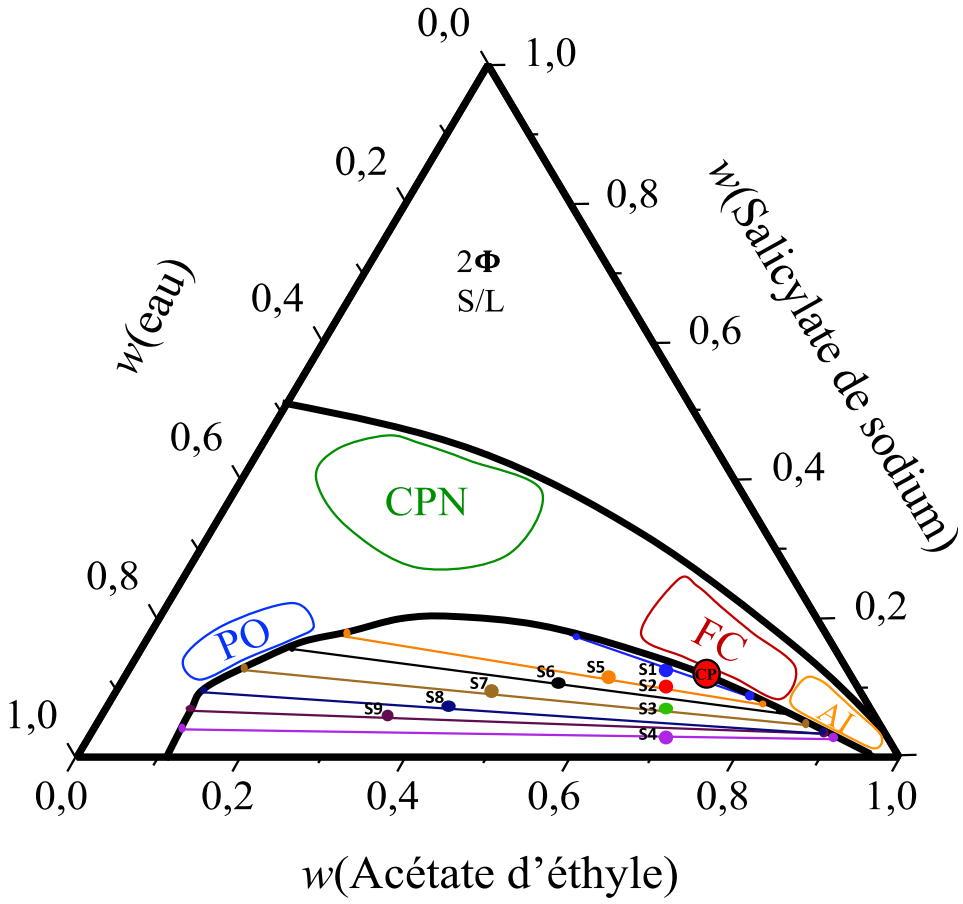




El Maangar, A.; Theisen, J.; Penisson, C.; Zemb, T.; Gabriel, J.-C. P.: **A Microfluidic Study of Synergic Liquid-Liquid Extraction of Rare Earth Elements.** PCCP 2020, 22 (10), 5449–5462. doi.org/10.1039/c9cp06569e.

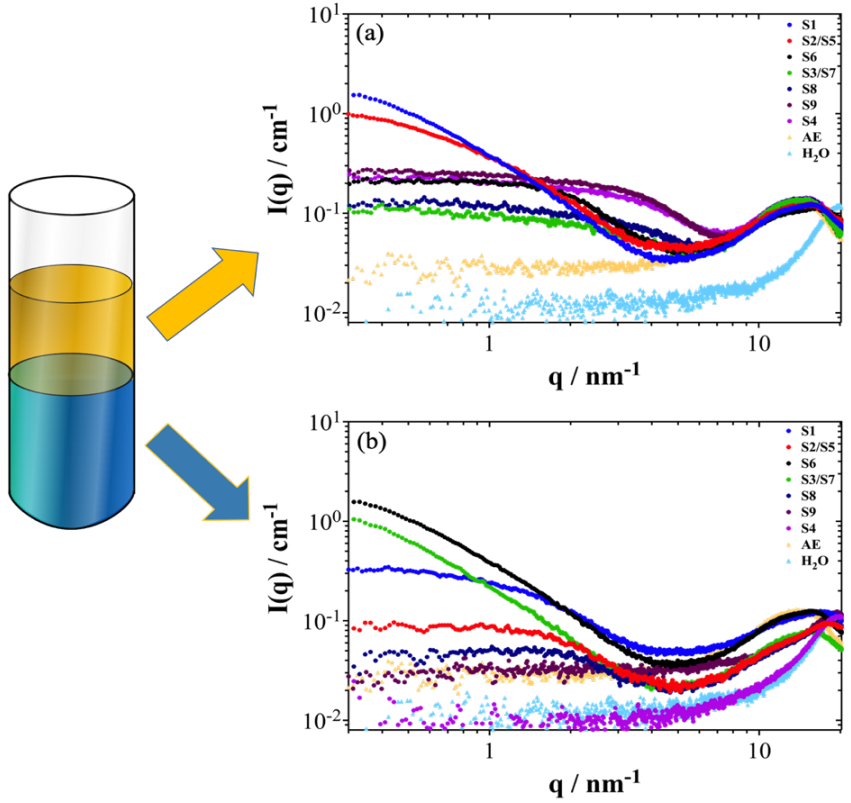
Precision in ln D using the "ienaic" approach

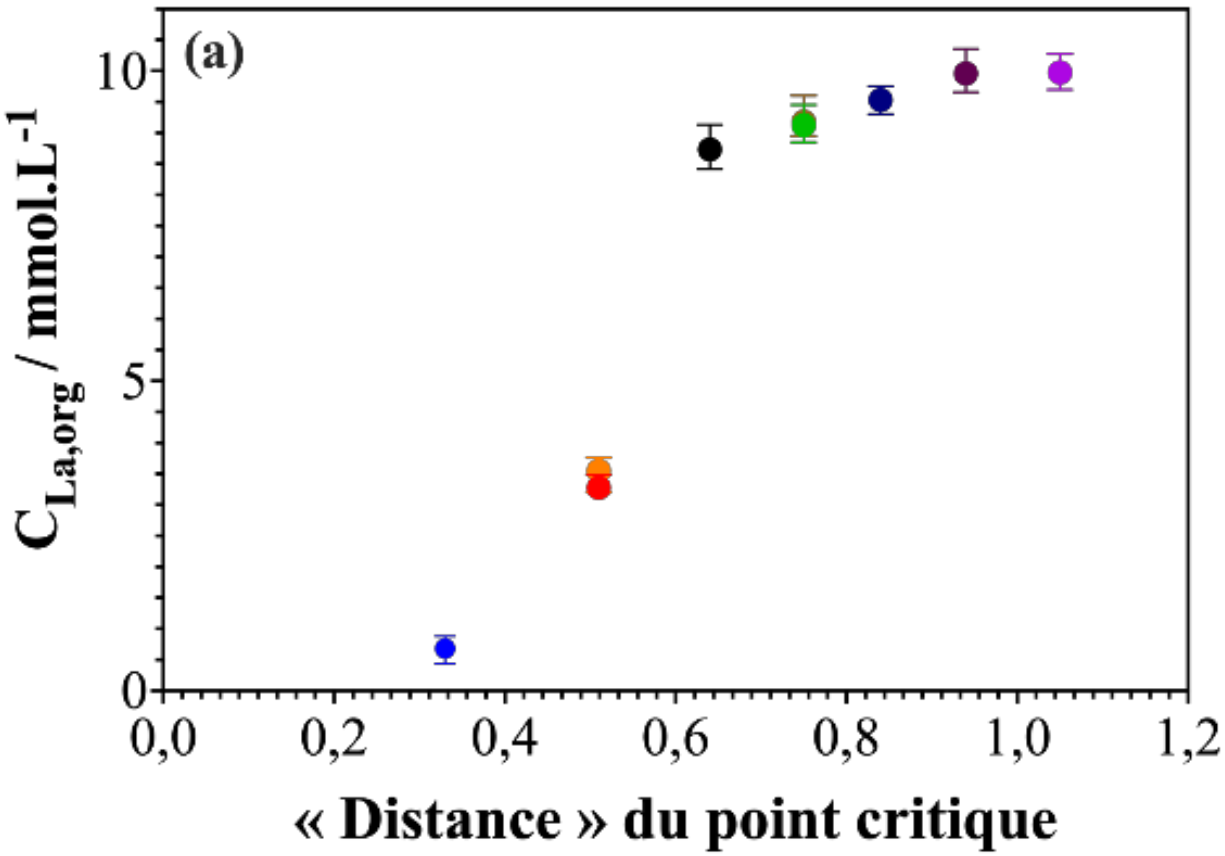
°97%+:-2 % « : means Incertitude in RTln means D between 0.01 and 0.05 this means ln D is between 3 and 4.6 while target is determlination of ΔG_{ext} to less than $0.5k_bT$ = XRF of both phases is the only knonw technique to achieve the precision required !



El Maangar, A. , Lopian, T., Dourdain, S., Kunz, W. & Zemb, T. **Diluent effects on the stability range of w/o micellar systems and microemulsions made with anionic extractants** EPJ Nuclear Sci. Technol. 8, 28 (2022), doi.org/10.1051/epjn/2022025

What is the yield in extraction: Yeild decreases with increase of extractant in the solvent phase !!!!

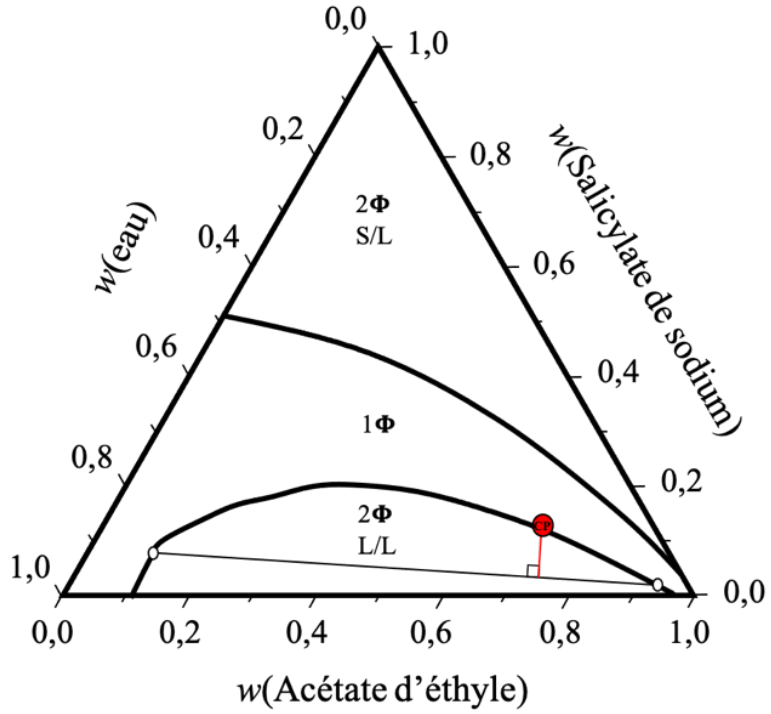


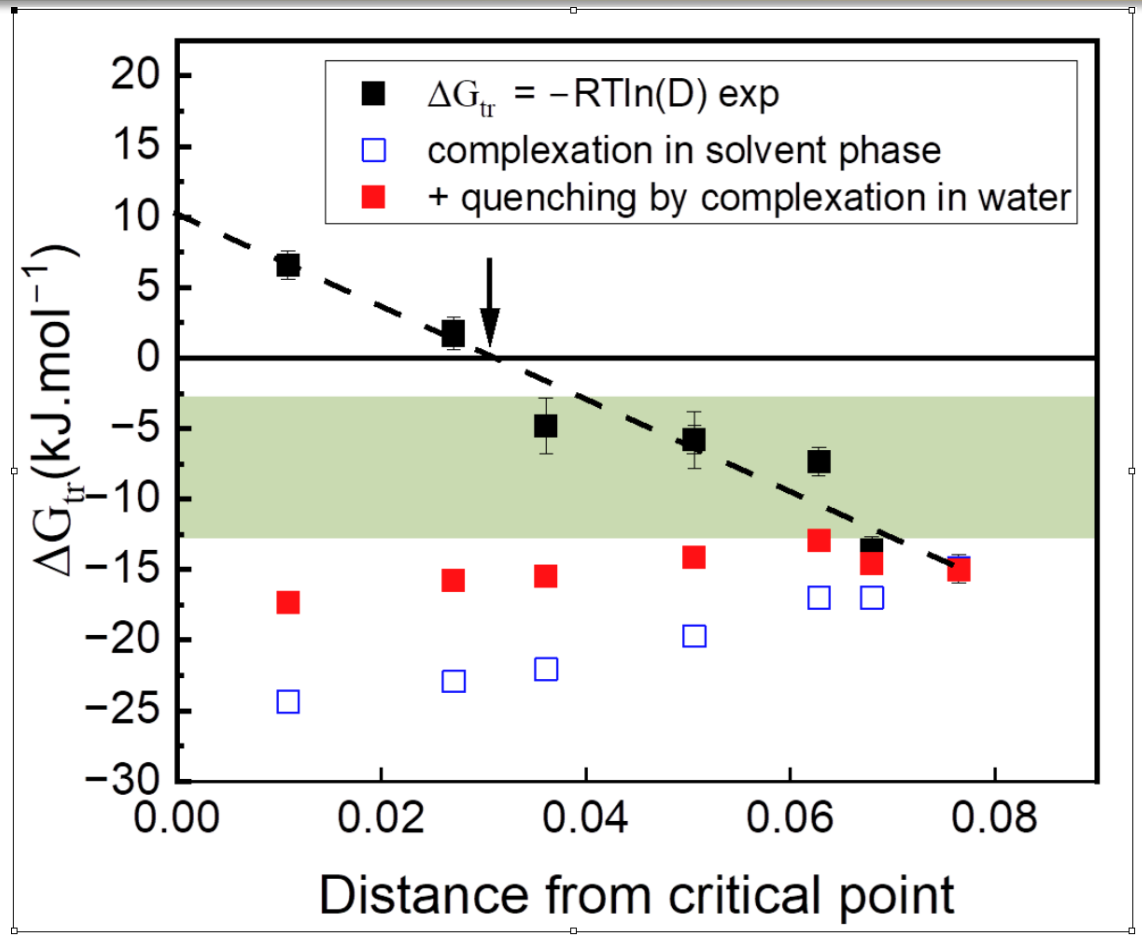


Identification of aggregation : i.e; self- assembly (Or not) in coexisting phases..

- **El Maangar, A.**; Degot, P.; Huber, V.; Causse, J.; Berthault, P., Touraud, D.; Kunz, W.; Zemb, T., ***Pre-nucleation cluster formation upon ethyl acetate addition to an aqueous solution of an anionic hydrotrope, Journal of molecular liquids***, 2020, 310 : 113240, DOI : 10.1016/j.molliq.2020.113240.

Ienaics approach: complexation plus solvent structure @ TΔS

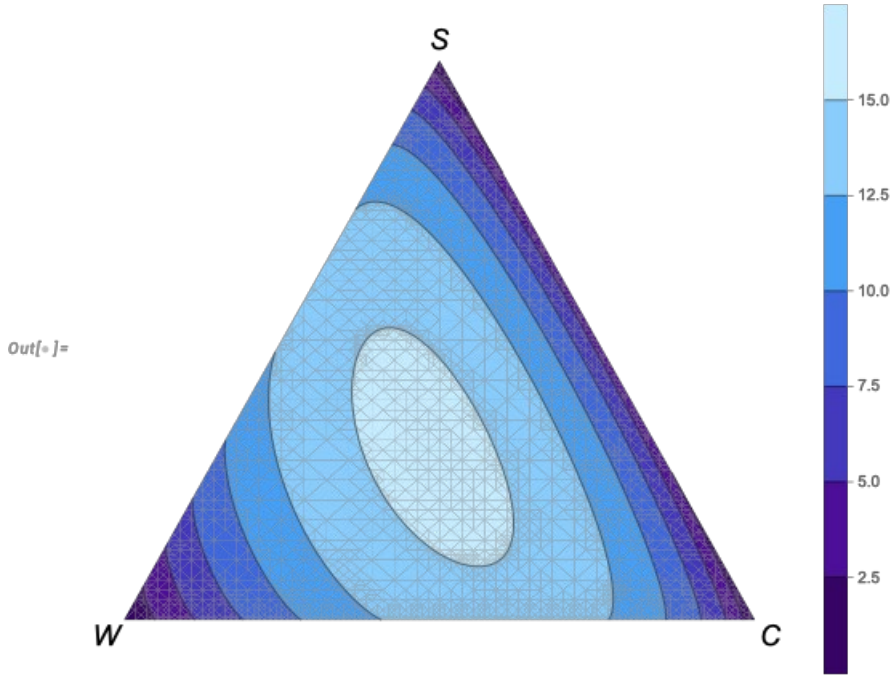


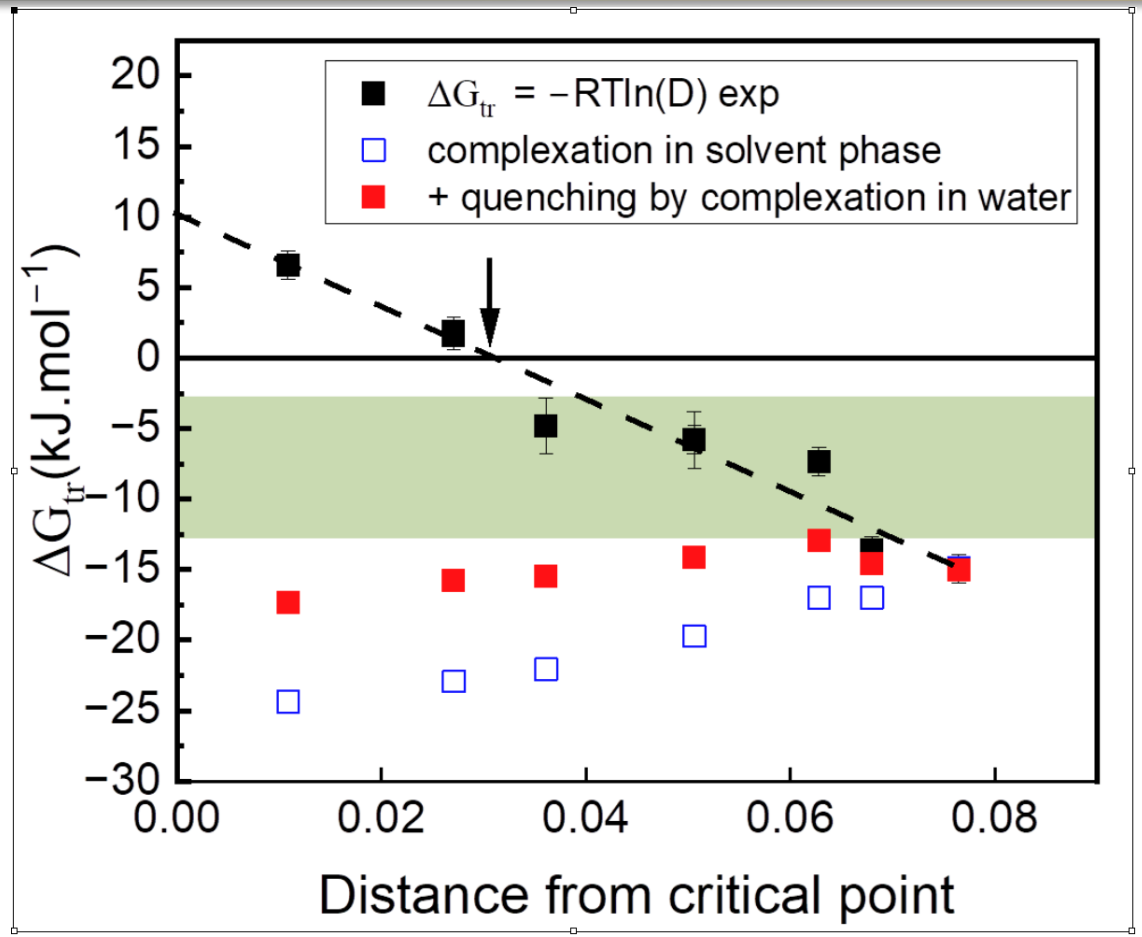


$$\Delta_{\mathrm{tr}}G^{\circ} = \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{complex}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{confin}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{apolar}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{lagg}} - T\Delta_{\mathrm{tr}}S^{\circ}_{\mathrm{pdisp}}$$

Why? **21 Lectures at the first Conference Bernard Bigot (2024): soon on Promethee web-site**

Ienaics approach: complexation plus solvent structure @ TΔS



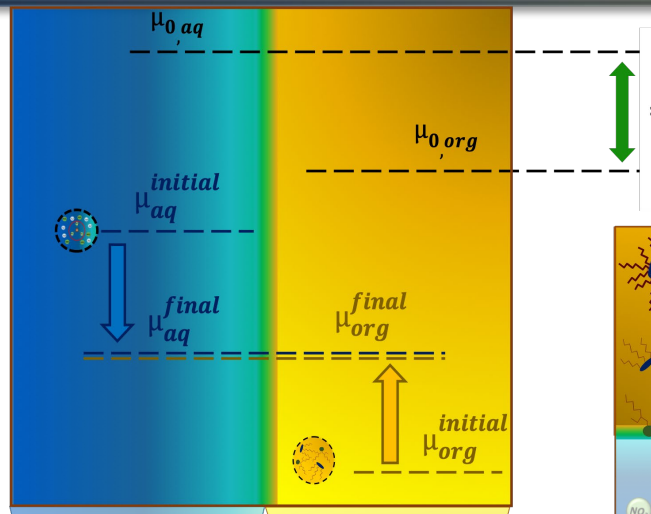


S. Marcelja (2017) Phys. Rev.
Extensive intrisnsic entropy of **ternary** fluids?
300 * 0.5 J/nm3. =>. 5-10 kJ/mol.
Compare to 40-60 60KJ/mole complexation

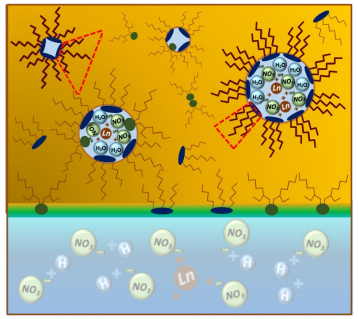
$$\Delta_{\mathrm{tr}}G^{\circ} = \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{complex}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{confin}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{apolar}} + \Delta_{\mathrm{tr}}G^{\circ}_{\mathrm{lagg}} - T\Delta_{\mathrm{tr}}S^{\circ}_{\mathrm{pdisp}}$$

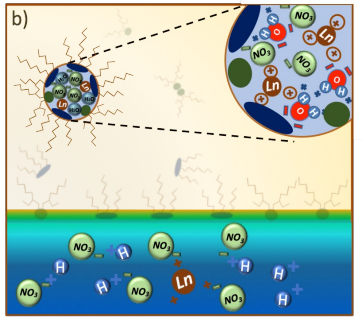
Why? **21 Lectures at the first Conference Bernard Bigot (2024): soon on Promethee web-site**

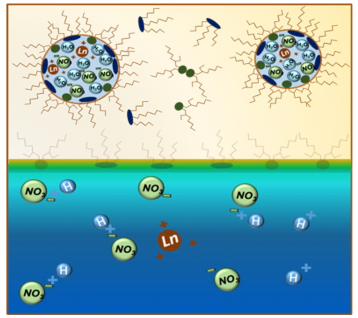
A new technology for liq-liq extraction using hydrotopes as diluent modifier & co-complexant emerges

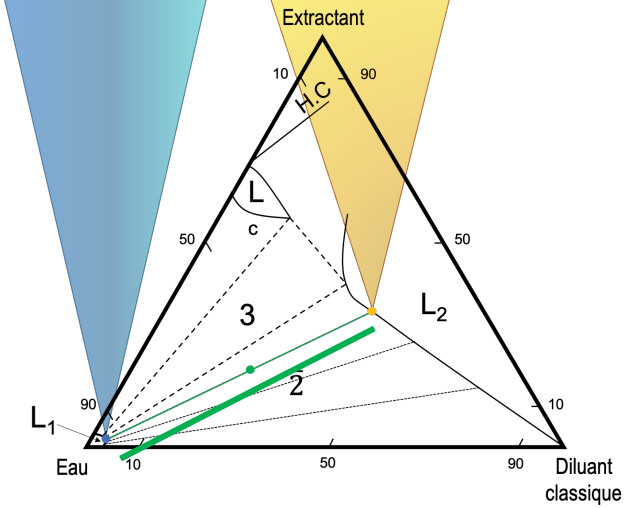


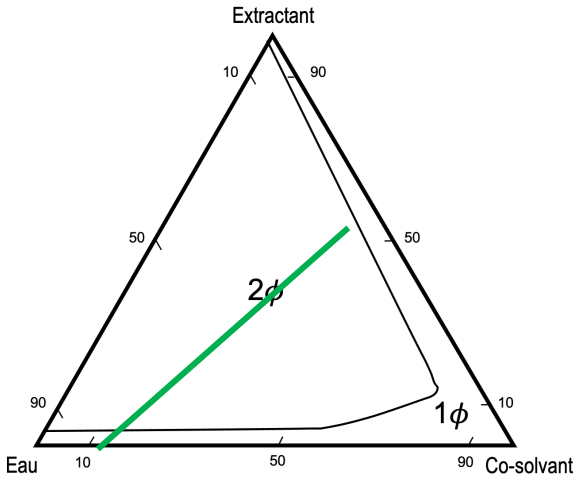
$$= \Delta G_{Extraction} = + \Delta G_{Complexation} + \Delta G_{chain} + \Delta G_{droplet}$$

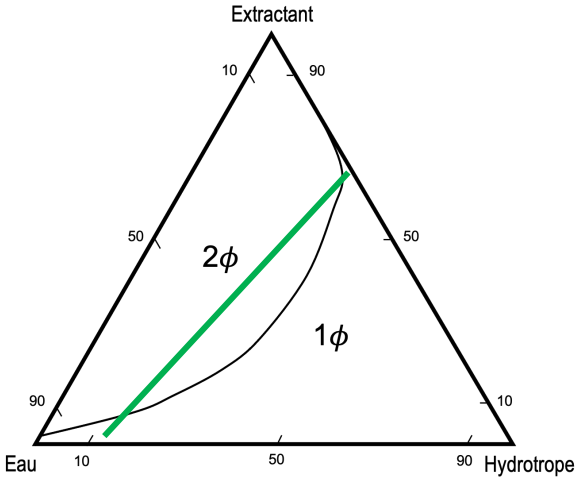












hydrotrope assisted “peri-critical” extraction : WO2023/078989 and 79055 11/5/2023