Phase Separation mechanisms in an Acidic Biphasic Solution

Gautier Meyer[1], Jean-François Dufrêche[2], Isabelle Billard[3] and Marie Plazanet[1]

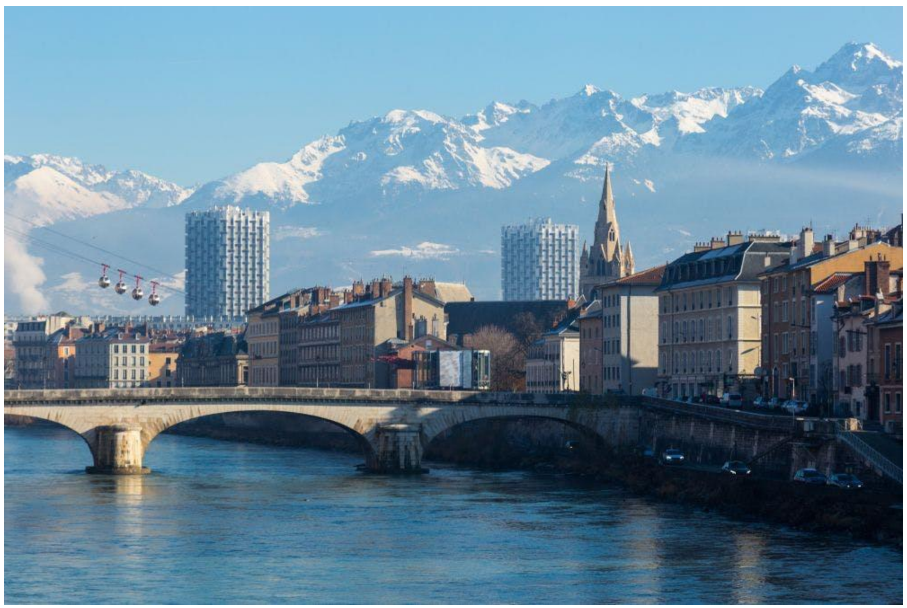
[1]LIPhy, CNRS and Univ. Grenoble-Alpes, Grenoble

[2]Institut de Chimie Séparative, Marcoule

[3]LEPMI, CNRS and Univ. Grenoble-Alpes, Grenoble

MC13
Effets d'environnement et de solvatation sur les processus moléculaires

Phase Separation mechanisms in an Acidic Biphasic Solution



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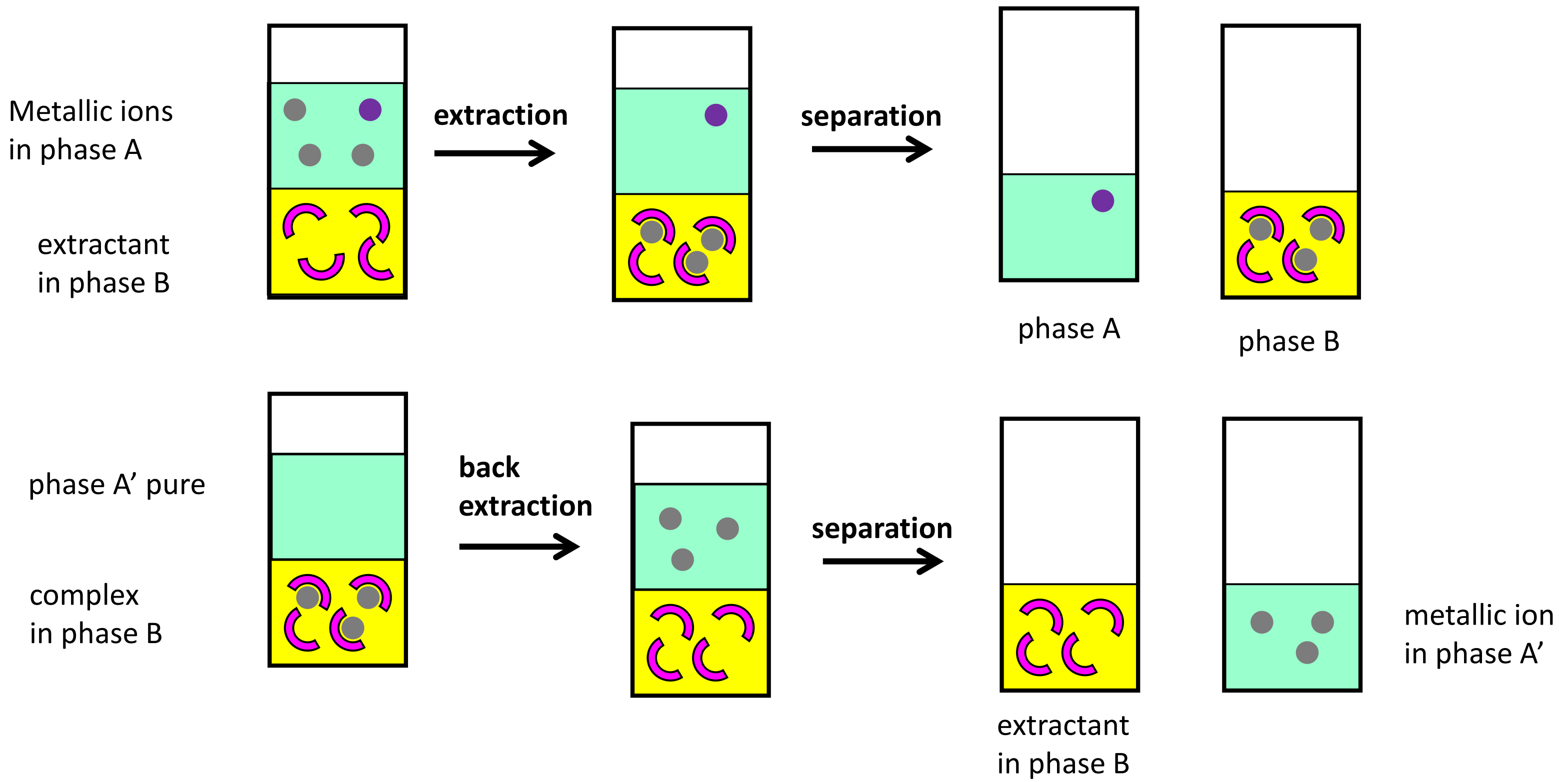
leaching with strong acids…
mixture of H_2O, Ni(II), Cu(II), Ln(III), Fe(III), Cr(VI), Pt(IV), SO_4^{2-}, Cl^-, NO_3^-, F^-…

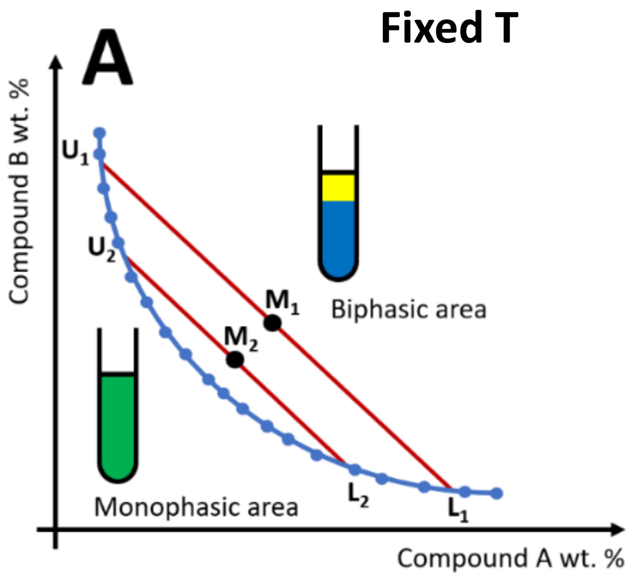
Liquid-liquid extraction



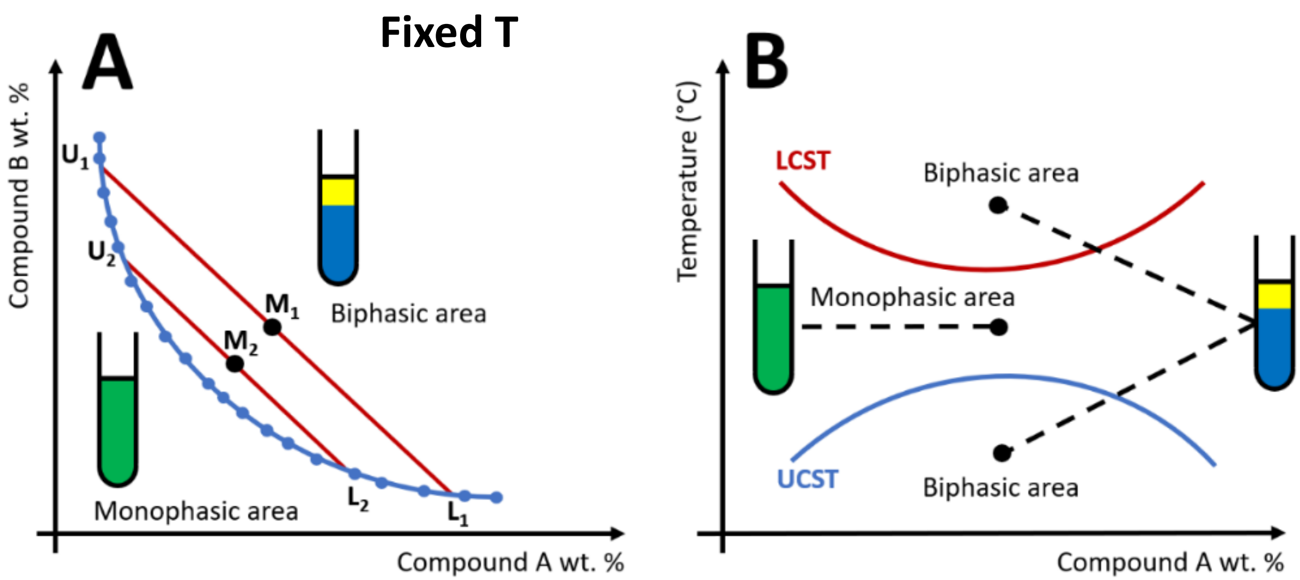
Chemicals in use:
-organic solvents (toluene, hexane….)
-extractants (TBP, DEHBA…)

Can we use less toxic solvents ? Aqueous biphasic solutions, DES, IL….

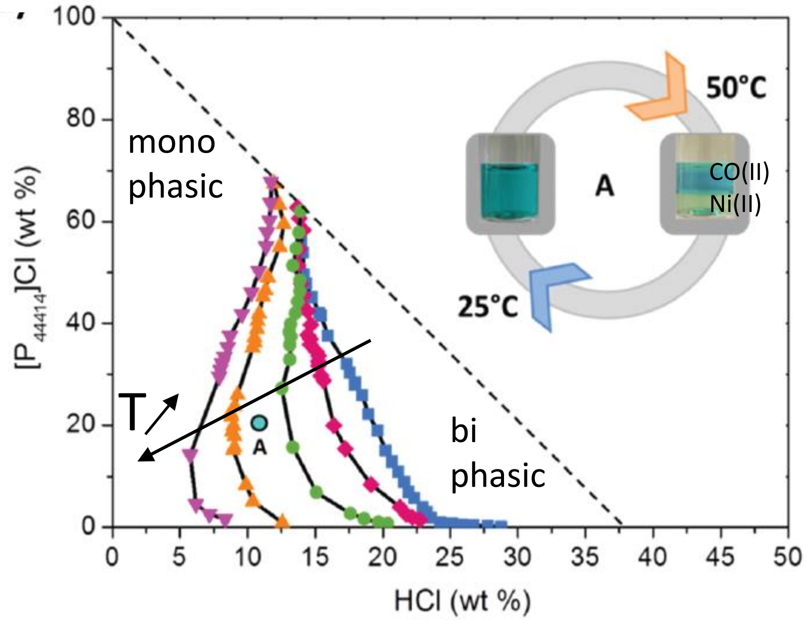
Aqueous Biphasic Systems (ABS) for liquid-liquid extraction



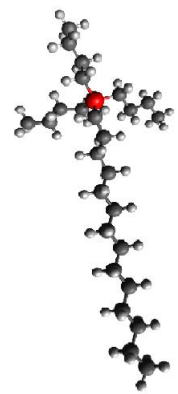
Aqueous Biphasic Systems (ABS) for liquid-liquid extraction



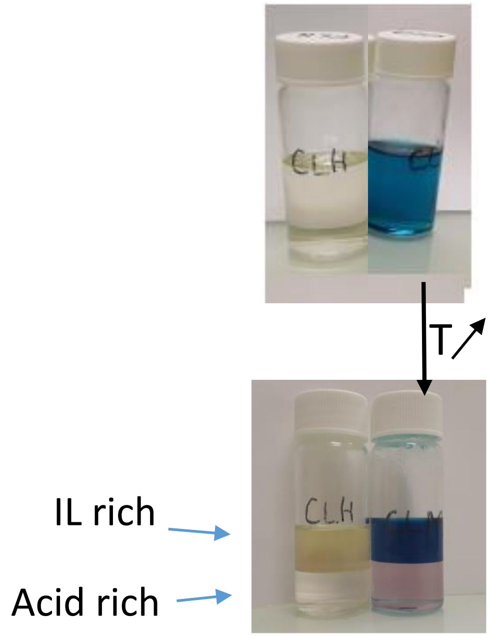
Acidic ABS : [$P_{4,4,4,14}$Cl] / HCl / H_2O



Matthieu Gras, … Joao Coutinho & Isabelle Billard, **Angew. Chem. Int. Ed., 57 (2018) 1563**.

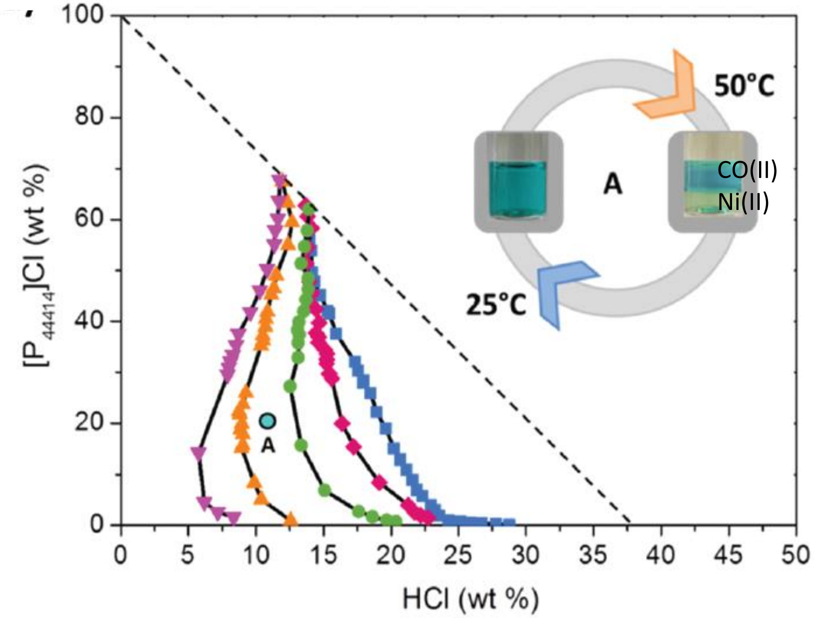


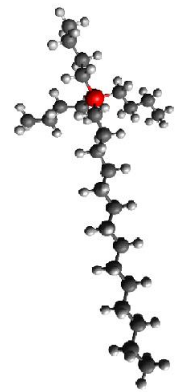
[$P_{4,4,4,14}$]Cl



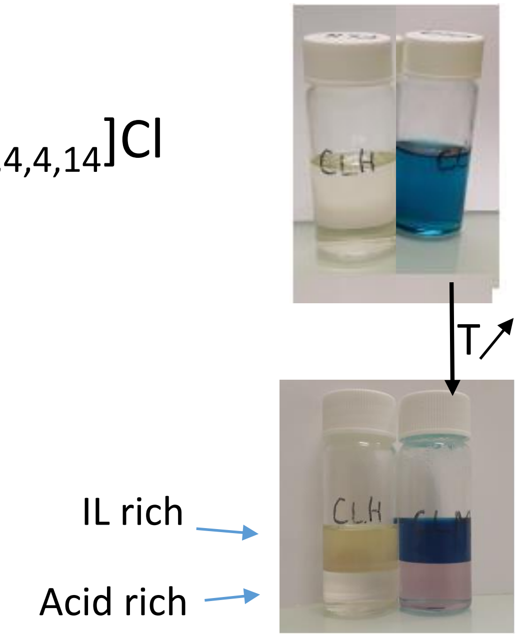
- Thermomorphic, acidic
- Low Critical Solution Temperature (LCST) : phase separation upon temperature rise
- ABS in presence of HCl or NaCl

Acidic ABS : $[P_{4,4,4,14}Cl]$ / HCl / H_2O





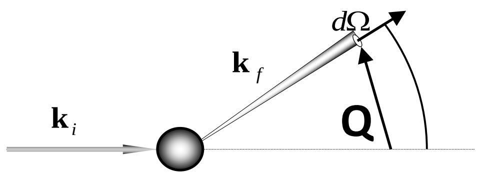
$[P_{4,4,4,14}]Cl$



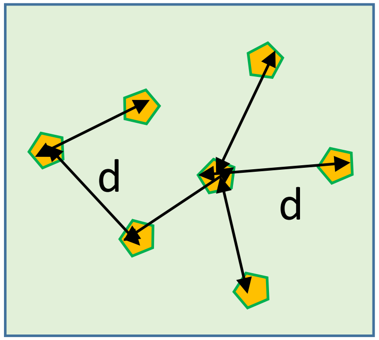
- Phase separation mechanisms vs T and [ions] ?
  - IL structural organisation
  - behaviour of free ions

- Liquid-liquid interface

Structural investigation : SANS
(Small Angle Neutron Scattering)

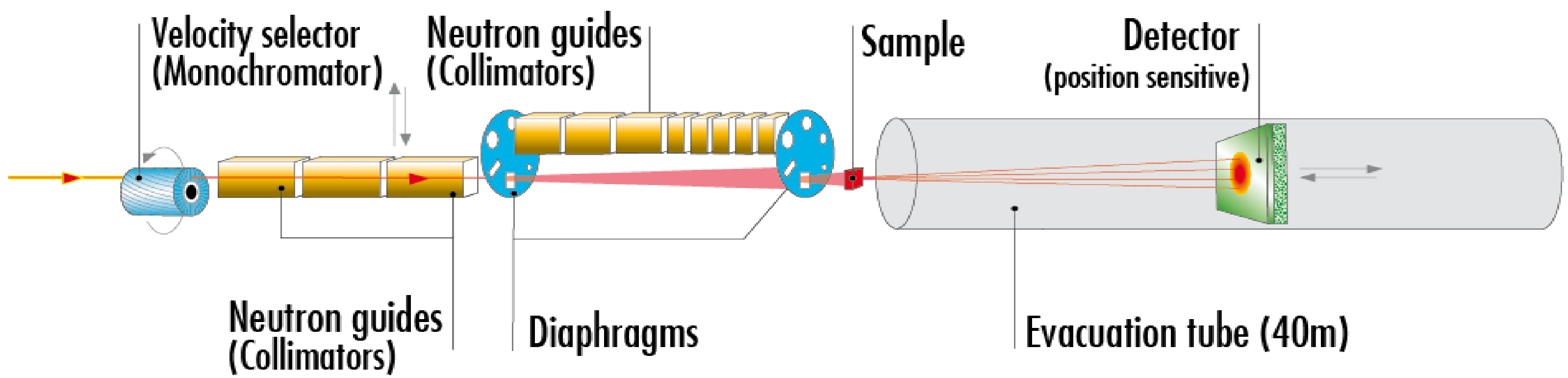


Correlation length d: $Q \sim \frac{2\pi}{d}$



$I(Q) \sim P(Q).S(Q)$

P(Q) : form factor (shape of the objects)
S(Q) : structure factor (organization)

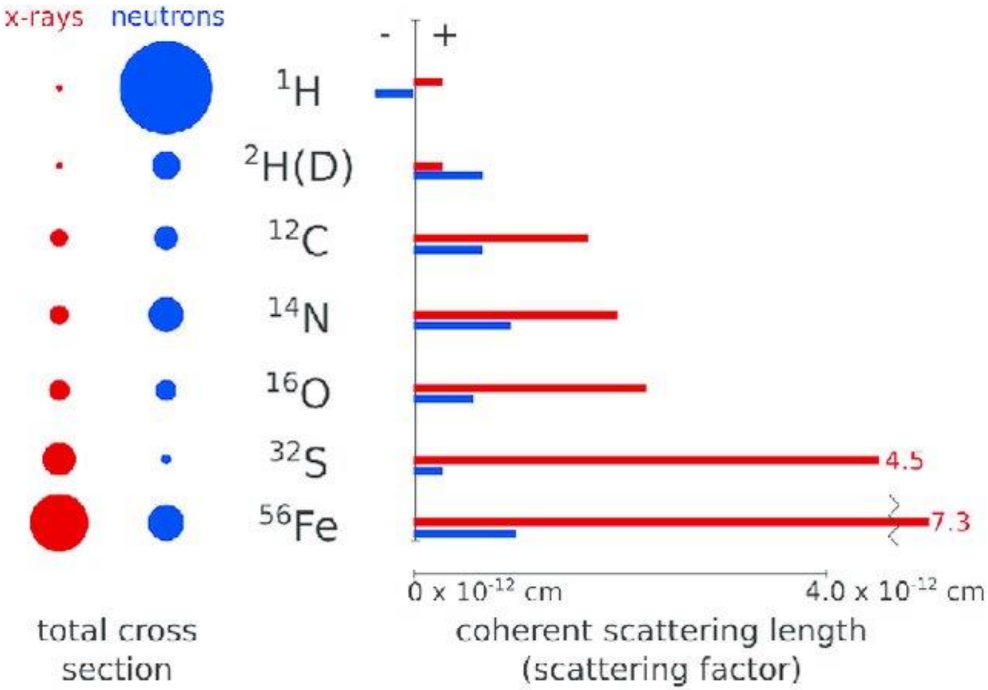


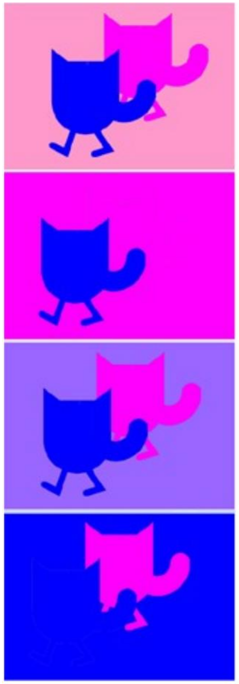
Distances ~ 1-500 nm

D11, ILL (Grenoble, France)

Structural investigation : SANS
(Small Angle Neutron Scattering)

H/D contrast with neutron scattering

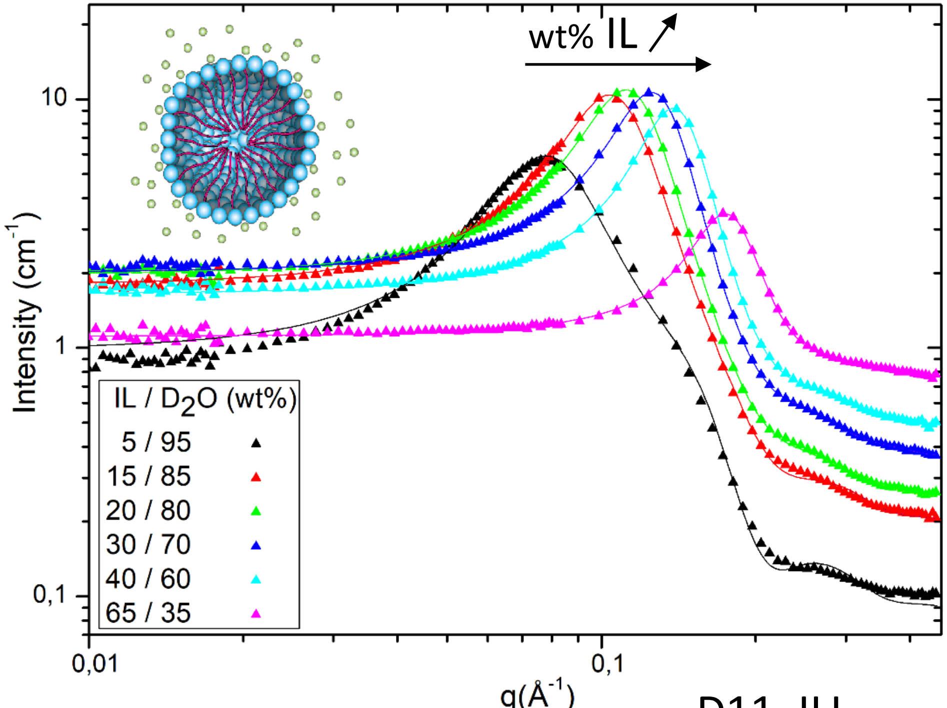




>>> Hydrogenated IL in deuterated solvent.

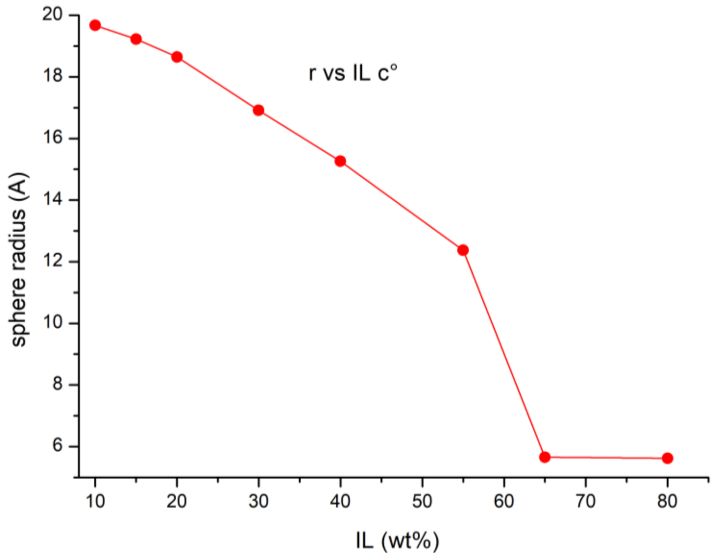
Binary mixture [$P_{4,4,4,14}Cl$] / D_2O

Structure from SANS



D11, ILL

Micelles radius ~ 17 Å :
~ length of the cation

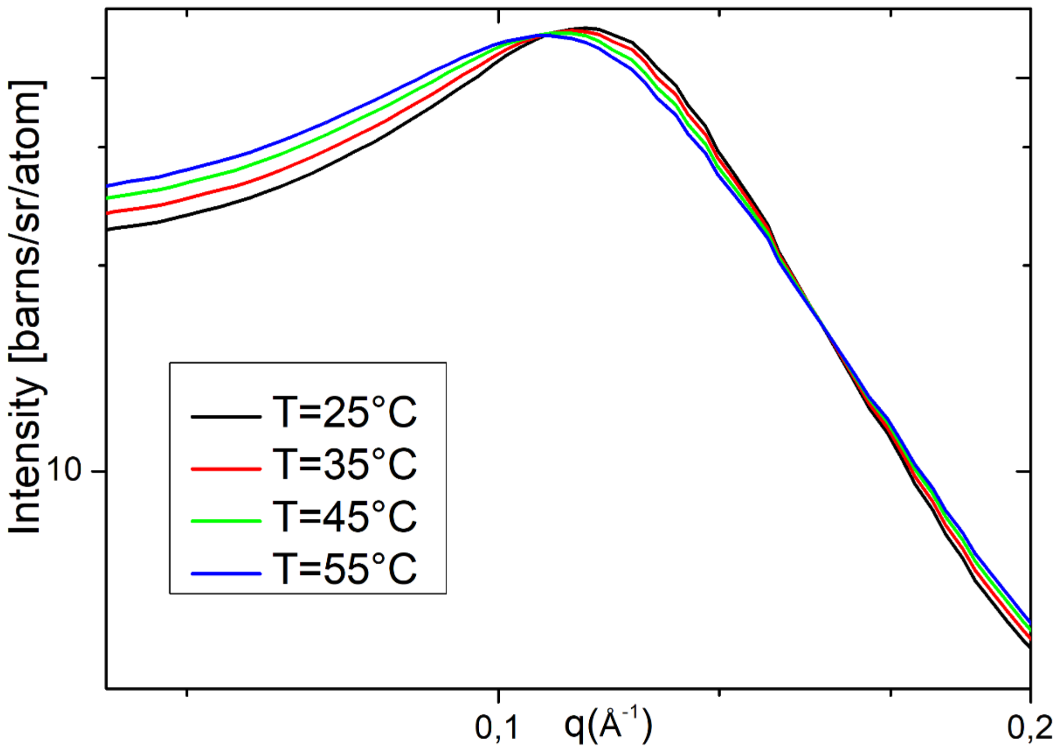


Spherical micelles dispersed in solution due to electrostatic interactions

Form factor : hard spheres (micelles)
Structure factor : hard spheres (larger radius)

Binary mixture [$P_{4,4,4,14}$Cl] / D_2O

Temperature dependence



no structural modification over the temperature range of the phase separation in corresponding acidic solutions

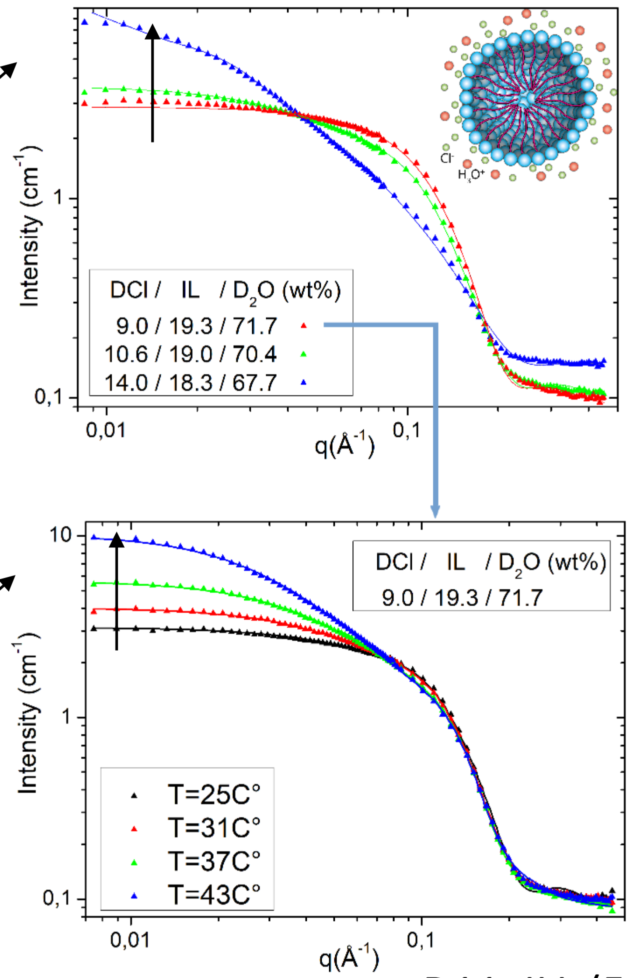
Nimrod, ISIS (UK)

Acidic ABS : [$P_{4,4,4,14}$Cl] / DCl / D_2O

Structure from SANS

wt% HCl ↗

temperature ↗

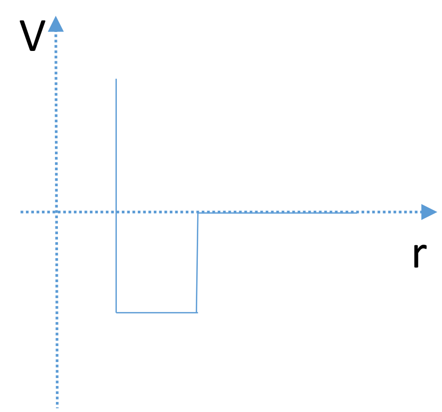


D11, ILL (France)

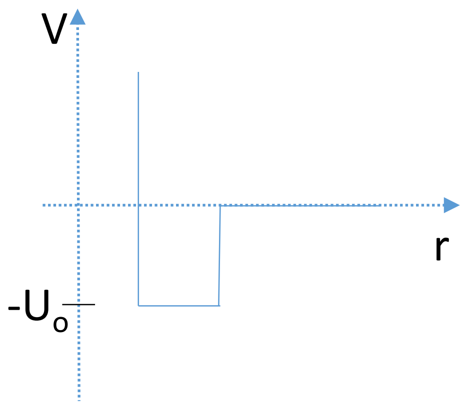
Micelles aggregation upon acid addition or temperature rise

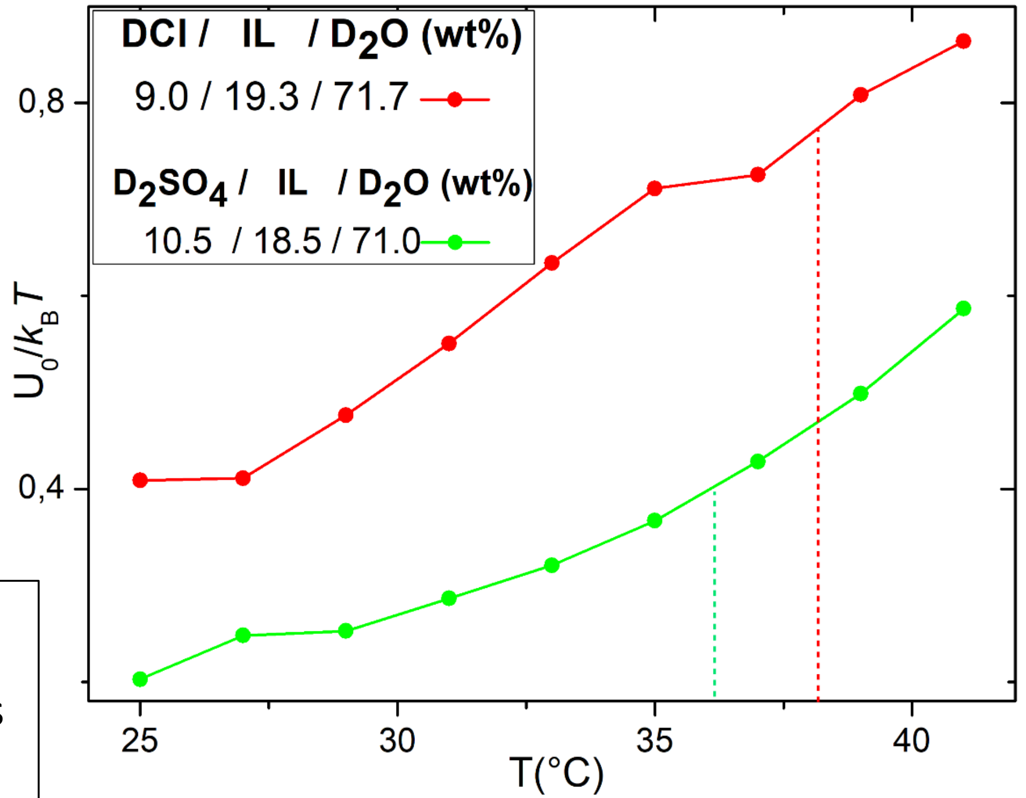
Form factor : hard spheres (**spherical micelles**)

Structure factor : **sticky hard spheres** (larger radius)



Acidic ABS : [$P_{4,4,4,14}$Cl] / DCl / D_2O





Stickiness ~ kT

>> aggregation of the micelles

>> phase separation.

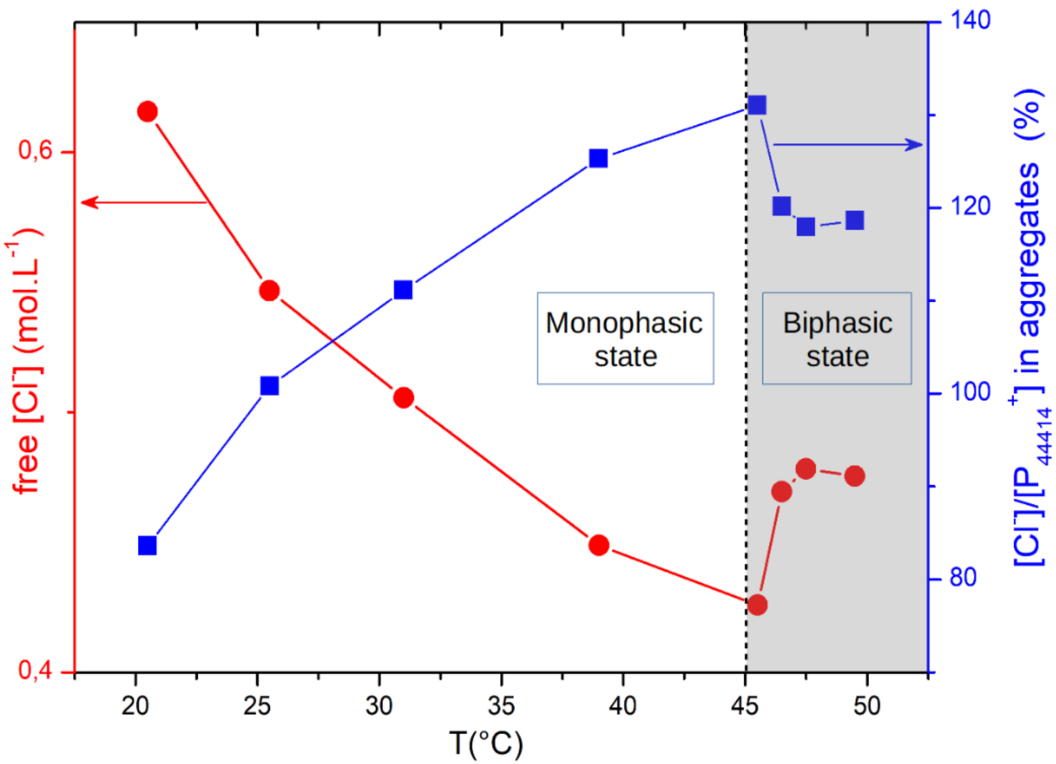
Phase separation temperature

Phase separation mechanisms with temperature?

What causes the increase of stickiness ?
>> increase of electrostatic screnning

[$P_{4,4,4,14}$Cl], NaCl, H_2O

Free Cl^- titration



free [Cl^-] decreases with temperature:

Cl^- exothermic adsorption at the micelle surface ΔH_{ads}~ 12 kJ/mol

⇓

Screening of electrostatic repulsion

⇓

micelle aggregation

⇓

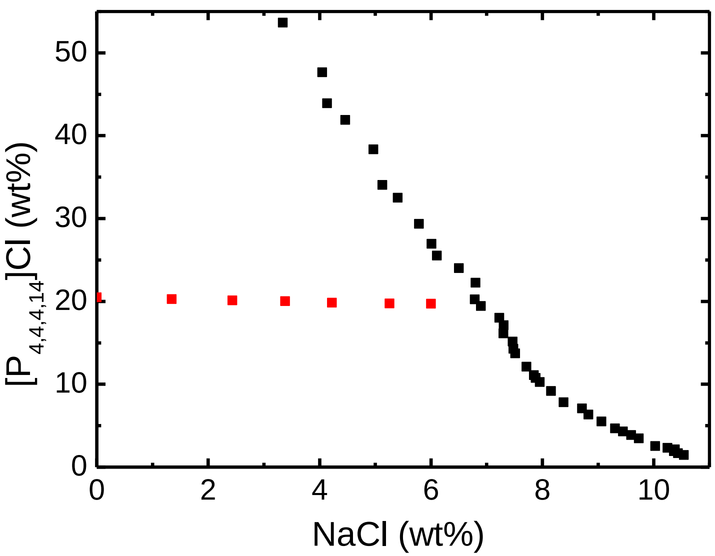
flocculation

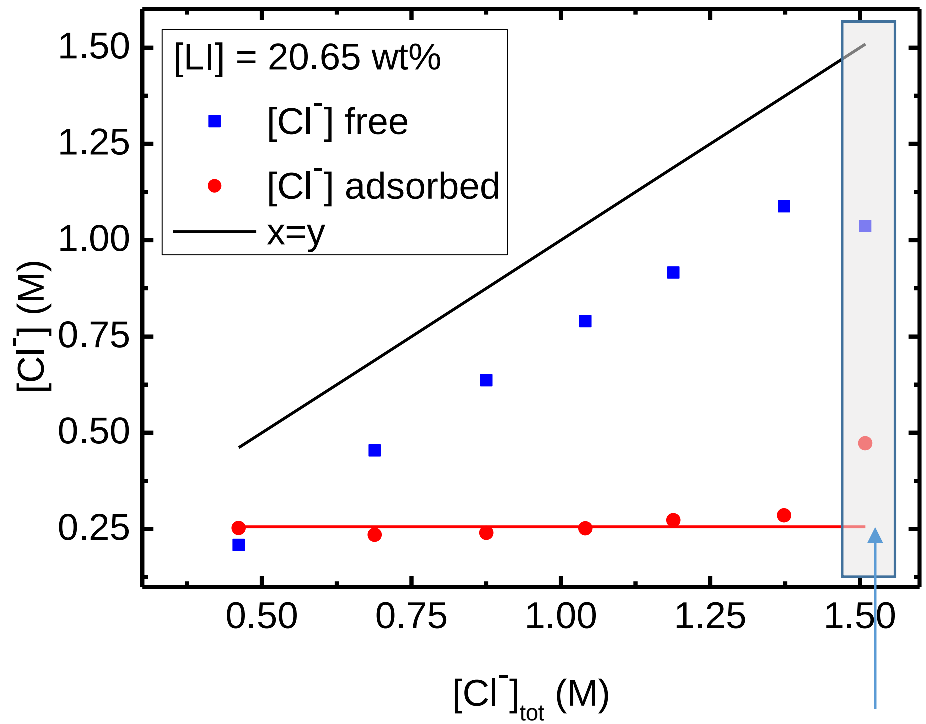
G. Meyer et al., J. Phys. Chem. Let. (2022), 13, 2731-2736.

Phase separation mechanisms with [ions] ?

Does the addition of charges also cause the adsorption at the micelle surface ?

Free Cl^- titration



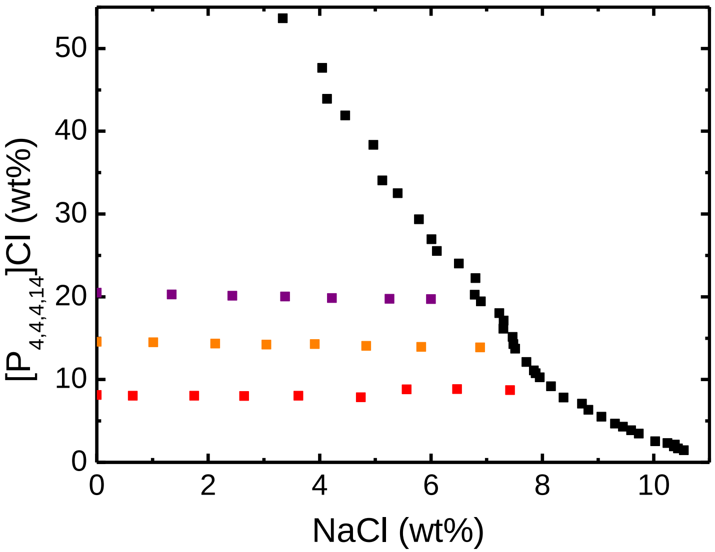


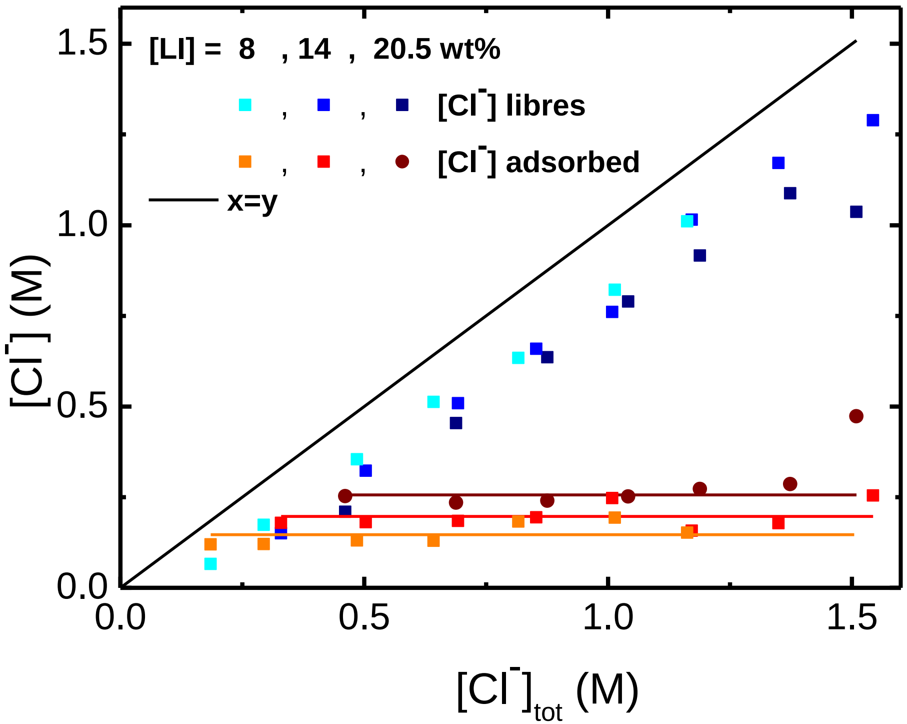
$$[Cl^-]_{ads}=1-[Cl^-]_{free}$$

Specific Cl^- electrode limit of linearity

Phase separation mechanisms with [ions] ?

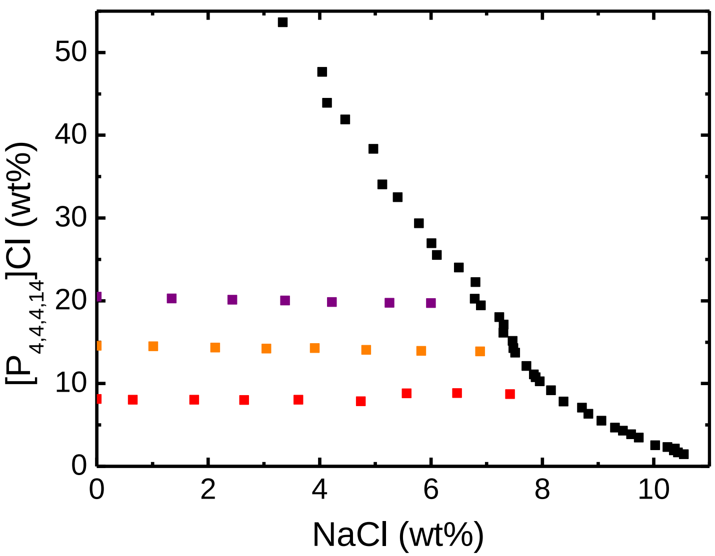
Does the addition of charges also cause the adsorption at the micelle surface ?

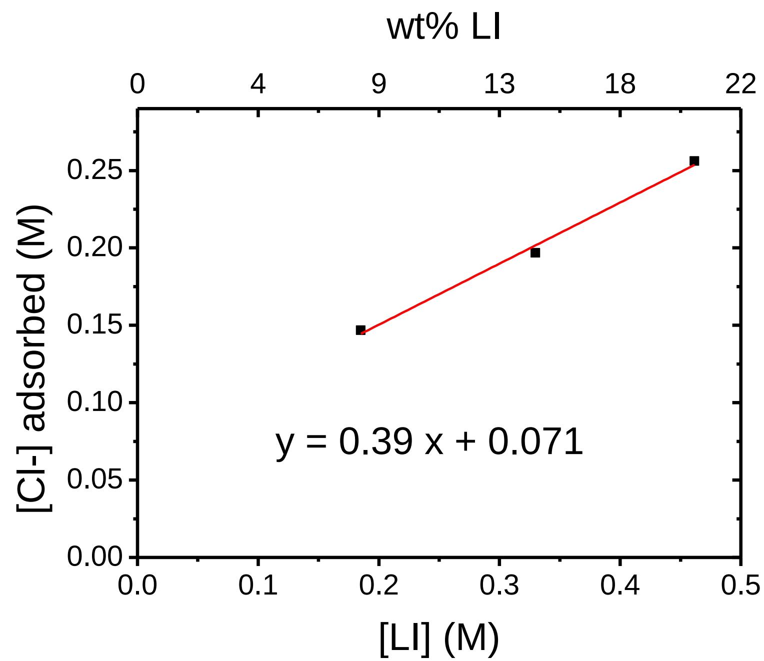




Phase separation mechanisms with [ions] ?

Does the addition of charges also cause the adsorption at the micelle surface ?





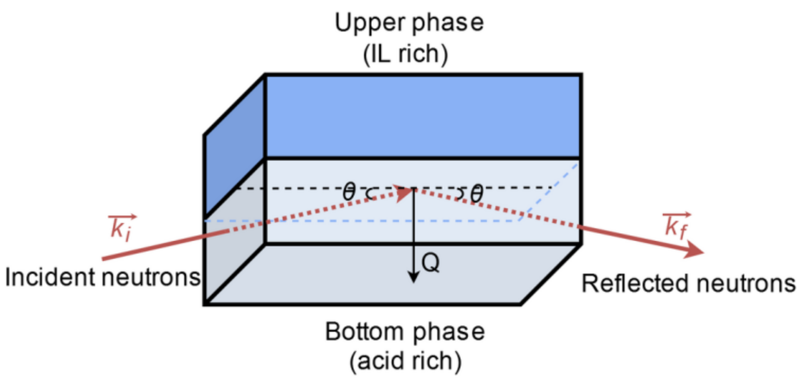
40% Cl$^-$ adsorbed at the micelle surface, independent of [NaCl] :

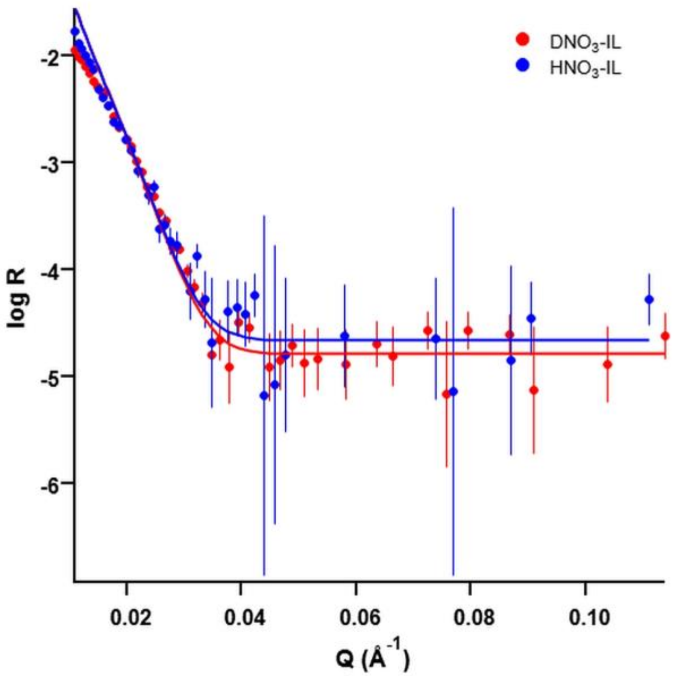
screening of the interactions through the ionic strength of the solution

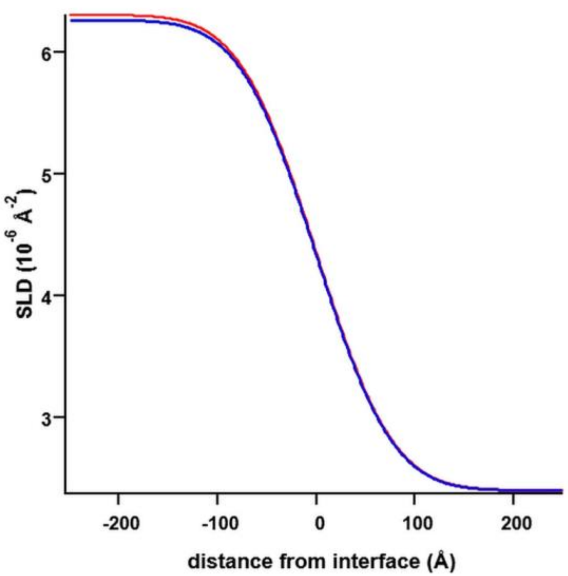
→ *Modelling of electrostatic interaction through regulation charge therory in order to understand the role of solvent, electrical double layer and adsorption.*

Liquid-liquid interface

Neutron reflectometry







IL/DNO_3 /D_2O (29,4/4,8/65,8 wt%)

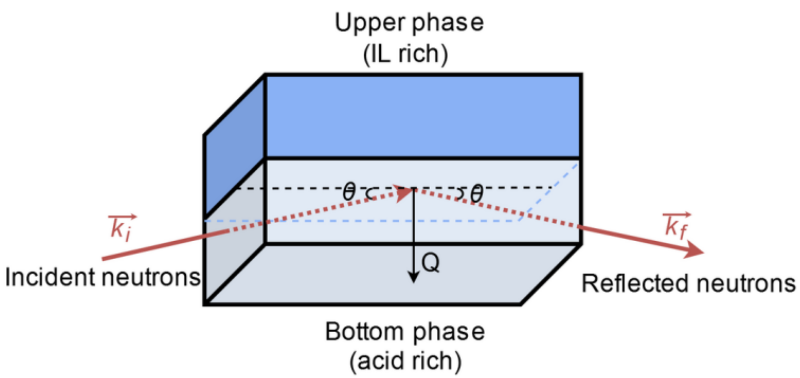
Data from FIGARO (ILL)

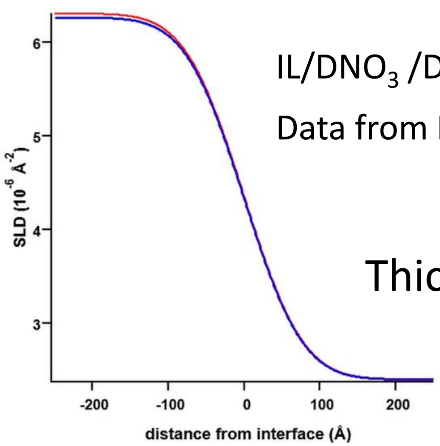
Thickness of the interface :

$$\sigma = 65 \text{ Å}$$

Liquid-liquid interface

Neutron reflectometry





IL/DNO_3 /D_2O (29,4/4,8/65,8 wt%)

Data from FIGARO (ILL)

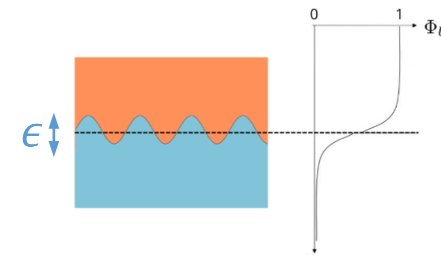
Thickness of the interface :

$$\sigma = 65\ \text{Å}$$

Surface tension ~ 0.7 mN/m

-> amplitude of capillary wave:

$$\epsilon^2 = \frac{k_B T}{2\pi\gamma} \ln\left(\frac{\Lambda}{\xi}\right)$$



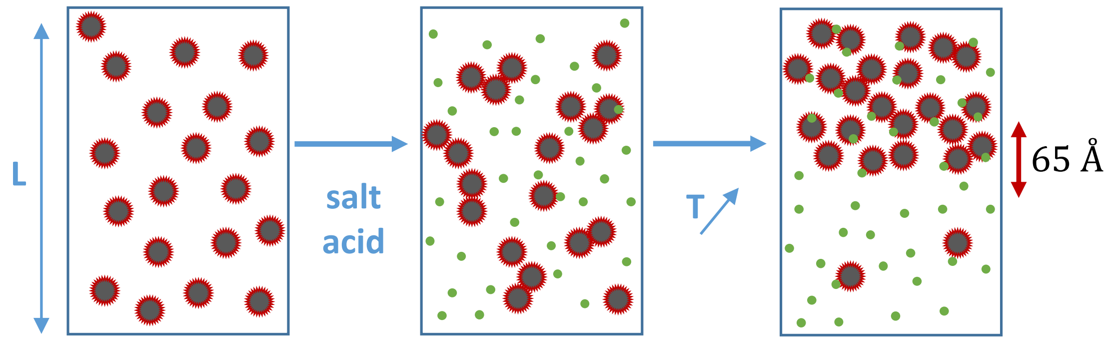
With $\Lambda = \sqrt{\dfrac{\gamma}{\Delta\rho g}}$ capillary length

ξ : characteristic molecular length

$$\epsilon \sim 40\ \text{Å}$$

>> can we discriminate between a model of fluctuating surfactant at the surface with amplitude of 4 nm, or micelle coencentration decreasing over the length of 2 micelles diameters (= 6 nm) ?

Summary and perspectives



Phase separation in acidic [$P_{4,4,4,14}$][Cl] LCSTsolution:

- **Self-aggregation** of IL in water in micelles dispersed by electrostatic interactions
- **Different screening** mechanism in presence of ions (acid or salt) with concentration and temperature
- **exothermic adsorption of Cl^-** ions compensates for the entropy loss

- **ionic/molecular adsorption at the micelle surface** is a possible general mechanism for the LCST in molecular systems.

> Do complexed **metallic ions migrate** toward their preferential phase in following the same mechanism ?

Collaborators

G. Meyer, PhD

Isabelle Billard,
LEPMI, Grenoble

J-F. Dufreche,
ICSM & U. Montpellier

Ralf Schweins, ILL

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Philip Gutfreund, ILL (France)
Tristan Youngs, ISIS (UK)

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