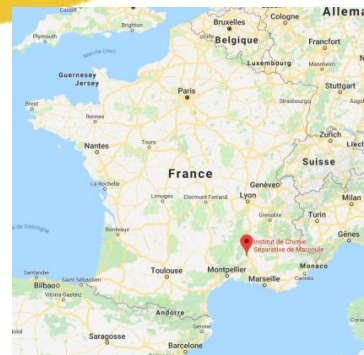
Institut de Chimie Séparative de Marcoule

Small Angle X-ray and Neutron Scattering for solvent extraction

S. Dourdain, O. Pecheur, Z. Lu, L. Ginot, E. Guerinoni, A. El Maangar, T. Zemb, S. Pellet-Rostaing



École Doctorale Sciences Chimiques Balard

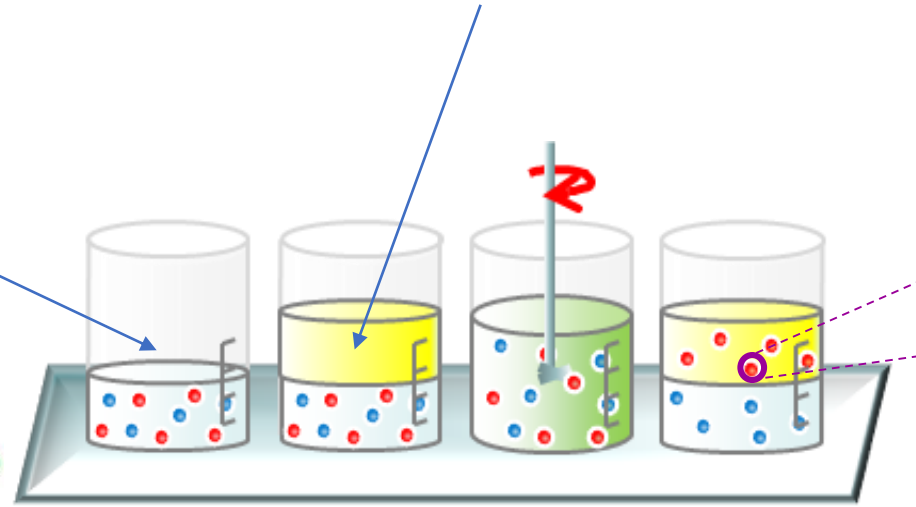
UNIVERSITÉ DE MONTPELLIER

ENS Chimie Montpellier

Solvent extraction

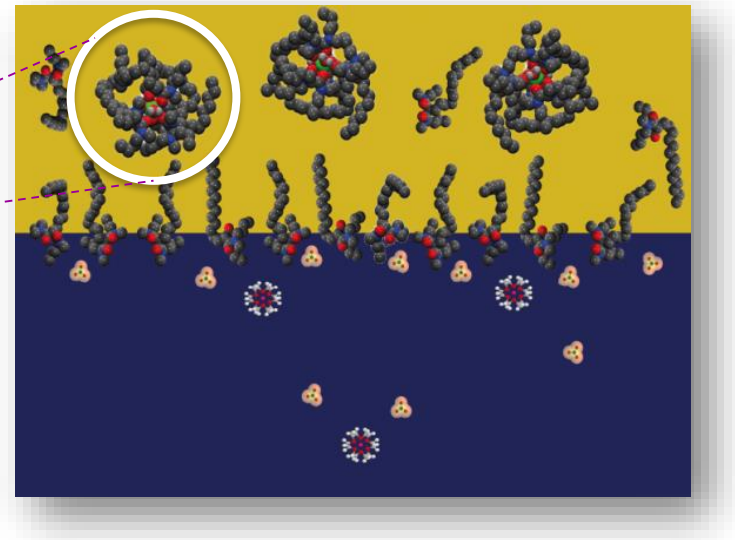
- Ores mining,
- Nuclear waste treatment,
- Electronic waste recycling, …

Extractants + Organic diluent



Design and optimization

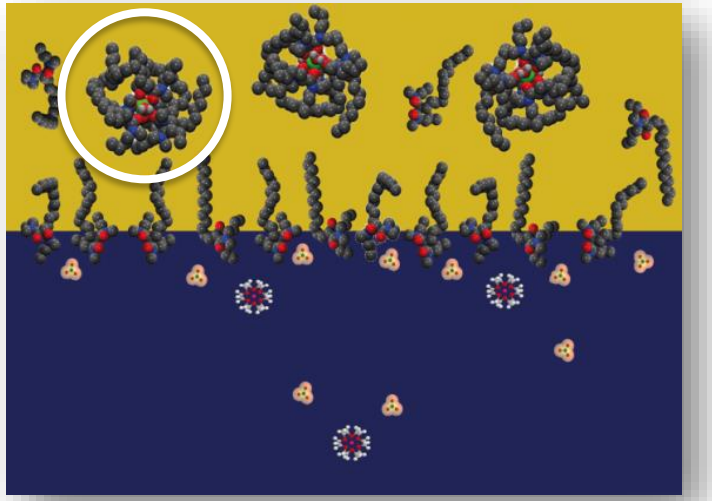
→ understand solvent extraction mechanisms



Complexes or reverse micelles ?

Extractant/Surfactant analogy

Complexes or reverse micelles ?



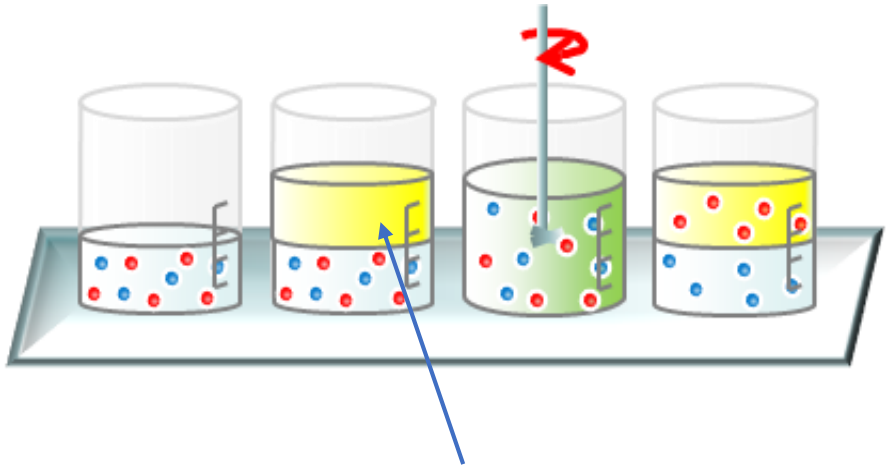
	Surfactants	Extractants
Surfactant = Surface Active Agent	Decrease Interfacial Tension	
Amphiphilic	V_{apol} l_c a_0	V_{apol} a_0
W/O micro-emulsion	Able to solubilize water and solutes	

Packing parameter

$$P = \frac{V_{apol}}{a_0 l_c}$$

➢ **Need to characterize the structure of the organic phase**

SAS for solvent extraction



1- To characterize aggregation and understand SX mechanisms

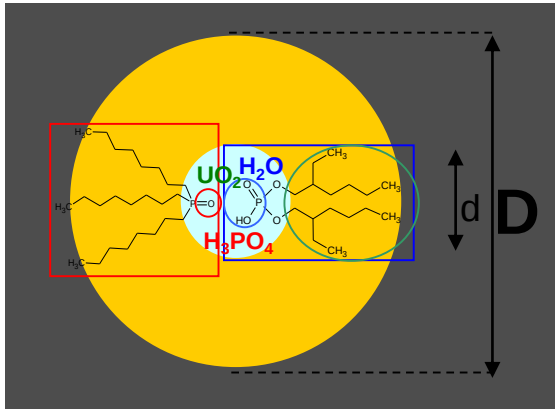
2- To understand 3rd phase problems

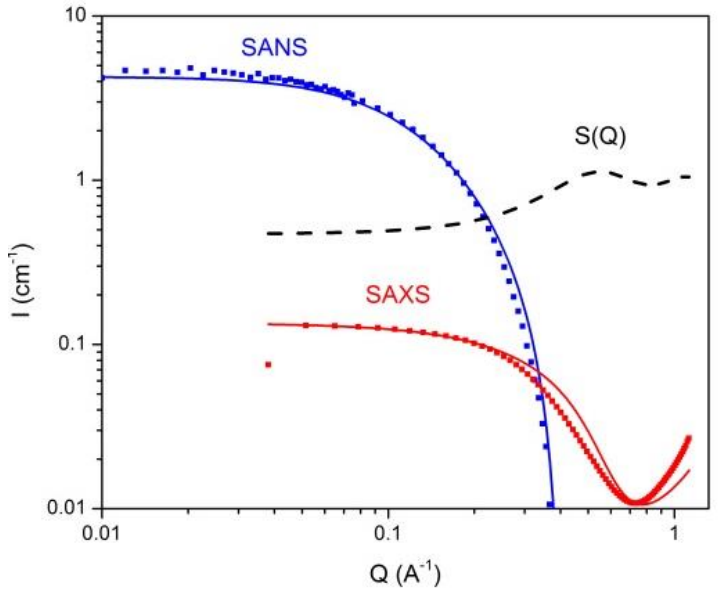
SAXS and SANS: Fitting data with complementary techniques

SA**N**S and SA**X**S

Neutrons

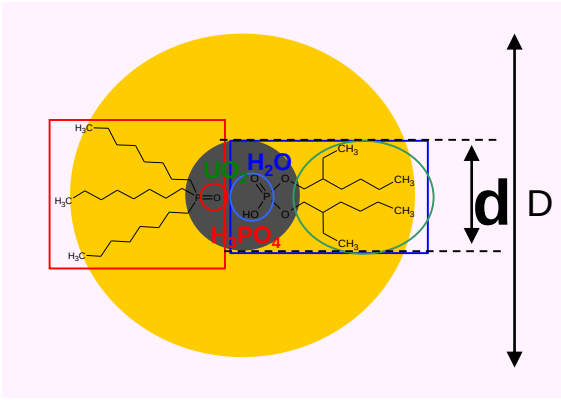
protons → deuterated solvent → diameter **D**





X-rays

electrons → high Z (metals,…) → diameter **d**



Fitting two set of data with same parameters

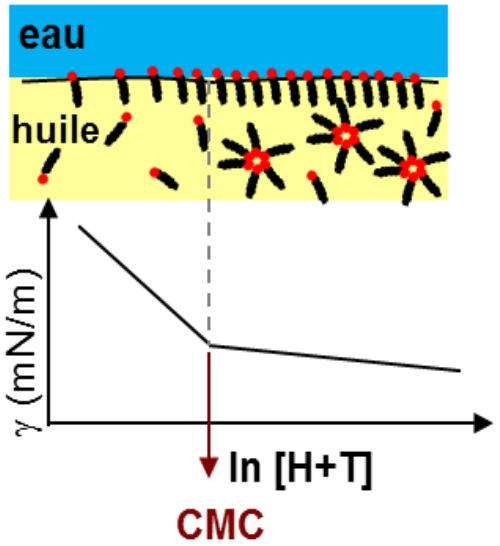
$$I(Q) = \frac{N_a(C - CAC)}{N} V^2(\Delta\rho)^2 P(Q) S(Q)$$

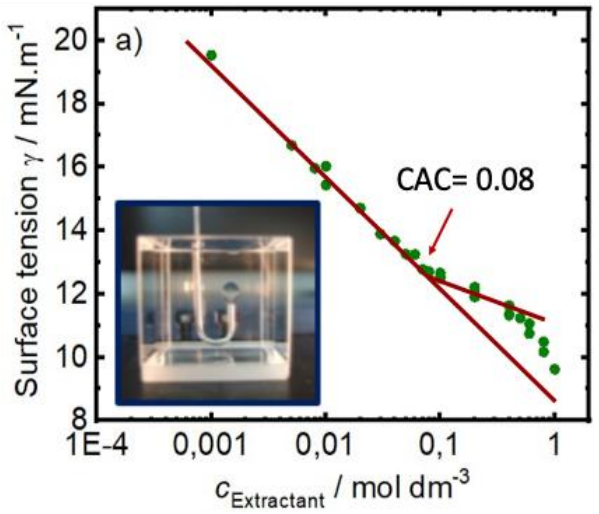
➢ V, $\Delta\rho$, CAC, Nag

- **Aggregates size: Rcore, Ragg, Nagg**
- **Interactions between aggregates,**
- **Diluent penetration in the aggregate's shell**
- **CMC/CAC**

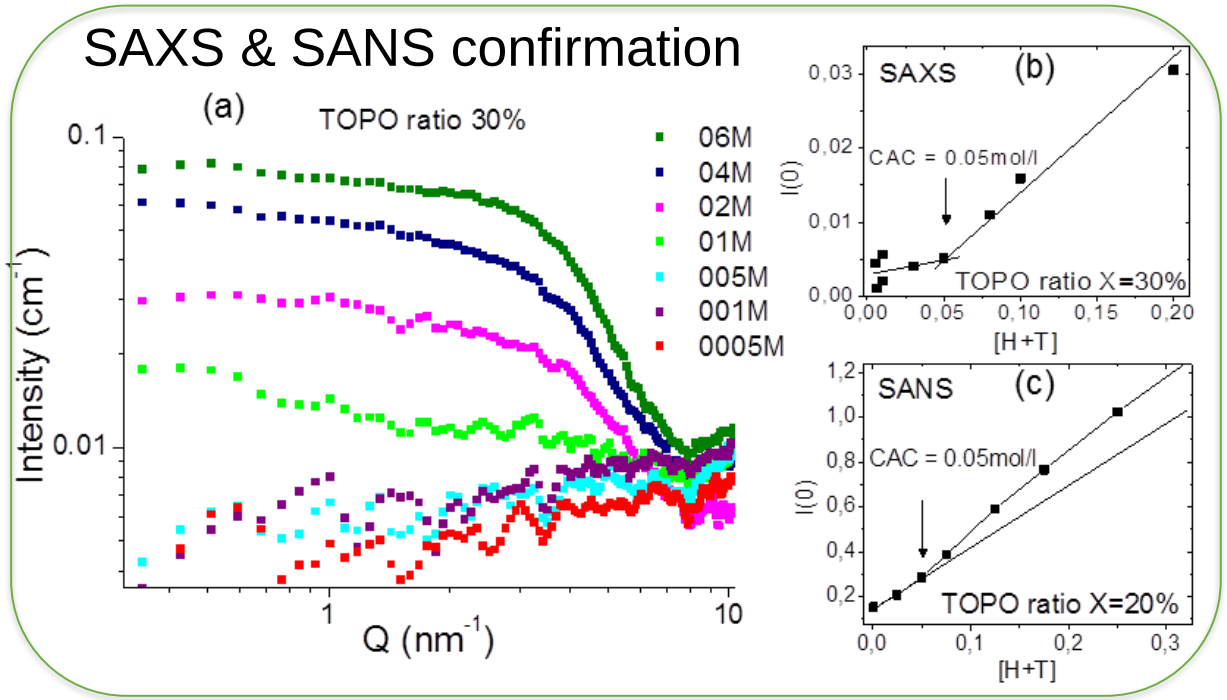
SANS to determine CMC / CAC

Surface tension measurement





SAXS & SANS confirmation



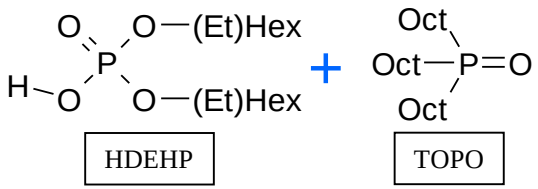
S. Dourdain, I. Hofmeister, O. Pecheur, J-F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing, T. Zemb, *Langmuir* **2012**

SANS to determine CMC / CAC

URPHOS

Non conventionnal mine for uranium

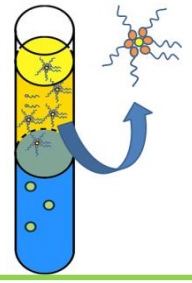
Phosphoric acid, Fertilizers

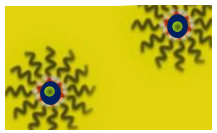


Mixture of extractants

→Synergistic extraction

Organic phase of solvent extraction



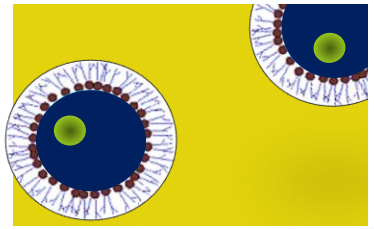


Complexes / aggregates

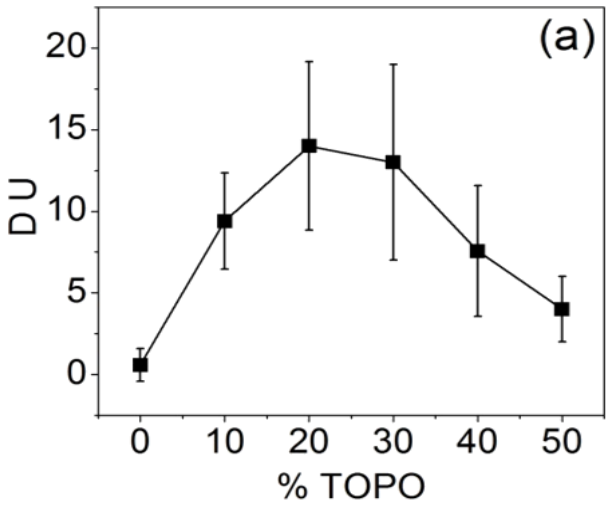
Analogie

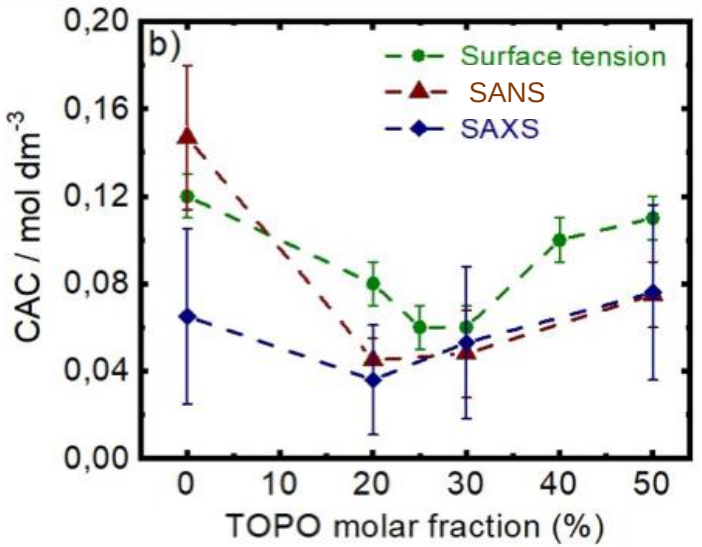
$$\Delta G^{0}_{aggregation} = RT \ln CAC$$

W/O Microemulsion



Reverse micelles

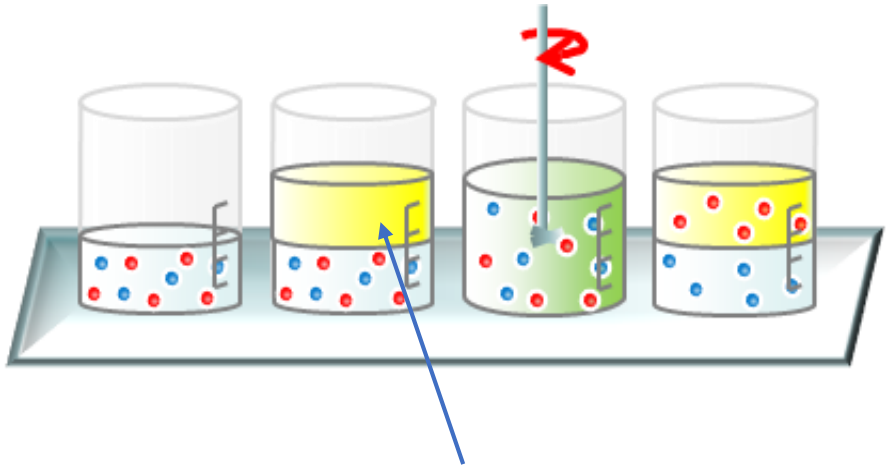




➢ CAC Minimization = synergistic aggregation concomitant with synergistic extraction

S. Dourdain, I. Hofmeister, O. Pecheur, J-F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing, T. Zemb, *Langmuir* **2012**

SAS for solvent extraction

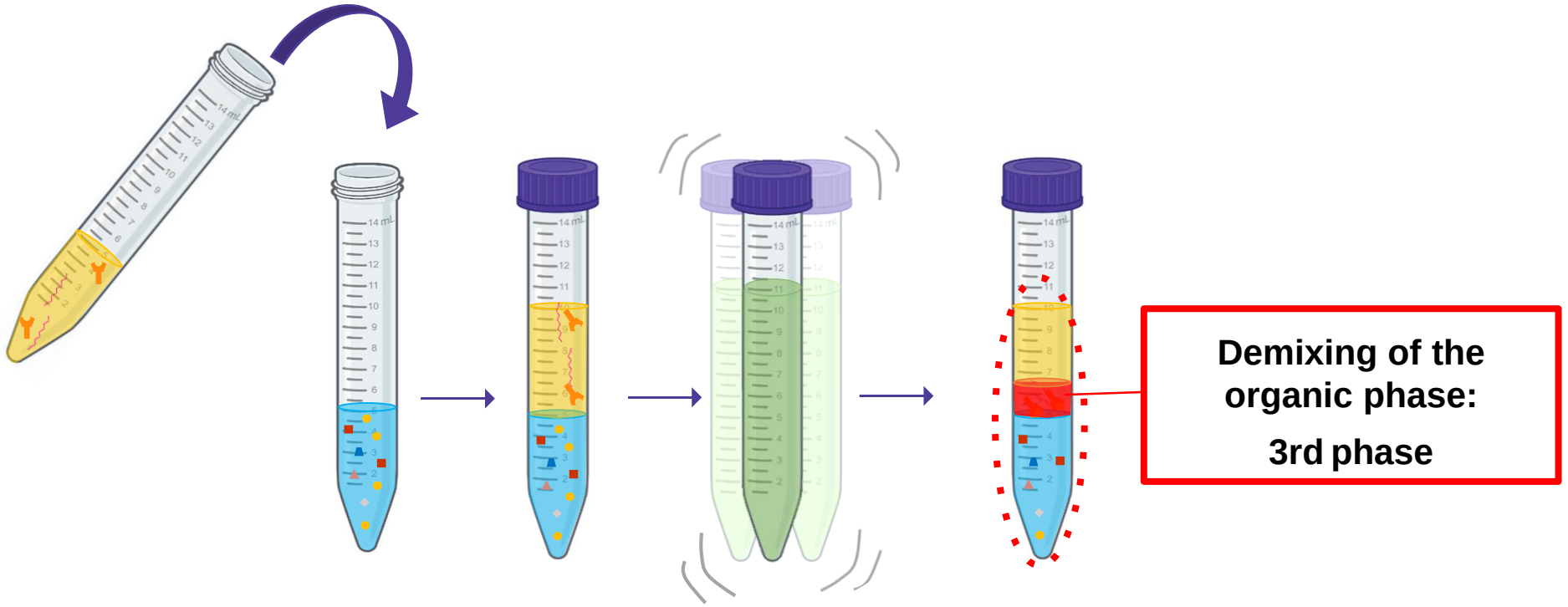


1- To characterize aggregation and understand SX mechanisms

2- To understand 3rd phase problems

- **origins of phase demixing**
- phase modifiers

3rd phase problem



Supra-molecular interpretation of the third phase formation

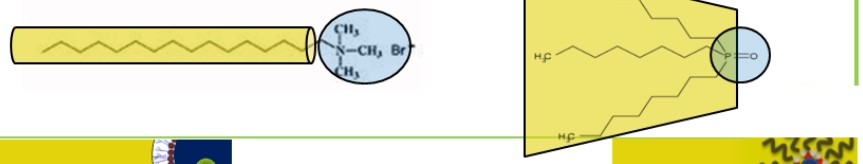
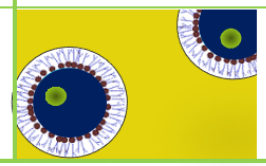
RESEARCH PAPER

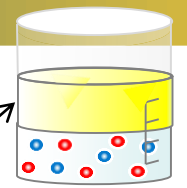
Supramolecular organisation of tri-*n*-butyl phosphate in organic diluent on approaching third phase transition

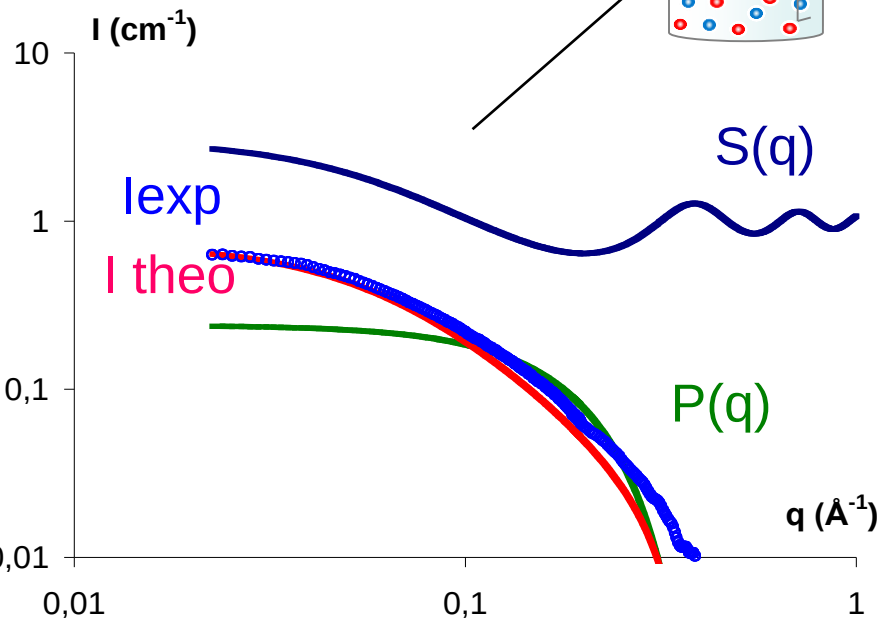
S. Nave,[a] C. Mandin,[a] L. Martinet,[a] L. Berthon,[b] F. Testard,[a] C. Madic[c] and Th. Zemb*[a]

[a] CEA, DS...
E-mail: ze...
[b] CEA, DE...
Bagnols-s...
[c] CEA, DE...

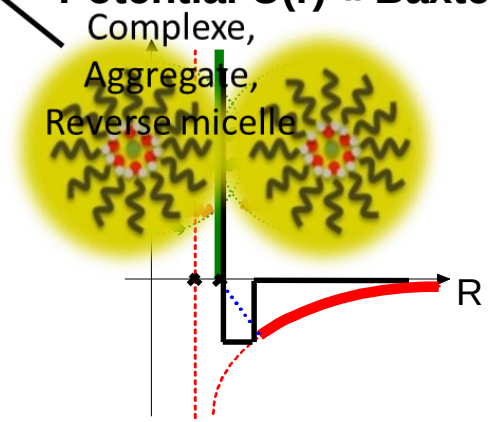
Third Phase Formation Revisited: The U(VI), HNO_3–TBP, *n*-Dodecane System[#,§]

	Surfactants	Extractants
Surfactant = Surface Active Agent	Decrease Surface Tension	
Amphiphilic		
W/O micro-emulsion	 Able to solubilize water and solutes	





Potential U(r) « Baxter »



- Attractive interactions between the polar cores of aggregates due to Van des Walls interactions

Solvent Penetration and Sterical Stabilization of Reverse Aggregates based on the DIAMEX Process Extracting Molecules: Consequences for the Th... Phase Formation

L. Berthon and L. Martinet
CEA ValRhô, DEN/DRCP/SCPS/LCSE, Bagnols-su...

F. Testard
CEA Saclay, DSM/DRECAM/SCM/LIONS, Gif-sur-Yvette

C. Madic
DEN-DDIN, CEA-Saclay, Gif-sur-Yvette, France

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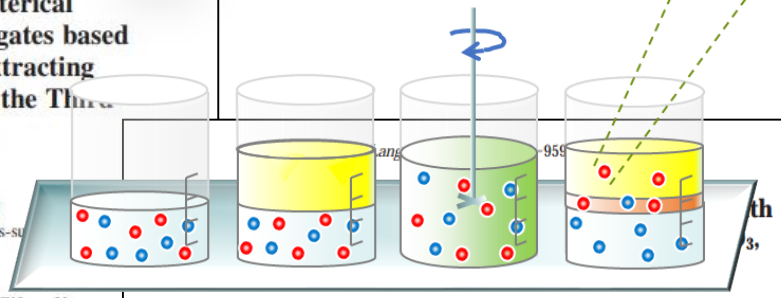

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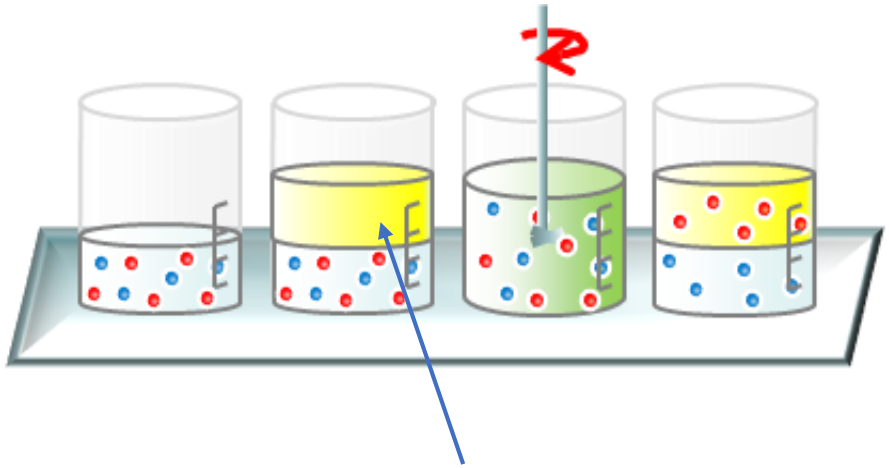
Chemistry Division and IPNS Division, Argonne National Laboratory, Argonne, Illinois 60439

Received April 11, 2003. In Final Form: August 25, 2003

Small-angle neutron scattering (SANS) data for the tri-*n*-butyl phosphate (TBP)−*n*-dodecane, HNO_3–$UO_2(NO_3)_2$ solvent extraction system have been interpreted using the Baxter model for hard spheres with surface adhesion. The increase in the scattering intensity in the low *Q* range observed when increasing

SAS for solvent extraction

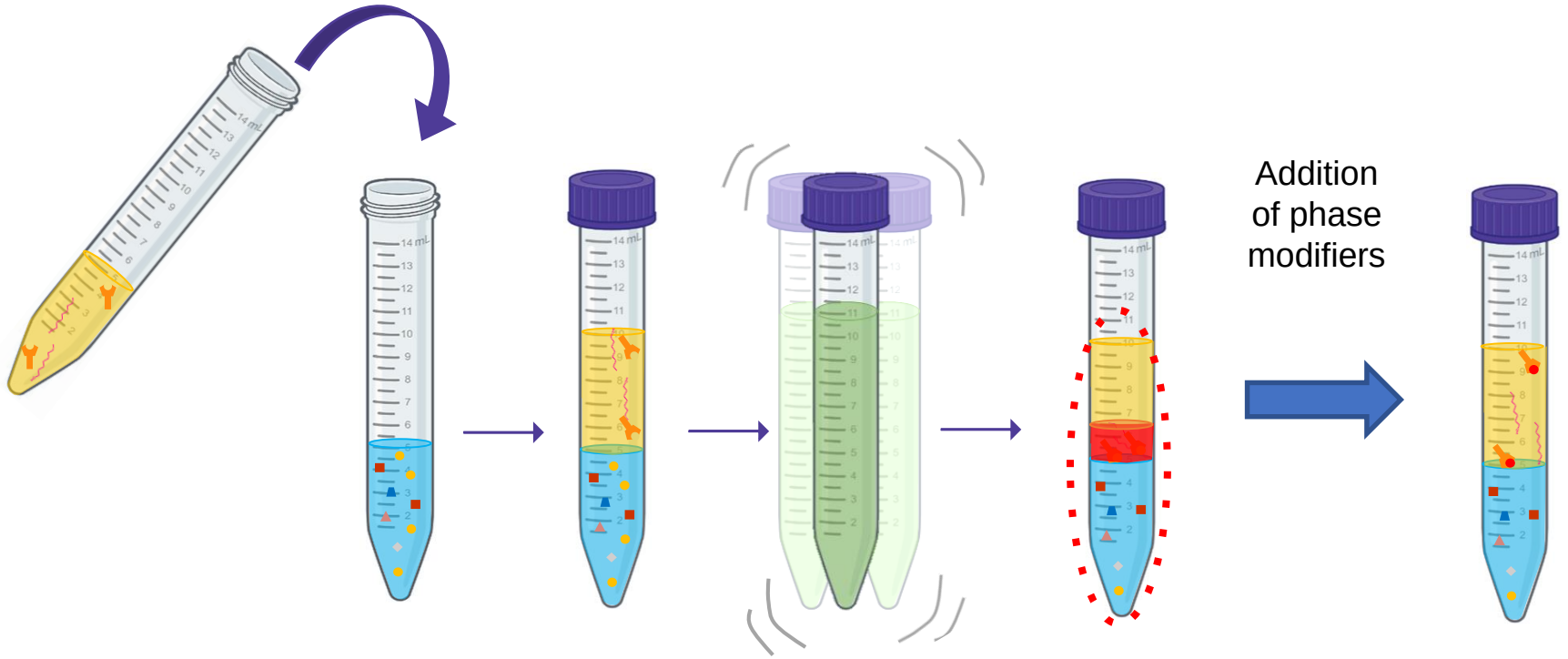


1- To characterize aggregation and understand SX mechanisms

2- To understand 3rd phase problems

- origins of phase demixing
- **phase modifiers**

3rd phase problem



Fatty alcohol
as 1-octanol

➢ Mechanisms of phase modifier effect on 3rd phase ?

How does the phase modifier act on 3rd phase formation ?

No study on modifier effect in solvent extraction conditions

Langmuir **2005,** *21,* 6769−6775

Unified Concept of Solubilization in Water by Hydrotropes and Cosolvents

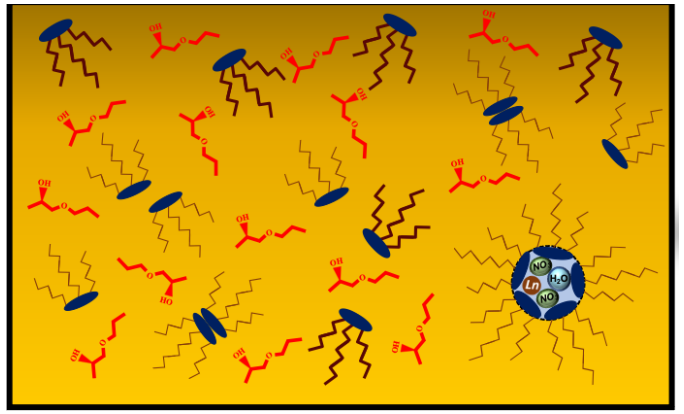
P. Bauduin, A. Renoncourt, A. Kopf, D. Touraud, and W. Kunz*

Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany

Langmuir **2003,** *19,* 6638−6644

Effect of *n*-Octanol on the Structure at the Supramolecular Scale of Concentrated Dimethyldioctylhexylethoxymalonamide Extractant Solutions

B. Abécassis,† F. Testard,*,† Th. Zemb,† L. Berthon,‡ and C. Madic§

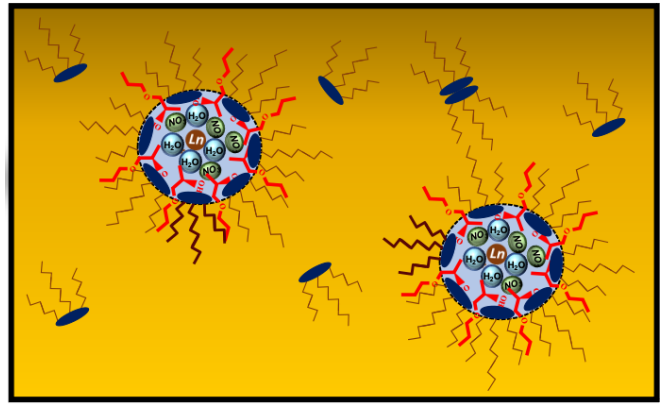


In surfactant microemulsions, modifiers play as:

- **co-solvent**: increase the solubility of surfactant, increase Critical Micellar Concentration (CMC).

OR

- **co-surfactant**: penetrate inside the shells of aggregates and increase the surface per polar head, and decrease the CMC.



- Great interests to use such colloidal approach to understand the effect of phase modifiers in solvent extraction!

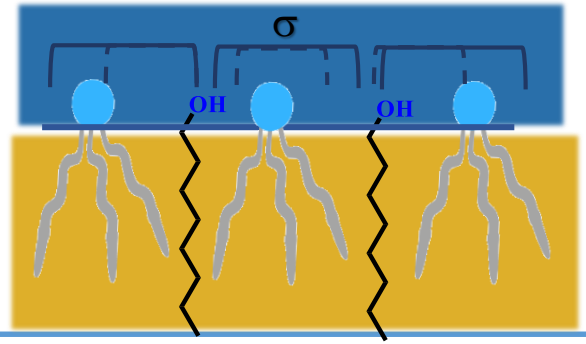
Does it act as a co-surfactant?

Studied system

Organic phase
0-0.4 M TOA in dodecane with 1-5 % vol. 1-octanol

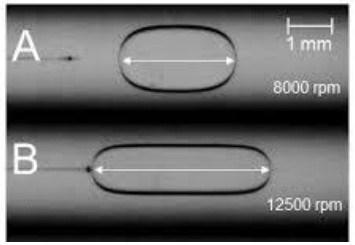
Aqueous phase
0.1 M H_2SO_4 + 0.1 M Li_2SO_4 + 250 ppm (or 1.05 mM) U(VI) + 250 ppm (or 4.48 mM) Fe(III). A/O = 1

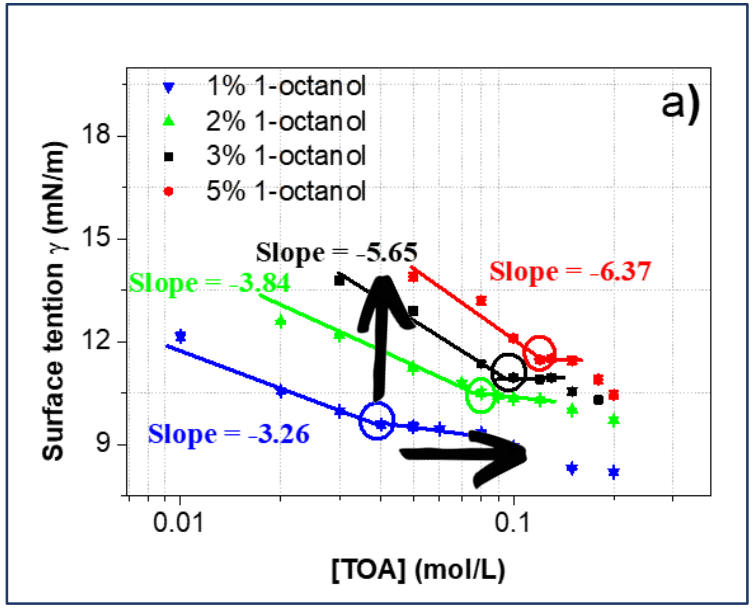
A co-surfactant?



1-octanol is not located between the extractant. It does not act as a co-surfactant

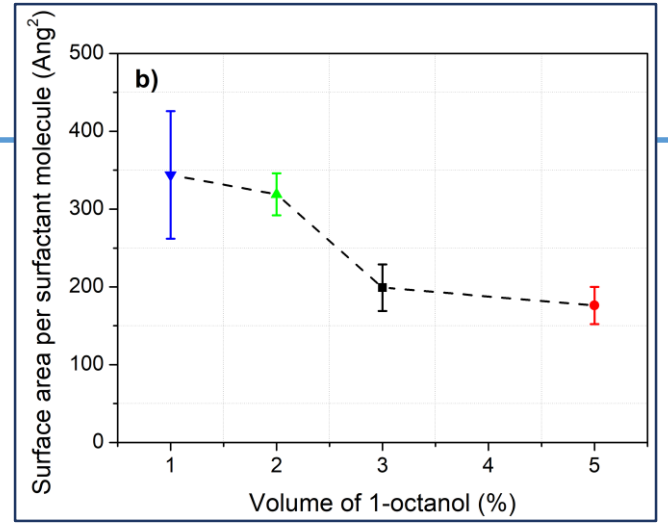
Surface tension measurement:





When % of octanol increases, γ and CAC increase.

σ Surface area per TOA molecule at the interface



Instead of increasing, σ decreases!

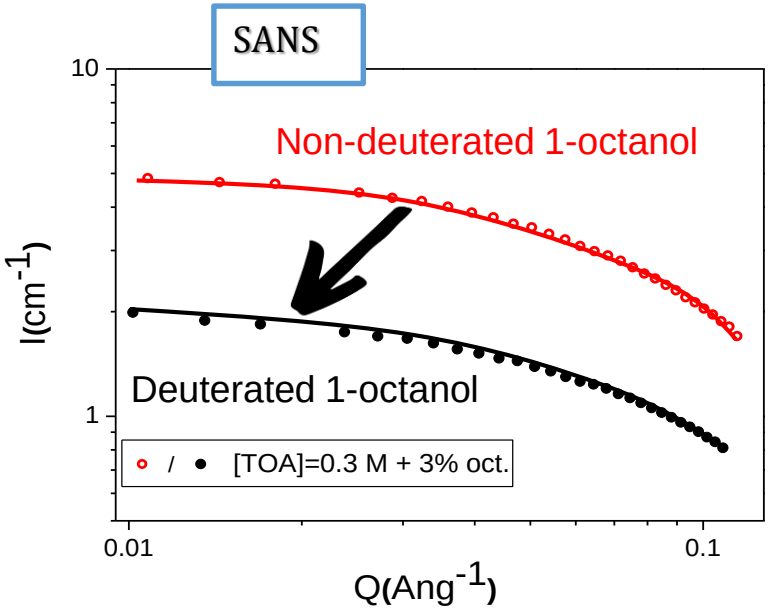
- Is octanol a co-solvent ?
- Identifying its location with SANS

Location of phase modifiers in aggregates?
Small-angle X ray and neutron scattering

Studied system

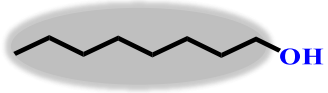
Organic phase
0-0.4 M TOA in dodecane with 1-5 % vol. 1-octanol

Aqueous phase
0.1 M H_2SO_4 + 0.1 M Li_2SO_4 + 250 ppm (or 1.05 mM) U(VI) + 250 ppm (or 4.48 mM) Fe(III). A/O = 1



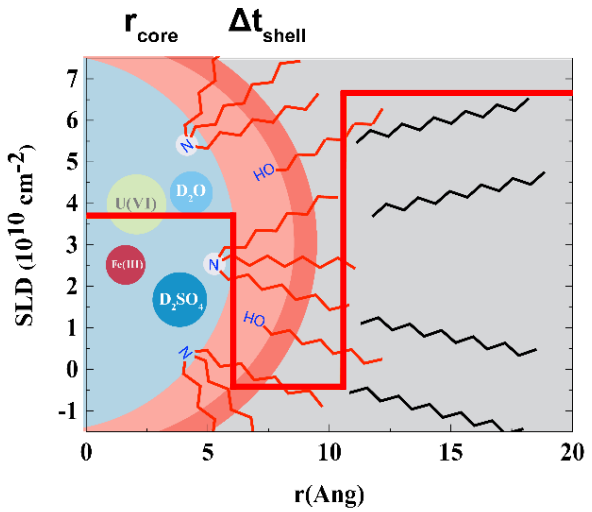
Non-deuterated 1-octanol:

Deuterated

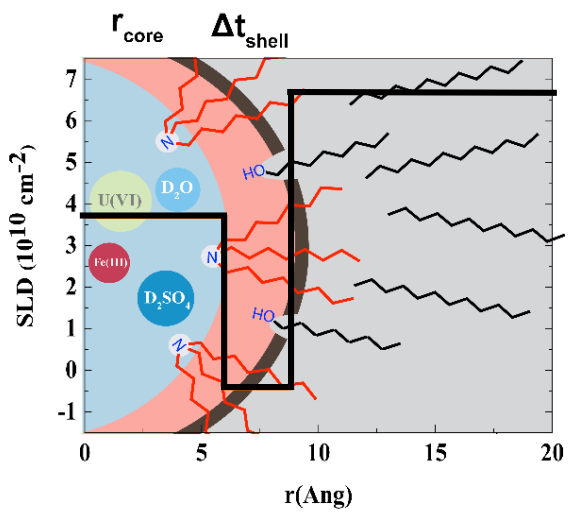


Decrease of scattering intensity → decrease of the aggregates size

With non-deuterated 1-octanol



With deuterated 1-octanol



→ Modelling of SANS data

- **Octanol is located around the apolar shell**
- **Octonal addition : Decrease interactions (τ^{-1})**
  - → **Neither co-surfactant nor co-solvent**
  - → **Repells the 3rd phase by creating a shielding barrier between the aggregates**

- Z. Lu , S. Dourdain, S. Pellet-Rostaing, Langmuir 2020

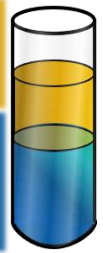
15

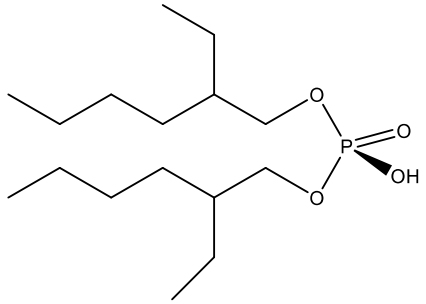
Attempt of Generalization ?

Phase stability with PnP as phase modifier

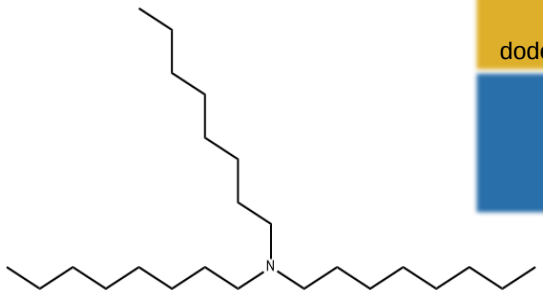
Phase organique:
0,1 – 2 M **HDEHP** dans dodécane avec 1 – 10 % PnP

Phase aqueuse:
100 mM $Eu(NO_3)_3$
30 mM $Fe(NO_3)_3$
0,03 M HNO_3





HDEHP

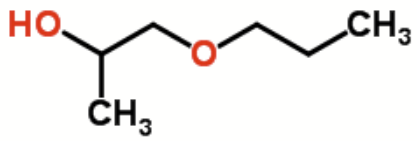


TOA

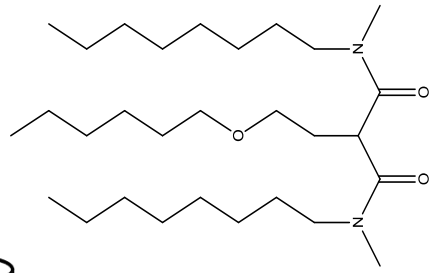
Phase organique:
0,1 – 2 M **TOA** dans dodécane avec 1 – 10 % PnP

Phase aqueuse:
10 mM $U(SO_4)_2$
30 mM F(III)
0,3 M H_2SO_4

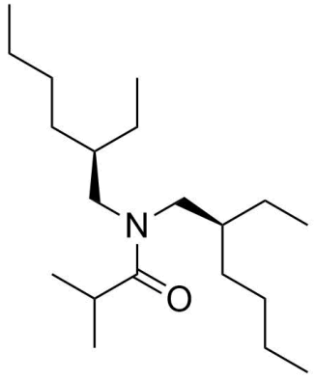
PnP :
A small hydrotrop commonly used in industry



PnP : 1-propoxy-2-propanol



DMDOHEMA



DEH*i*BA

Phase organique:
0,1 – 2 M **DMDOHEMA** dans dodécane avec 1 – 10 % PnP

Phase aqueuse:
100 mM $Eu(NO_3)_3$
30 mM $Fe(NO_3)_3$
4 M HNO_3

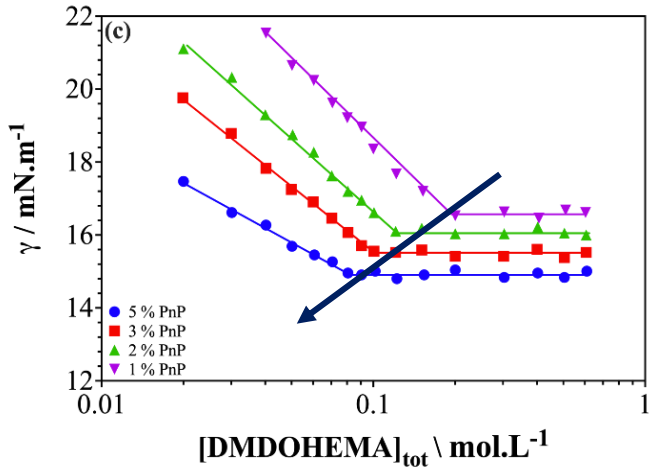
Phase organique:
0,1 – 3 M **DEH*i*BA** dans dodécane avec 1 – 10 % PnP

Phase aqueuse:
100 mM $UO_2(NO_3)_2$
30 mM $Fe(NO_3)_3$
6 M HNO_3

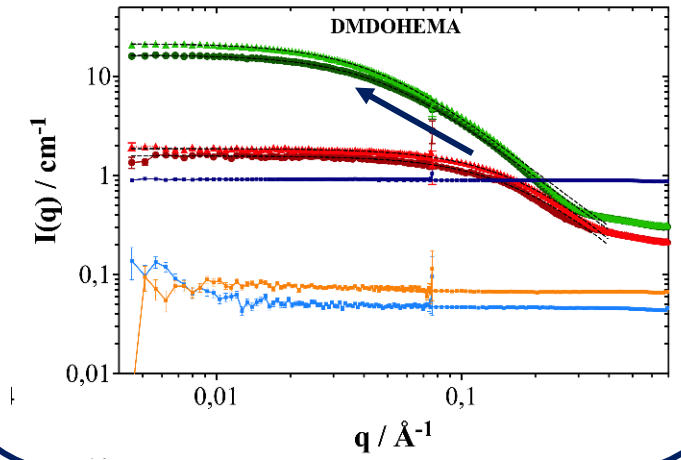
Molecular driving force preventing the 3rd phase ?

DMDOHEMA and DEHiBA

Tension de surface

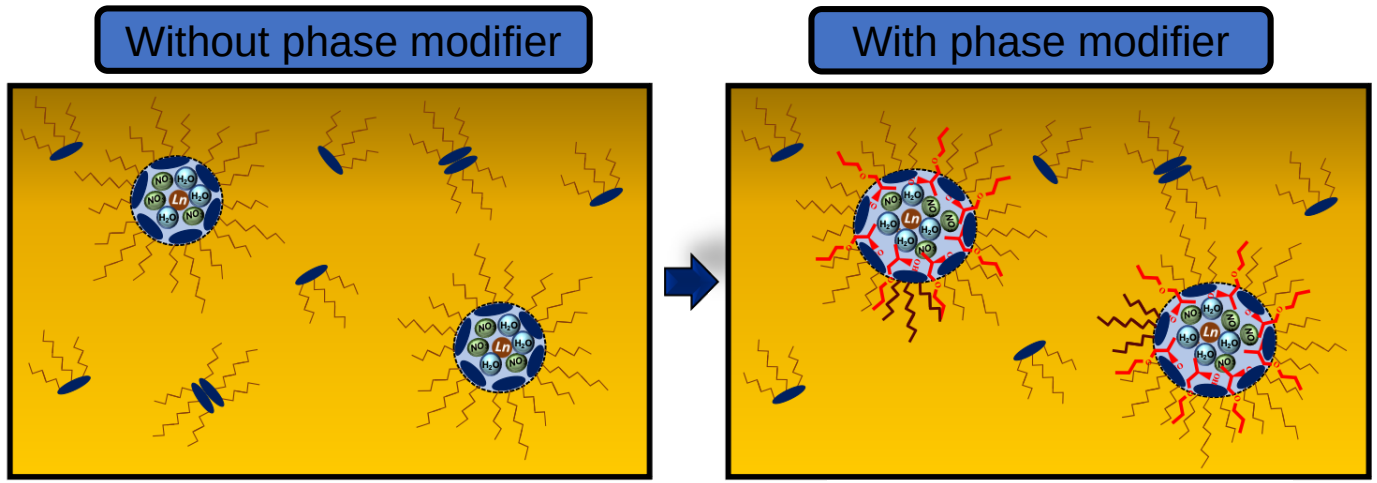


SANS



- **CAC decrease**
- **Surface tension decrease, σ increase**
- **Increase of R_{agg} and N_{agg}**

Co-surfactant

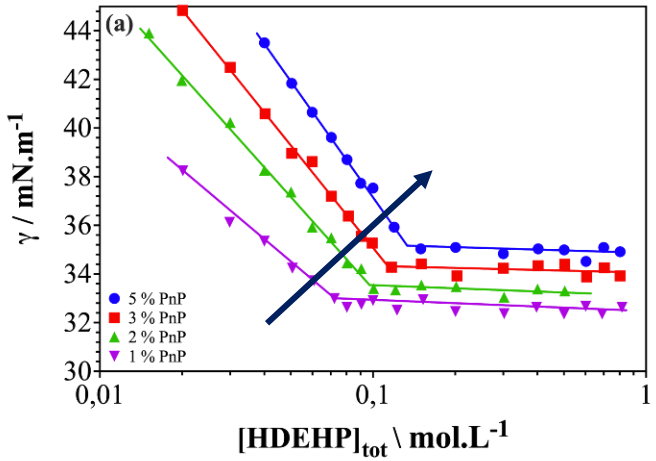


- El Maangar, A.; Prévost, S.; Dourdain, S.; Zemb, T., *CRAS* (2022)

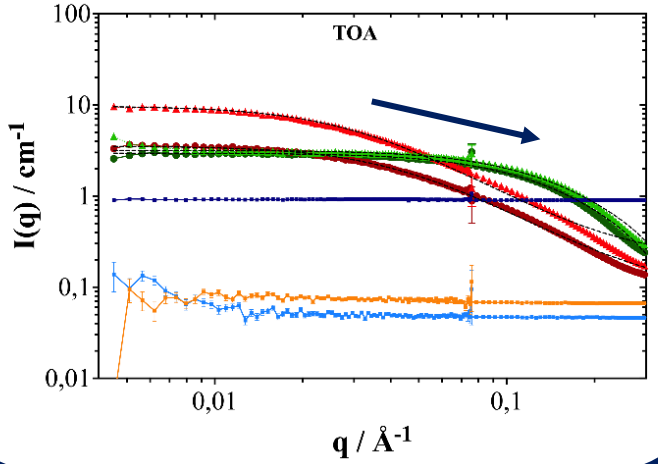
Molecular driving force preventing the 3rd phase ?

HDEHP and TOA

Surface tension

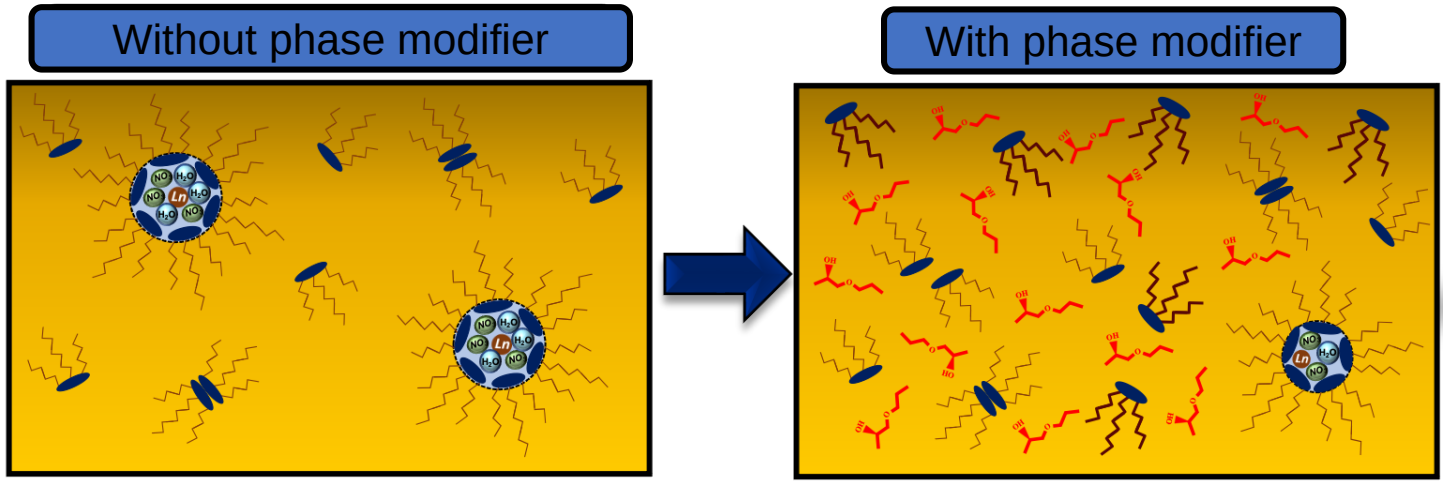


SANS



- **CAC increase**
- **Surface tension increase, σ decrease**
- **Decrease of R_{agg} and N_{agg}**

Co-solvent



- El Maangar, A.; Prévost, S.; Dourdain, S.; Zemb, T., *CRAS* (2022)

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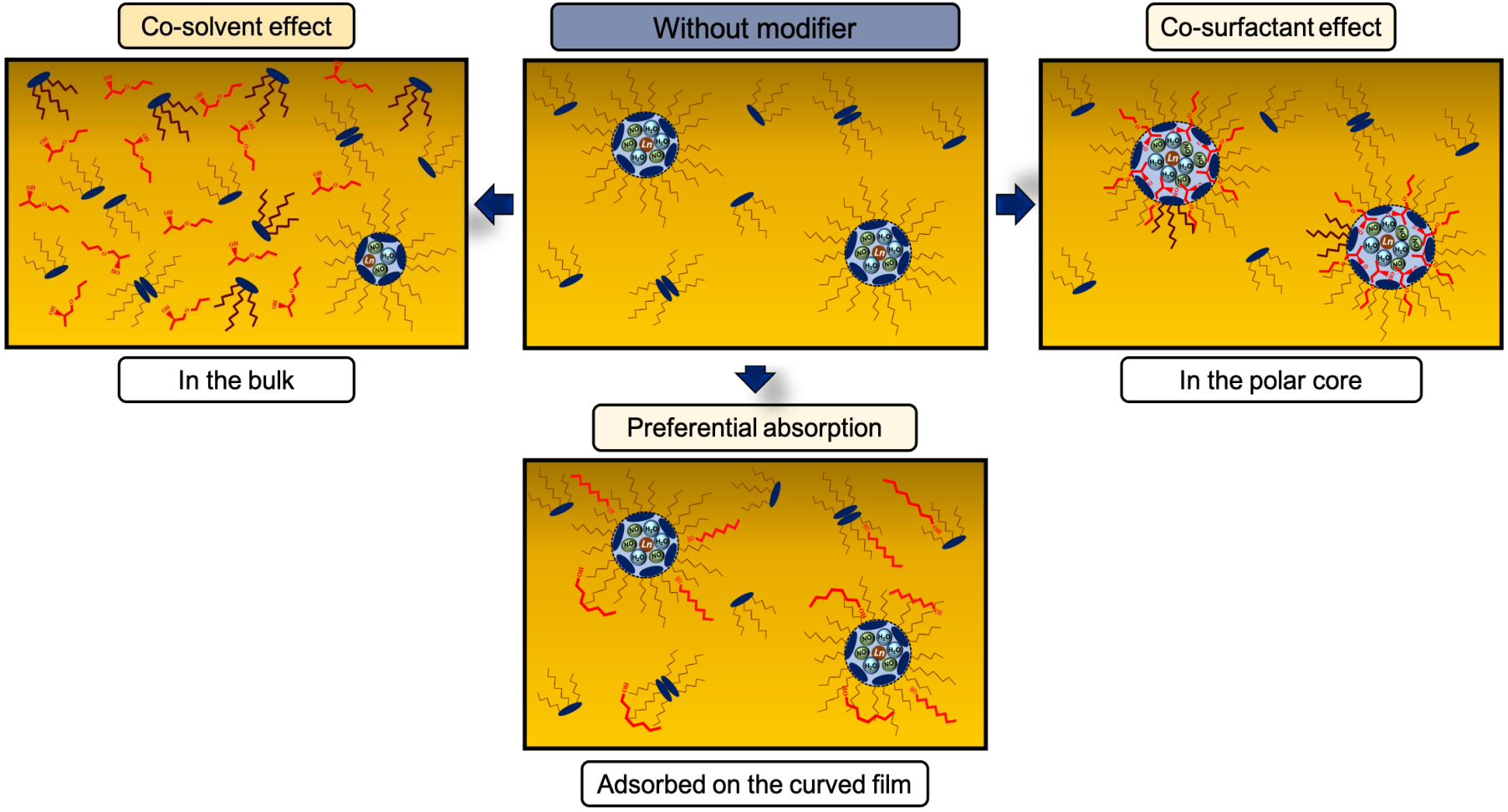
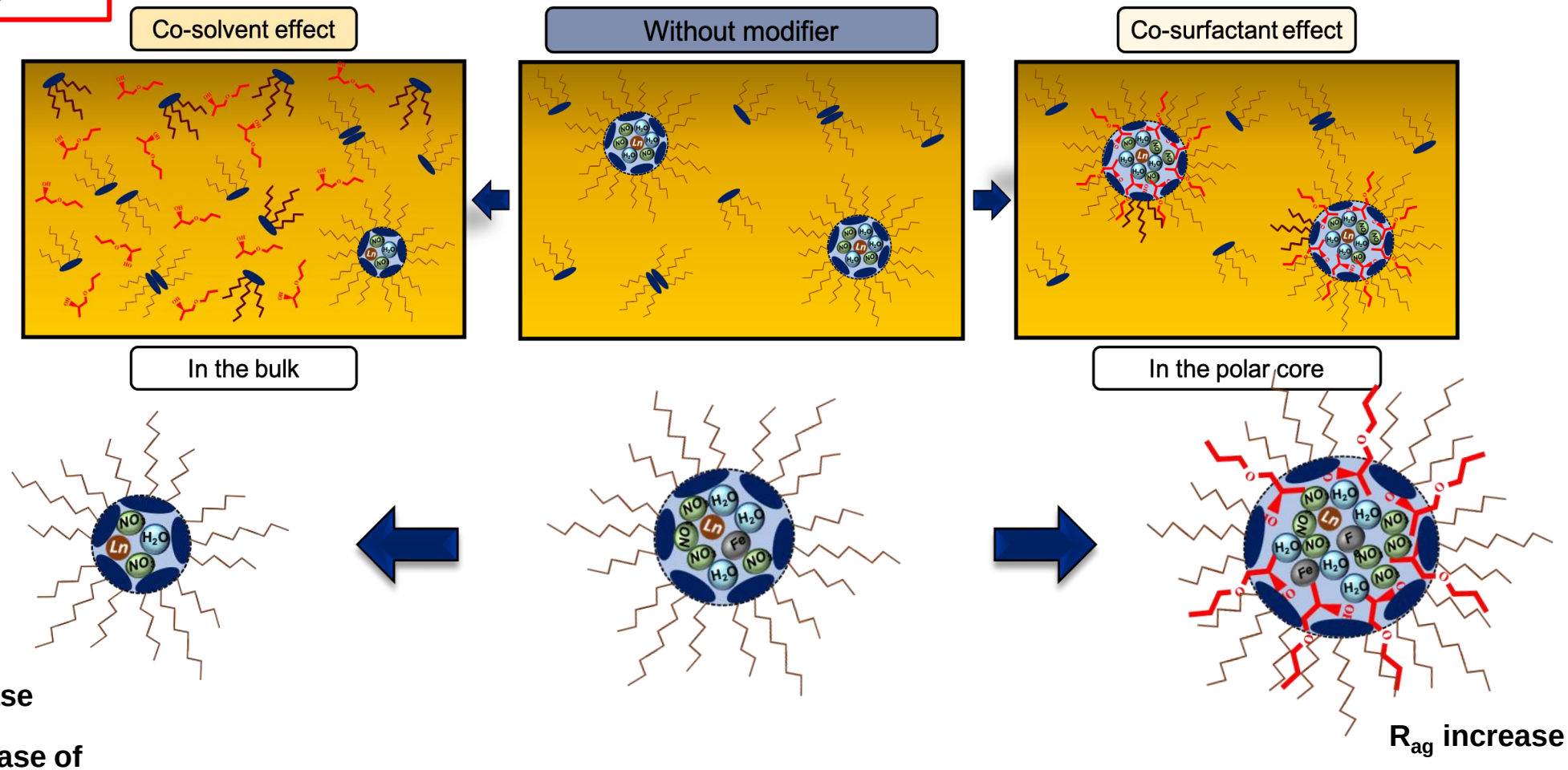
How does the phase modifier act on 3rd phase formation ?

Three action modes to repell the 3rd phase



How does the phase modifier act on 3rd phase formation ?

Three action modes to repell the 3rd phase



R_{ag} decrease

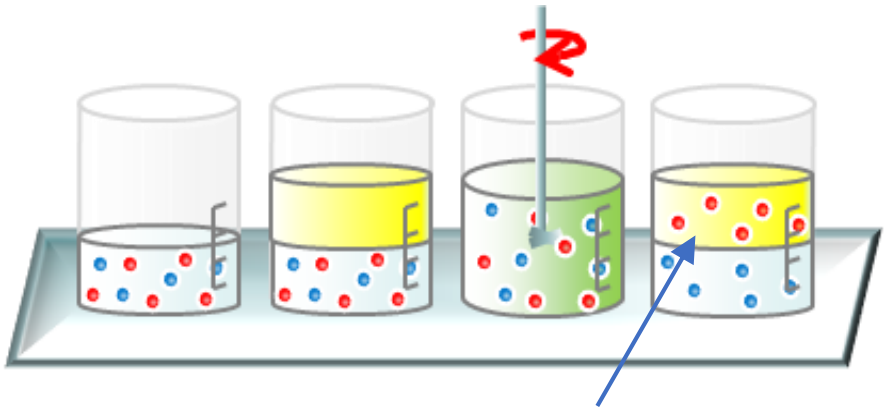
HDEHP: increase of separation factors Eu/Fe ou U/Fe

Control of the polar core size, → Control of selectivity

R_{ag} increase

DMDOHEMA: Decrease of Separation factors Eu/Fe ou U/Fe

Small Angle X-ray and Neutron Scattering for solvent extraction



To characterize aggregation and understand SX mechanisms
To understand 3rd phase problems & effect of phase modifiers