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Molecular Recognition of Radionuclides, St-Petersburg, 2009

# Supramolecular assemblies in the solvent extraction systems and modelling of metal distribution isotherms

G. Cote

Chimie Paris - ParisTech



**A first objective of the present paper is**

- to give a rapid overview of supramolecular and colloidal speciation in aqueous/organic liquid-liquid extraction systems;
- to underline the links between this speciation and macroscopic behaviours such as third phase formation, kinetics of metal extraction and crud formation.

**A second objective of this paper is**

- to give a state of the art on the modelling of the partition of solutes (metal species) between the feed aqueous solutions and the self-organised organic phases.



## Content

- **Supramolecular species & colloids and separation techniques**
- **Effect of supramolecularity in liquid-liquid extraction processes**
- **Tools for supramolecular speciation**
- **Solutes distribution modelling in supramolecular based systems**

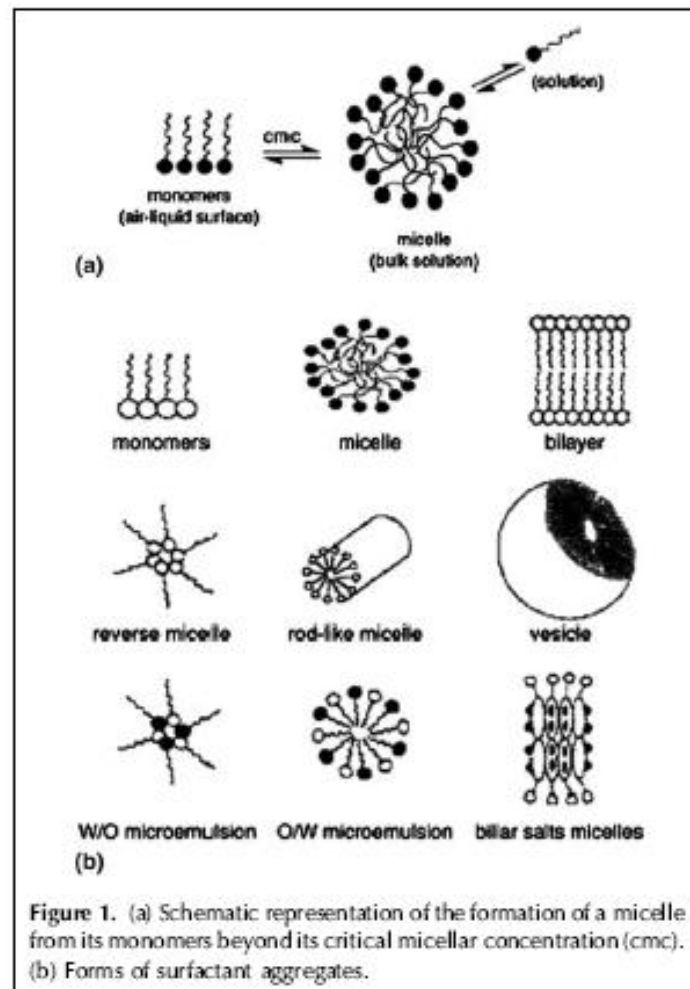


## **Supramolecular species & colloids and separation techniques**

## Supramolecular species & colloids and separation techniques

Evangelos K. Paleologos,  
Dimosthenis L. Giokas,  
Miltiades I. Karayannis

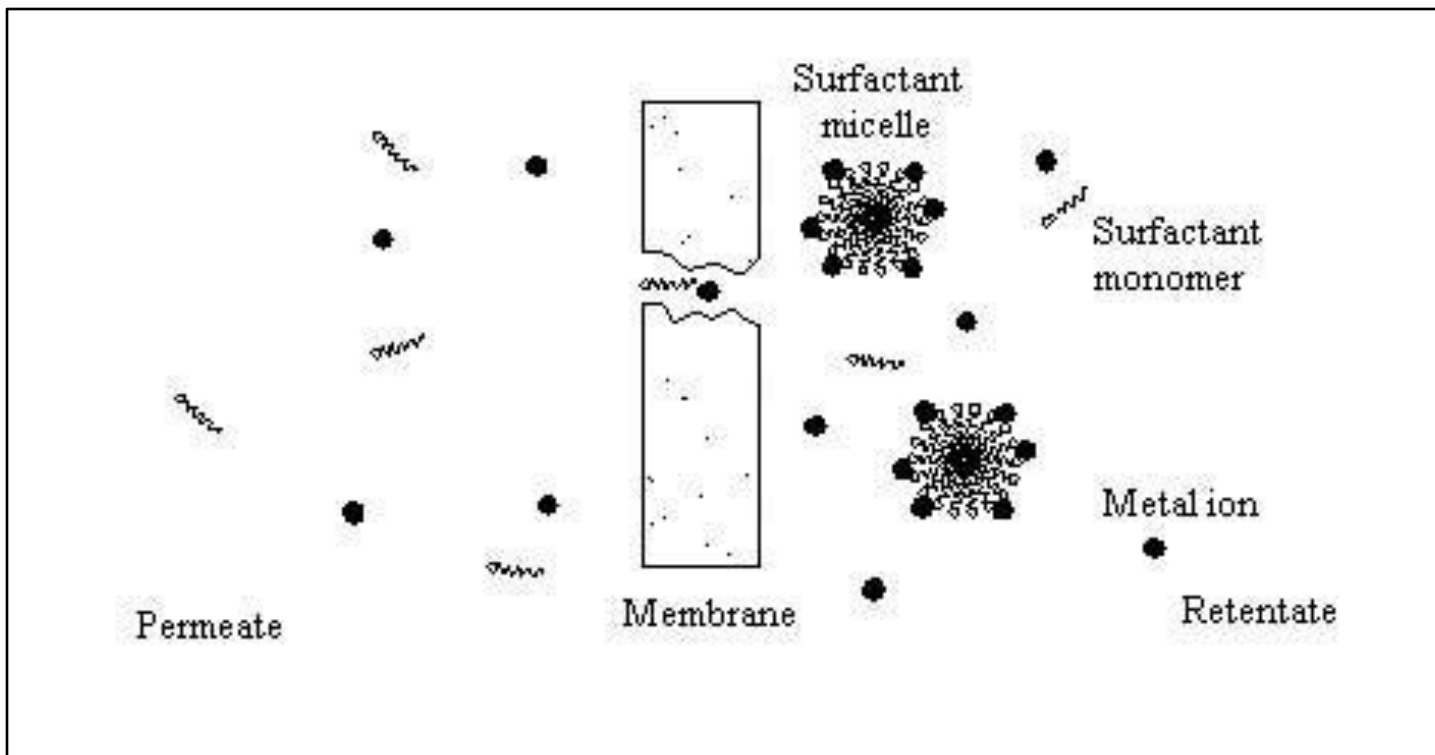
Trends in Analytical Chemistry, Vol. 24, No. 5, 2005



## Supramolecular species & colloids and separation techniques

Techniques	State versus supramolecularity	Type and role of supramolecular species	Field of application
<b>Micellar enhanced ultrafiltration (MEUF)</b>	<b>Technique intrinsically based on micelles</b>	<b>Adsorption of solutes onto micelles and removal of loaded micelles by ultrafiltration</b>	<b>Laboratory scale</b>
Cloud point extraction	Technique intrinsically based on micelles	Nonionic surfactants aggregate on heating and constitute an extraction phase	Solute preconcentration
Liquid-liquid extraction	Technique <b>not</b> intrinsically based on micelles	From micelles/small aggregates to swollen micelles	Worldwide used in hydrometallurgy

## Supramolecular species in Micellar Enhanced Ultrafiltration



## Supramolecular species & colloids and separation techniques

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## Supramolecular species in cloud point extraction

*S. Shariati, Y. Yamini / Journal of Colloid and Interface Science 298 (2006) 419–425*

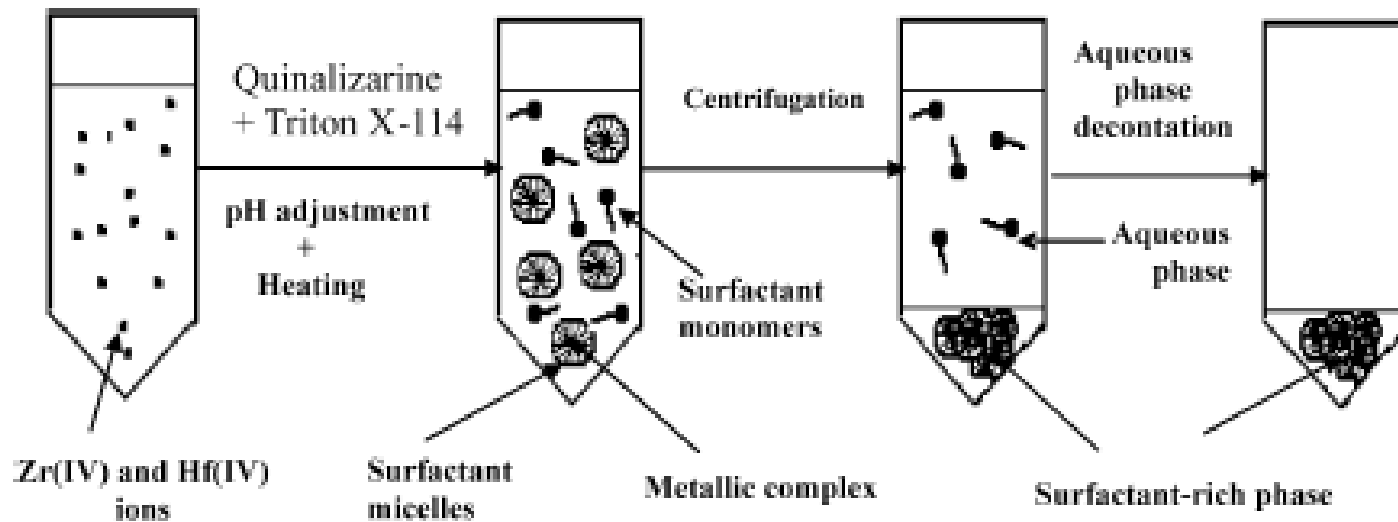
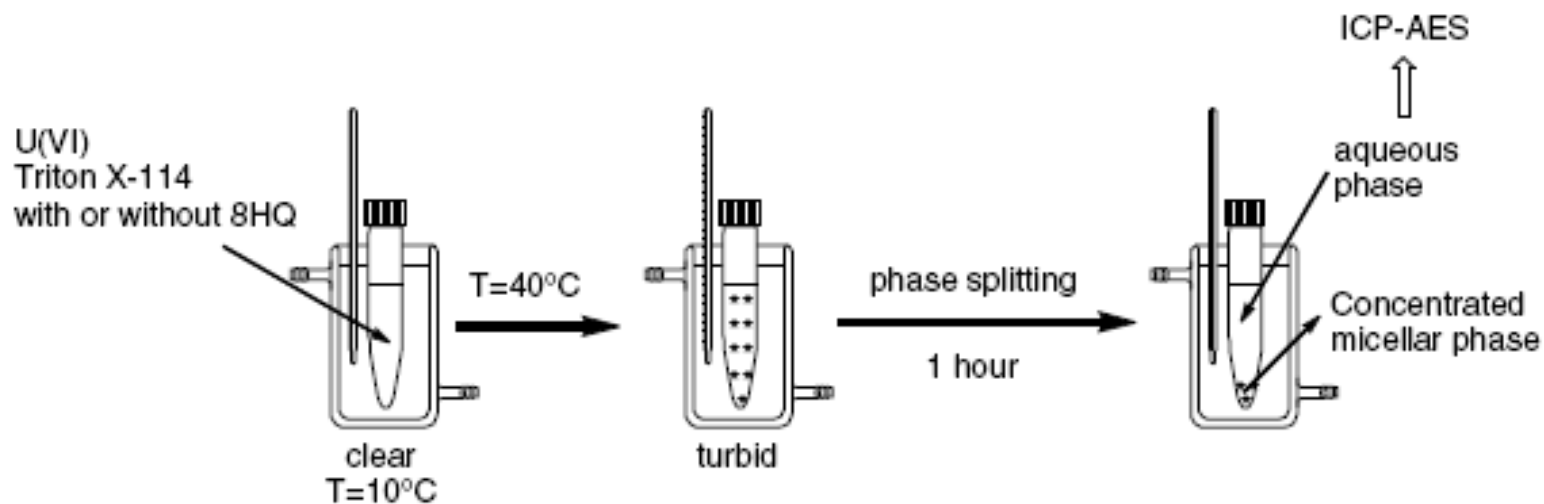


Fig. 1. Experimental schemes of zirconium and hafnium pre-concentration by CPE method.

## Supramolecular species in cloud point extraction

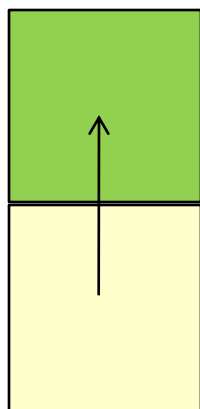


Alain Favre-Réguillon,<sup>1</sup> Denis Murat,<sup>2</sup> Gérard Cote,<sup>3</sup> Jacques Foos<sup>2</sup> and  
Micheline Draye<sup>4\*</sup>

*J Chem Technol Biotechnol* **81**:1872–1876 (2006)

## Supramolecular species & colloids and separation techniques

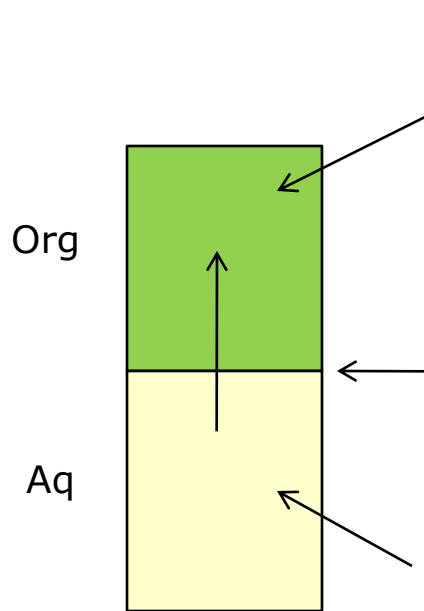
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Organic  
phase

- **Extractant** : Driving force for solute(s) transfer
- **Diluent** : Physical properties  
(density, viscosity, ...)
- **Phase modifier** : Several objectives
  - improvement of metal complexes solubility
  - 3rd phase formation delayer

## Ideal system



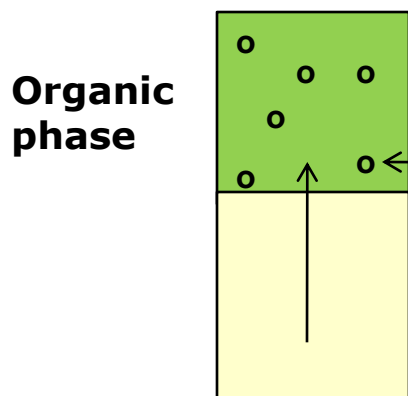
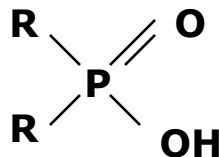
- Two phase system
- Limpid organic phase
- High selectivity towards target solute(s)
- High loading capacity for target solute(s)
- Sharp extraction isotherms (high  $K_{ex}$ )
- **Clear interface**
- Very low losses of organic phase (solubility – mechanical entrainment)

**Rapid  
Settling  
(<1 min)**

## Examples

### HDHP

Di-*n*-hexylphosphoric acid



**Monomer**  
**Dimer**  
**Trimer**  
**Tetramer**

# HDHP

## Di-*n*-hexylphosphoric acid

$$\beta_2 = 158 \text{ mol}^{-1}, \quad \beta_3 = 158 \text{ mol}^{-1}, \quad \beta_4 = 1.10^5 \text{ mol}^{-1}$$

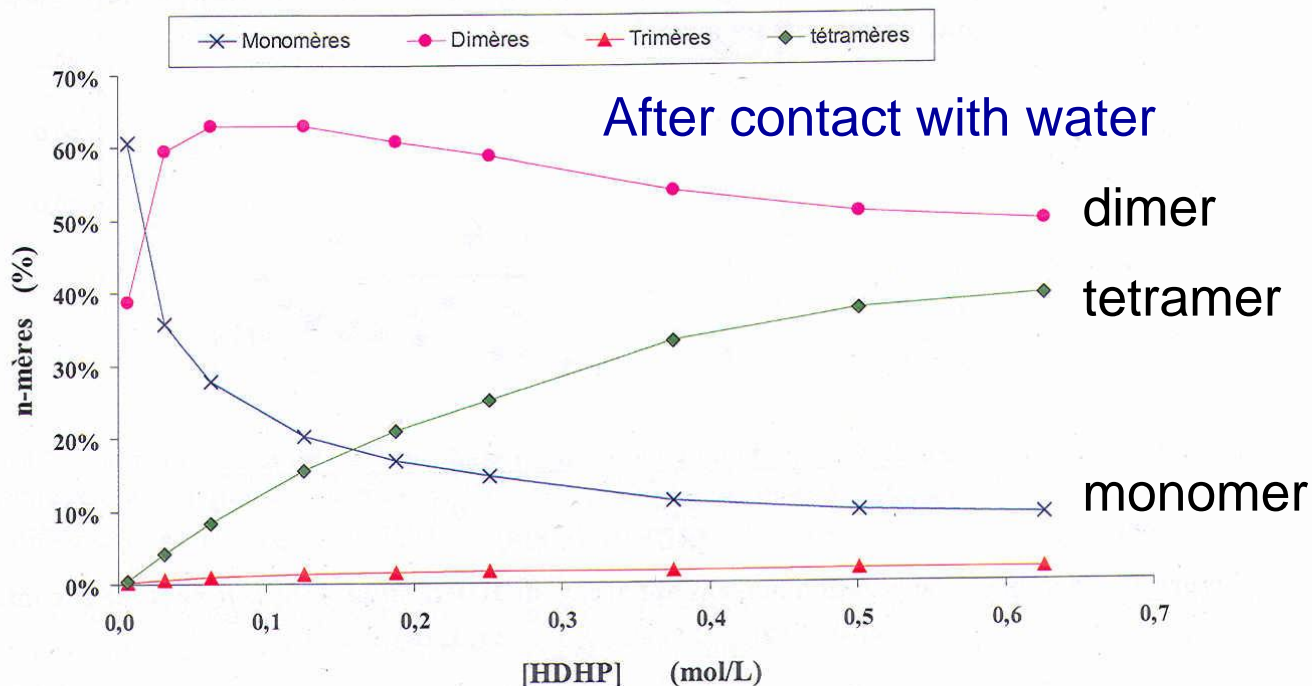


Figure 44 : Répartition des molécules de HDHP dans les agrégats en phase organique, en fonction de la concentration de HDHP dans le *n*-pentane, mis en contact avec de l'eau, à 24°C.

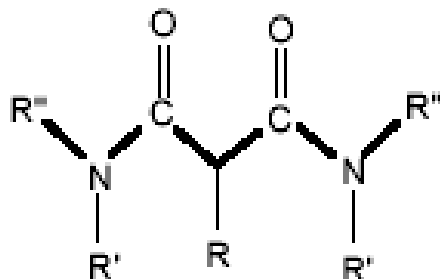
B. Gannaz, PhD,  
University Paris 6  
2006

# HDHP

## Di-*n*-hexylphosphoric acid

Tableau 21 : Bilan des résultats obtenus sur la spéciation supramoléculaire de phases organiques de HDHP.

Phase aqueuse	VPO ( <i>n</i> -pentane)	DNPA ( <i>n</i> -dodécane)	DXPA ( <i>n</i> -dodécane)
H <sub>2</sub> O	Constantes d'agrégation Diagramme de spéciation : Dimères majoritaires, et pour [HDHP] <sub>tot</sub> > 0,4 mol/L : [tétramères] ~ [monomère] ~ [dimère]/2 [H <sub>2</sub> O] <sub>org</sub> ↑ avec [HDHP] <sub>tot</sub>	(HDHP) <sub>2</sub> majoritaire Ø <sub>cœur polaire</sub> = 6 à 7 Å Ø <sub>dimère</sub> = 12 Å	Ø <sub>cœur polaire</sub> = 7 Å
HNO <sub>3</sub>	Effet modéré sur l'agrégation N ↑ légèrement	Agrégation stable (H <sub>2</sub> O) <sub>org</sub> remplacée par HNO <sub>3</sub> ([HNO <sub>3</sub> ] <sub>org</sub> + [H <sub>2</sub> O] <sub>org</sub> constante)	pas d'influence : Ø <sub>cœur polaire</sub> = 7 Å
HNO <sub>3</sub> /M <sup>3+</sup>	(DHP) <sub>3x</sub> (HDHP) <sub>y-3x</sub> M <sub>x</sub> (H <sub>2</sub> O) <sub>w</sub> , avec y = 3(x+w) M <sup>3+</sup> remplace (H <sub>2</sub> O) <sub>org</sub> (x + w = constante)  (HDHP.DHP) <sub>3</sub> M(H <sub>2</sub> O) majoritaire	N = 4 tétramère ou moyenne hexamère - dimère Ø <sub>cœur polaire</sub> = 7 Å Ø <sub>agrégat</sub> = 15 Å	Polydispersité faible  Complexe = agrégat  Ø <sub>cœur polaire</sub> = 6 à 8 Å



$R' = \text{méthyl } R'' = \text{butyl } R = \text{dodécyl} : \text{DMDBDDMA}$

$R' = \text{méthyl } R'' = \text{butyl } R = \text{tétradécyl} : \text{DMDBTDMA}$

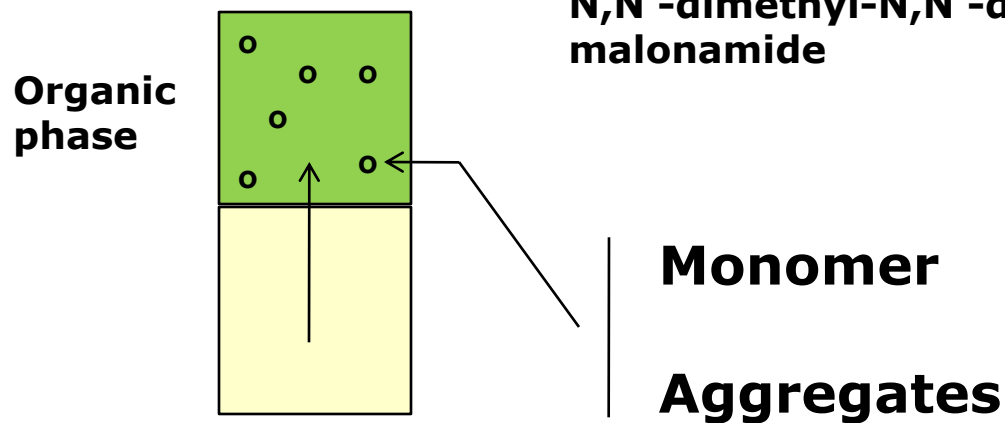
$R' = \text{méthyl } R'' = \text{butyl } R = \text{octadécyl} : \text{DMDBODMA}$

$R' = \text{méthyl } R'' = \text{octyl } R = \text{hexylethoxy} : \text{DMDOHEMA}$

## Examples

### DMDOHEMA

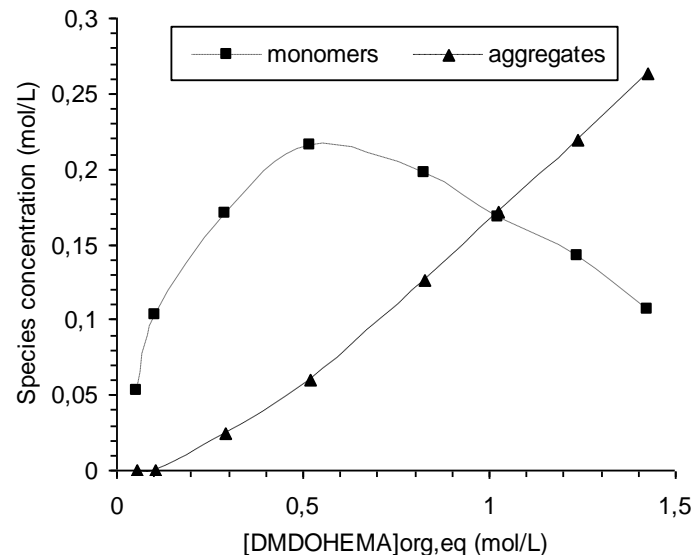
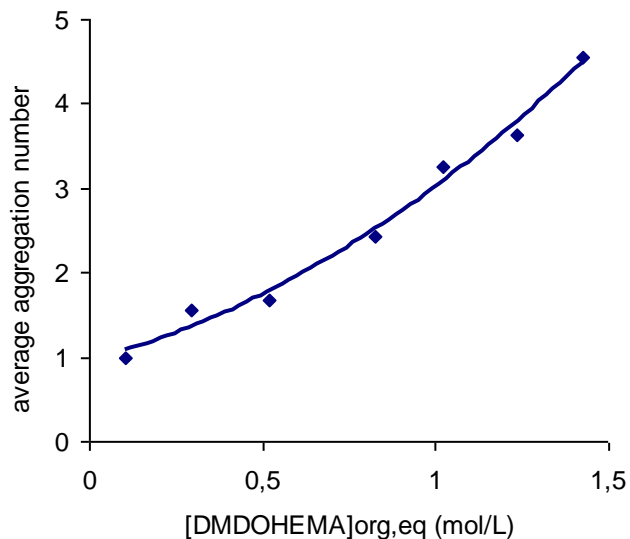
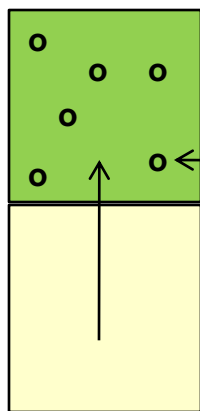
*N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy  
malonamide



## Examples

### DMDOHEMA

#### N,N'-dimethyl-N,N'-dioctylhexylethoxy malonamide



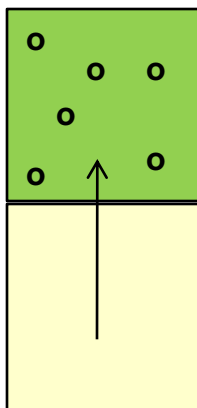
Aggregation properties of DMDOHEMA diluted in *n*-heptane in contact with a 3 M LiNO<sub>3</sub> aqueous phase.  
 L. Berthon, Y. Meridiano, S.Lagrave, X. Crozes, C. Sorel, N. Zorz, F. Testard, Th. Zemb,  
 ISEC 2008, Tucson, Arizona September 15 - 19, 2008

## Examples

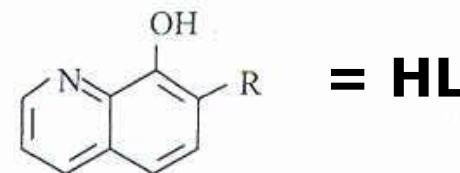
### Kelex 100

in alkaline media in presence of long chain alcohol,  
in kerosene

Organic  
phase



Kelex<sup>®</sup>100  
*R* = 3,3,5,5-tetramethyl-1-ethenyl  
 hexyl

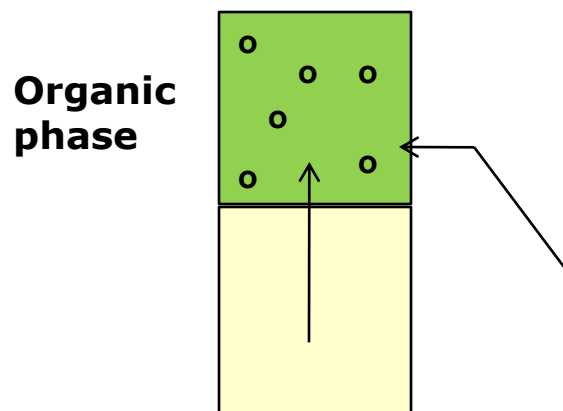


## Examples

### Kelex 100

in alkaline media in presence of alcohol,  
in kerosene

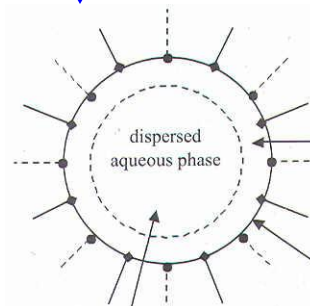
### From micelles to swollen micelles



Micelles :  $(L^-, Na^+)_3(ROH)_5(H_2O)_6$   $\Phi_{core} < 1\text{nm}$

↓ + Na octanoate

Swollen micelles



$\Phi_{core} = 2 - 8\text{ nm}$

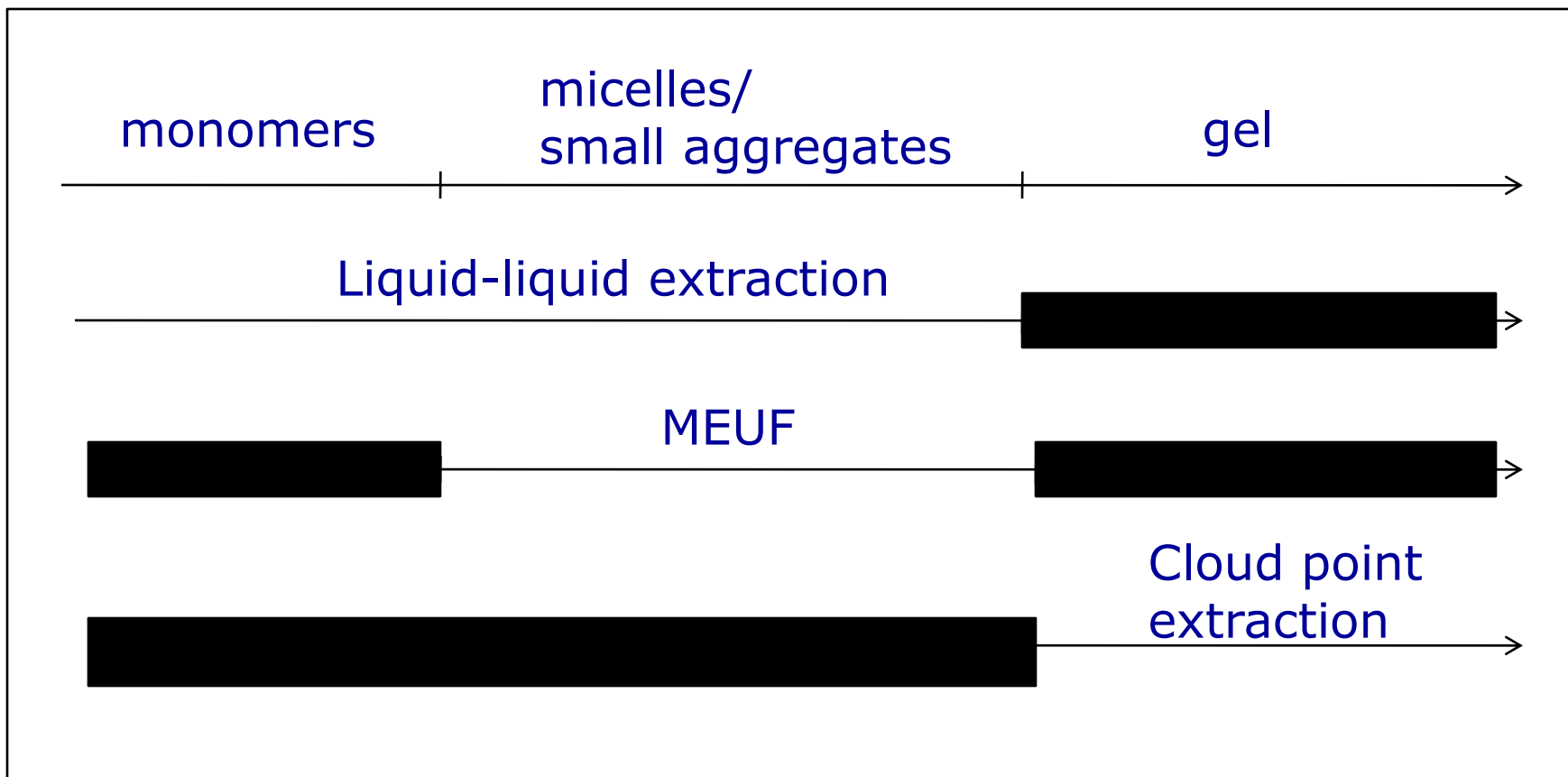
$\Phi_{hydro} = 4 - 10\text{ nm}$



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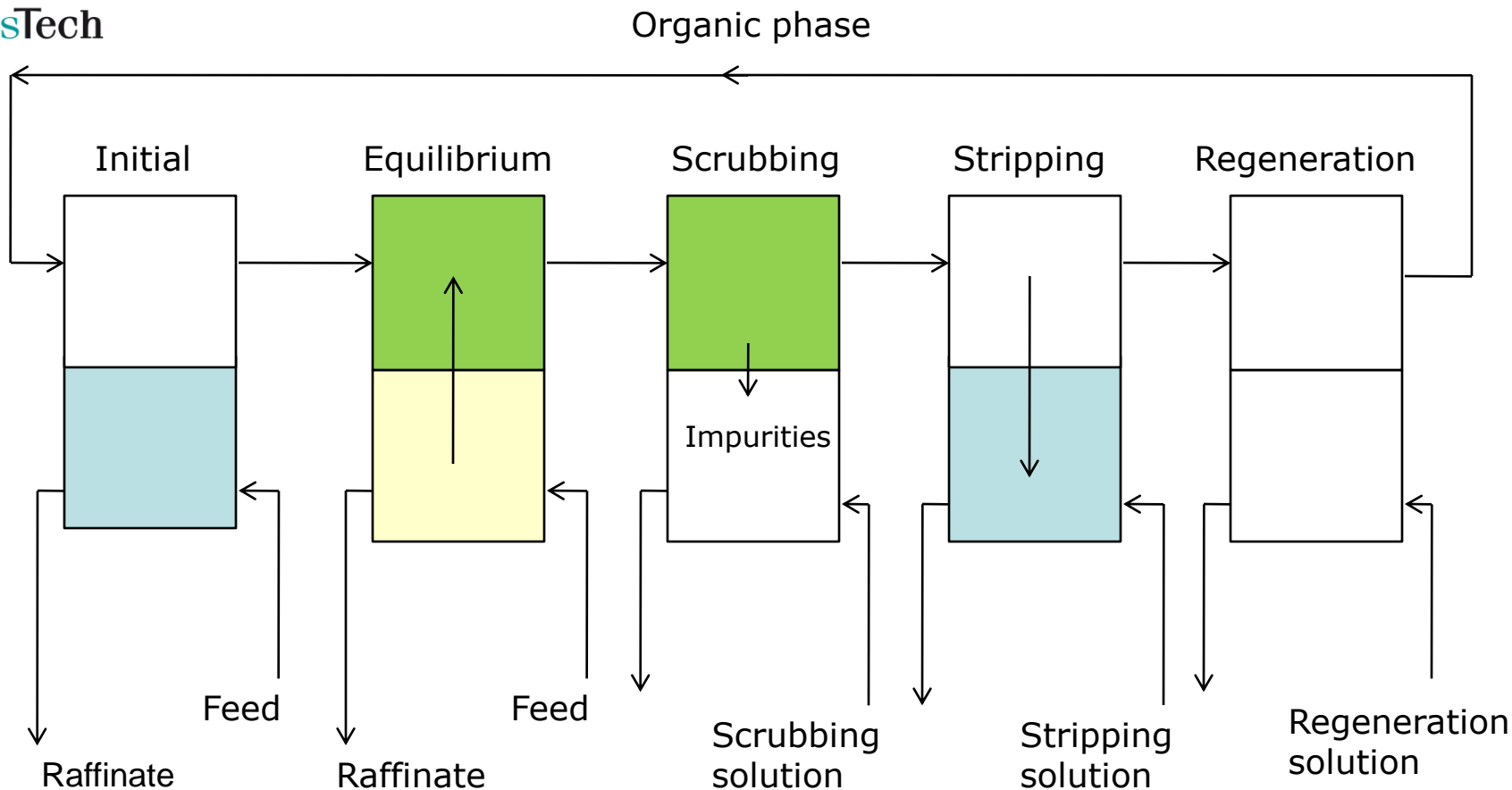
## Colloids in aqueous phases

- **Silica**
- **Humic substances**
- **Dust from air**



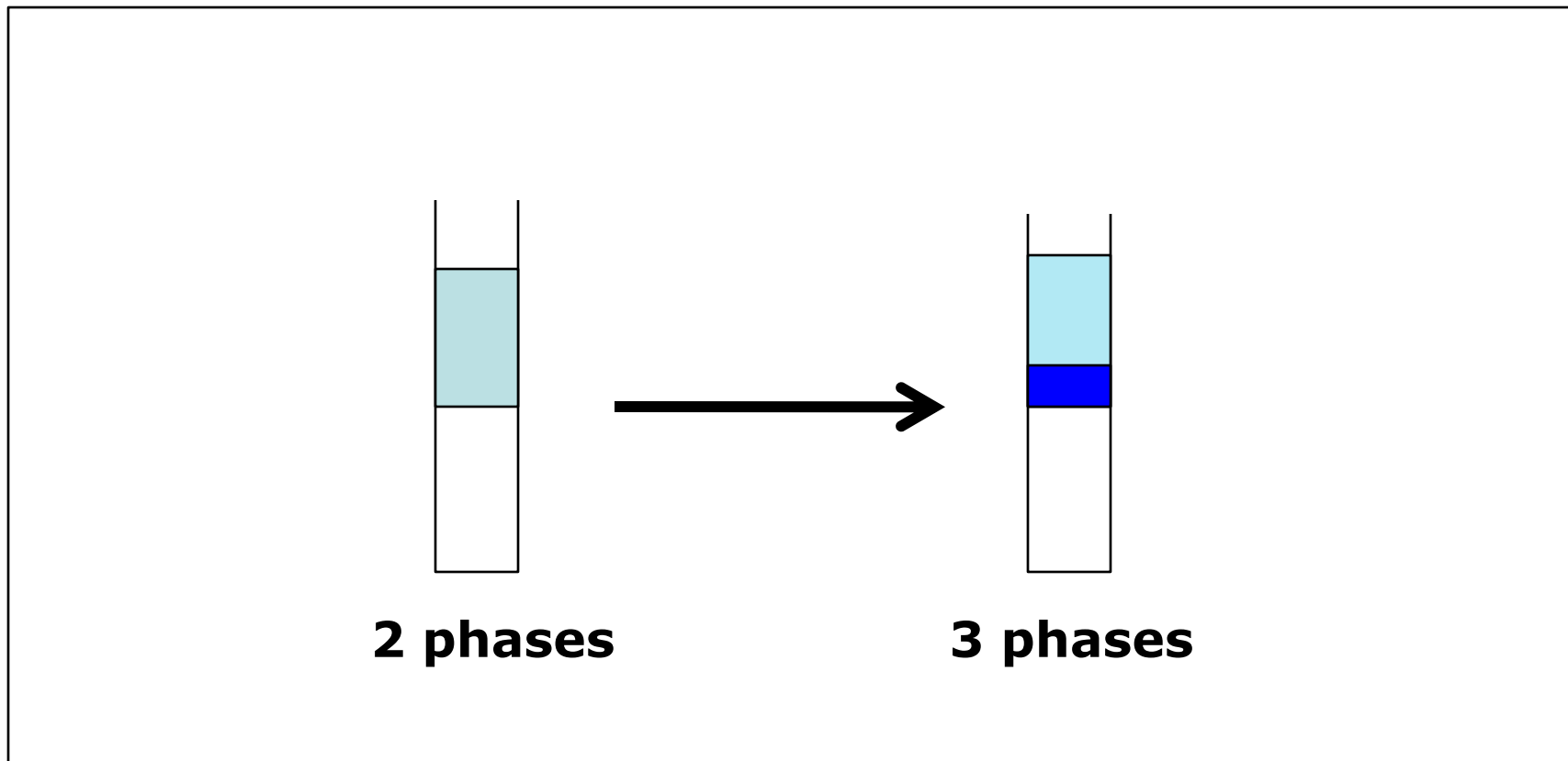


## Effect of supramolecularity in liquid-liquid extraction processes





## 3rd phase formation



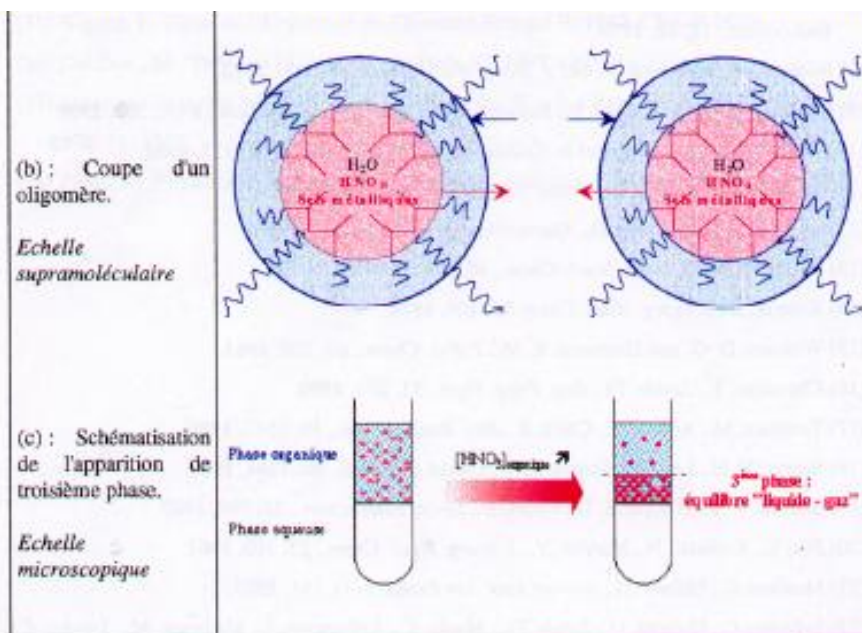


Figure III-22 : Organisation du diamide dans la phase organique - de l'échelle moléculaire (a) à l'échelle microscopique (c).

C. Verdier-Erlinger, Thèse, Université Paris XI, 1998

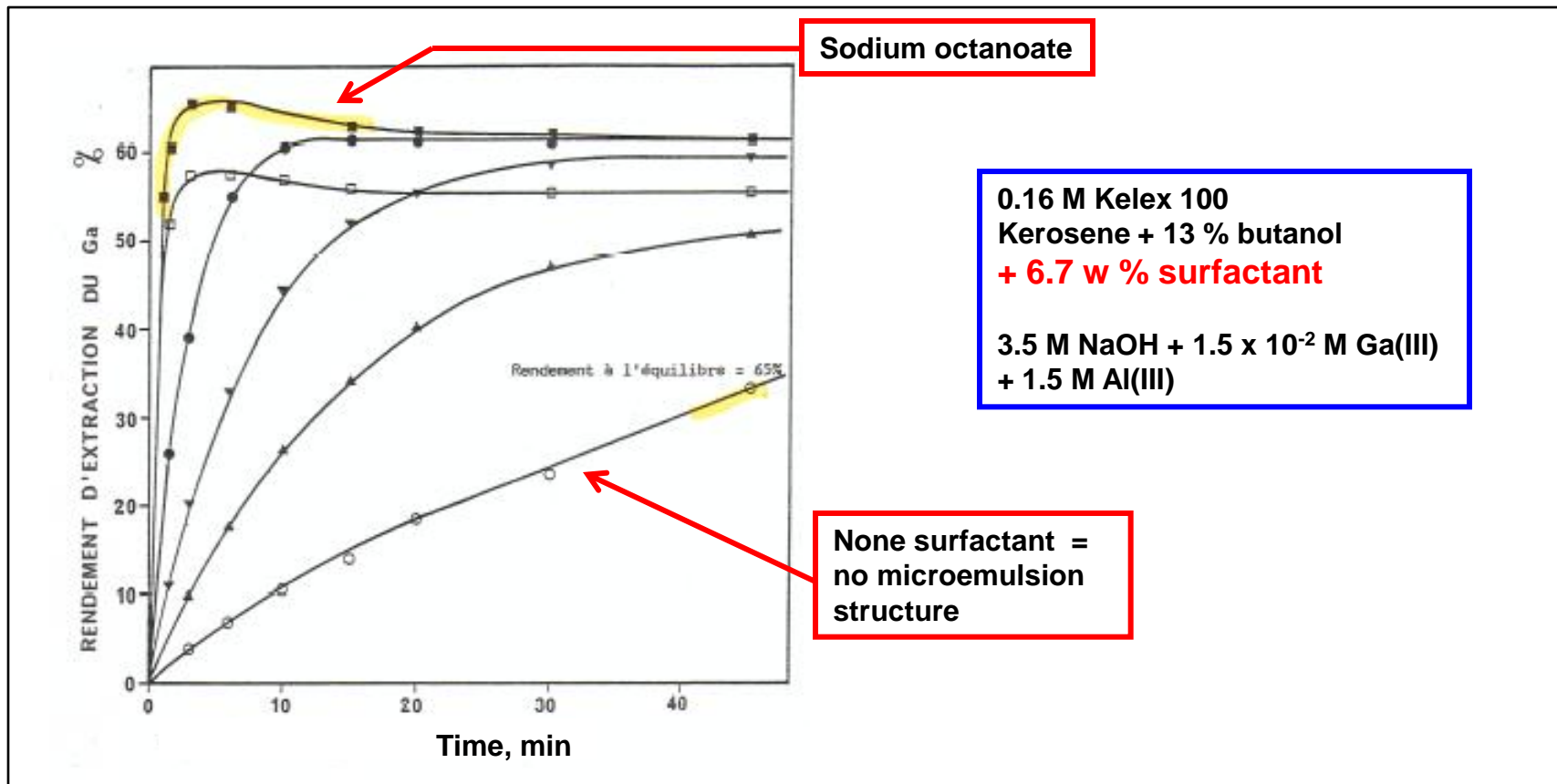


## Kinetic effects

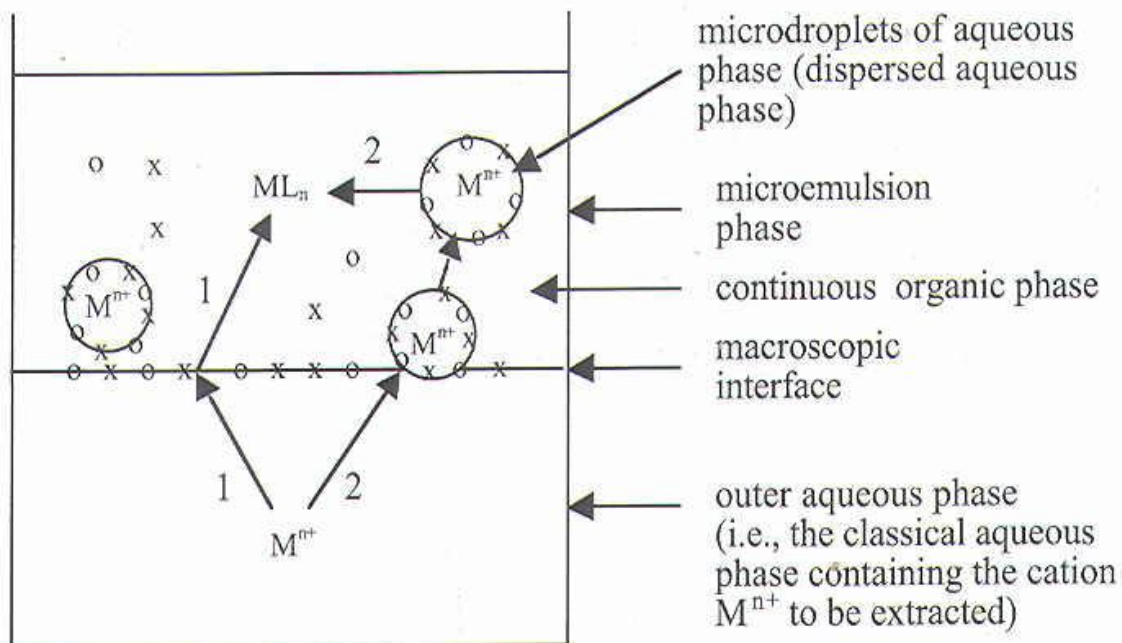
Kelex<sup>®</sup>100  
*R* = 3,3,5,5-tetramethyl-1-ethenyl  
 hexyl

**0.16 M Kelex 100**  
**Kerosene + 13 % butanol**  
**+ 6.7 w % surfactant**

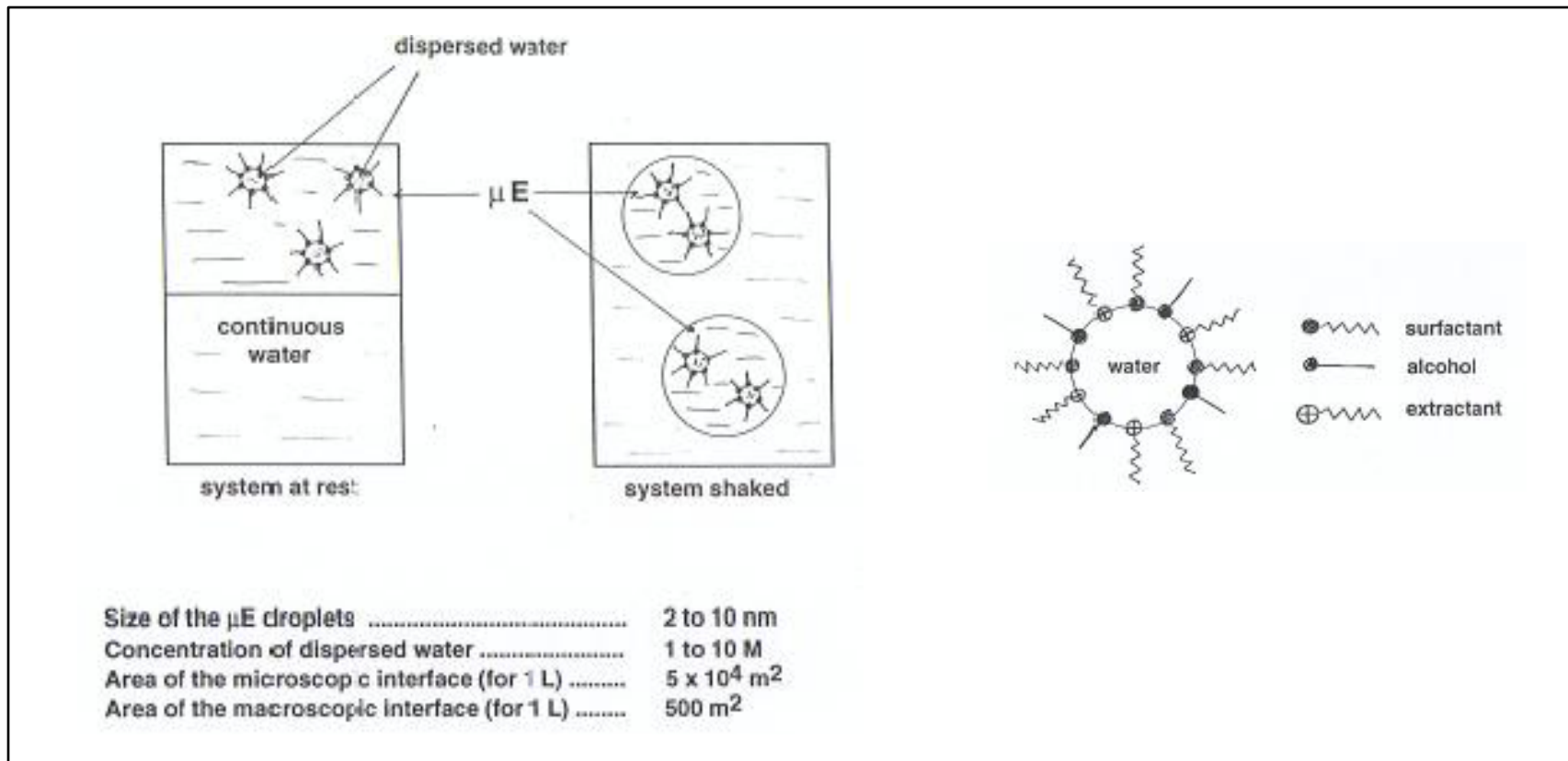
**3.5 M NaOH + 1.5 x 10<sup>-2</sup> M Ga(III)**  
**+ 1.5 M Al(III)**



**Possible routes for the liquid-liquid extraction of a metal cation when the organic phase is a water-in-oil microemulsion (Cote, 2003)**



**x = extractant molecules; o = surfactant or alcohol molecules  
(for the sake of simplicity, the alkyl chains of reagents have been omitted)**



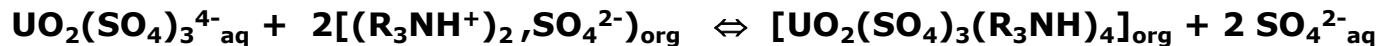
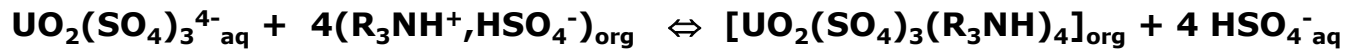


## Cruds formation

**Crud is defined as the material resulting from the agitation of an organic phase, an aqueous phase, and fine solid particles, that form a stable mixture**

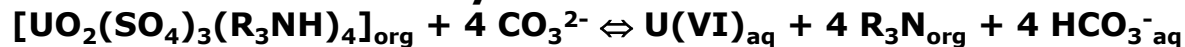
## An example : Chemistry of uranium extraction and stripping

### Extraction :



### Stripping :

**In the absence of molybdenum :**



**In the presence of molybdenum**

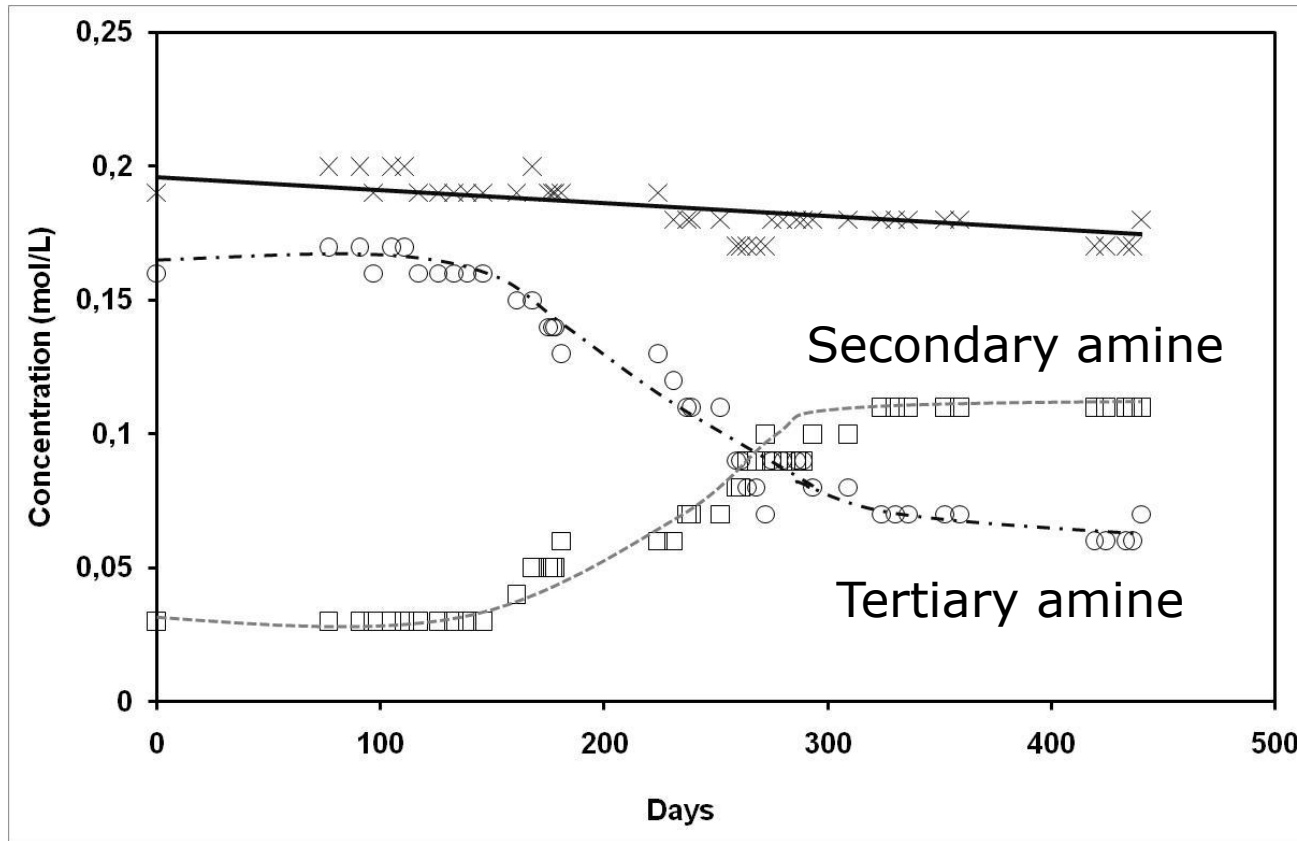


**Molybdenum is then stripped with  $\text{Na}_2\text{CO}_3$**



## The main encountered troubles

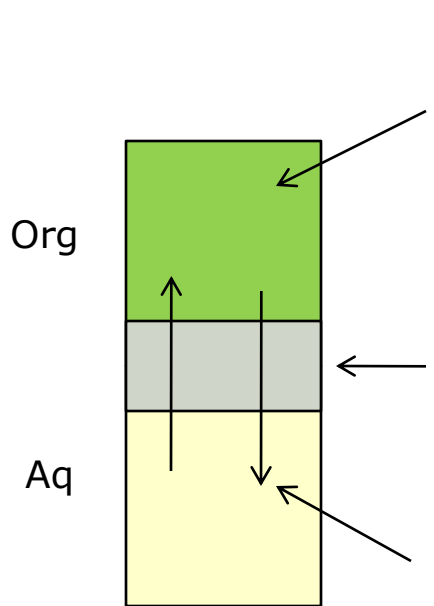
- A significant degradation of the tertiary amine into dioctylamine due to the presence of vanadium, chromium,...
- A subsequent loss of uranium loading capacity
- **The appearance of unbreakable cruds at the stripping stage, due to molybdenum co-extracted by the decomposition products of the tertiary amine (mainly secondary amine)**
- An increased loss of organic phase by immobilization in the cruds



**Formation of secondary amines by degradation of Alamine®336 during the uranium solvent extraction in a solvent extraction plant. ○: Tertiary amine; □: Secondary amine; ×: Total (t=0 corresponds to a solvent reloaded with tertiary amine but not a fresh solvent, which explains the presence of secondary amine at that time).**

**(A. Chagnes et al., J. Chem. Technology. Biotechnology, 2009, in press)**

## Real system (time $t$ – scale of years)



- Ageing of the organic phase
- Losses of organic phase by physical phenomena
- Loss of loading capacity of the target solute(s)
- Loss of selectivity
- **Appearance of cruds**
- Variation of ore composition with progression in the mines or quarries

**Slow settling and difficult phase separation**

## Cruds



**Stripping problems (cruds) with amine 0,22M and alcohol 5%**



## Tools for supramolecular speciation



<b>Techniques</b>	<b>Information</b>
Water determination	Mass balance $[H_2O]_{org}$ vs $a_{H_2O}$
VPO	Aggregation
SANS, SAXS	Size, shape, interaction between aggregates
ESI-MS	Determination of species
Ultracentrifugation	Size, composition of aggregates

Tableau 31 : Bilan des résultats obtenus sur la spéciation supramoléculaire de phases organiques DMDOHEMA-HDHP. D = DMDOHEMA et HP = HDHP.

Phase aqueuse	VPO ( <i>n</i> -pentane)	DNPA ([D] = 0,7 + [HP] = 0,3 mol/L) dans le <i>n</i> -dodécane	DXPA
H <sub>2</sub> O	existence d'agrégats mixtes [H <sub>2</sub> O] <sub>org</sub> ↑ avec [espèces]	extraction H <sub>2</sub> O synergique dans le cœur polaire de micelles inverses mixtes $\varnothing_{\text{cœur polaire}} = 11 \text{ \AA}$ $\varnothing_{\text{agrégat}} = 24 \text{ \AA}$	
HNO <sub>3</sub>	[HNO <sub>3</sub> ] = 0,1 mol/L + [NaNO <sub>3</sub> ] = 2,9 mol/L  Effet très faible de l'acidité sur l'agrégation  N ↑ légèrement	extractant minoritaire = co-surfactant majoritaire = oriente les propriétés synergisme/extraction de l'eau	$\varnothing_{\text{cœur polaire}} \uparrow$ avec l'acidité Interactions ↑ (↑ HNO <sub>3</sub> dans cœurs polaires)
		[HNO <sub>3</sub> ] = 0,1 mol/L (D) <sub>2</sub> HP(H <sub>2</sub> O) <sub>1,5</sub>	$\varnothing_{\text{cœur polaire}} = 11 \text{ \AA}$
		[HNO <sub>3</sub> ] = 1 mol/L (D) <sub>3</sub> HP(H <sub>2</sub> O) <sub>3</sub> HNO <sub>3</sub>	$\varnothing_{\text{cœur polaire}} = 13 \text{ \AA}$
		[HNO <sub>3</sub> ] = 3 mol/L (D) <sub>5</sub> (HP) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (HNO <sub>3</sub> ) <sub>3</sub>	$\varnothing_{\text{cœur polaire}} = 14 \text{ \AA}$

B. Gannaz, PhD, University Paris 6, 2006

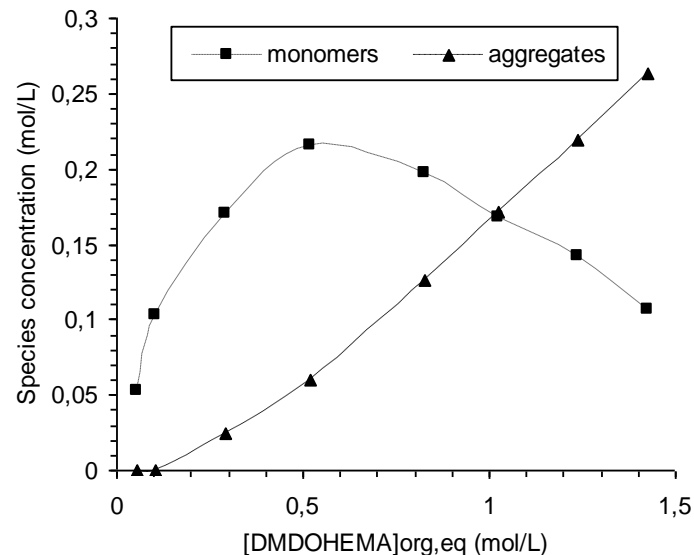
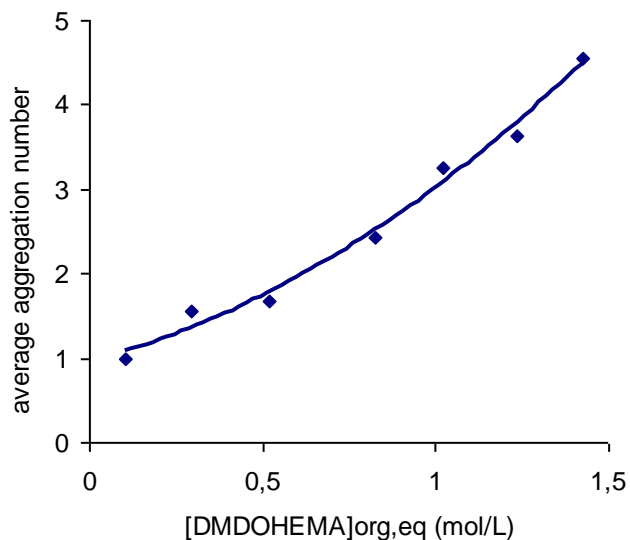
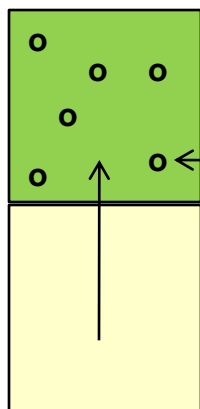
Tableau 31 : Bilan des résultats obtenus sur la spéciation supramoléculaire de phases organiques DMDOHEMA-HDHP. D = DMDOHEMA et HP = HDHP.

<b>HNO<sub>3</sub></b>  <b>M<sup>3+</sup></b>	[HNO <sub>3</sub> ] = 0,1 mol/L + [NaNO <sub>3</sub> ] = 2,9 mol/L	Effets conjugués de l'acidité et de [M <sup>3+</sup> ] Agrégation/LiNO <sub>3</sub> similaire à H <sub>2</sub> O	Interactions ↑ (M <sup>3+</sup> et HNO <sub>3</sub> dans cœurs polaires)
	Ce <sup>3+</sup> remplace (H <sub>2</sub> O) <sub>org</sub> ([Ce <sup>3+</sup> ] <sub>org</sub> + [H <sub>2</sub> O] <sub>org</sub> constante)	[HNO <sub>3</sub> ] = 0,1 mol/L Nd(NO <sub>3</sub> )(D) <sub>4</sub> (P) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> HNO <sub>3</sub> Ø <sub>cœur polaire</sub> = 12 Å / Ø <sub>agrégat</sub> = 21 Å.	Ø <sub>cœur polaire</sub> = 10 Å
	Capacité de charge liée à :	[HNO <sub>3</sub> ] = 1 mol/L Nd(D) <sub>6</sub> (P) <sub>3</sub> (H <sub>2</sub> O) <sub>5</sub> (HNO <sub>3</sub> ) <sub>2</sub> Ø <sub>cœur polaire</sub> = 15 Å / Ø <sub>agrégat</sub> = 24 Å.	Ø <sub>cœur polaire</sub> = 13 Å
	[extractant] + organisation supramoléculaire	[HNO <sub>3</sub> ] = 3 mol/L Nd <sub>2</sub> (D) <sub>16</sub> (P) <sub>6</sub> (HP)(H <sub>2</sub> O) <sub>15</sub> (HNO <sub>3</sub> ) <sub>14</sub> Ø <sub>cœur polaire</sub> = 21 Å / Ø <sub>agrégat</sub> = 33 Å.	Ø <sub>cœur polaire</sub> = 14 Å

**B. Gannaz, PhD, University Paris 6, 2006**

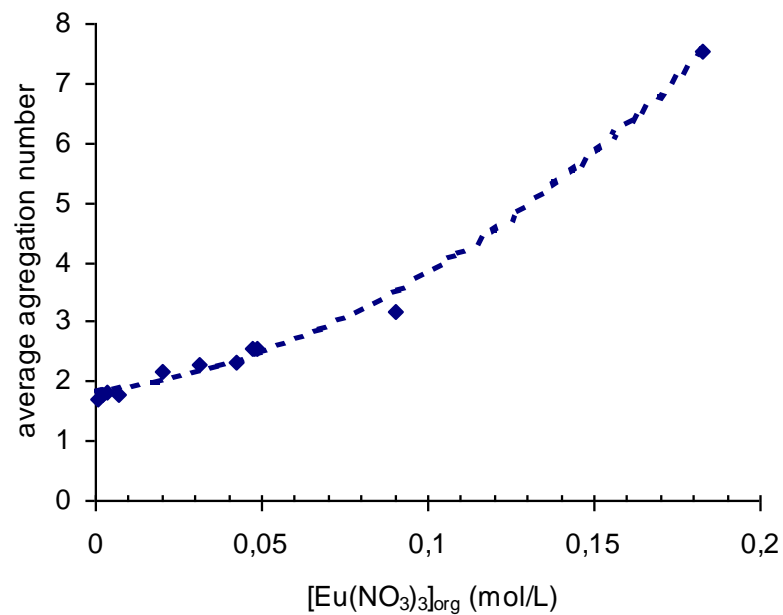
# DMDOHEMA

## N,N'-dimethyl-N,N'-dioctylhexylethoxy malonamide



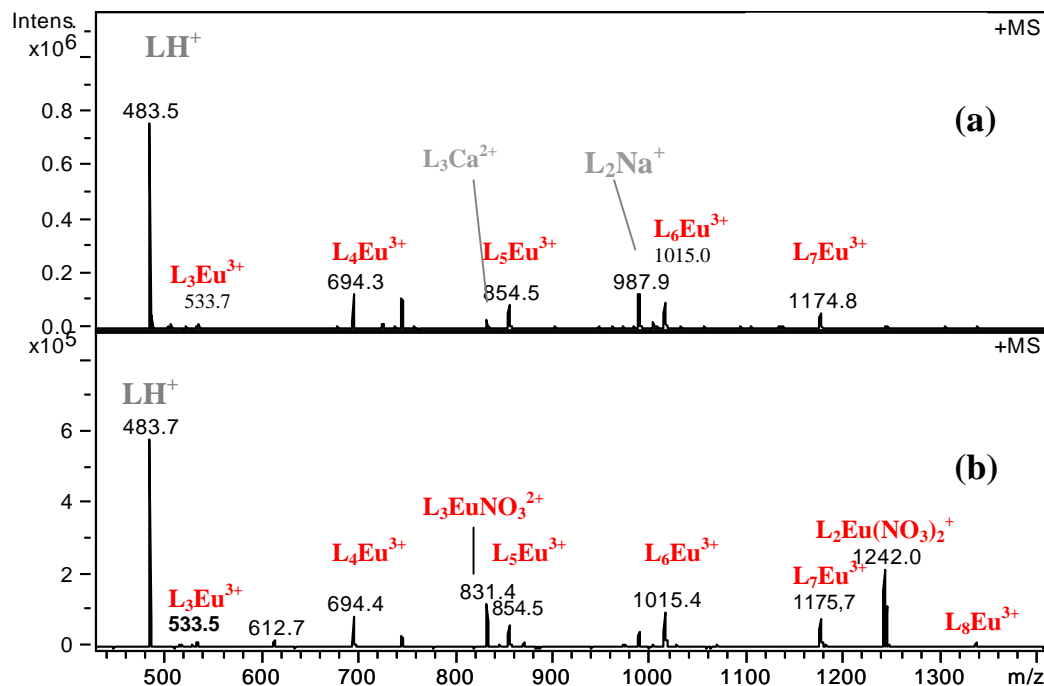
Aggregation properties of DMDOHEMA diluted in *n*-heptane in contact with a 3 M LiNO<sub>3</sub> aqueous phase.  
 L.Berthon, Y. Meridiano, S.Lagrave, X. Crozes, C. Sorel, N. Zorz, F. Testard, Th. Zemb,  
 ISEC 2008, Tucson, Arizona September 15 - 19, 2008

Average aggregation number as a function of europium concentration in organic phase for 0.5M DMDOHEMA in *n*-heptane.  
 a/Aqueous phase: europium nitrate in 3 M LiNO<sub>3</sub>  
 b/Water activity in aqueous phase:  $a_{\text{H}_2\text{O}} = 0,86$



## ESI-MS

Positive ESI mass spectrum for 0.5 M DMDOHEMA in *n*-dodecane after equilibration with  
 (a) 0.1 M  $\text{Eu}(\text{NO}_3)_3$  in 3 M  $\text{LiNO}_3$  or  
 (b) 0.4 M  $\text{Eu}(\text{NO}_3)_3$  in 3 M  $\text{LiNO}_3$

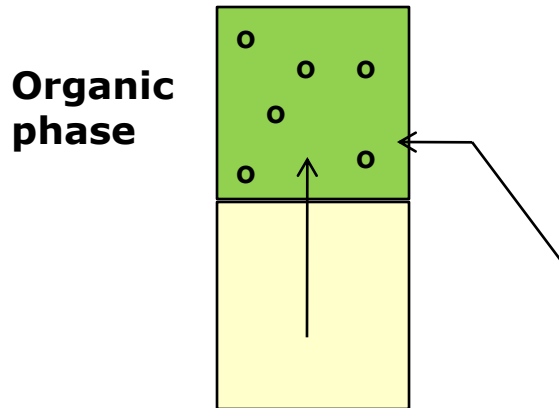


## Ultracentrifugation

### Kelex 100

in alkaline media in presence of alcohol,  
in kerosene

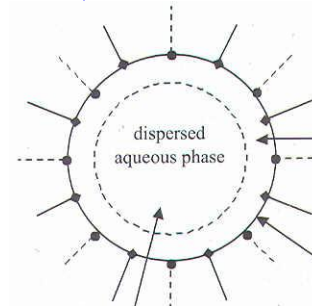
### From micelles to swollen micelles



Micelles :  $(L^-, Na^+)_3(ROH)_5(H_2O)_6$   $\Phi_{core} < 1\text{nm}$

↓ + Na octanoate

Swollen micelles

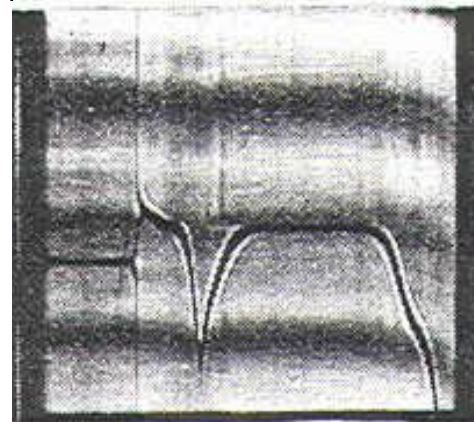


$\Phi_{core} = 2 - 8\text{ nm}$

$\Phi_{hydro} = 4 - 10\text{ nm}$

## Ultracentrifugation

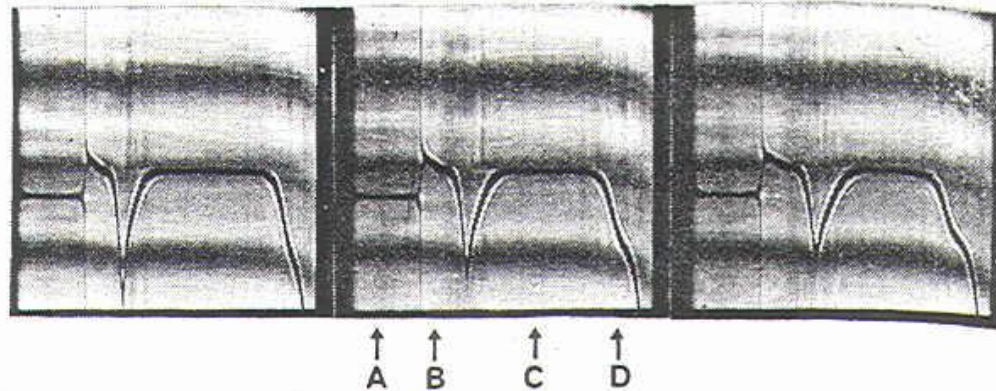
  $\omega = 52000 \text{ rpm}; 4 - 36 \text{ hours}$



↑ A    ↑ B    ↑ C    ↑ D

**Figure 5.** Typical ultracentrifugation patterns, system III of Table II.

# Ultracentrifugation

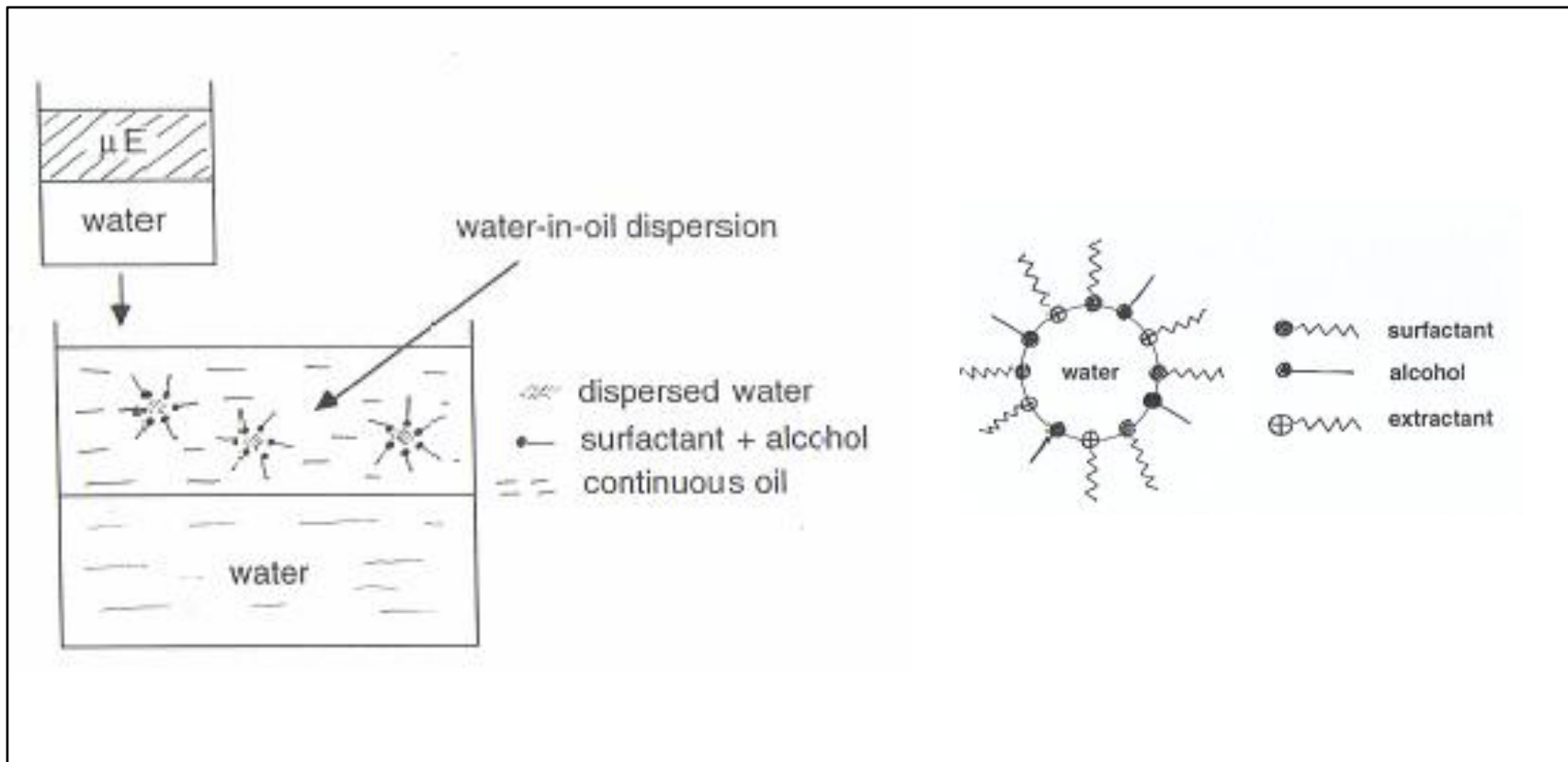


**Figure 5.** Typical ultracentrifugation patterns, system III of Table II.

Region A corresponds to the air present in the cell.  
 In region B, between the meniscus and the peak, no water droplets exist, but only the continuous organic phase.  
 Region C, after the peak, nearly corresponds to the initial microemulsion.  
 Region D is a region rich in droplets.

$$r_h^2 = \frac{9}{2} \frac{\eta S_0}{\rho_g - \rho_c}$$

where  $S_0 = (1/\omega^2 R)(dR/dt)$  is the sedimentation coefficient at infinite dilution.

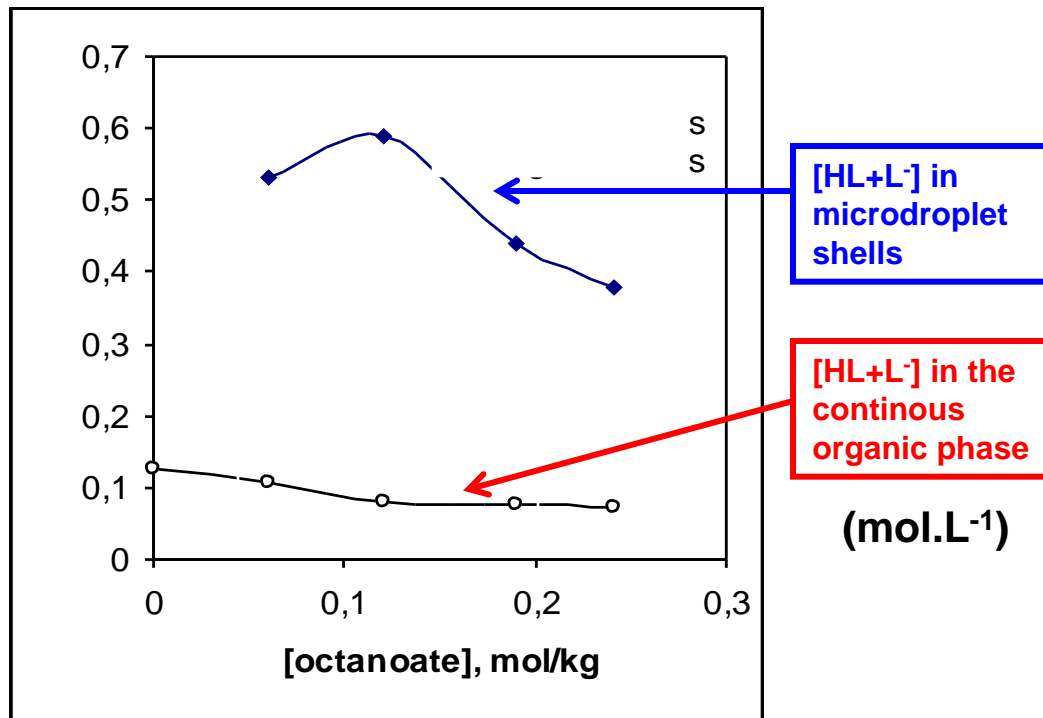


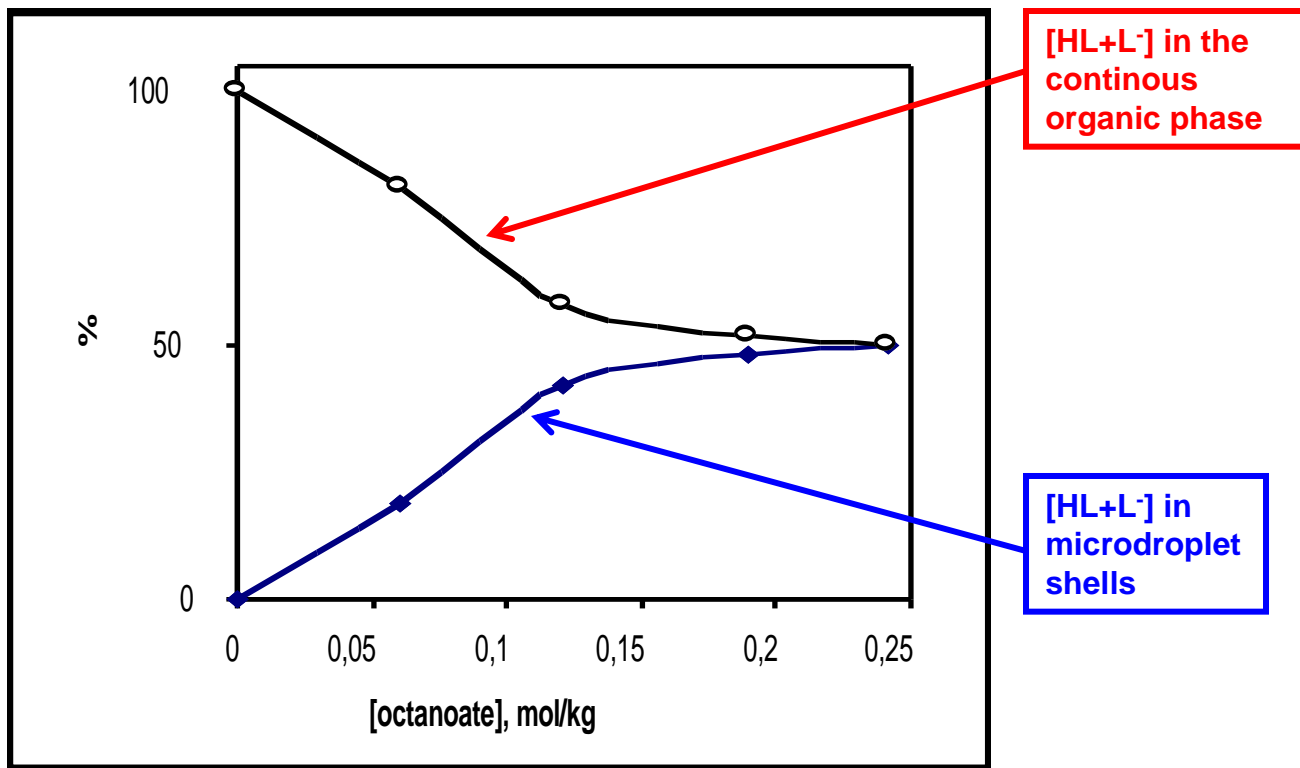
666 • ANALYTICAL CHEMISTRY, VOL. 55, NO. 4, APRIL 1983

Table III. Variation of Fraction  $f_d$  of RHOx Adsorbed on Droplets and of RHOx Concentration ( $[RHOx]_d$ ) on Droplets vs. Octanoate Concentration <sup>a</sup>

[octanoate], mol·kg <sup>-1</sup>	[RHOx] <sub>μE</sub> , M	[RHOx] <sub>αφ</sub> , M	volume fraction α	$f_d$	[RHOx] <sub>d</sub> , M
0.06	0.127 ± 0.001	0.108 ± 0.003	0.045 ± 0.005	0.19 ± 0.04	0.5 ± 0.15
0.12	0.125 ± 0.001	0.080 ± 0.003	0.090 ± 0.009	0.42 ± 0.035	0.5 ± 0.1
0.24	0.124 ± 0.001	0.074 ± 0.002	0.165 ± 0.017	0.50 ± 0.035	0.3 ± 0.05

<sup>a</sup> [Octanoate]/[butanol] = 0.112; aqueous phase, NaOH 3.5 M.







## **Solutes distribution modelling in supramolecular based systems**

## Classical approach based on full speciation and mass action law

Gannaz et al.  
Solvent Extr. Ion Exch.  
25, 2007, 313

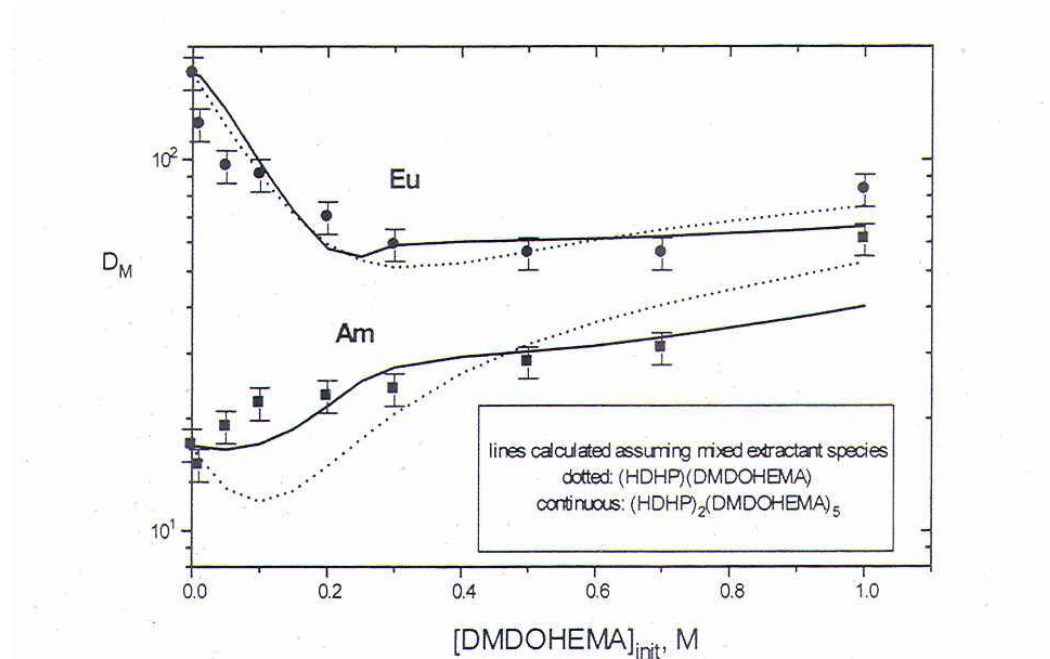


Figure 11. DMDOHEMA concentration dependencies for the extraction of  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  in the presence of constant 0.1 M HDHP in *n*-dodecane with 0.10 M  $\text{HNO}_3$  and 3 M  $\text{NaNO}_3$  in the aqueous phase and  $T = 25^\circ\text{C}$ .



## Classical approach based on full speciation and mass action law



**HA = HDHP; B = DMDOHEMA**

## Alternative approach based on surface sorption

The ions are considered to adsorb on a surface  $\Sigma$ , which is related to the area per extractant molecule  $\sigma$  simply by:  $\Sigma = c_{\text{ext}}\sigma$ , where  $c_{\text{ext}}$  is the extractant concentration in the solvent, excluding the macroscopic solvent–water interface in the case of emulsified systems.

**Testard *et al.*, C.R. Chimie 10 (2007) 1034**

Taking into account that the extractants can exist in four different states of aggregation, the adsorption isotherm has now to be written as the simultaneity of four adsorption isotherms (Eq. (2)):

$$\theta = \frac{1}{[E]_{\text{tot}}} \sum_{\text{pp}} [E] \frac{{}^{\text{pp}}K_{\text{ad}}M_{\text{pp}}}{1 + {}^{\text{pp}}K_{\text{ad}}M_{\text{pp}}} \quad (2)$$

where “pp” stands for the sum of the contributions of the four pseudophases: monomers, micelles, networks and tactoids,

**Testard *et al.*, C.R. Chimie 10 (2007) 1034**

## Alternative approach based on surface sorption

When only an average organization is considered, the adsorption isotherm is defined by an *average* adsorption constant (Eq. (3)):

$$\theta = \frac{\langle K_{\text{ad}} \rangle M_{\text{pp}}}{1 + \langle K_{\text{ad}} \rangle M_{\text{pp}}} \quad (3)$$

Testard *et al.*, C.R. Chimie 10 (2007) 1034

## Alternative approach based on surface sorption

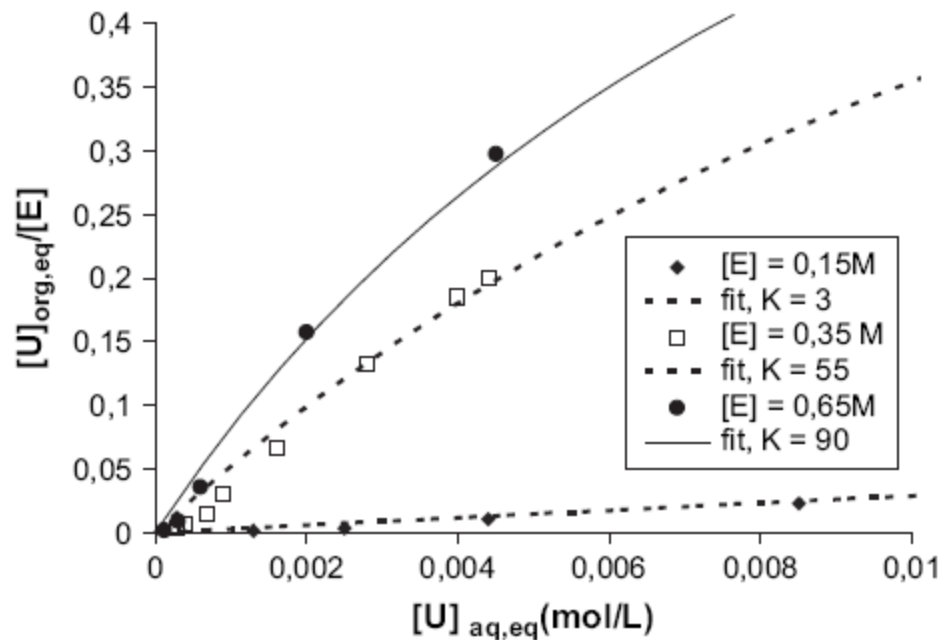


Fig. 3. Effect of the extractant concentration on the extraction isotherm for uranyl extraction by a solution of diamide (noted “E”) in hexane.



**Both methods allow good fitting, but contain a certain degree of uncertainty**

- Uncertainty about speciation in the first case
- Use of average sorption constants in the second case



# Acknowledgements

## GDRI SupraChem