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Stir Bar Sorptive Extraction modelling for hydrometallurgical extracting molecules, and LC-MS analytical method for environmental applications

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2nd workshop SBSE

Paris, February 12th, 2013

Plan

Context

D2EHPA extraction modelling with PDMS

- *Thermodynamics approach*
- *Kinetics aspects*

Experimental validation of the model

- *A LC-MS method to quantify D2EHPA in aqueous solutions*
- *Experimental kinetics aspects*
- *Extraction modelling versus experimental data*

Conclusions

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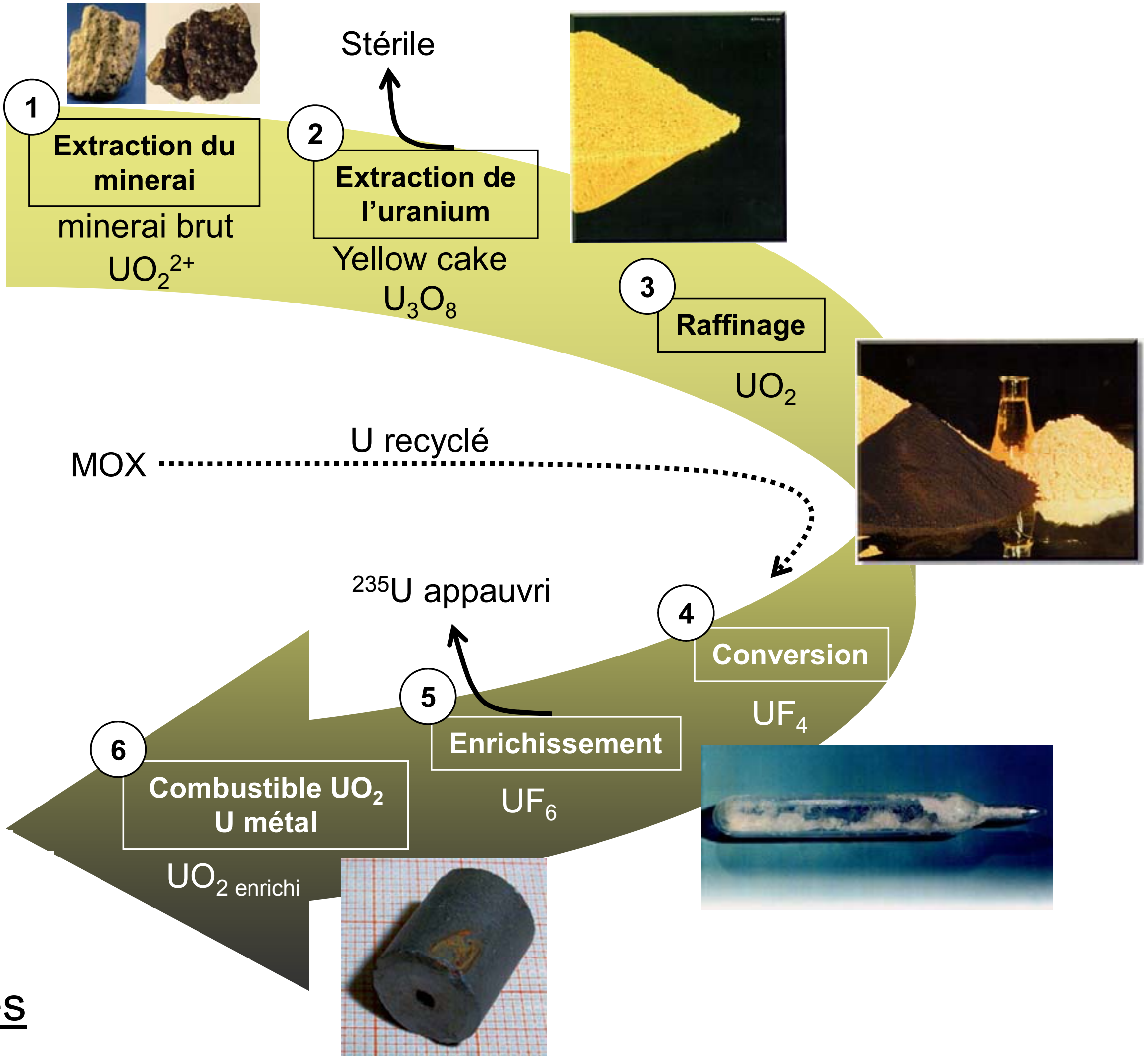
Industrial and analytical context

Detection of extracting molecules at ppb concentration levels in aqueous samples.

Modelling of the sampling conditions for general applications

Hydrometallurgical process for uranium production : *From ore mining to spent fuel reprocessing plants*

Ore mining



1 **Extraction du minerai**

minerai brut

UO_2^{2+}

Stérile

2 **Extraction de l'uranium**

Yellow cake

U_3O_8

3 **Raffinage**

UO_2

MOX

U recyclé

4 **Conversion**

UF_4

^{235}U appauvri

5 **Enrichissement**

UF_6

6 **Combustible UO_2**
U métal

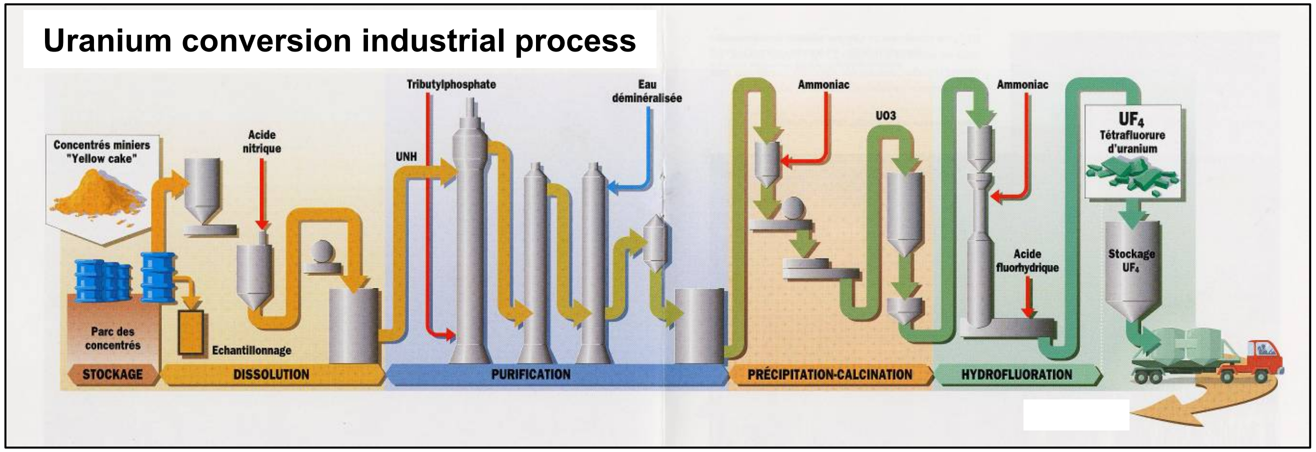
$UO_{2\ \text{enrichi}}$

Power plants, and spent fuel reprocessing facilities

Hydrometallurgical process for uranium production :
From ore mining to spent fuel reprocessing plants

Production of uranium or plutonium by Purex*-like hydrometallurgical processes

*Purex : PURification by EXtraction



Uranium conversion industrial process

- Yellow cake dissolution
- Liquid-liquid extraction
- Uranium nitrate
- Ammonium diuranate
- Calcination
- Uranium dioxide
- Hydrofluorination
- Uranium hexafluoride

$$\text{"Yellow cake"} \xrightarrow{[HNO_3]_{concentré}} 2\,NO_3^- + UO_2^{2+}$$

$$2\,NO_3^- + UO_2^{2+} \rightleftharpoons [UO_2(NO_3)_2],\,H_2O \rightleftharpoons [UO_2(NO_3)_2](TBP)_2$$

$$[UO_2(NO_3)_2](TBP)_2 \rightleftharpoons [UO_2(NO_3)_2],\,H_2O$$

$$2\,(UO_2(NO_3)_2) + 6\,NH_4OH \longrightarrow (NH_4)_2U_2O_7 + 4\,NH_4NO_3 + 3\,H_2O$$

$$(NH_4)_2U_2O_7 \longrightarrow 2\,UO_3 + 2\,NH_3 + H_2O$$

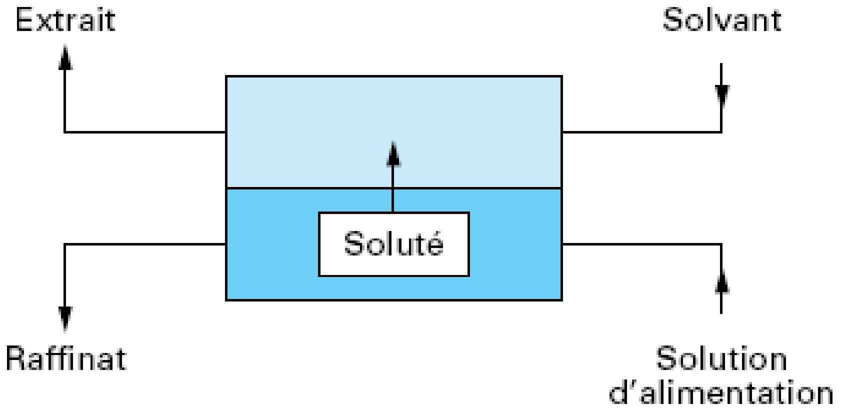
$$UO_3 + H_2 \xrightarrow{N_2} UO_2 + H_2O$$

$$UO_2 + 4\,HF \longrightarrow UF_4 + 2\,H_2O$$

$$UF_4 + F_2 \longrightarrow UF_6$$

Hydrometallurgical process for uranium production : *Two-phase equilibrium and extraction mechanism*

Two-phase process
(Liquid-liquid process)



Molecular extraction mechanism
(complex formation and partition equilibria)

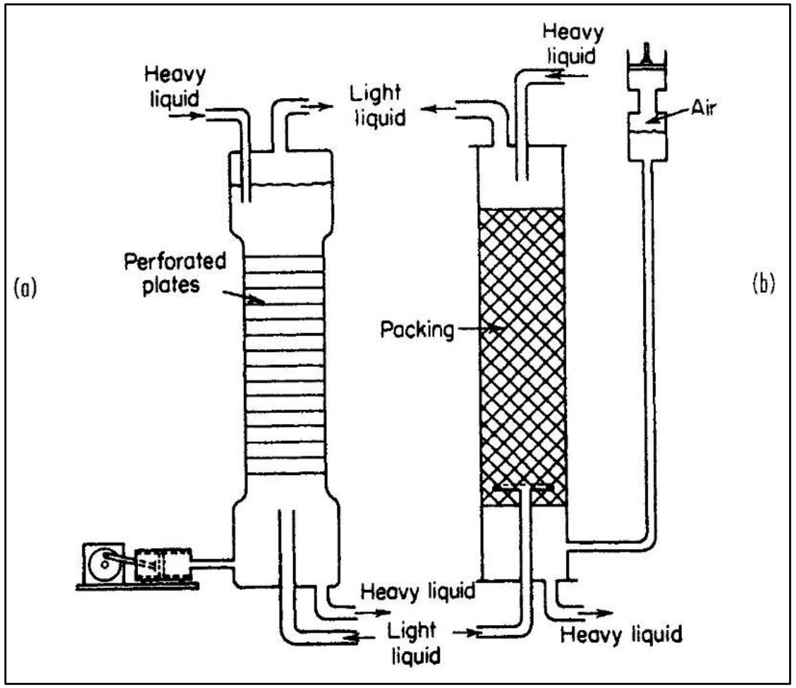
$HL \Leftrightarrow \overline{HL}$ avec $K_D(HL) = C_{\overline{HL}} / C_{HL}$

$HL \Leftrightarrow H^+ + L^-$ avec $K_a = C_{H^+} C_{L^-} / C_{HL}$

$2\,\overline{HL} \Leftrightarrow \overline{H_2L_2}$ avec $K_d = C_{\overline{H_2L_2}} / (C_{\overline{HL}})^2$

$M^{n+} + n\,L^- \Leftrightarrow ML_n$ avec $\beta_n = C_{ML_n} / [C_{M^{n+}} (C^n_{L^-})]$

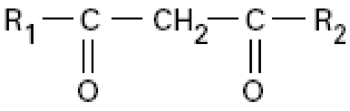
$ML_n \Leftrightarrow \overline{ML_n}$ avec $K_D(ML_n) = C_{\overline{ML_n}} / C_{ML_n}$



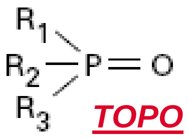
Pulsed columns for counter-flow liquid-liquid extraction

Hydrometallurgical process for uranium production : *Two-phase equilibrium and extraction mechanism*

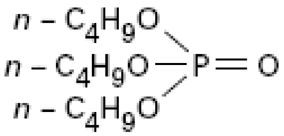
Typical extracting molecules



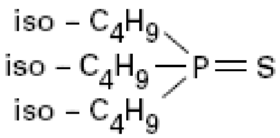
β-dicetones

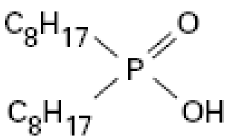


TOPO
(phosphine oxides)

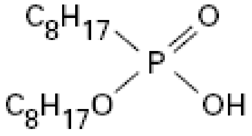


TBP
(phosphoric acid ester)

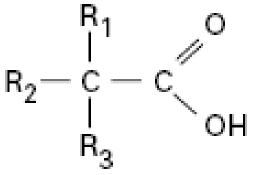




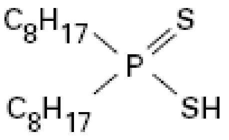
(phosphinic acids)

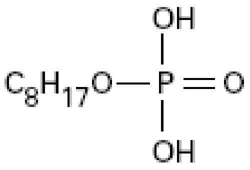


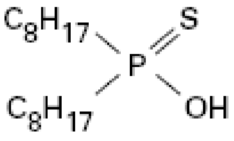
(phosphonic acids)

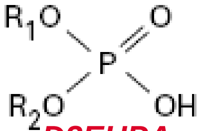


(Carboxylic acids)



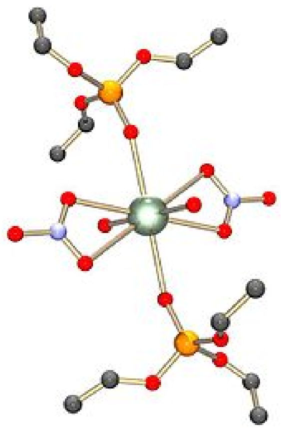






D2EHPA
(phosphoric acids)

Extracted metal ion complex structure

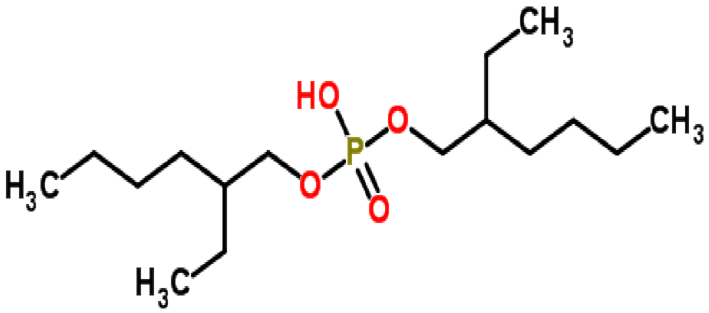


$UO_2(NO_3)_2$, 2TBP

Typical extraction solvents

SOLVESSO 150
SHELLSOL AB
SOLVANTAR 340
SOLVAREX 10
VARSOL 80
SHELLSOL H
WHITE-SPIRIT W.S 17/18
WHITE-SPIRIT 5 HPE
EXXSOL D80
NORPAR 12
SHELLSOL D70
SPIRDANE D40
SHELLSOL D40
SHELLSOL TD
ISOPAR L
KERDANE D65
ISOPAR H
ISANE IP 175

D2EHPA : bis-(2-ethylhexyl) phosphoric acid



D2EHPA is a very good liquid-liquid extraction agent for uranium in phosphoric acid media, it has potential environmental impact which requires analytical methods for environmental monitoring at trace concentration levels (µg/L),

Important today : Development of efficient analytical procedures based on green analytical chemistry (solvent-free methods, direct and rapid analysis procedures),

Due to its physical and chemical properties (hydrophobic and acidic properties, dimerization in organic solvents, complex equilibria with uranyl ions,…), D2EHPA is a good standard for extraction process modelling.

Aim of this R&D project

Development of green analytical methods for D2EHPA detection at trace levels :

- On site and solvent-free sampling technique (no sample or solvent transportation),
- Optimization of sampling conditions, from modelling concepts,
- Development of a versatile model that could be applied for other extracting agents,
- Analytical method permiting rapid detection and quantification at trace levels (µg/L),

- **Sampling by Stir Bar Sorptive Extraction,**
- **Application of basic analytical chemistry and liquid-liquid partition equilibria for extraction modelling,**
- **LC-MS analytical method development.**

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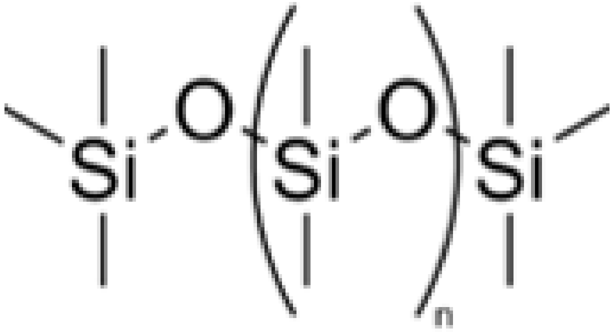
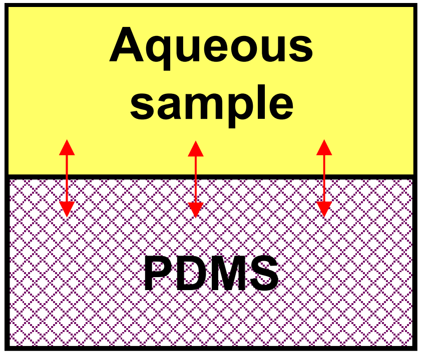
D2EHPA extraction modelling with PDMS

D2EHPA extraction modelling : thermodynamics approach

<u>Starting point of the model</u> : polydimethylsiloxan (PDMS) is considered as a non-polar solvent, where chemical equilibria occur similarly compared with other organic liquid solvents

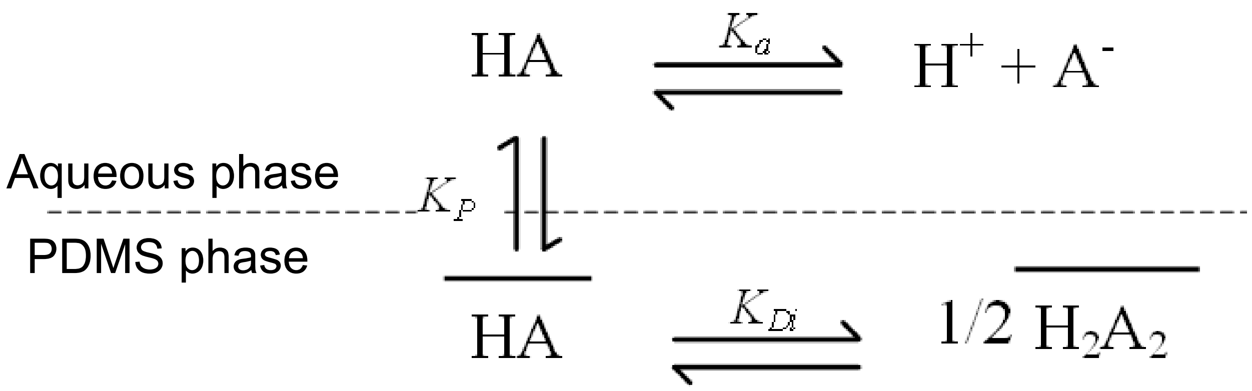




Chemical equilibria considered for D2EHPA partition modelling
(from known chemical properties)

$HL \Leftrightarrow \overline{HL}$	with $K_D(HL) = C_{\overline{HL}} / C_{HL}$	(Two-phase partition equilibrium)
$HL \Leftrightarrow H^+ + L^-$	with $K_a = C_{H^+} C_{L^-} / C_{HL}$	(Acid-base equilibrium in aqueous phase)
$2\,\overline{HL} \Leftrightarrow \overline{H_2L_2}$	with $K_d = C_{\overline{H_2L_2}} / (C_{\overline{HL}})^2$	(Dimerization equilibrium in organic phase)

D2EHPA extraction modelling : thermodynamics approach



The extraction process is thermodynamically ruled by three physical and chemical equilibria based on thermodynamic constants :

$$K_a = \frac{\left|H^+\right|_{eq}\left|A^-\right|_{eq}}{\left|HA\right|_{eq}} = 10^{-1,47}$$

$$K_P = \frac{\left|\overline{HA}\right|_{eq}}{\left|HA\right|_{eq}} = 10^{6,07}$$

K_p=K_{ow} (hypothesis)

$$K_{Di} = \frac{\left|\overline{H_2A_2}\right|_{eq}}{\left|\overline{HA}\right|^2_{eq}} = 10^{4,50}$$

D2EHPA extraction modelling : thermodynamics approach

Application of the <u>law of mass action</u> and the <u>law of conservation of matter</u> to calculate the extraction yield :

Distribution coefficient

$$D = \frac{[\overline{HA}]_{eq} + 2[\overline{H_2A_2}]_{eq}}{[HA]_{eq} + [A^-]_{eq}}$$

$$\frac{n_{PDMS}}{n_0} = \frac{n_{\overline{HA}eq} + 2n_{\overline{H_2A_2}eq}}{n_0}$$

Extraction yield

$$\frac{n_{PDMS}}{n_0} = \frac{1}{C_0}\left(- \frac{\left(1 + \frac{10^{pH-pKa}}{\gamma_{A^-}} + \frac{K_P}{\beta}\right) - \sqrt{\left(1 + \frac{10^{pH-pKa}}{\gamma_{A^-}} + \frac{K_P}{\beta}\right)^2 + \frac{8C_0 K_{Di} K_P^2}{\beta}}}{4K_{Di}K_P} \right)\left(1 - \beta\frac{\left(1 + \frac{10^{pH-pKa}}{\gamma_{A^-}} + \frac{K_P}{\beta}\right) - \sqrt{\left(1 + \frac{10^{pH-pKa}}{\gamma_{A^-}} + \frac{K_P}{\beta}\right)^2 + \frac{8C_0 K_{Di} K_P^2}{\beta}}}{2K_P} \right.$$

Three modelling parameters depending of the molecule extracted

K_a , K_p , K_{Di}

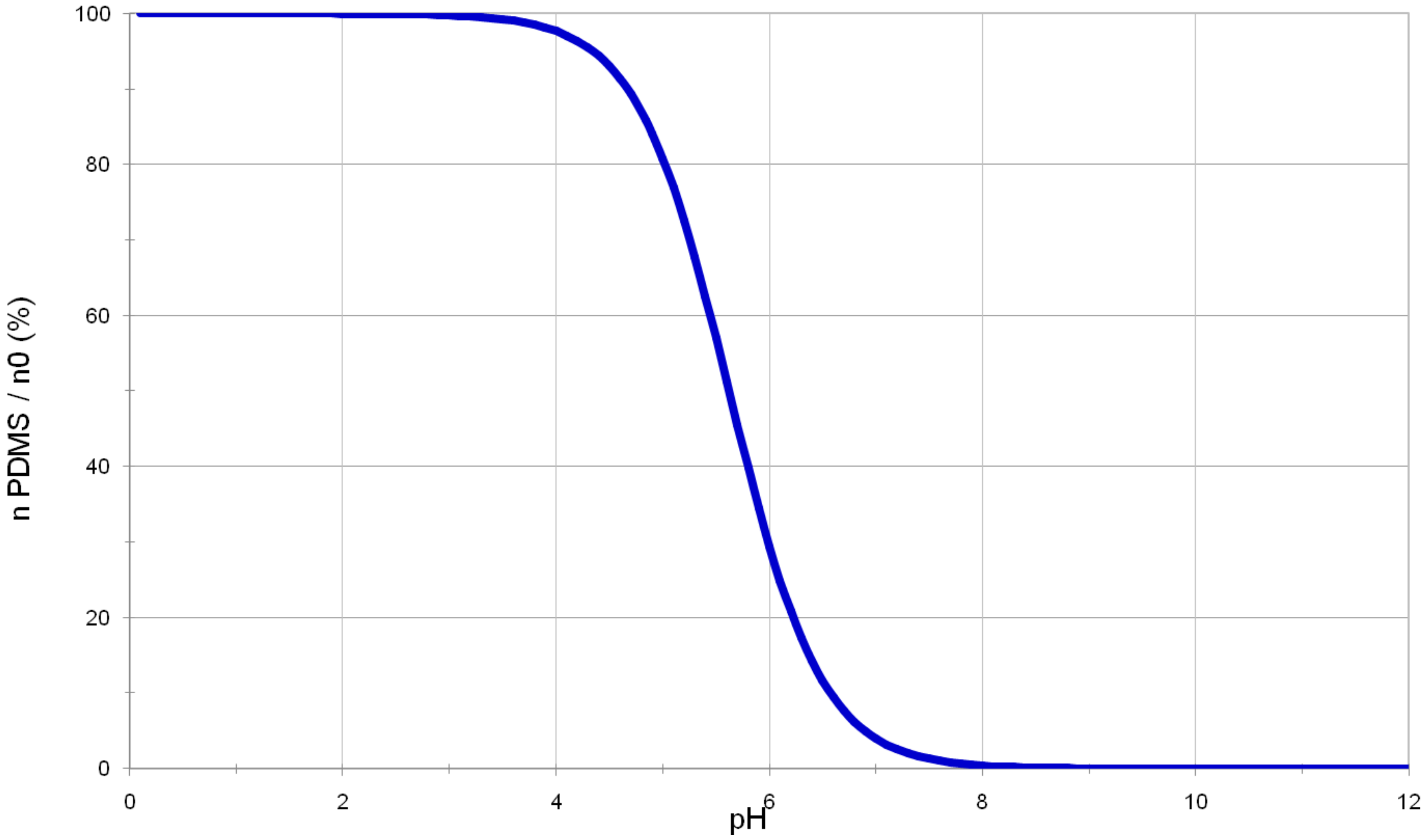
Three operating parameters to optimize the extraction

γ_{A-}: activity coefficient (aqueous media)

β : volume ratio for the two phases (V_{sample} / V_{PDMS})

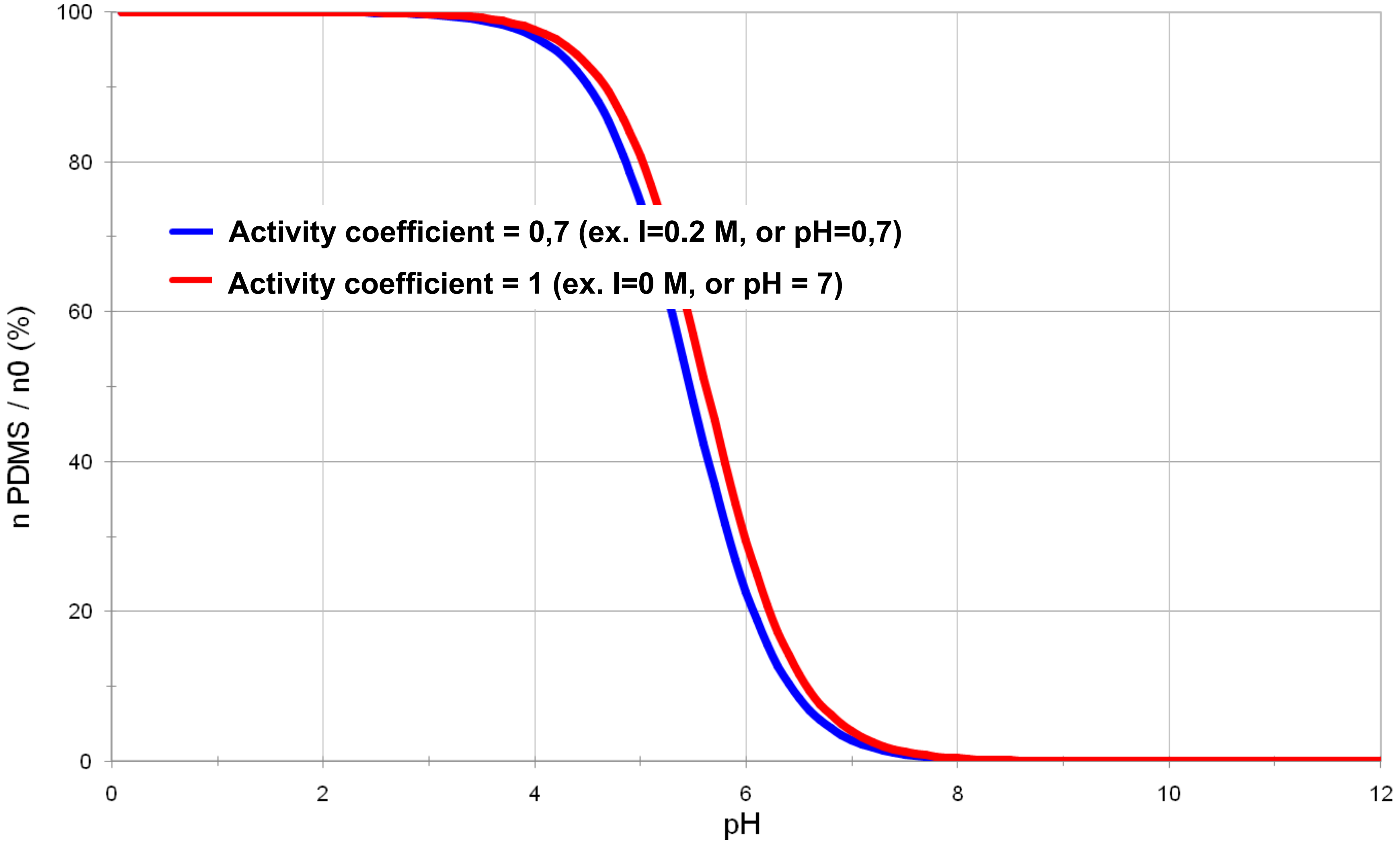
pH: pH of the aqueous solution (sample)

D2EHPA extraction modelling : thermodynamics approach



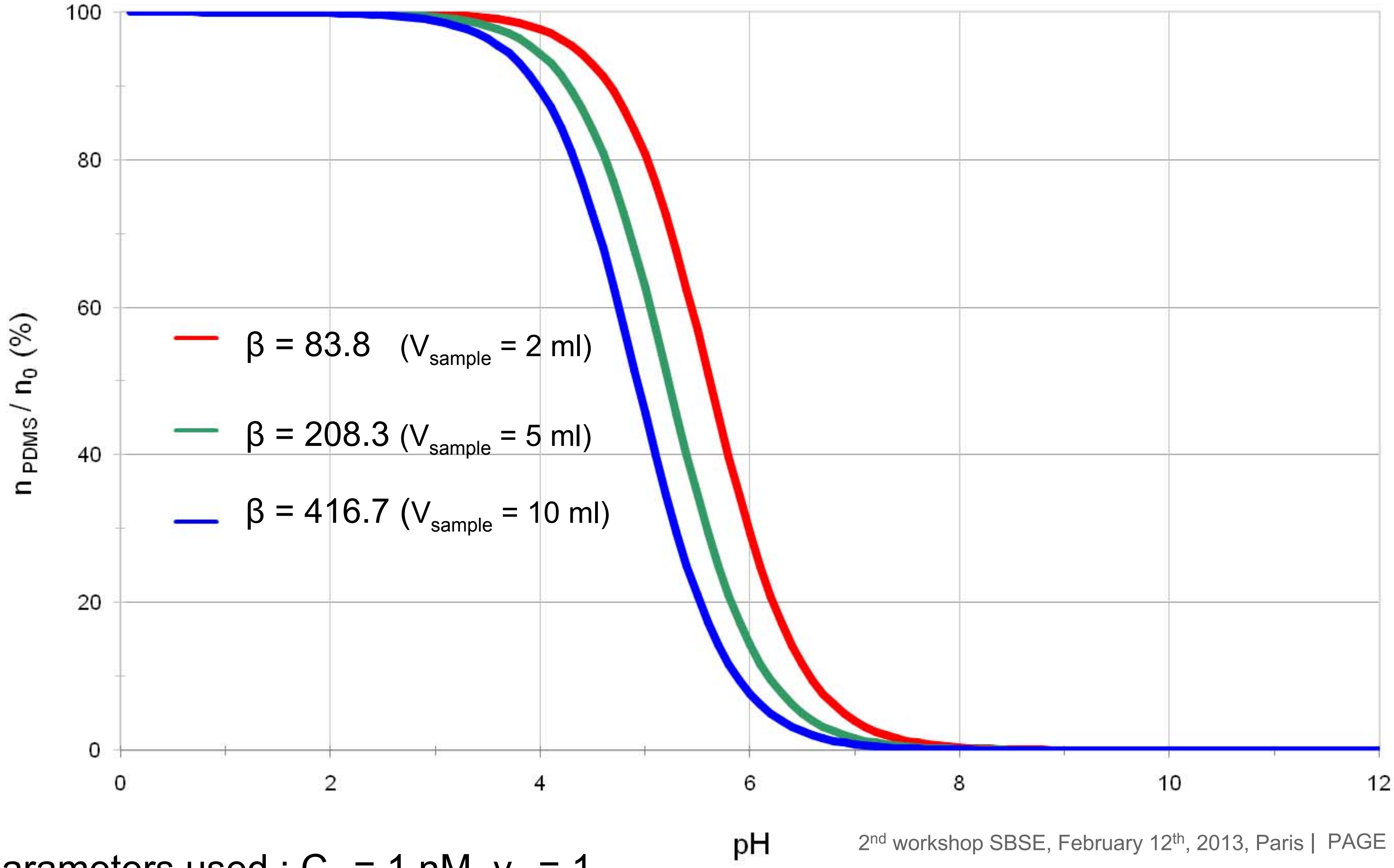
Parameters used : C_0 = 1 nM, β = 83.3 , γ_{A^-}=1

D2EHPA extraction modelling : thermodynamics approach



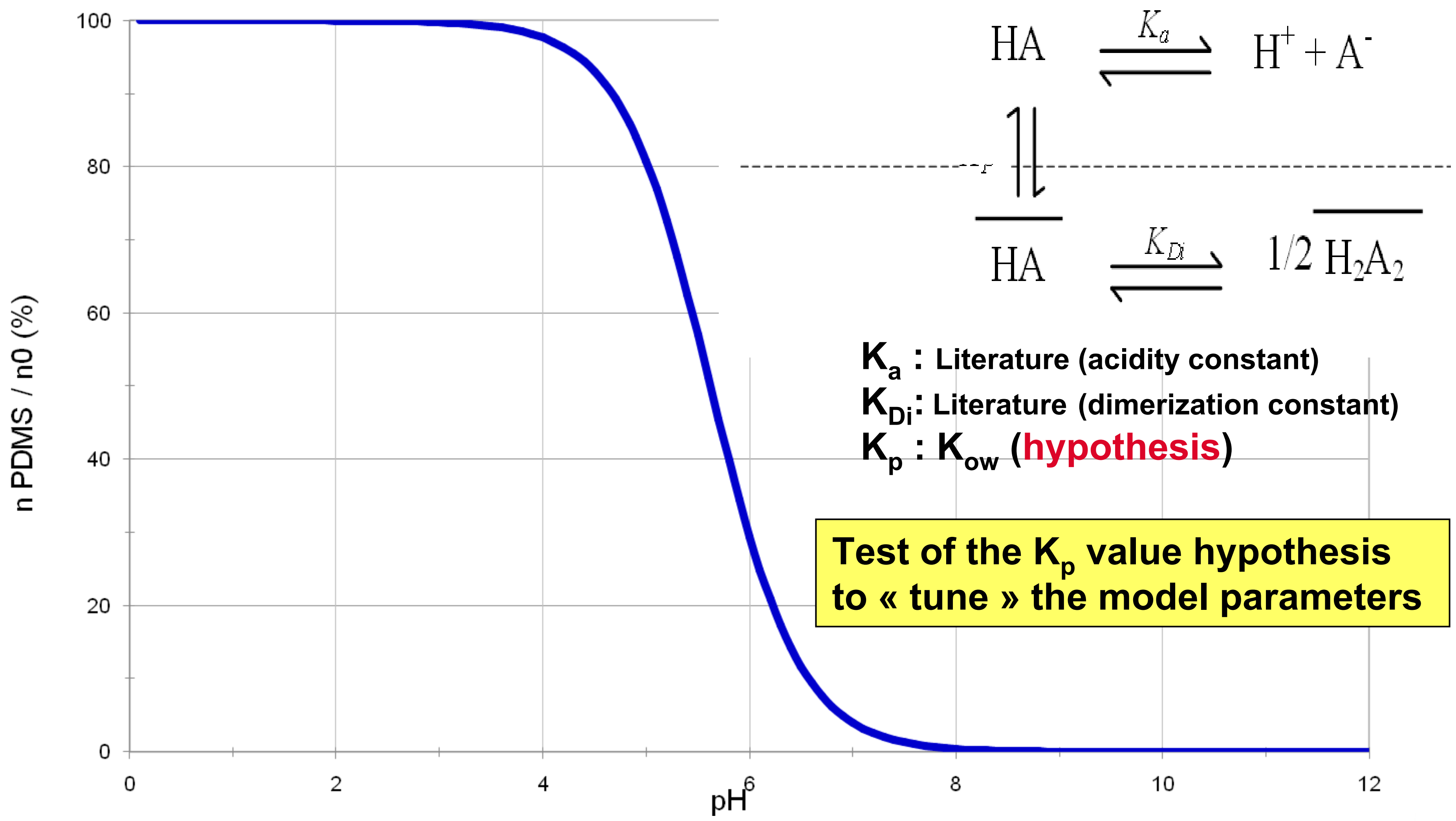
Parameters used : C_0 = 1 nM, β = 83.3

D2EHPA extraction modelling : thermodynamics approach



Parameters used : C_0 = 1 nM, γ_{A^-} = 1

D2EHPA extraction modelling : thermodynamics approach



K_a : Literature (acidity constant)

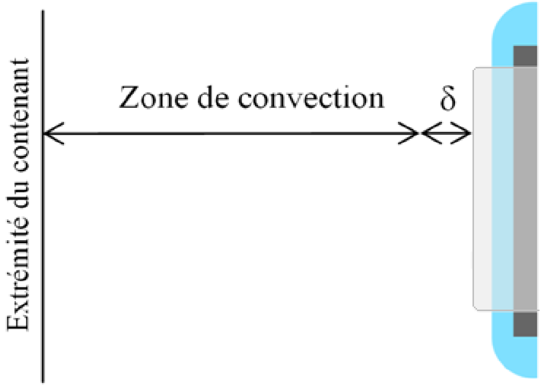
K_{Di}: Literature (dimerization constant)

K_p : K_{ow} (hypothesis)

Test of the K_p value hypothesis to « tune » the model parameters

D2EHPA extraction modelling : kinetics aspects

« ***La thermodynamique impose, la cinétique dispose*** »



In the convection zone, the solution is homogeneous

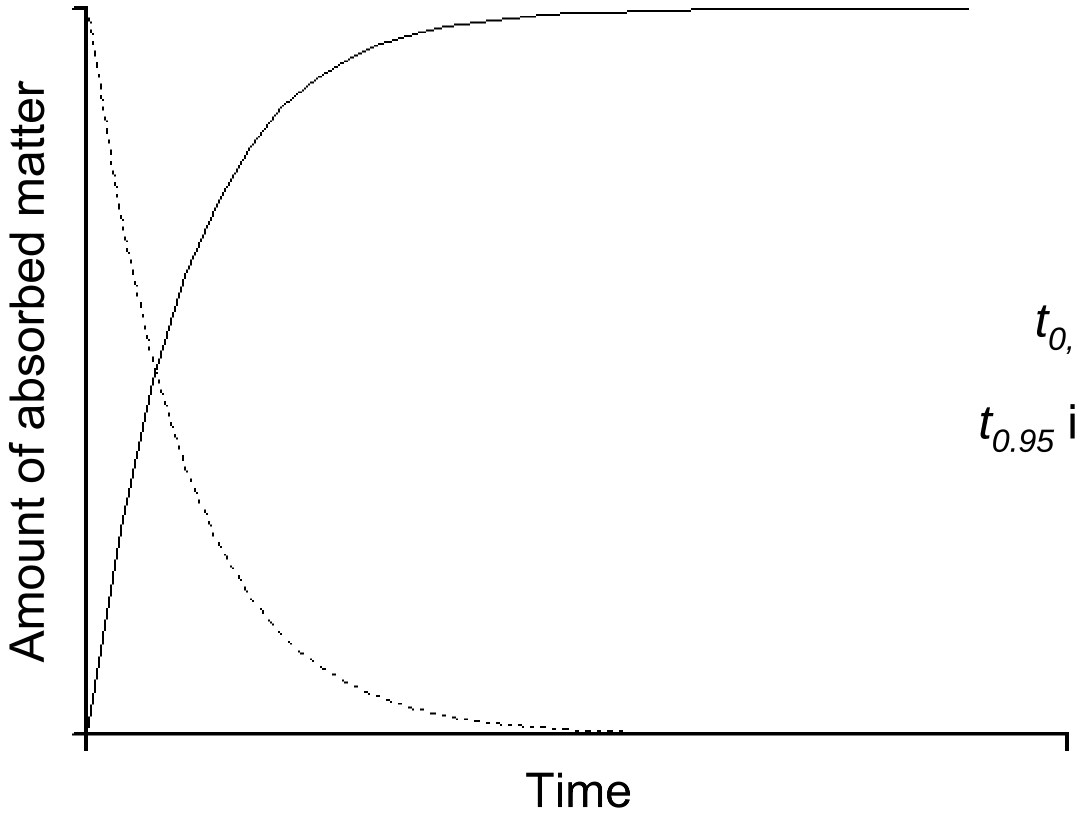
In the diffusion zone (or diffusion layer) (with thickness δ), pure diffusion of matter occurs according to Fick's law : $\vec{J} = -D\,\overrightarrow{grad}C$

Simplified empirical model similar to first order kinetics model :

$$\frac{dA}{dt} = -k.A \Rightarrow A_{abs}(t) = A_0\left(1 - e^{-\frac{t}{\tau}}\right)$$

A. Prietoa, O. Basauria, R. Rodilb, A. Usobiagaa, L.A. Fernándeza, N. Etxebarriaa, O. Zuloagaa, Stir-bar sorptive extraction: A view on method optimisation, novel applications, limitations and potential solutions, Journal of Chromatography A, 1217, 2642-66, (2010)

D2EHPA extraction modelling : kinetics aspects



$$A_{abs}(t) = A_0\left(1 - e^{-\frac{t}{\tau}}\right)$$

$t_{0,95} = -\tau \times \ln(0.05) = 2.99 \times \tau$

$t_{0.95}$ is a pseudo-equilibrium time

Operating parameters with an impact on the equilibrium time

- **Temperature** (Viscosity, Brownian movement of molecules)
- **Sample volume** (Amount of matter to absorb, transfer kinetics of matter toward the sample-twister interface)
- **Rotation speed of the twister** (Sample mixing and diffusion layer thickness)
- **Sample vial** (Sample mixing efficiency)

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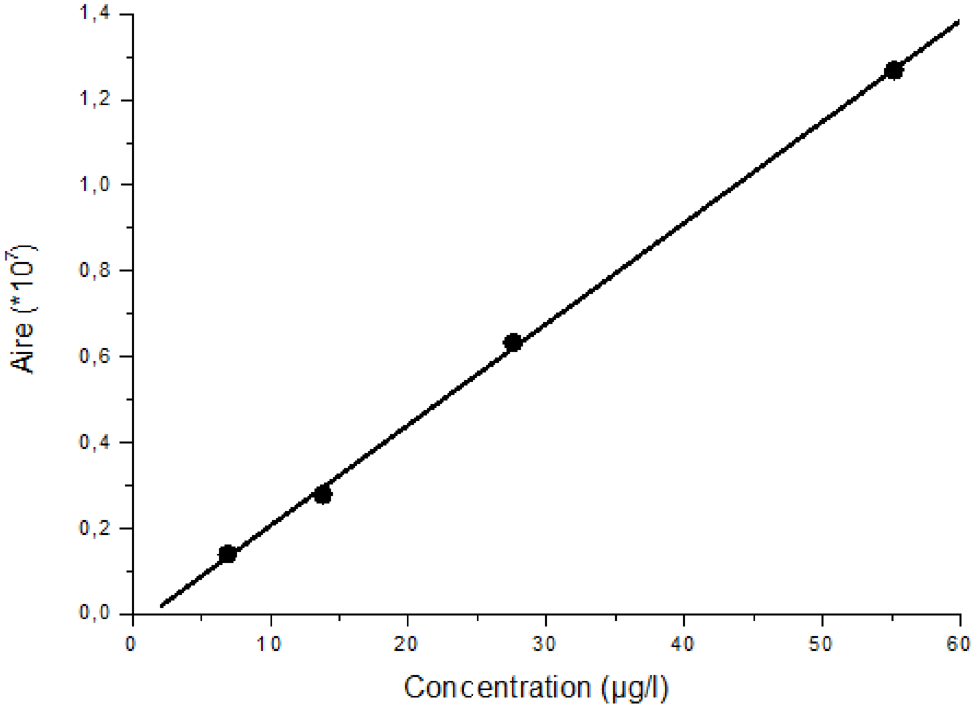
Experimental validation of the model

A LC-MS method to quantify D2EHPA in aqueous solutions

Chromatography (elution) conditions:

Mobile phase : Methanol / ammonium acetate 50 mM (70/30 – v/v); Flow rate: 1ml/min^{-1}
Column : Poursuit ® C18 (250x4,6 mm – d_p:5µm)
Retention time for D2EHPA : 34 min.

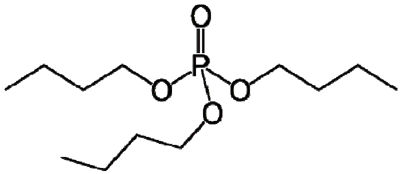
MS detection by APCI
(atmospheric pressium chemical ionisation) :
Ionization mode : negative mode
D2EHPA detected at : *m/z* = 321u.

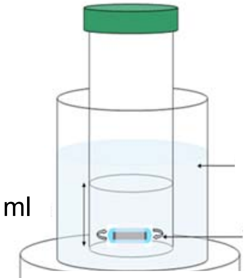


Limit of detection   : 3,0 µg/l
Limit of quantitation : 7,0 µg/l

D2EHPA extraction modelling : experimental kinetics aspects

Tributylphosphate (TBP)





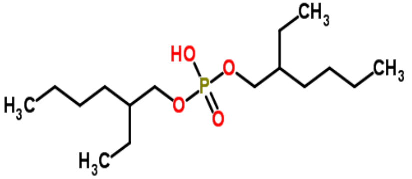
Sample volume : 2 ml

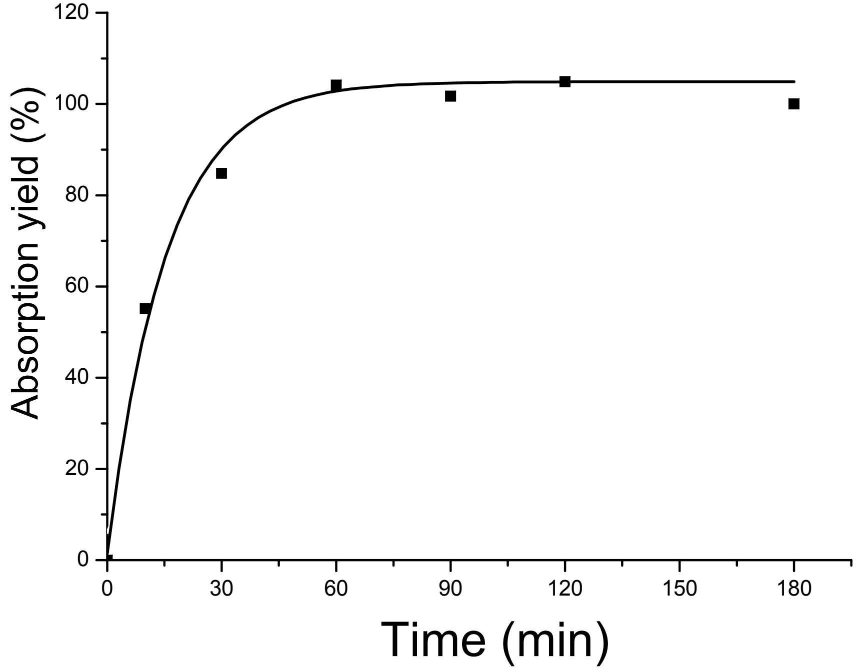
Bath temperature : 25°C

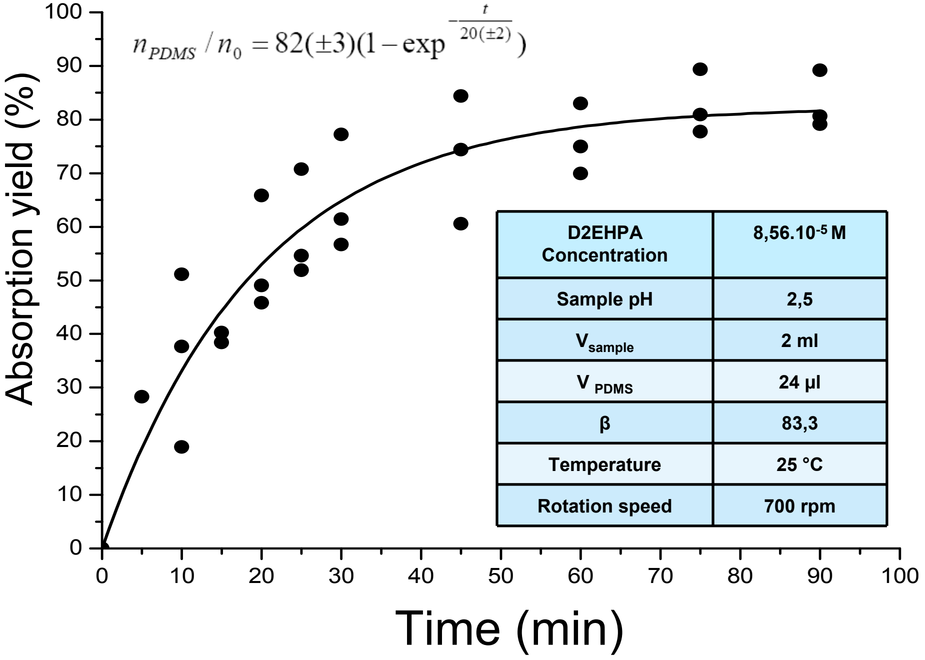
Rotation speed of the twister : 700 rpm

Magnetic stirrer

D2EHPA







$$n_{PDMS}/n_0 = 82(\pm3)(1-\exp^{-\frac{t}{20(\pm2)}})$$

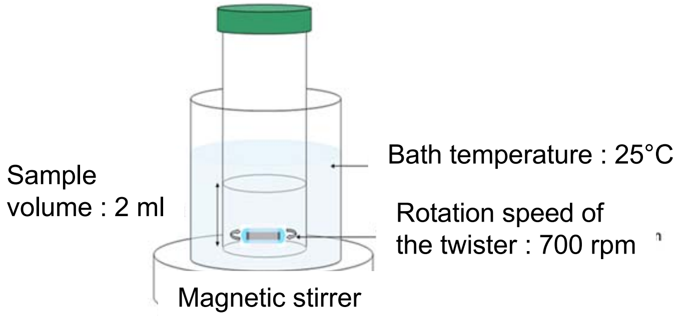
D2EHPA Concentration	$8{,}56.10^{-5}$ M
Sample pH	2,5
V_{sample}	2 ml
V_{PDMS}	24 µl
β	83,3
Temperature	25 °C
Rotation speed	700 rpm

Pseudo-equilibrium time ($t_{0.95}$) estimate : 60 (±6) min

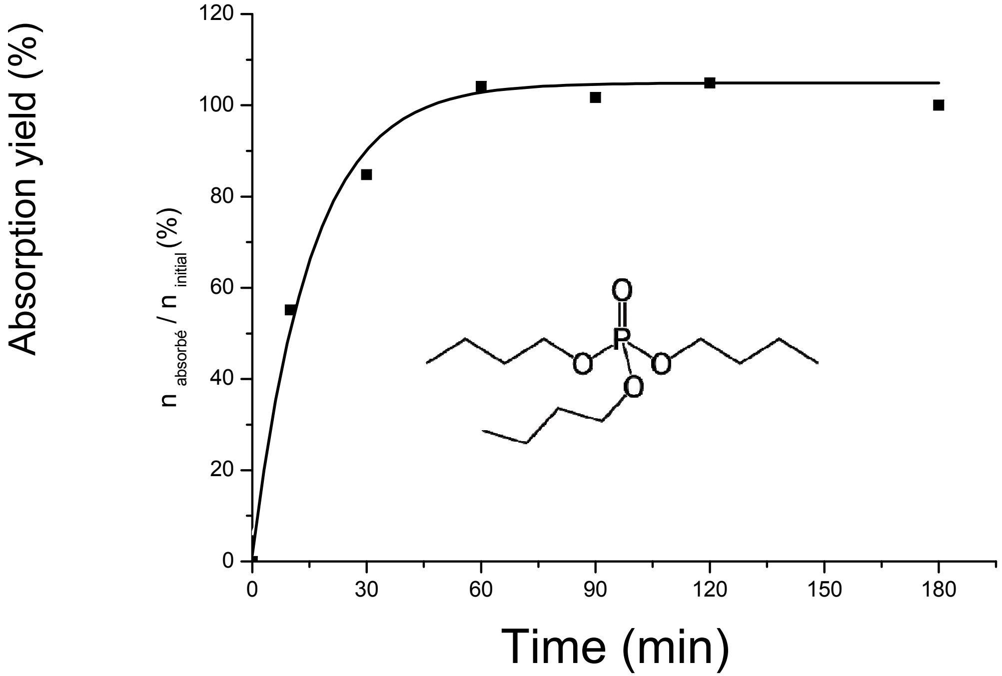
Use of an effective time of 70 min to carry out further model validation experiments

D2EHPA extraction modelling : experimental kinetics aspects

Influence of operating conditions evaluated with ***TBP*** *due to faster analytical procedures if compared with those for D2EHPA*



Temperature (°C)	$t_{0.95}$ (min)
5	83
25	32
50	15

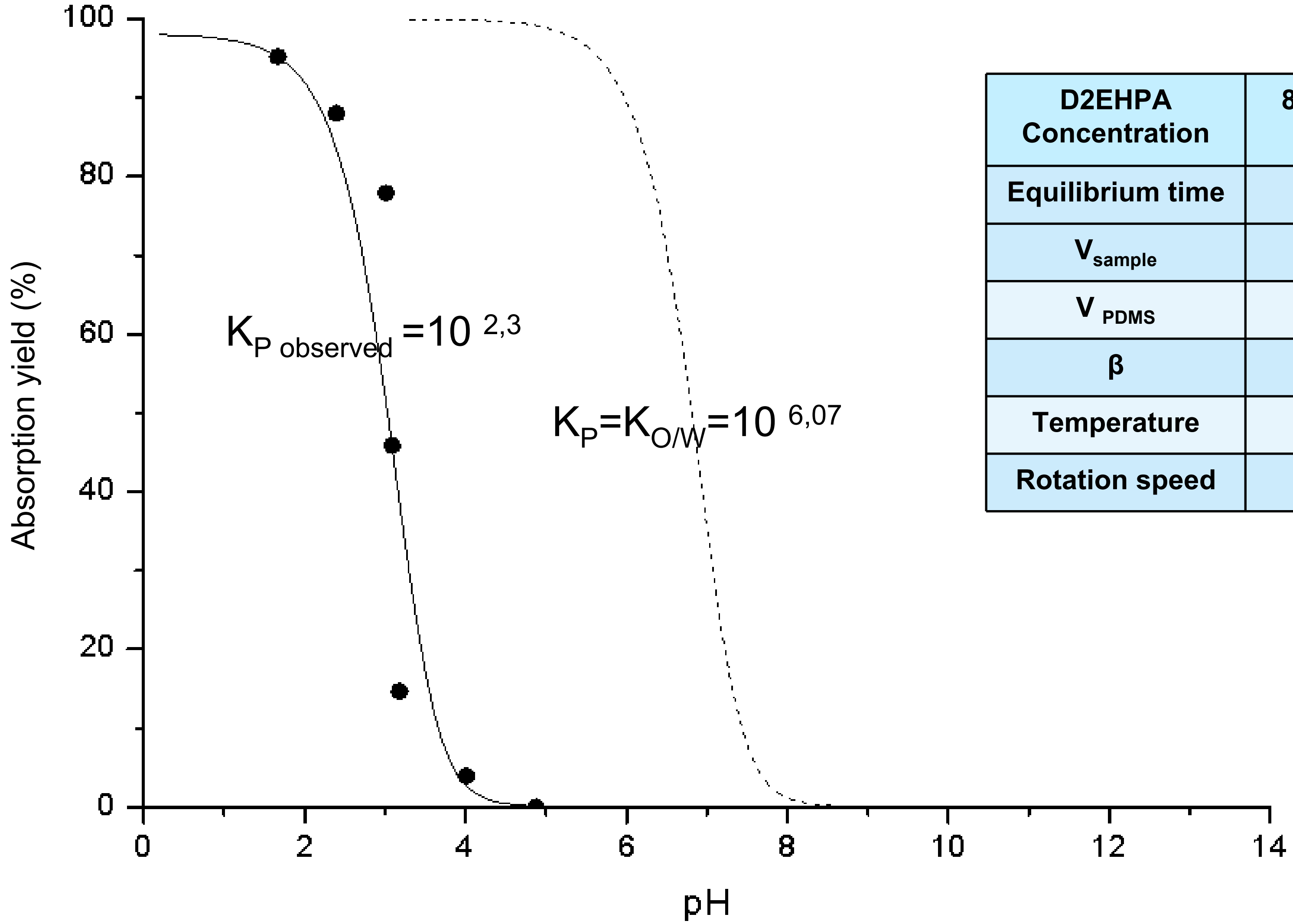


Sample composition	$t_{0.95}$ (min)	Equilibrium time ratio
Water	42	1
Buffered water	46	

Sample volume (ml)	$t_{0.95}$ (min)	Equilibrium time ratio
2	42	2
10	94	

Rotation speed of (rpm)	$t_{0.95}$ (min)	Equilibrium time ratio
700	42	2
70	86	

D2EHPA extraction modelling versus experimental data



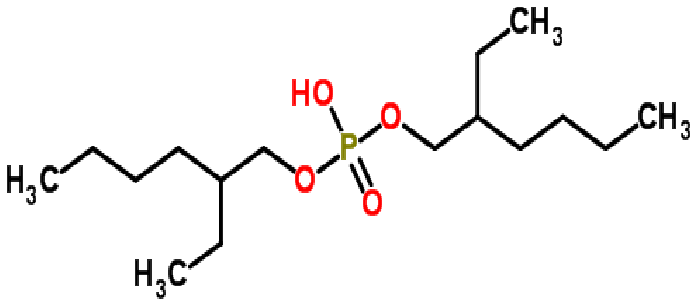
D2EHPA Concentration	**8,56.10^{-5} M**
Equilibrium time	**70 min**
V_{sample}	**2 ml**
V_{PDMS}	**24 µl**
β	**83,3**
Temperature	**25 °C**
Rotation speed	**700 rpm**

Why $K_{o/w}$ cannot be used in our model ?

Publication by Paul Ruelle :

P. Ruelle, The n-octanol and n-hexane/water partition coefficient of environmentally relevant chemicals predicted from the mobile order and disorder (MOD) thermodynamics, Chemosphere, ***40****, 457-512, (2000)*

PDMS is not octanol ! For polar molecules (ex. R-OH or molecules with proton exchange properties), $K_{O/W}$ and $K_{Hexan/W}$ are different

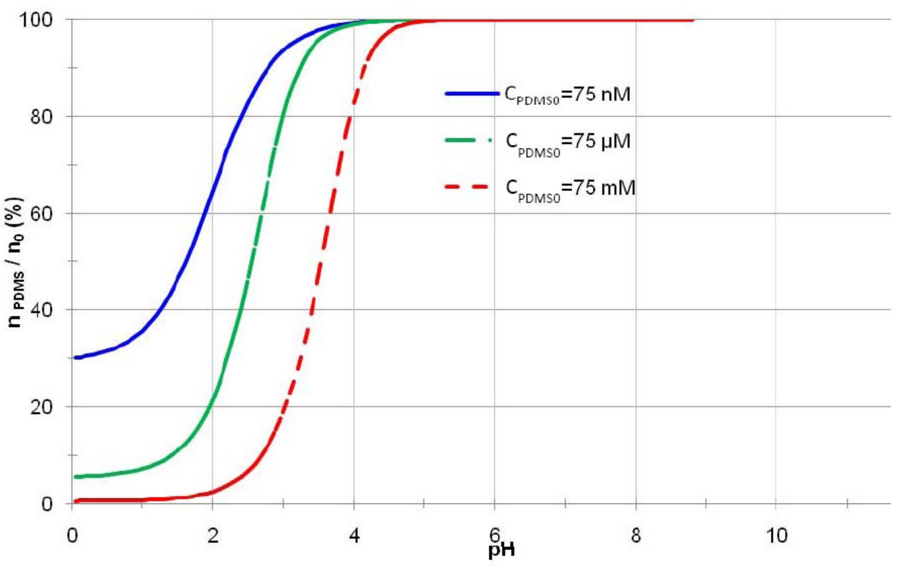


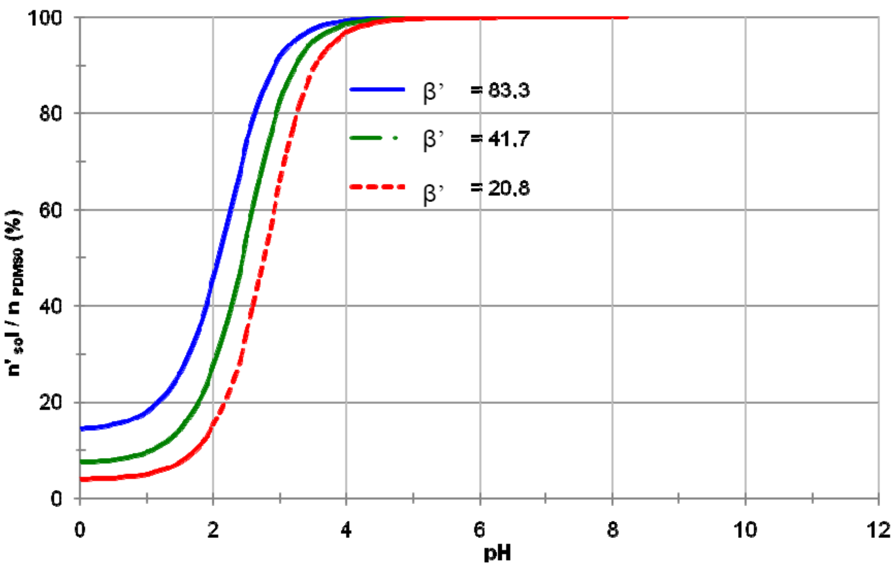
Molecule	Log $K_{H/W}$	Log $K_{O/W}$
4-ethylphenol	0.39	2.58
Heptanol	1.00	2.64
4,4'-Cl_2-bisphenol F	0.15	4.00

But the $K_{H/W}$ value for D2EHPA is not available, at the moment !

D2EHPA back-extraction modelling

$$\frac{n'_{sol}}{n_{PDMS_0}} = \beta' \frac{\left(1+\frac{10^{pH-pKa}}{\gamma_{A^-}}\right) \times \left[-\beta'\left(1+\frac{10^{pH-pKa}}{\gamma_{A^-}}\right) - K_P + \sqrt{\left(\beta'\left(1+\frac{10^{pH-pKa}}{\gamma_{A^-}}\right)+K_P\right)^2 + 8K_{Di}K_P^2C_{PDMS0}} \right]}{4C_{PDMS0}K_{Di}K_P^2}$$





D2EHPA back-extraction yield : 50 to 80% after 4 to 5 replicate leaching.
The method probably suffers a kinetics-limited reverse process.
Hypothesis : is it due to slow diffusion of D2EHPA in PDMS ?

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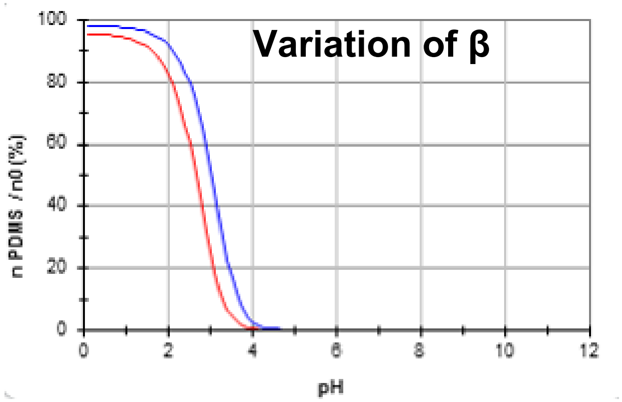
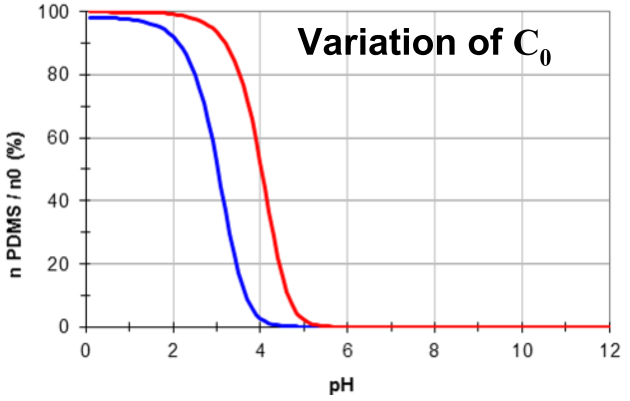
Conclusions

Conclusions

Modelling of D2EHPA extraction by PDMS (twister) achieved, from solution chemistry and liquid-liquid extraction basic concepts,

But the impact of other operating parameters must be evaluated,





Application of such model to other similar molecules should be possible (to be continued),

But data for molecules in PDMS (as a solvent) are lacking ($K_{PDMS/W} \neq K_{O/W}$),

And the back-extraction seems to be limited (kinetics limitation ? hypothesis to confirm).

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Thank you for your attention