Extraction and back-extraction of Cesium Picrates with the 1,3 bis-benzo-crown 6-Calix[4]arene using membrane contactor

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Introduction

Recovery, separation of metal ions by solvent extraction

Recent advances to improve the extraction performances

- ***New macrocyclic extractants***
- ***Non dispersive solvent extraction (HFNDSX)***

Feasibility of the cesium picrate recovery with a calixarene using two membrane contactors

Outline

1 – Background

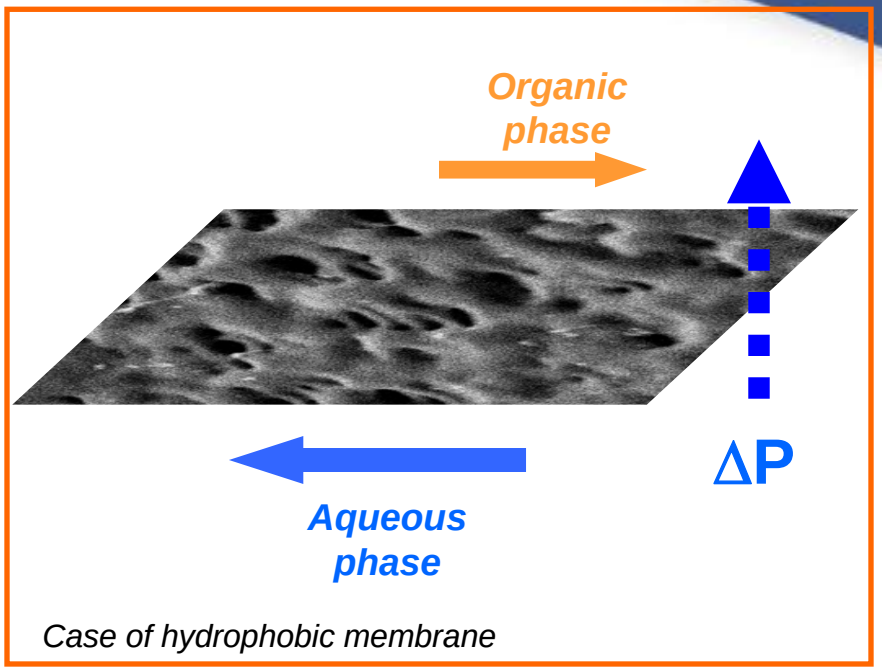
- *Non dispersive solvent extraction*
- *Membrane contactor*
- *Macrocycles*
- *Membrane contactor and macrocycles association*
- *Equilibrium and mass transfer*

2 - Material and methods

3 – Results and discussion

Non Dispersive Solvent Extraction

- Non supported liquid membrane
- Both phases flow continuously
- Interface immobilized in the pores
- Hydrophobic or hydrophilic

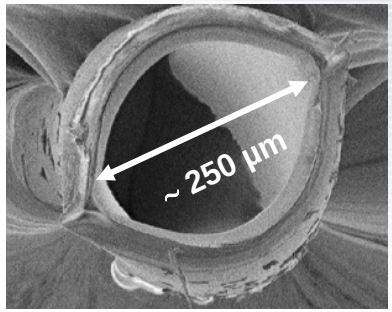


Case of hydrophobic membrane

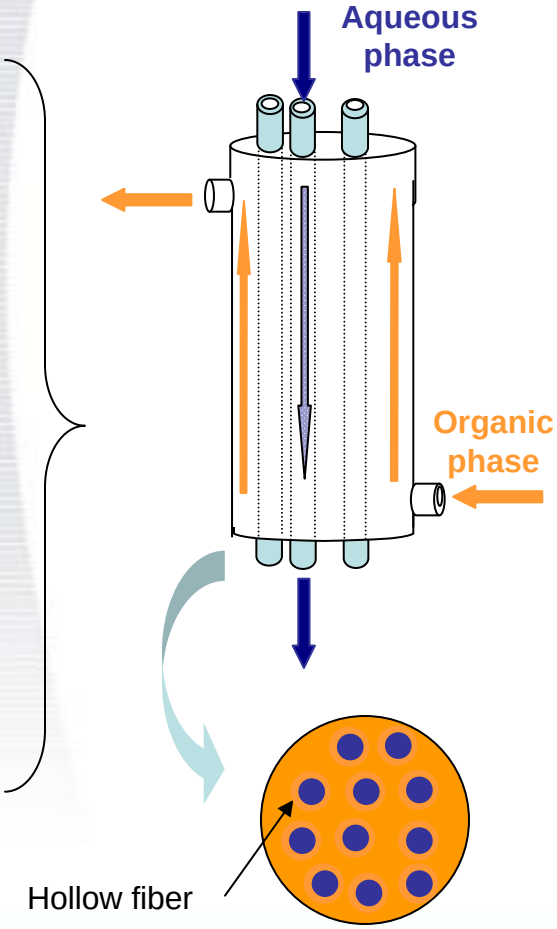
Hollow fiber contactor

Membrane contactor

Hollow fibers



Cross section of fiber

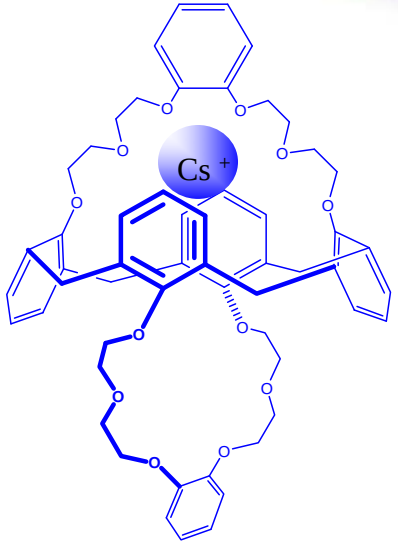


Advantages

- Area known, constant, independent / flow rates
- Area/volume is high, *1600 – 6500 $m^2.m^{-3}$* *(Packed towers : 30 – 350 $m^2.m^{-3}$)*
- Scale up is straightforward with membrane contactor
- Reduction emulsion

Macrocycles

- **Extractant**
  - **- Selective (cavity sizes)**
  - **- Ionophore (carrier)**



- **Treatment of radioactive waste**

  1,3 bis-benzo-crown-6-calix[4]arene / cesium

- **But …expensive and**

  low solubility in conventional industrial diluent !!

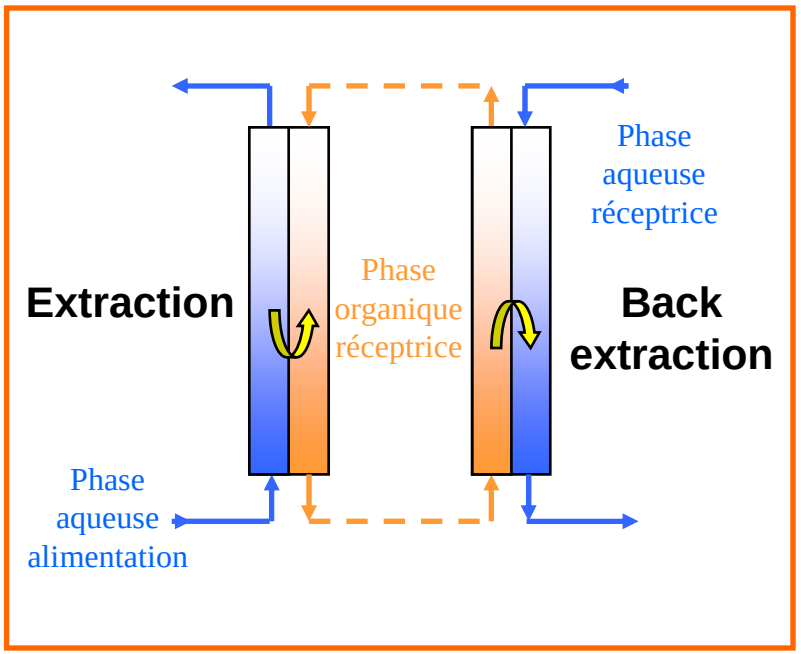
Macrocycles – membrane contactor association

➢ **Supported Liquid Membrane (SLM) containing calixarene**

But loss of extractant

➢ **Integrated membrane process with 2 hollow fiber contactors**

- **Small solvent volume**
- **No solvent loss**
- **Recovery of calixarene**



Equilibrium and Mass transfer

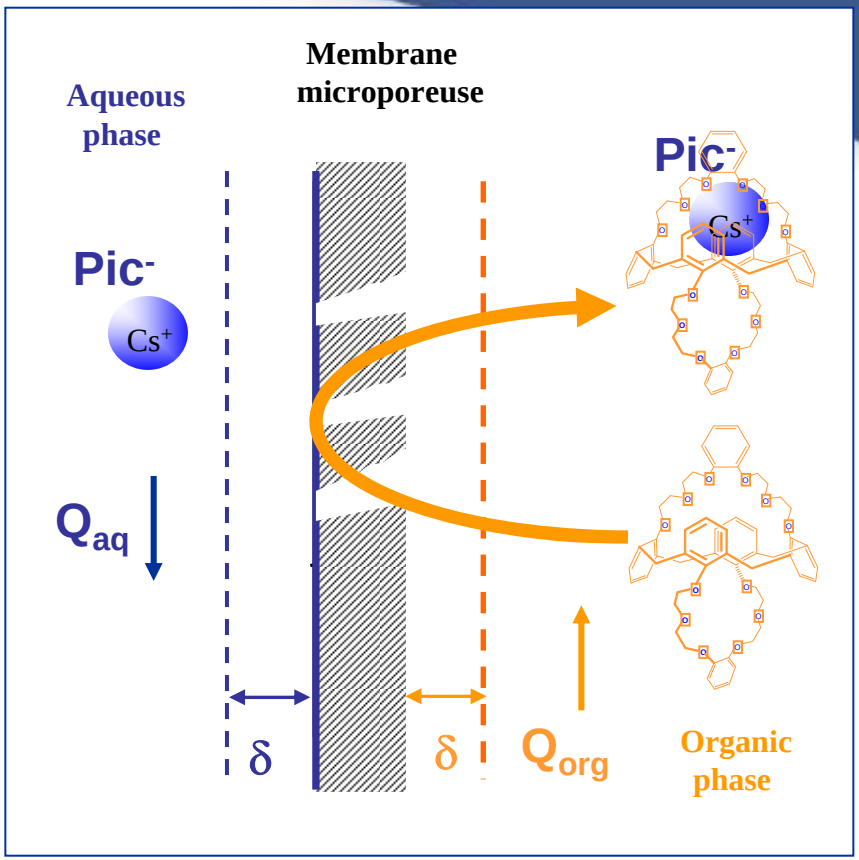
➢ Equilibrium

$$L_{org} + Pic^-_{aq} + Cs^+_{aq} \rightleftharpoons CsLPic_{org}$$

$$H = \frac{(CsLPic)^{eq}_{org}}{(CsPic)^{eq}_{aq}}$$

$$\mathbf{R = R_{aq} + R_m + R_{org}}$$

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{d_{in}}{H\,k_m\,d_{lm}} + \frac{d_{in}}{H\,k_s\,d_{out}}$$



Reaction is considered faster than diffusion

Outline

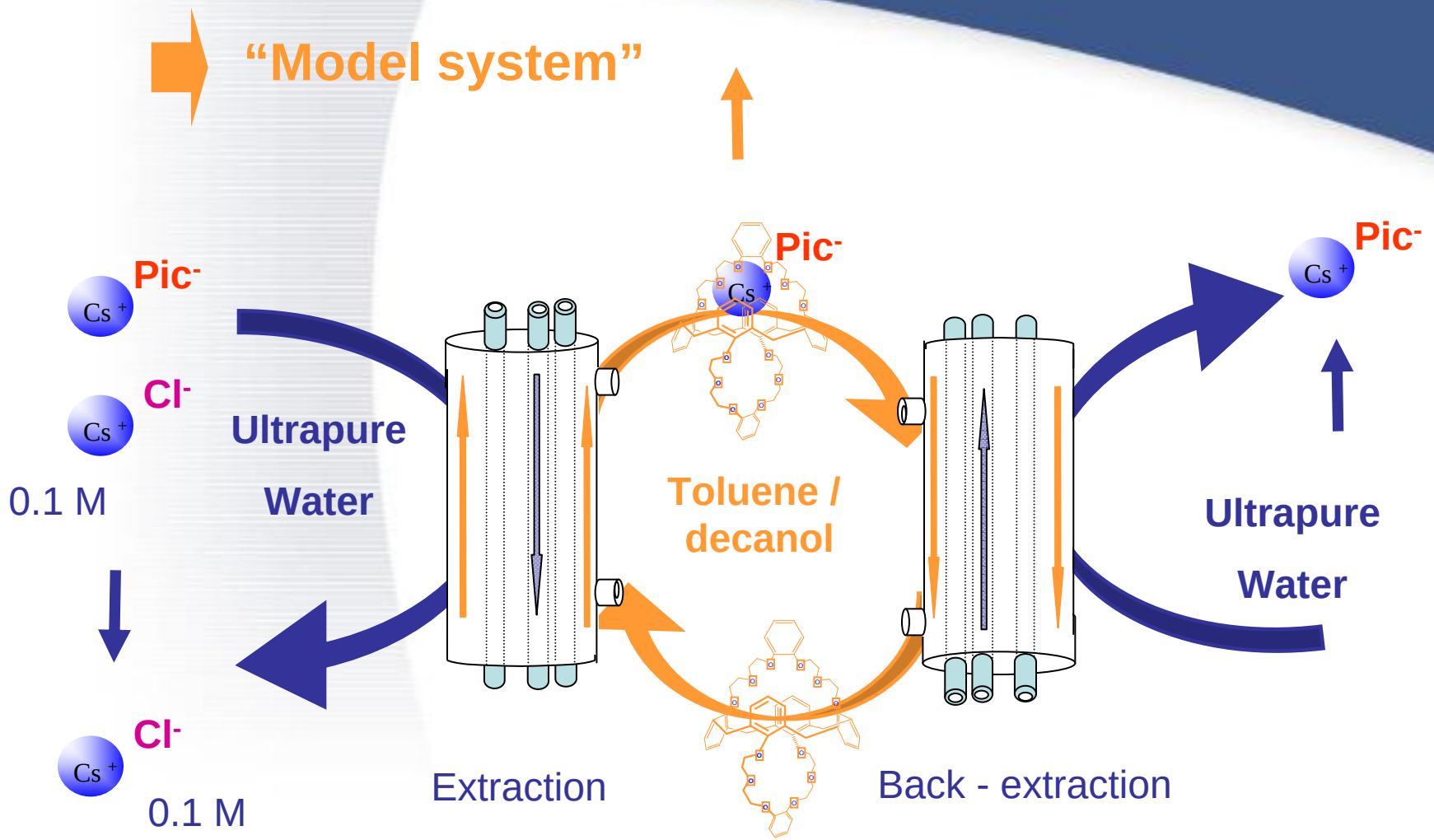
1 - Background

2 - Material and methods

- *Extraction system*
- *Characteristics of hollow fiber module*
- *Set up*

3 – Results and discussion

Extraction system

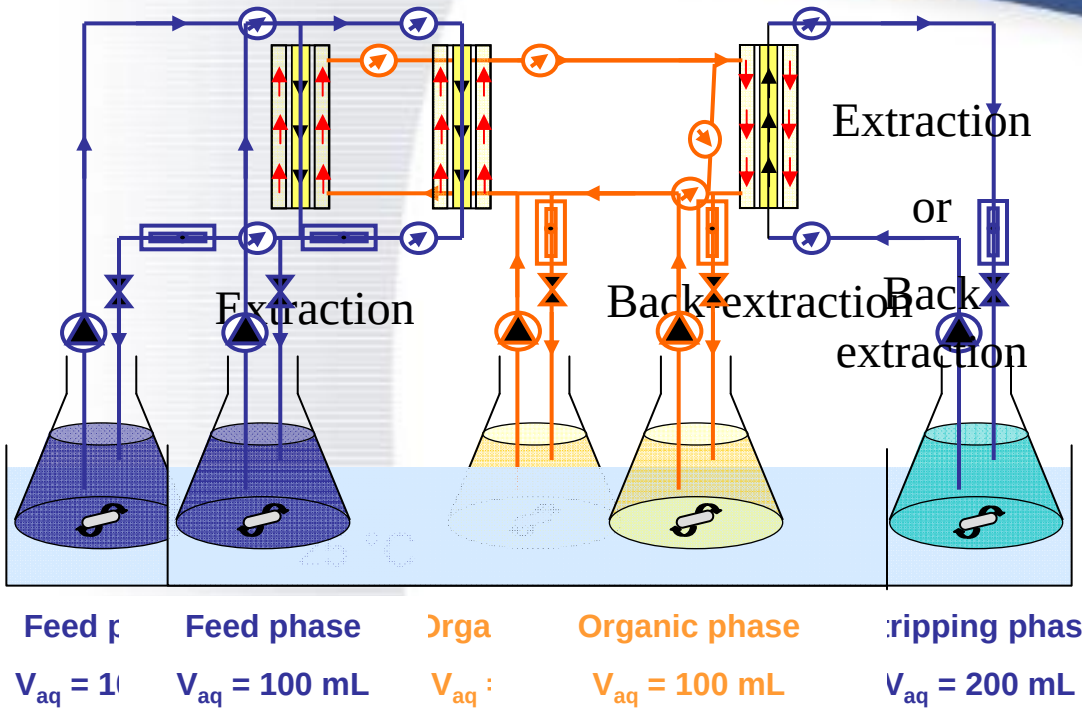


Characteristics of the hollow fibers module

Hollow fiber	
Name	Accurel PP 50/280
Material	polypropylene
Internal Diameter (D_{int})	280 µm
Thickness	50 µm
Pore size	0.05 µm
Porosity	50 – 55 %
Module	
Material	glass
Internal Diameter (D_{int})	4 mm
Length	22 cm
Number of hollow fibers	60
Exchange surface	0.426 cm^2
Total internal volume of the fibers	0.81 cm^3
Volume of the organic phase inside the module	1.27 cm^3
Specific exchange area	0.154 $cm^2.cm^{-3}$

Given by Menbrana Company

Set up



- ΔP = 0.4 bars
- Re_{aq} = 1200 *(Q_{aq}= 12 mL.min^{-1})*, Re_{org}= 1×10^{-3} *(Q_{org}= 12 mL.min^{-1})*
- UV-Visible *(Picrate)*

Outline

1 - Background

2 - Material and method

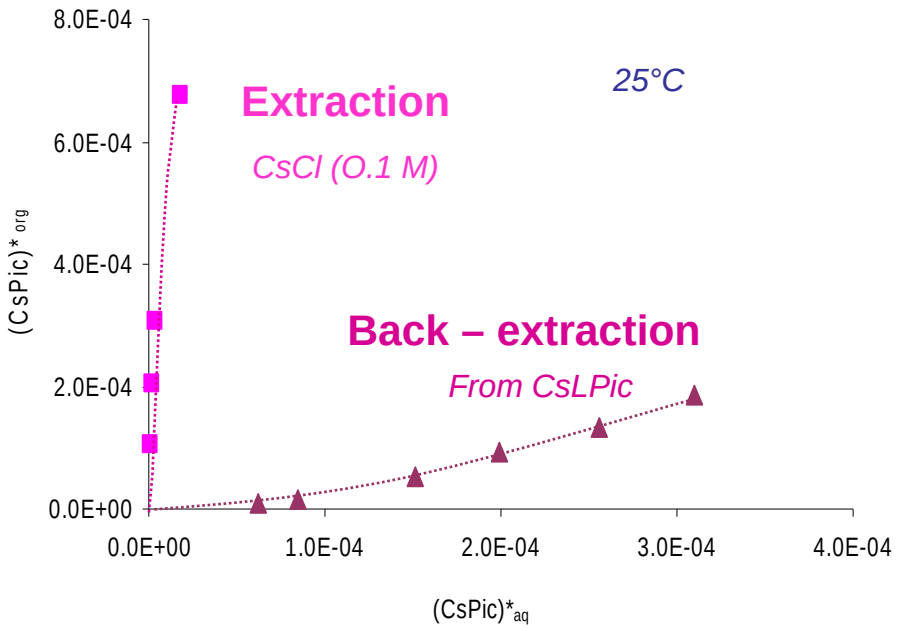
3 – Results and discussion

- ***Extraction equilibrium***
- ***Extraction with a single module***
- ***Extraction and simultaneous back-extraction***

Equilibrium isotherm

➢ **Equilibrium based separation process**

↳ **knowledge of the equilibrium isotherms**



➢ **Low solubility**

$(CsLPic)_{org} < 8.10^{-4}$ M

➢ $1.4 \times 10^{-4} < (CsPic)° < 1.0 \times 10^{-3}$

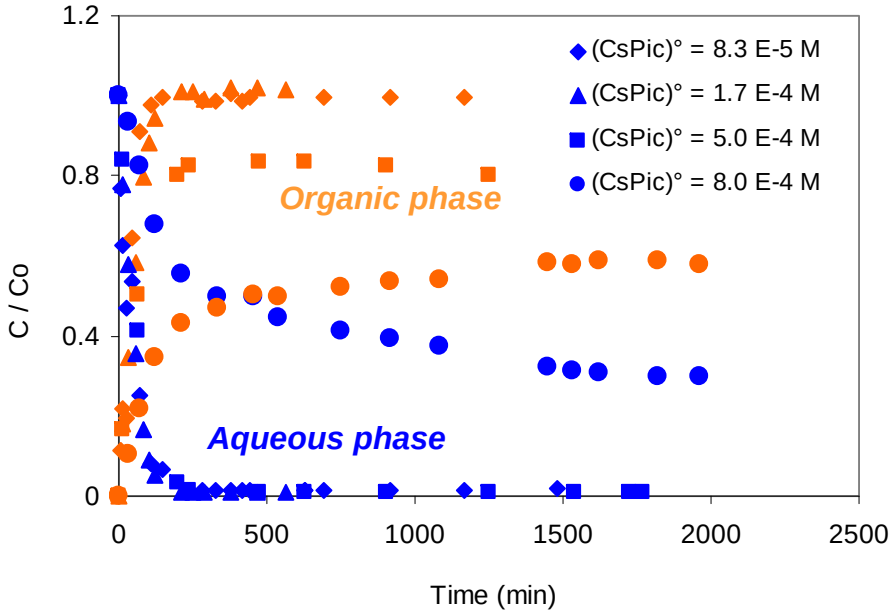
90 < H < 140 for the extraction

0 < H < 1 for the back extraction

Extraction kinetics with a single module

Extraction of CsPic with calixarene

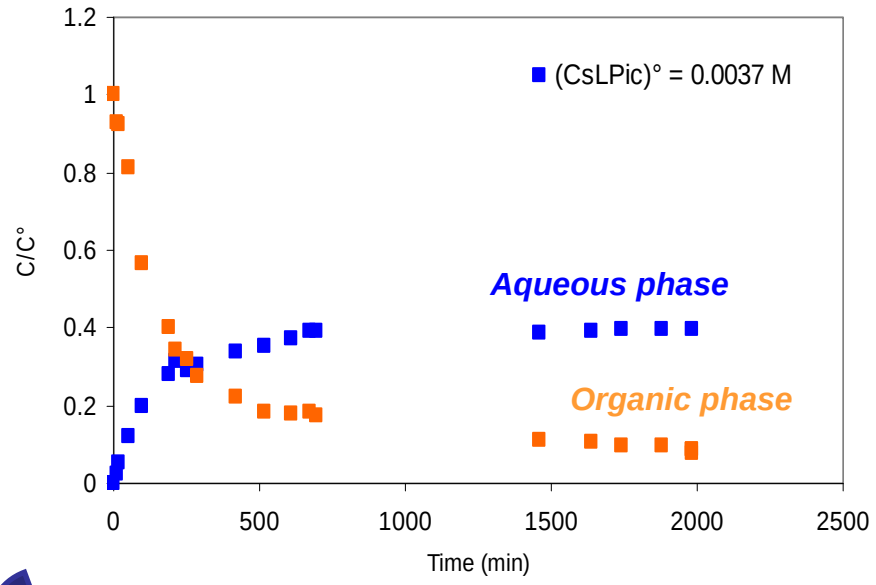
$(CsCl)_{aq}$ = 0.1 M



$$\frac{1}{K_w} = \frac{1}{k_w}$$

Back-extraction of CsPic with H_2O

From the calixarene complex (CsLPic)



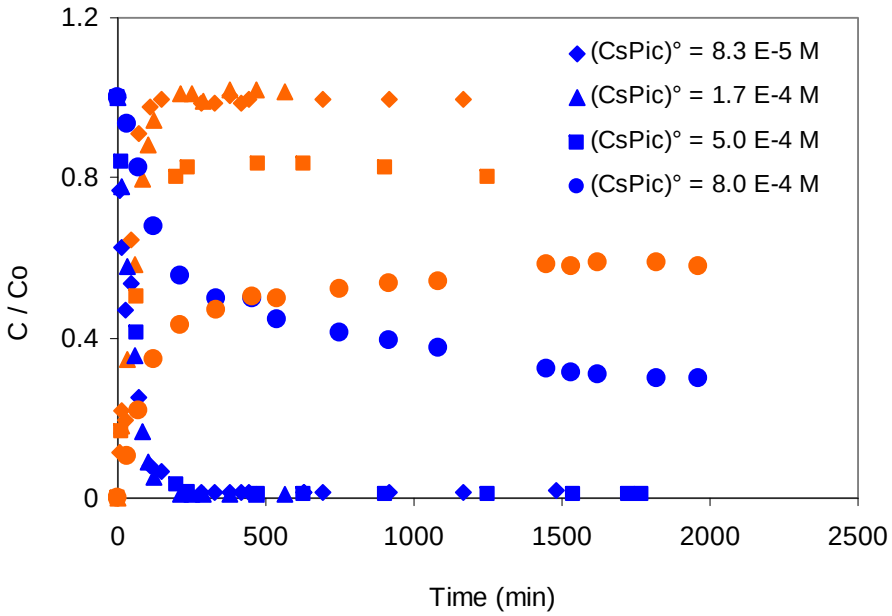
$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{d_{in}}{H\, k_m\, d_{lm}} + \frac{d_{in}}{H\, k_s\, d_{out}}$$

Effect of the concentration with a single module

Extraction of CsPic with calixarene

Mass balance for the extraction of CsPic with calixarene

$(CsCl)_{aq}$ = 0.1 M



Mass balance no checked

↳ **Mass loss**

Saturation of organic phase*

↳ **Solid third phase in pores**

Another resistance !!

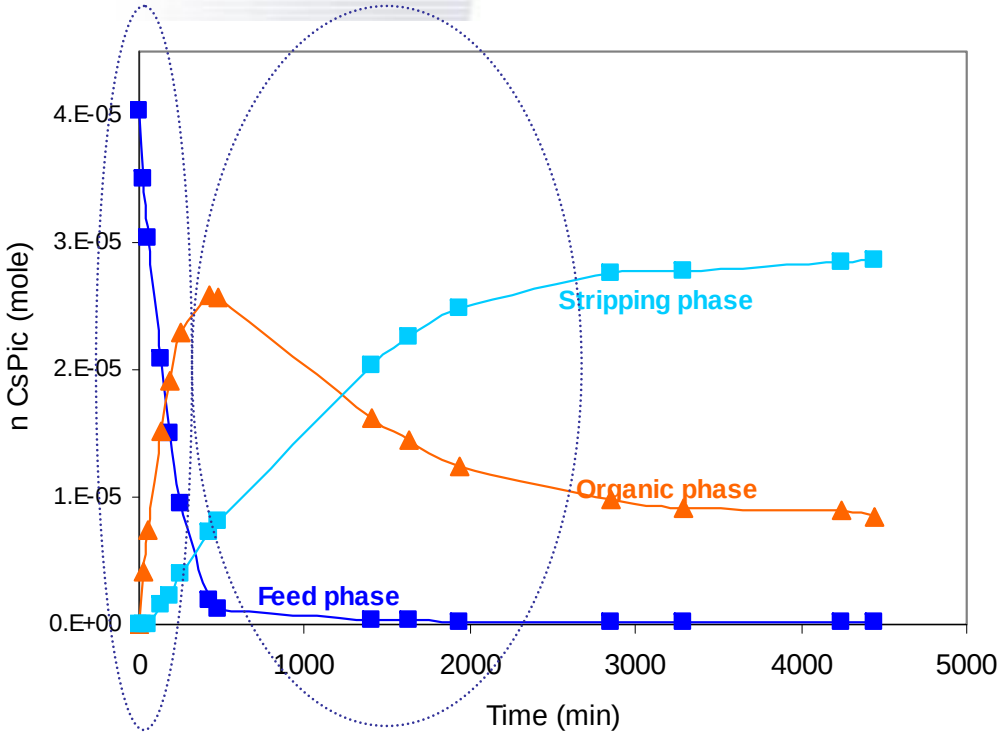
↳ **Kinetic ↘**

Extraction–simultaneous back extraction would avoid the third phase

** Equilibrium Concentrations in Membrane Contactors from Non-Linear Distribution Curves: Alkali Picrates Extraction with a Calix[4]arene. Z. Albaraka, Z. Asfari, J. M. Loureiro, M. Burgard, D. Trébouet , Sep. and Purif. Techn. in press.*

Extraction – simultaneous back extraction

$(CsPic)^{\circ} = 4.0 \times 10^{-4}$ M, $(CsCl)_{feed} = 1.0 \times 10^{-3}$ M



1st module
R minima

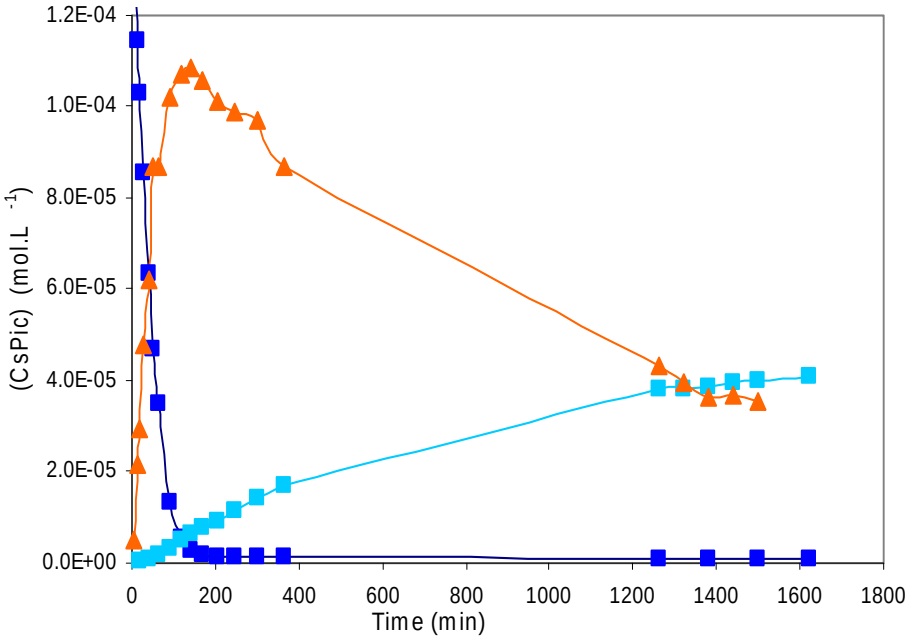
2nd module
R ↗

- "Common" kinetics
- Stable system in the time
  - No loss
  - No dispersion
- Stripping yield ~ 72 %
- Mass Balance ~ 90 %
- Slow process
  - 3 days to reach a steady state
  - 2nd module

Influence of initial concentration on kinetics

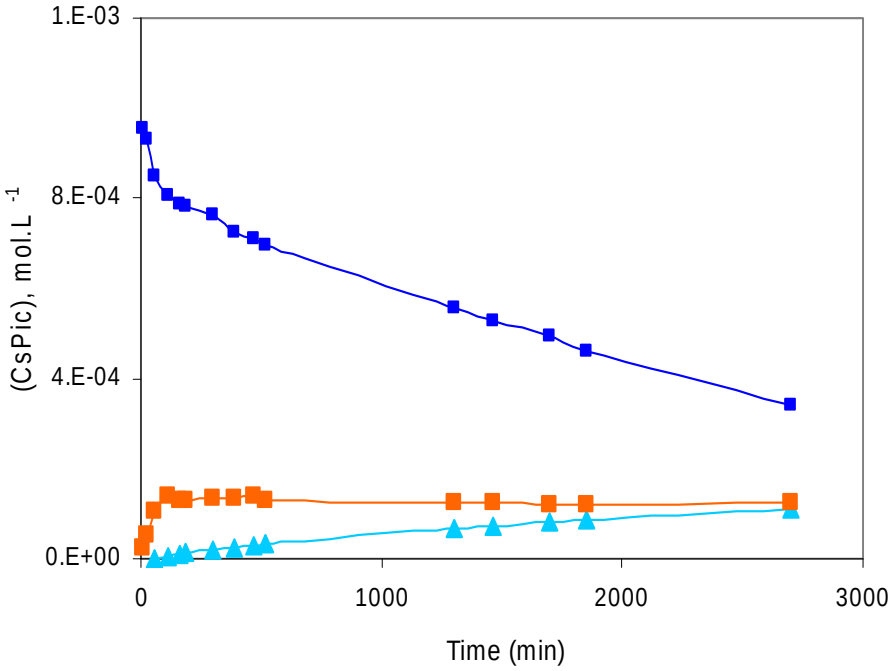
$(CsPic)°= 1.5\times10^{-4}$ M,

$(CsCl)_{feed} = 1.0 \times10^{-3}$ M



$(CsPic)°= 1.0\times10^{-3}$ M

$(CsCl)_{feed} = 1.0 \times10^{-3}$ M

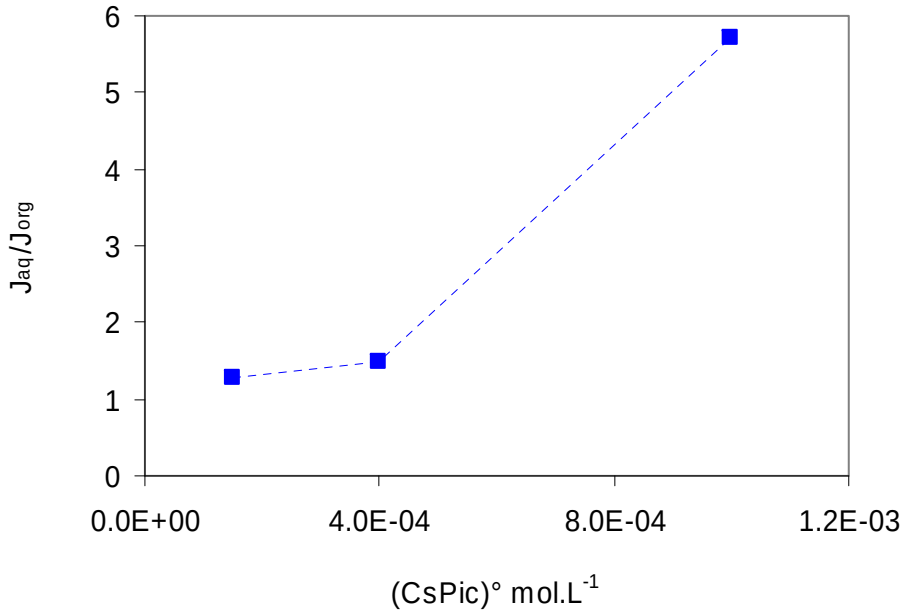


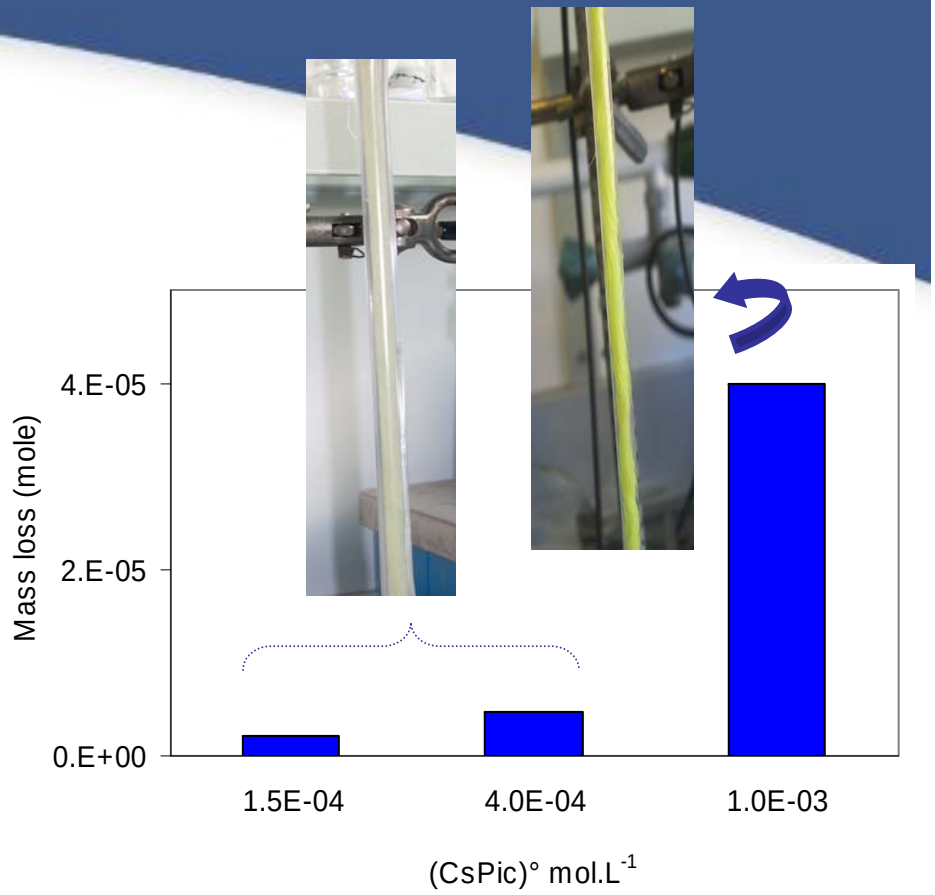
Different feed aqueous and organic phase kinetics

Mass flux and mass balance

Jaq /org versus the initial concentration

(CsCl) = 0.1 M

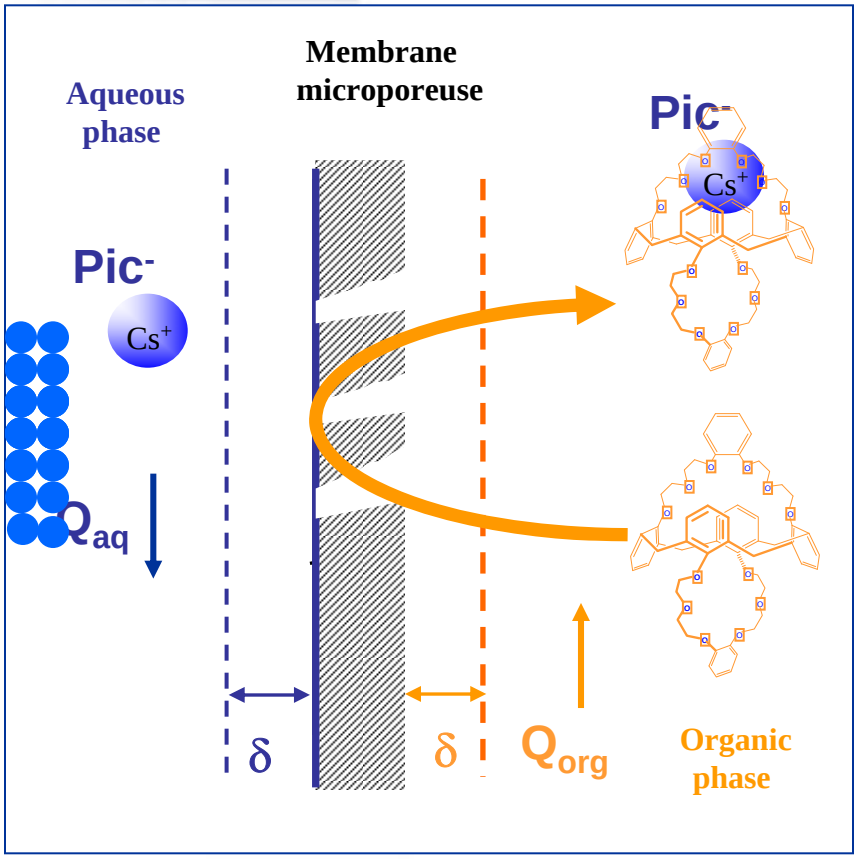




Low initial concentration : $J_{aq} \sim J_{org}$

High initial concentration : $J_{aq} > 6\ J_{org}$

Additional resistance



$$\frac{1}{K_w} = \frac{1}{k_w} + \text{Additional Resistance}$$

Conclusion

Extraction and Back-extraction with calixarene using module contactor

promising process.

Improvement of model extraction system :

H ↗ for the back extraction
Optimal calixarene (high solubility in industrial diluent)
Replace the cesium chloride
Hydrophilic membrane

Mass transfer modeling*

Albaraka Z., Trebouet D., Tuna M., Loureiro M.J., & Burgard M., Inter. J. Chem. Reactor Eng. (2008). 6. A13

Take account all the physicochemical phenomenon

Hydrometallurgy applications :

Bulk effluent (inorganic anions)

Thank for your attention

and

Thank SCI for its help !