Modelling of membrane and comparison to the experiment

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FROM RESEARCH TO INDUSTRY

Modelling of membrane and comparison in the case of pertraction experiments

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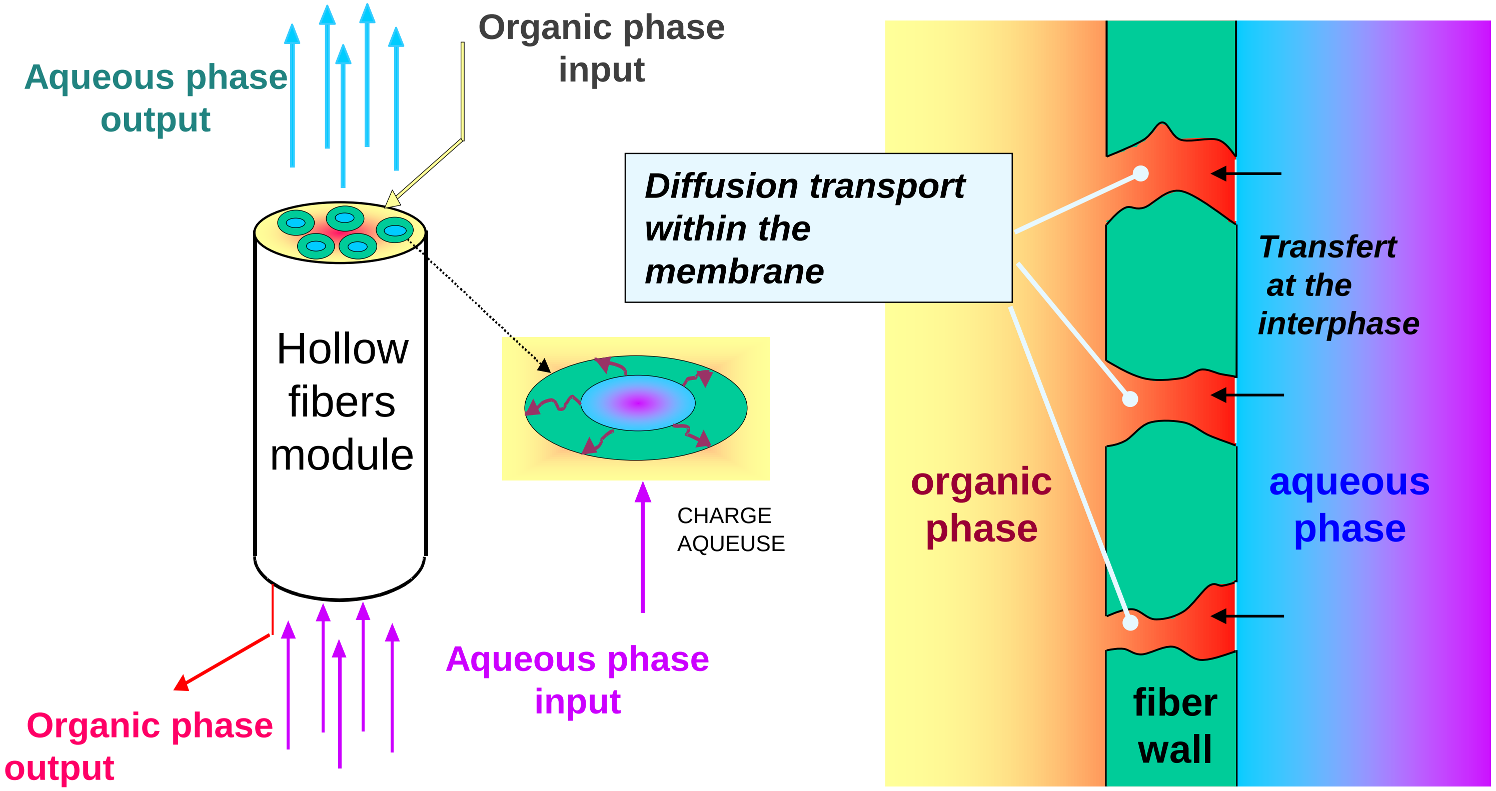
Pertraction principle

Liquid-liquid extraction across hollow fibers (membrane)

Interfacial area determined by the geometry of the device

No emulsion is generated



Liquid-liquid extraction across membrane

Advantages

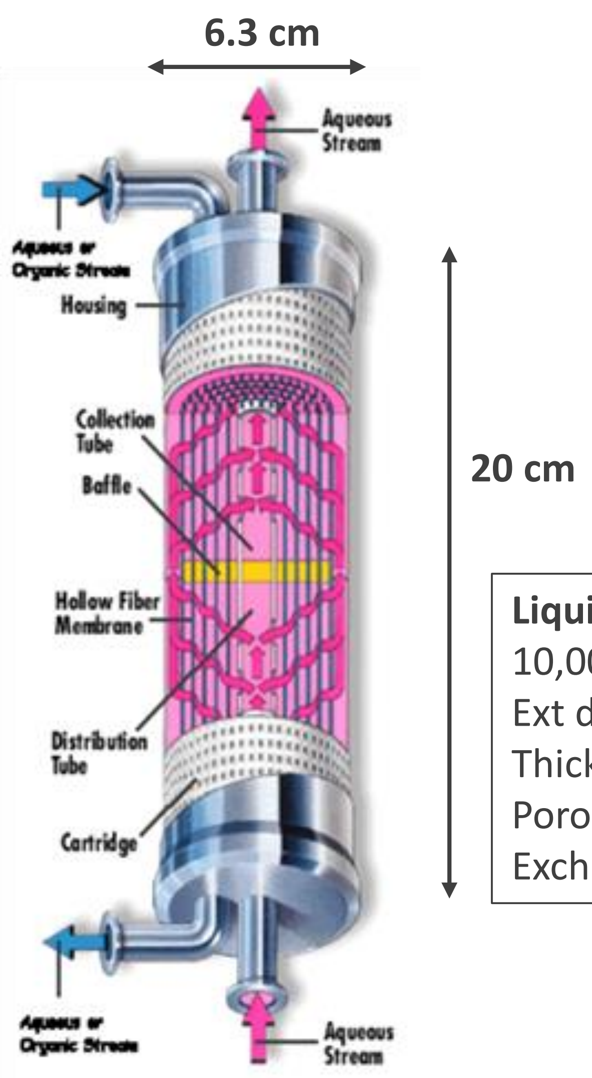
- No need for density difference between phases
- No problem of phase emulsification
- Well defined geometry: easy scale-up
- Co or counter-current configuration

Drawbacks

- Generally lower mass transfer flux compared to classical extraction devices (mixers-settlers, agitated columns, centrifuge extractors)
- Pressure in each phase must be well control to avoid phase entrainments

$$\Delta P < \frac{2\gamma cos\theta}{r}$$

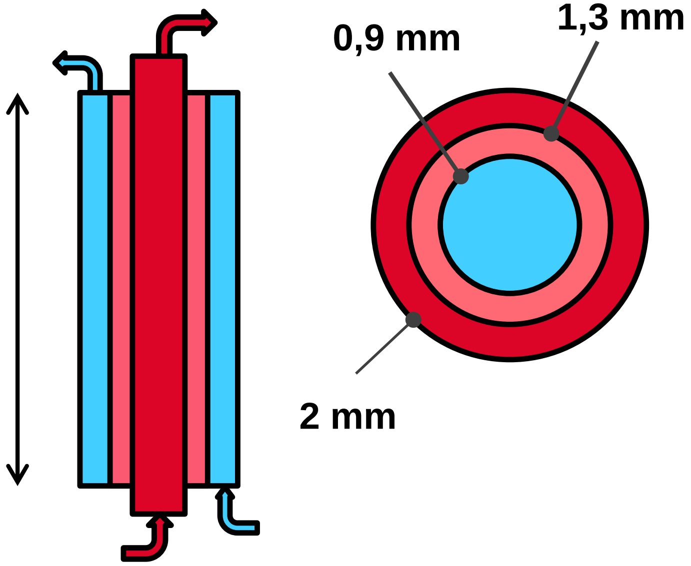
- Risk of clogging



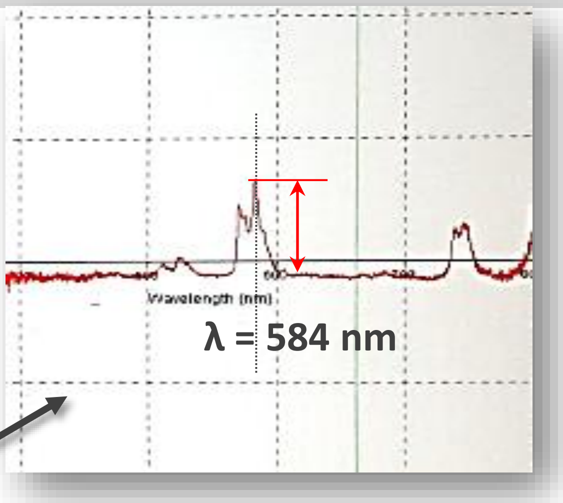
Liqui-Cel® contactor
10,000 fibers
Ext diam 0.3 mm
Thickness 30 µm
Porosity 30%
Exchange area 0,56 m²

Pertraction experimental setup

Extraction of Nd in co-current closed loop on solvent with HDEHP 0.5M



Online measurement of neodymium concentration in the output organic phase by spectrophotometry at λ = 584 nm



Characteristics of the membrane:

Material: Polypropylene

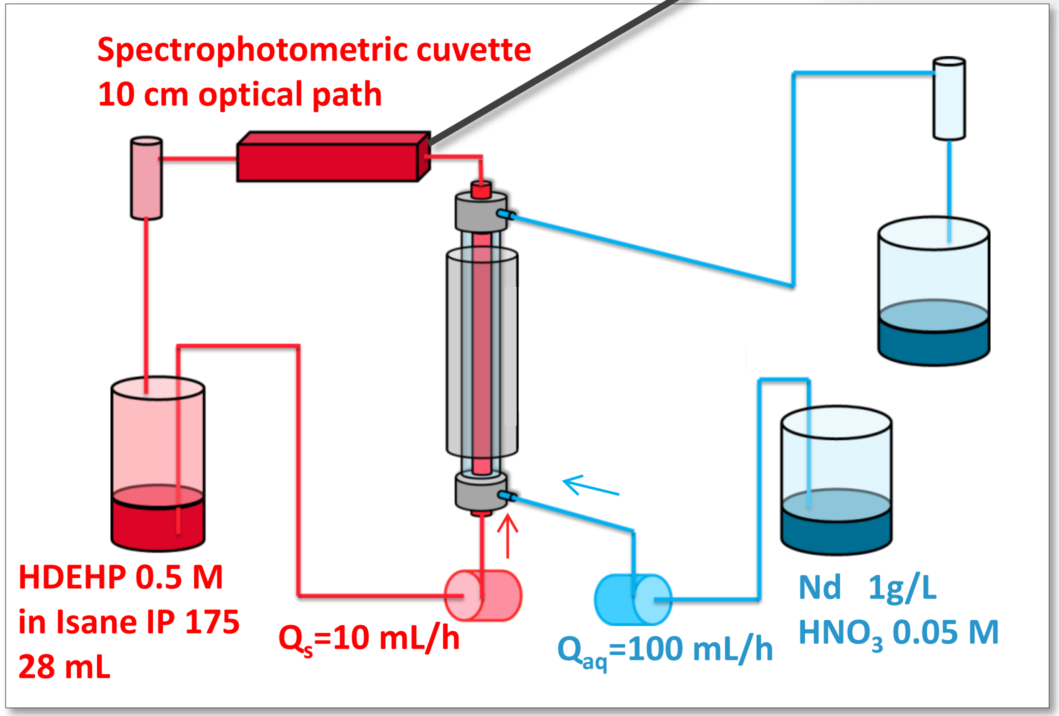
Pores size: 200 µm

Porosity: 72%

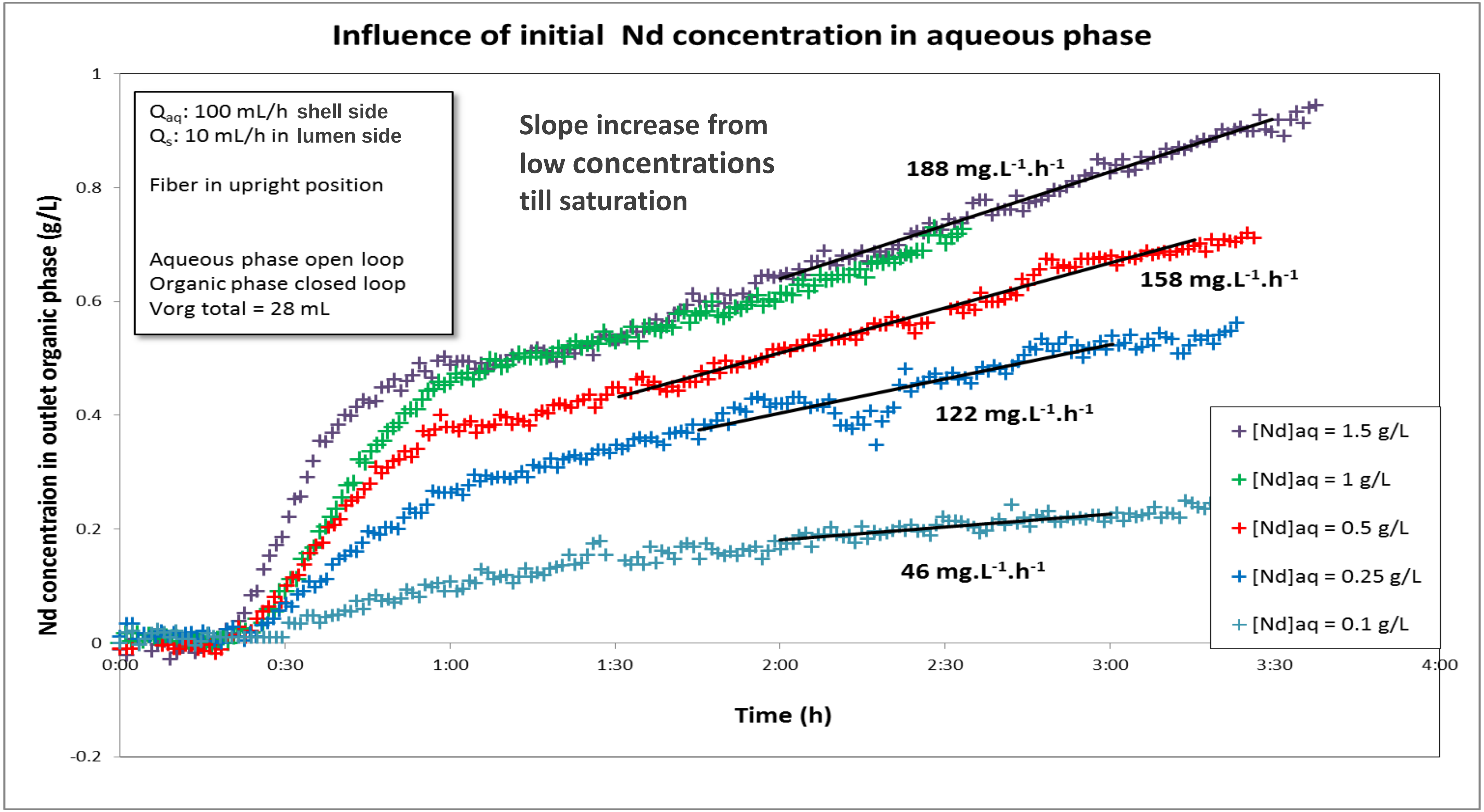
Tortuosity: ~ 2

Thickness: 400 µm

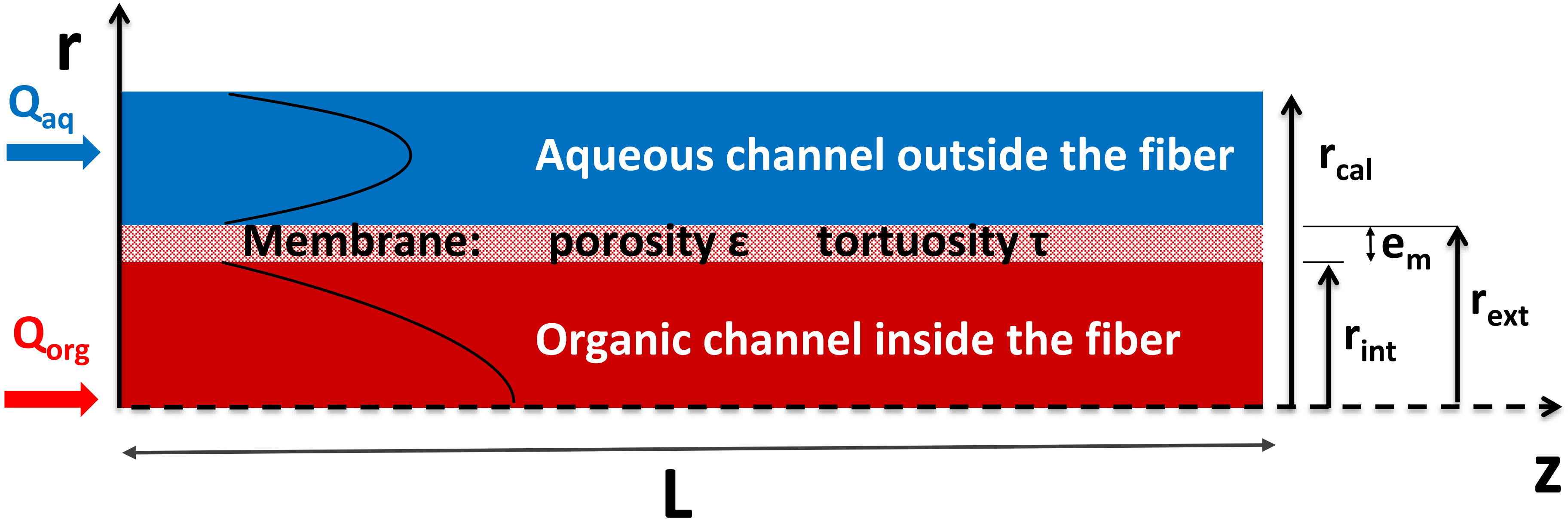
Manufacturer: Microdyn-Nadir



Evolution of Nd concentration in the outlet solvent



Modelling of extraction through a cylindrical hollow fiber (1/2)



Laminar flow (Re<1) → axisymmetric Hagen-Poiseuille flow

$$u(r) = \frac{2Q_{org}}{\pi r_{int}^2}\left(1 - \left(\frac{r}{r_{int}}\right)^2\right)$$ inside the fiber

$$u(r) = \frac{2Q_{aq}}{\pi}\frac{(r_{cal}^2 - r^2) + (r_{cal}^2 - r_{ext}^2)\dfrac{Ln\left(\frac{r}{r_{cal}}\right)}{Ln\left(\frac{r_{cal}}{r_{ext}}\right)}}{\left((r_{cal}^4 - r_{ext}^4) - \dfrac{(r_{cal}^2 - r_{ext}^2)^2}{Ln\left(\frac{r_{cal}}{r_{ext}}\right)}\right)}$$ outside the fiber

Modelling of extraction through a cylindrical hollow fiber (2/2)

- General transport equation of a solute in each phase

$$\frac{\partial C(r,z,t)}{\partial t} = -u(r,z)\frac{\partial C(r,z,t)}{\partial z} + D\left(\frac{\partial}{\partial z}\left(\frac{\partial C(r,z,t)}{\partial z}\right) + \frac{\partial}{\partial r}\left(\frac{\partial C(r,z,t)}{\partial r}\right) + \frac{1}{r}\frac{\partial C(r,z,t)}{\partial r}\right)$$

negligible

$D = D_{aq}$ in the aqueous channel

$D = D_{org}$ in the organic channel

$D = D_{mem} = \frac{D_{org}\,\varepsilon}{\tau}$ in the hydrophobic membrane (i.e. filled with organic phase)

- Kinetics of transfer at the interphase between the aqueous phase and the organic phase

$$\emptyset = \varepsilon k_v\left(C_{aq,i} - \frac{C_{org,i}}{K_d}\right)$$ mass transfer flux at the interphase

- Constant or variable distribution coefficient $K_d = \frac{C_{org,eq}}{C_{aq,eq}}$

- Discretization of equations with finite differences scheme and resolution of the matrix system with a time implicit scheme using Scilab software

- Transient calculation performed until equilibrium is reached

Resistance to mass transfer

Calculation of the mass transfer coefficients from concentration profiles

Determination of the influence of the different terms in the resistance to mass transfer

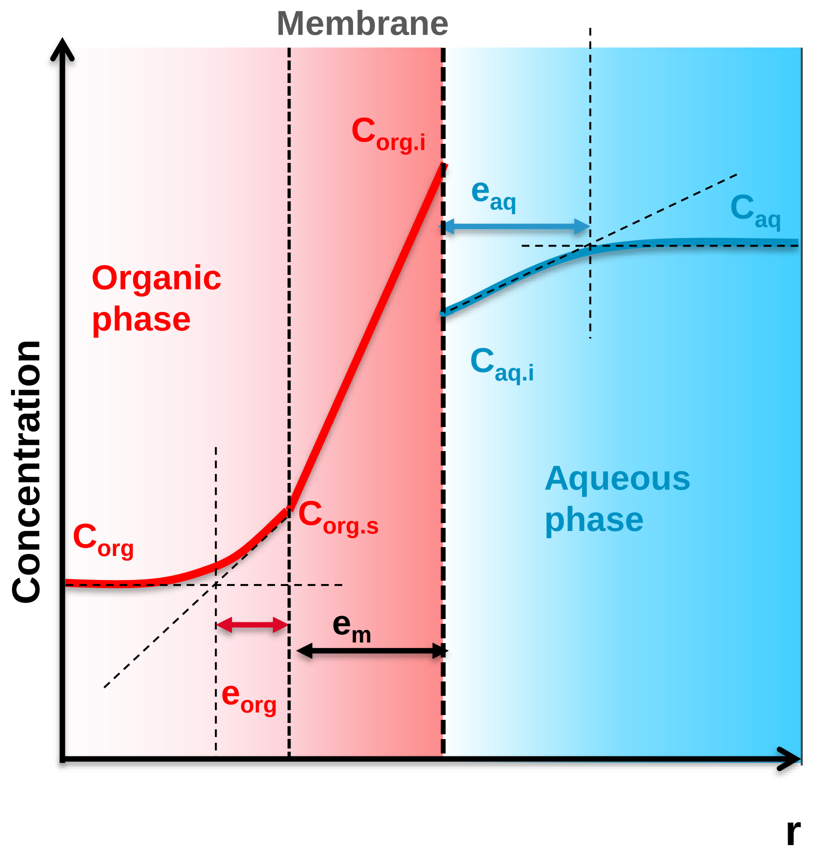
$$\emptyset = K_{aq}\left(C_{aq} - \frac{C_{org}}{K_d}\right) = k_{aq}\left(C_{aq} - C_{aq,i}\right) = D_{aq}\left(\frac{\partial C_{aq}}{\partial r}\right)_i$$

$$\emptyset = K_{org}\left(K_d C_{aq} - C_{org}\right) = k_{org}\left(C_{org.s} - C_{org}\right) = D_{org}\left(\frac{\partial C_{org}}{\partial r}\right)_s$$

$$\emptyset = \varepsilon k_v\left(C_{aq,i} - \frac{C_{org,i}}{K_d}\right) = \frac{\varepsilon D_{org}}{e_m \tau}\left(C_{org,i} - C_{org,s}\right)$$

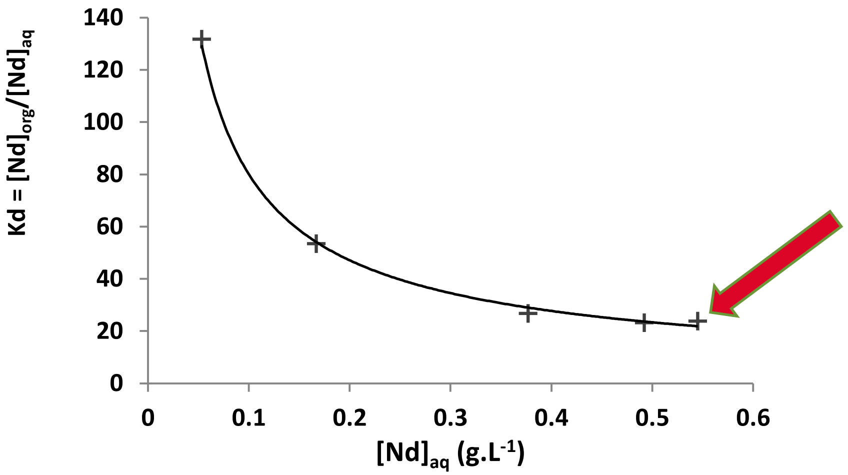
$$\frac{1}{K_{org}} = \frac{1}{k_{org}} + \frac{e_m \tau}{\varepsilon D_{org}} + \frac{K_d}{\varepsilon k_v} + \frac{K_d}{k_{aq}}$$

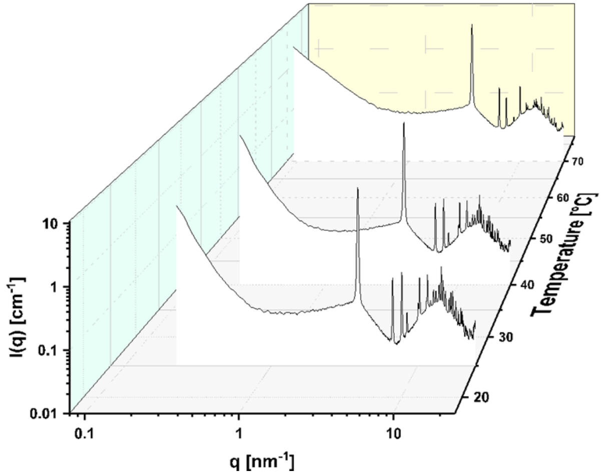
resistance in organic phase | membrane resistance | interfacial resistance | resistance in aqueous phase



Parameters of the model

Variation of distribution coefficient of Neodymium Kd





SAXS spectra of the third phase
crystalline phase

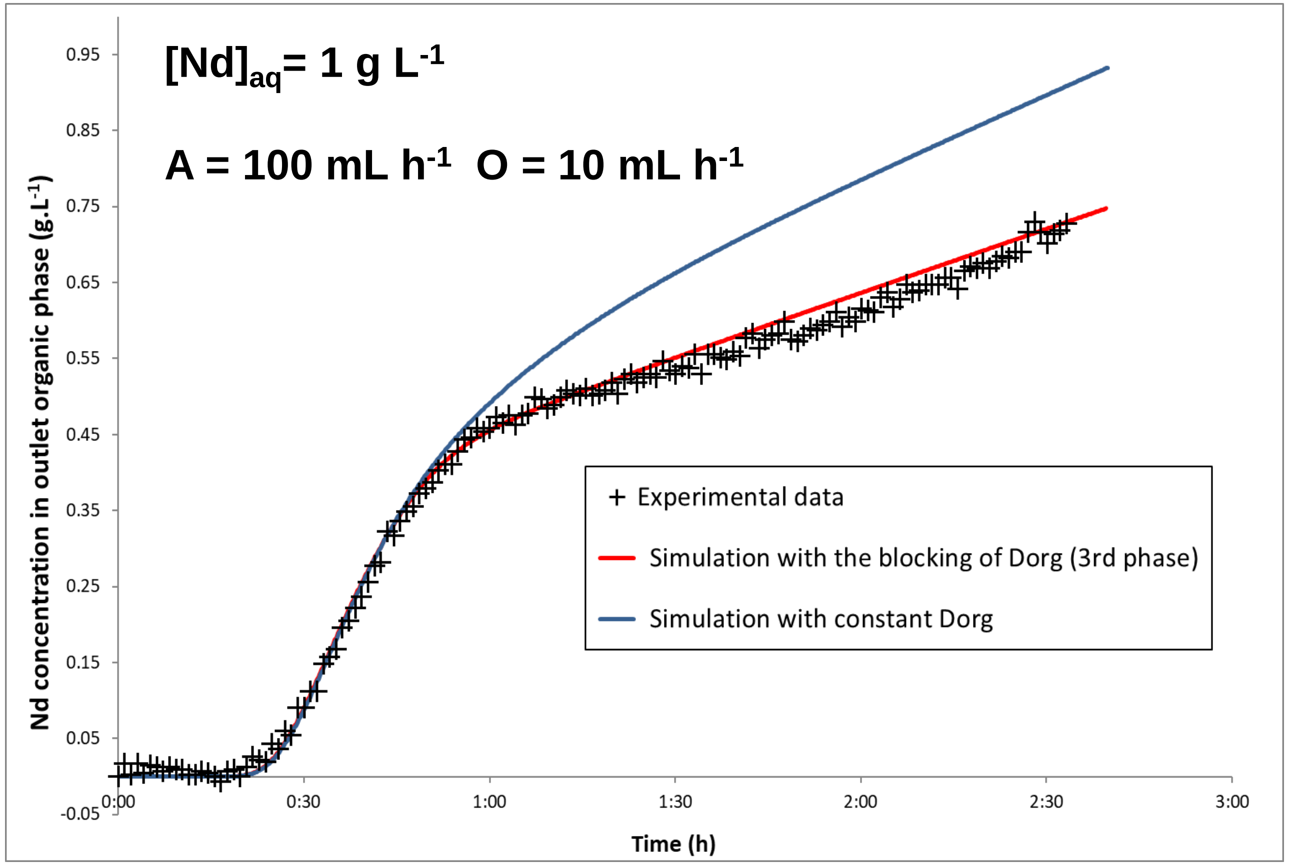
Set of parameters

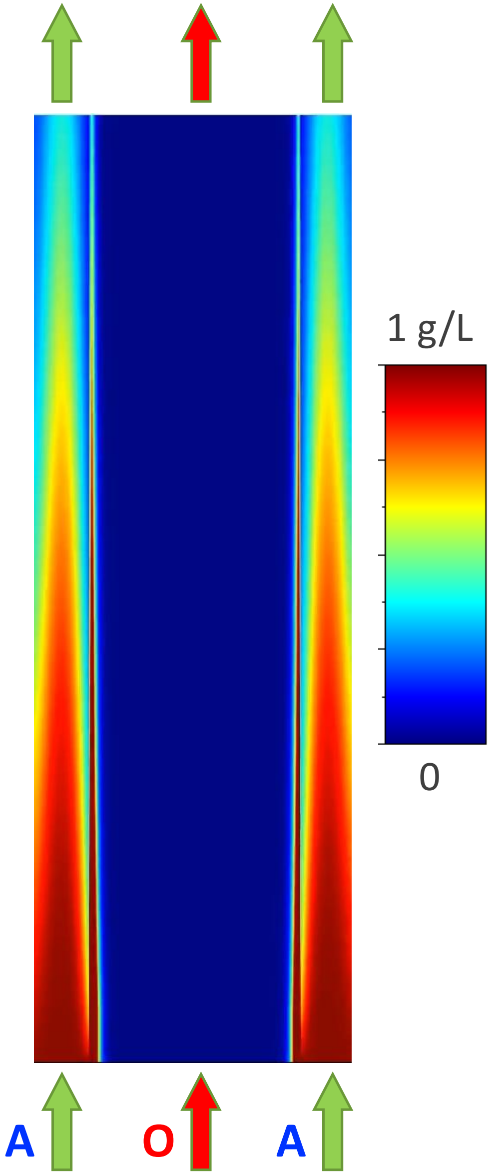
- D_{aq} = 5.8 10^{-10} m².s^{-1} (experimental value*)
- D_{org}= 10.6 10^{-11} m².s^{-1} (derived from experimental value* for [HDEHP] = 1 M and corrected for [HDEHP] = 0.5 M according to the variation of the viscosity)
- Porosity = 72% (Mercury porosimeter)
- Tortuosity = 2.6 Value adjusted to fit all the data (manufacturer's data ~ 2)

* *Etude des conditions de mise en œuvre de la pertraction pour l'extraction de métaux d'intérêt*, Moussa Touré, PhD Thesis, Montpellier University, 2015

Evolution of Nd concentration in the pertraction device

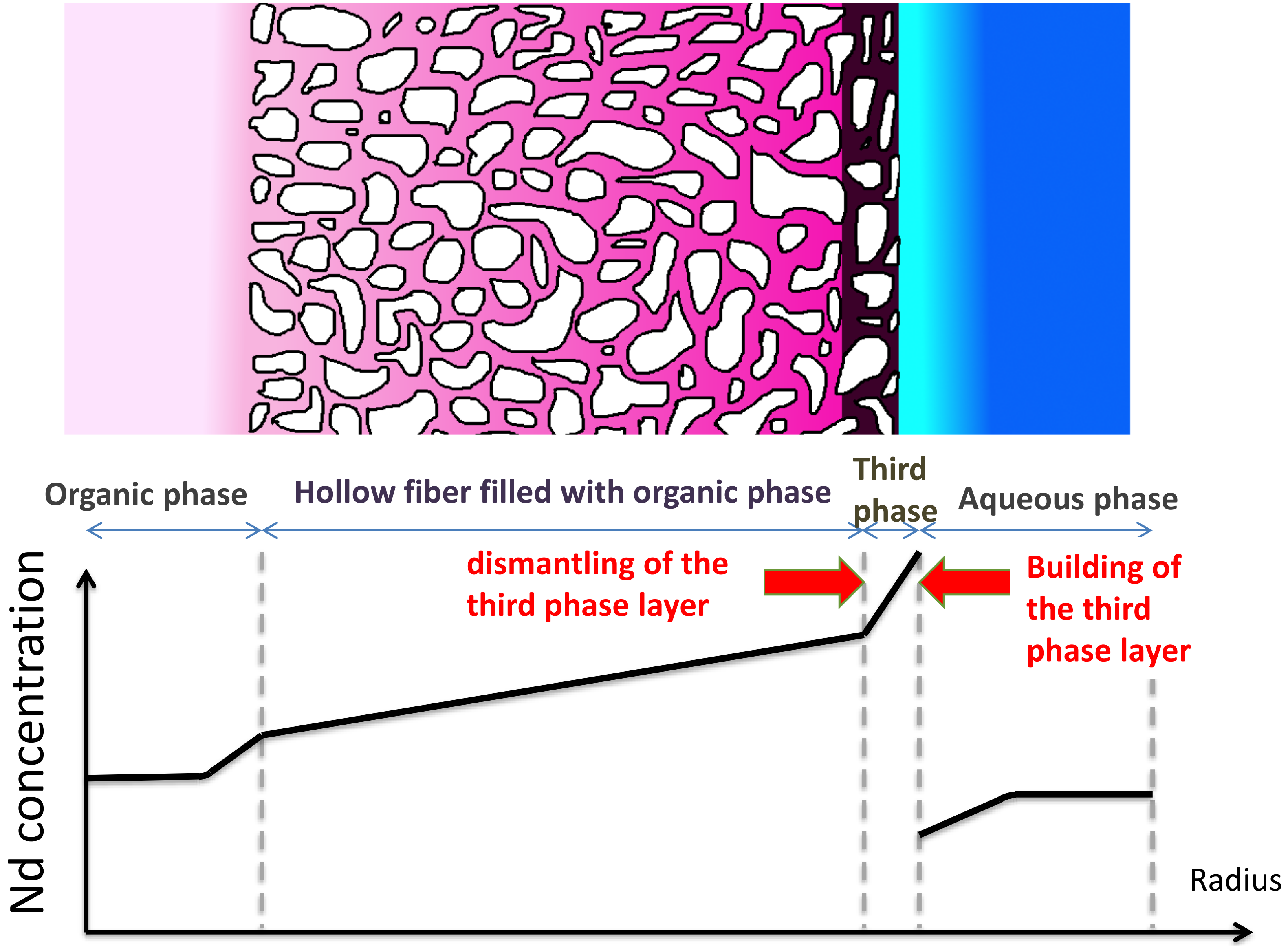
Nd concentration in the output organic phase (simulations/experiment)





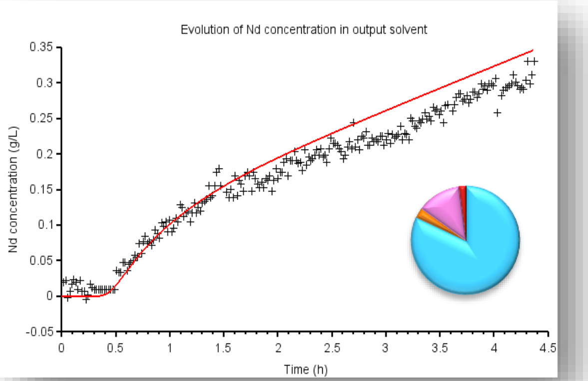
Blocking of the diffusion in the third phase layer must be taken into account to fit with experimental data.

Zoom inside the membrane

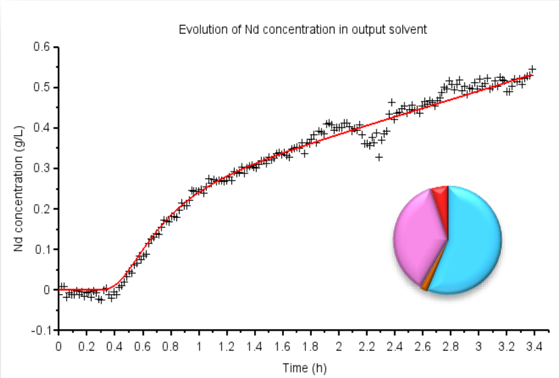


Comparison of experimental data versus simulation

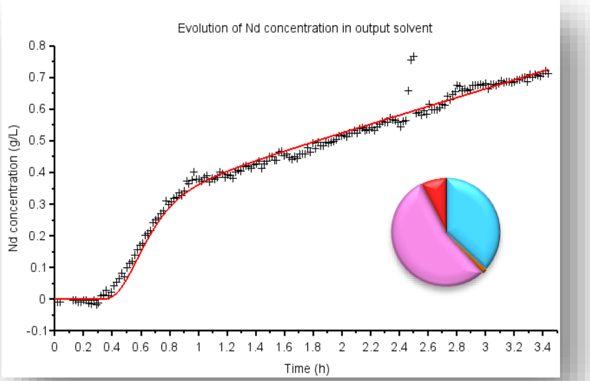
Run n° 22 $[Nd]_{aq}$= 0.1 g L^{-1}
A = 101.7 mL h^{-1} O = 10.7 mL h^{-1}



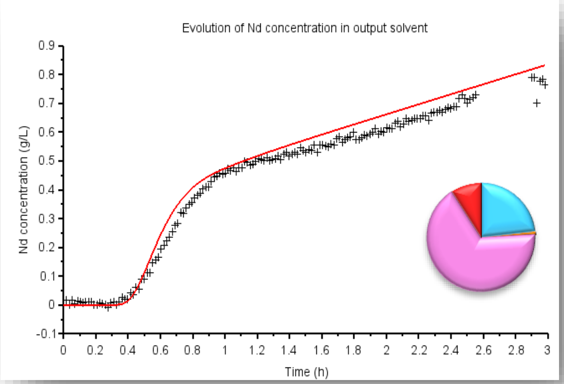
Run n° 19 $[Nd]_{aq}$= 0.25 g L^{-1}
A = 99.2 mL h^{-1} O = 10.1 mL h^{-1}



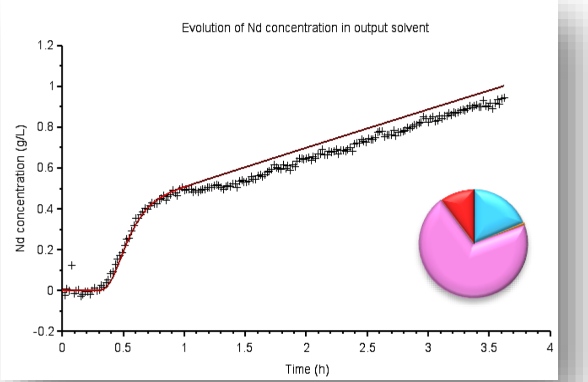
Run n°18 $[Nd]_{aq}$= 0.5 g L^{-1}
A = 98.3 mL h^{-1} O = 9.9 mL h^{-1}



Run n° 11 $[Nd]_{aq}$= 1 g L^{-1}
A = 100 mL h^{-1} O = 10 mL h^{-1}

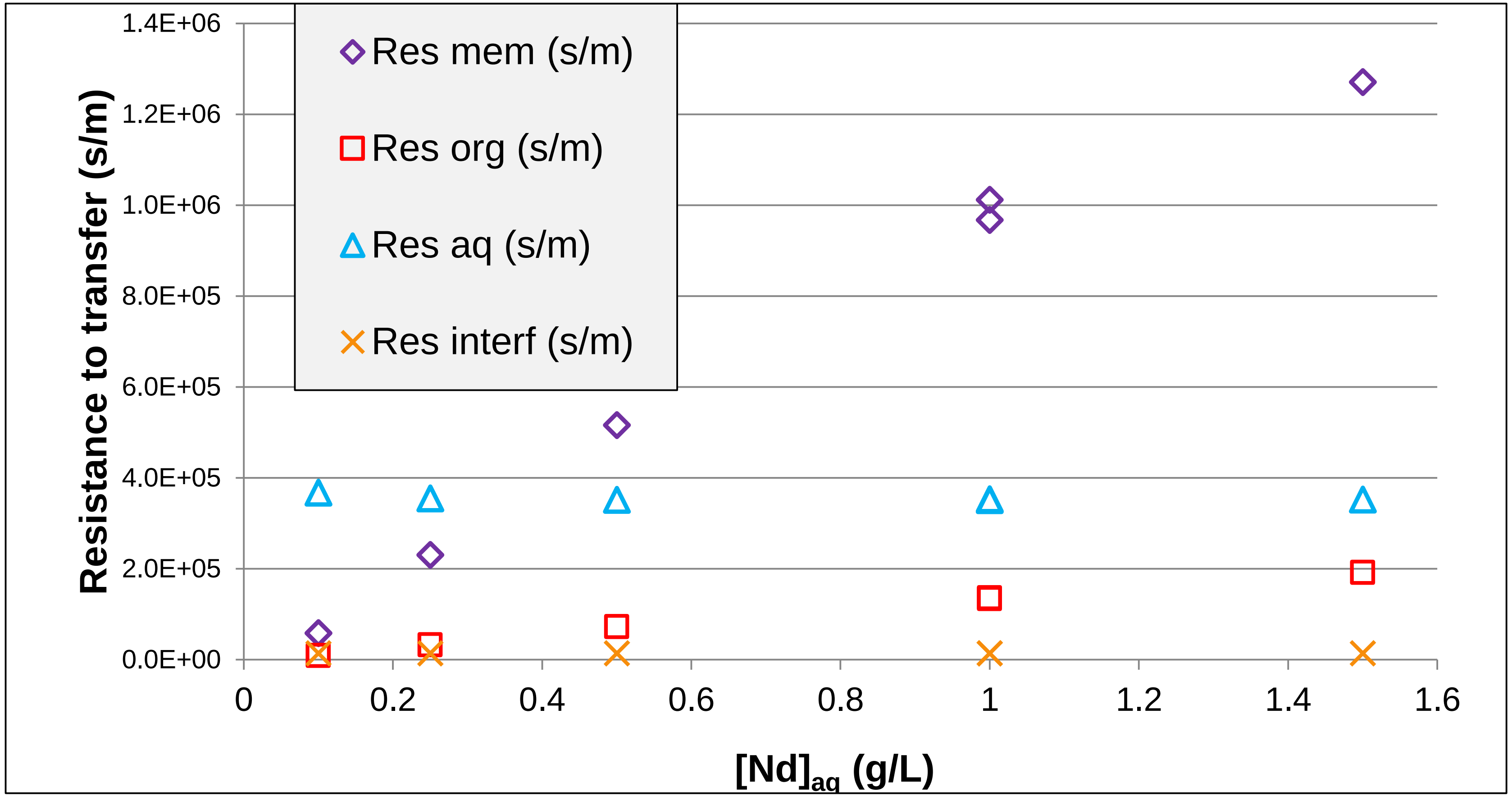


Run n° 21 $[Nd]_{aq}$= 1.5 g L^{-1}
A = 97 mL h^{-1} O = 10.9 mL h^{-1}



Res_aq Res_interf Res_mem Res_org

Evolution of resistance to mass transfer



Resistance to mass transfer increase in the membrane with Nd concentration because of the decrease of the distribution coefficient (lower gradient concentration in the solvent) and appearance of the third phase.

Conclusion and outlooks

- **Good agreement between experiments and simulation of neodymium pertraction with HDEHP**
  - No correlation needed for mass transfer coefficients
  - Modelling of the blocking of the diffusion in the membrane due to third phase formation fit well with experiments
  - The model can be used to design and scale-up pertraction process

- **More investigations should be done about the third phase layer:**
  - Can it be used to increase separation efficiency with other ions?
  - How can mass transfer be increased using ultrasonic external triggering?

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