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## A general approach for predicting the filtration of soft and permeable colloids: the Milk example

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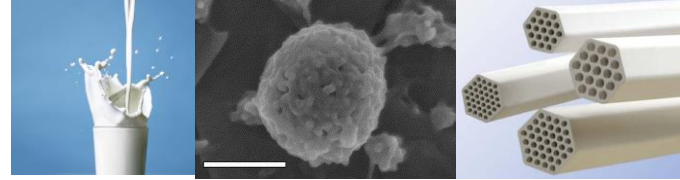
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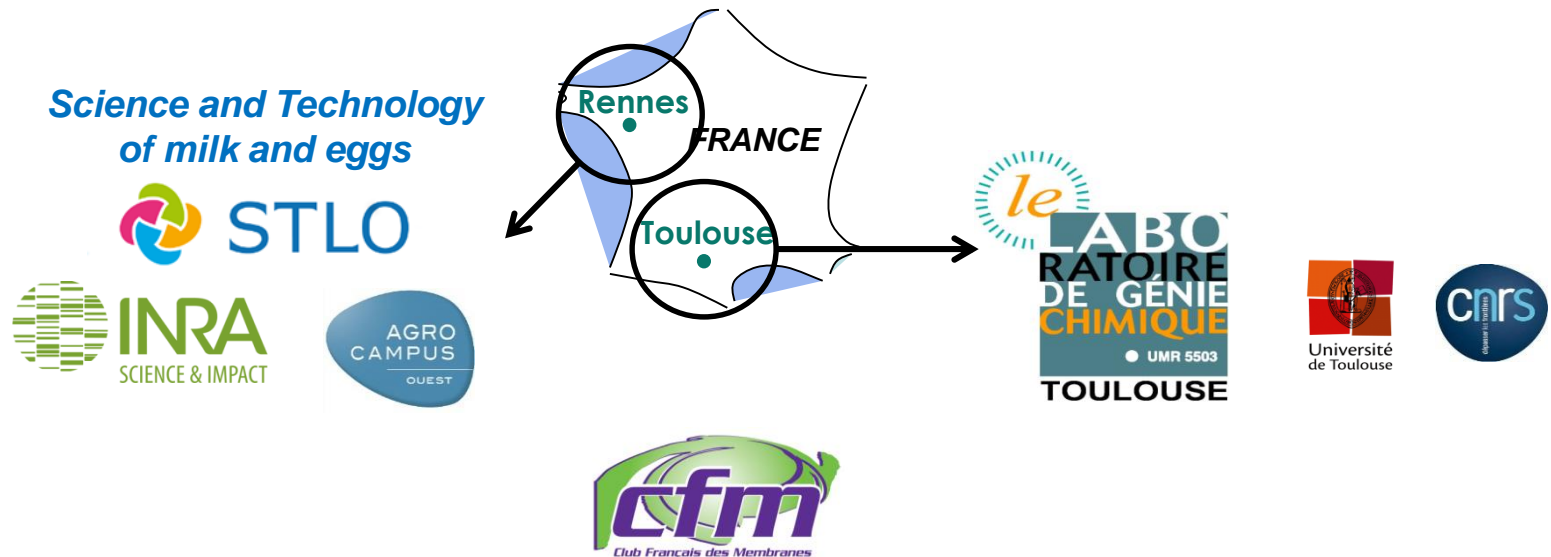
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# A general approach for predicting the filtration of soft and permeable colloids : the Milk example

A. Bouchoux, P. Qu, P. Bacchin, G. Gésan-Guiziou



## - Filtration in the dairy sector

- Operations largely used:  $\approx 40\%$  of the membrane area installed in food sector

**Concentration of milk components**  $\rightarrow$  Cheese manufacture, standardization, ...

**Fractionation of milk components**  $\rightarrow$  Ingredients with high added value



## Operations not well mastered & Performance impossible to predict

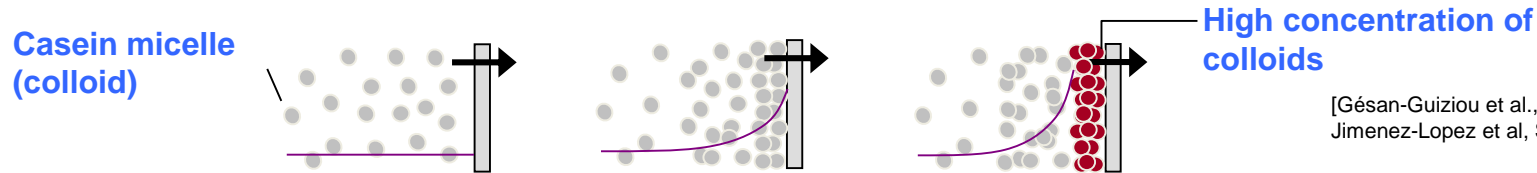
- Variability of production duration and quality of produced fractions
- Difficulties of cleaning

**High consumption of** | **water** (2-6 m<sup>3</sup> of water / 100 m<sup>2</sup> of membranes / cleaning operations)  
**detergents and energy...**

# Context

## - Micro- and Ultra- filtration (crossflow) of skimmed milk

- casein micelles = main contributor to accumulation at the membrane surface

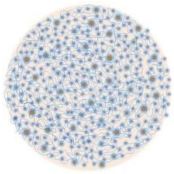


[Gésan-Guiziou et al., JMS, 1999; Jimenez-Lopez et al, SPT, 2008]

- Casein micelle = soft and porous « natural » colloid

~80% of milk proteins, C ≈ 25 g/L

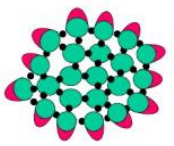
**Composition :** caseins :  $\alpha_{s1}$ ,  $\alpha_{s2}$ ,  $\beta$ ,  $\kappa$  (3:1:3:1)  
minerals : phosphate and calcium



[de Kruif et al., Adv. Colloid Interface Sci., 2012 ]

**Colloidal object (≈ sphere) :**

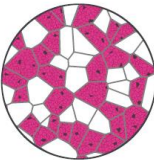
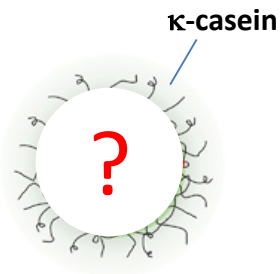
large size distribution ~50-250nm, average diameter ≈ 100nm  
highly hydrated (3.7g of water / g protein)



[Walstra, Int. Dairy. J., 1999 ]

**Structure :**

core → web of caseins + calcium phosphate nanocluster  
surface →  $\kappa$ -casein, highly charged



[Bouchoux et al., Biophys.J., 2010]

**The internal structure is not totally elucidated...**

# Objective

- **To propose a methodology for building a model that is able to predict the performance of the filtration (J, concentration gradient) of soft and permeable colloids**

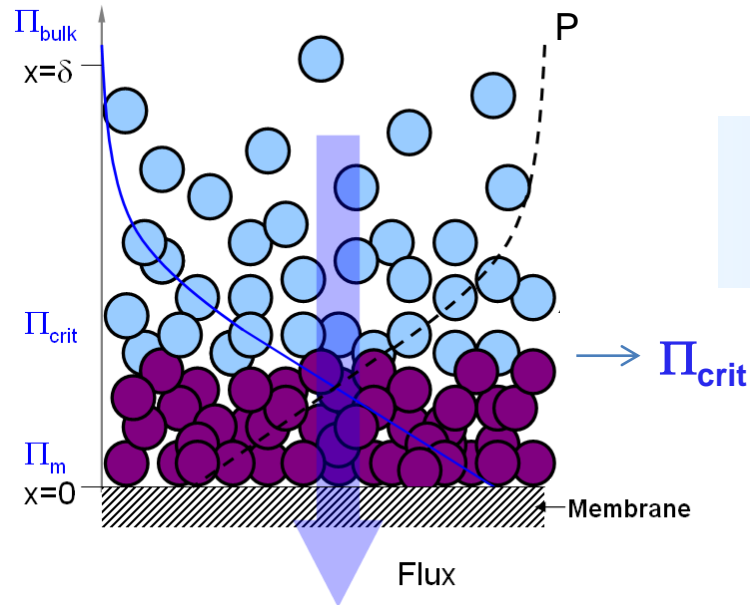
... by taking into account the approaches previously developed for non deformable and non permeable colloids (like hard spheres)

Note :

- dead-end filtration case only
- native « casein micelles » as model experimental system

# Filtration modeling for colloids

## - Theory



## Case of dead-end filtration

Diffusion and convection in polarized layer

$$J = -\frac{1}{\eta R_{PL}} \frac{d\Pi}{dx} = -\frac{k_{PL}}{\eta} \frac{d\Pi}{dx} = \frac{1}{\eta R_{PL}} \frac{dP}{dx}$$

Compression and permeation in a deposit/gel

$$J = \frac{k_{gel}}{\eta} \frac{dP}{dx} = -\frac{k_{gel}}{\eta} \frac{d\Pi}{dx}$$

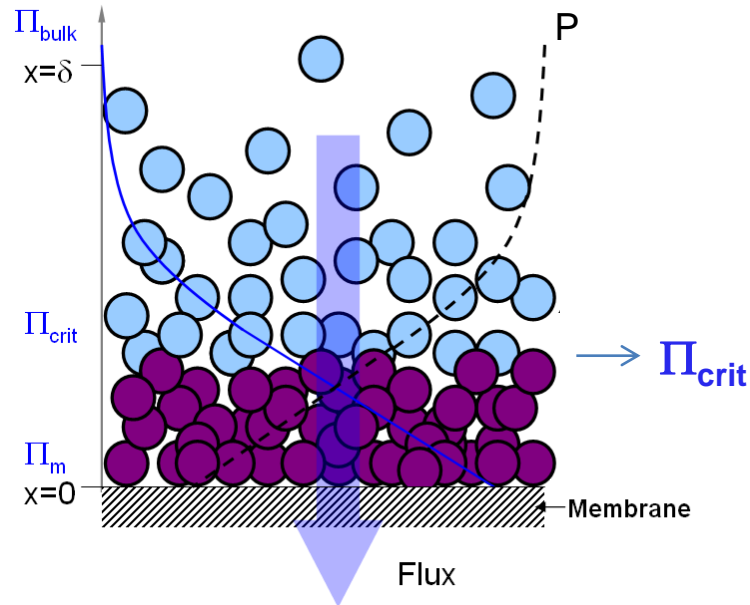
- $J \rightarrow$  permeation flux
- $P \rightarrow$  pressure
- $k(\phi) \rightarrow$  permeability
- $R_{PL} \rightarrow$  resistance of the polarized layer
- $\Pi \rightarrow$  osmotic pressure
- $\phi \rightarrow$  volume fraction
- $\eta \rightarrow$  dynamic viscosity of the solvent

$$\frac{dP}{dx} = \frac{-d\Pi}{dx}$$

[Bacchin, Gordon Research Conference Membranes, 2006]  
 [Bowen et Jenner, Chem. Engng.Sci., 1995]  
 [Bacchin et al., J.Membrane Sci., 2006]  
 [Elimelech et Bhattacharjee, J.Membrane Sci., 1998]

# Filtration modeling for colloids

## - Theory



→ **A single equation** to describe concentration polarisation and deposit layers

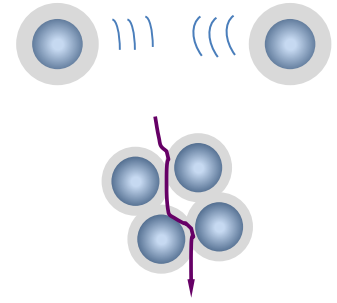
$$J = - \frac{k(\phi)}{\eta} \frac{d\Pi(\phi)}{dx}$$

- C → concentration
- J → permeation flux
- P → pressure
- k → permeability
- Π → osmotic pressure

→ **Two parameters** for the filtration modelling for colloids

Π (C/φ): Colloidal osmotic pressure (colloidal interactions)

k (C/φ): Hydraulic permeability (size, form, concentration)



# Filtration modeling for colloids

## - Theory: non-interacting hard spheres

### Permeability

Happel

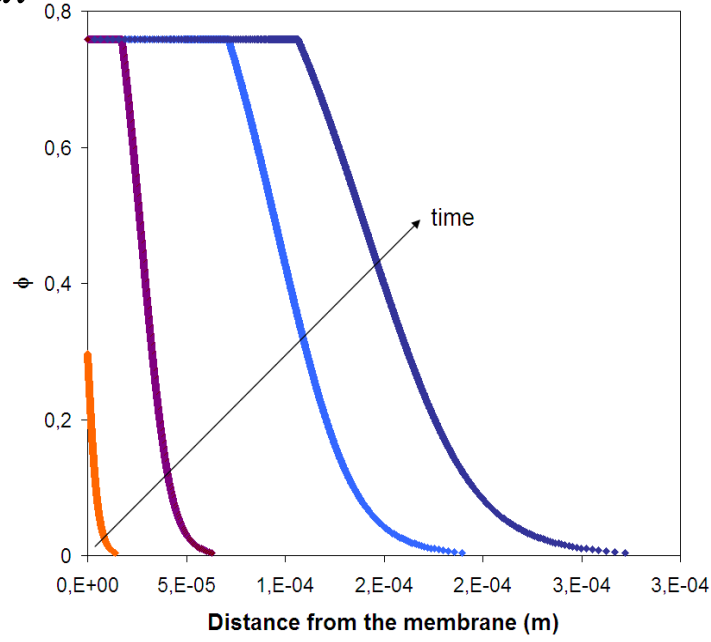
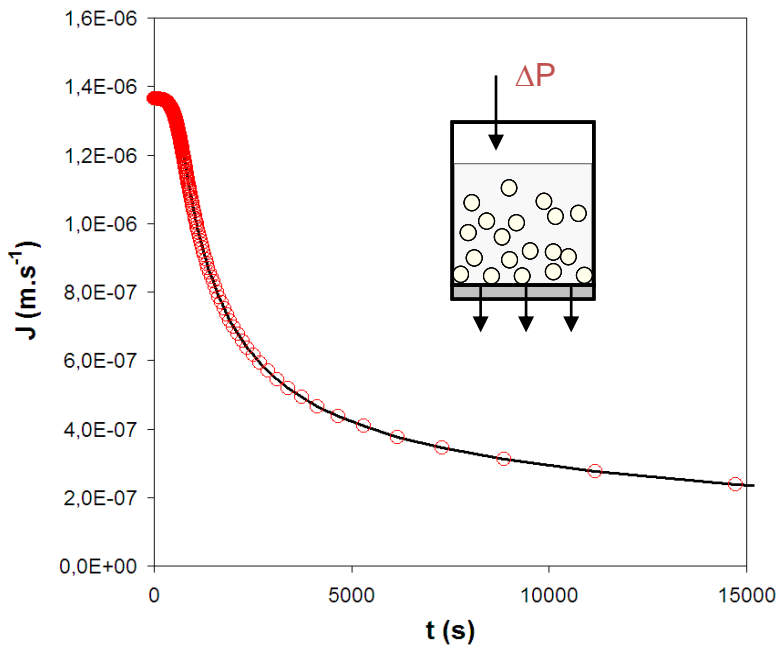
$$k_{happel} = \frac{2r_p^2}{9\phi} \cdot \frac{3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2}{3 + 2\phi^{5/3}}$$

### Osmotic Pressure

Carnahan-Starling

$$\frac{\Pi}{nkT} = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}$$

$$J = - \frac{k(\phi)}{\eta} \frac{d\Pi(\phi)}{dx}$$





# Filtration modeling for colloids

## - Theory: charged hard spheres

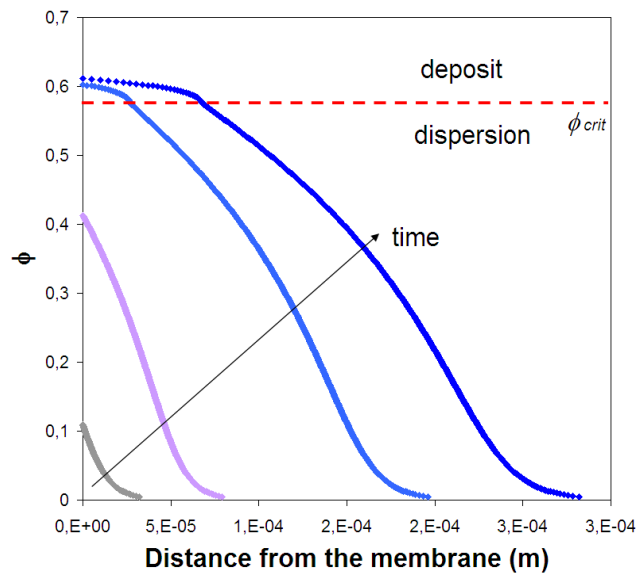
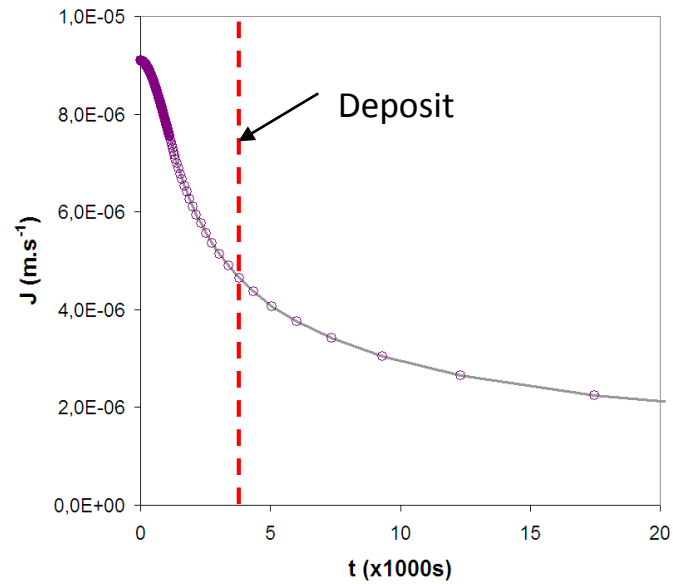
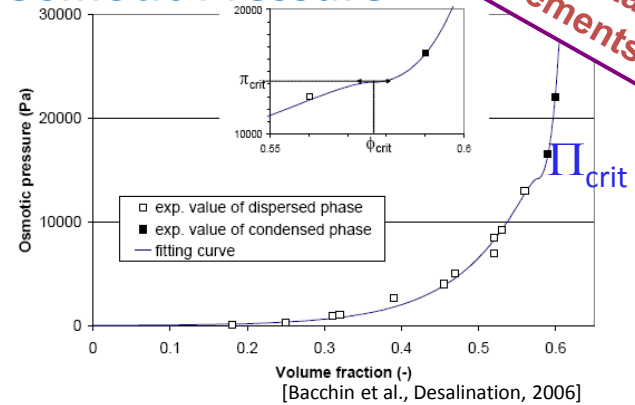
### Permeability

Happel

$$k_{happel} = \frac{2r_p^2}{9\phi} \cdot \frac{3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2}{3 + 2\phi^{5/3}}$$

$$J = - \frac{k(\phi)}{\eta} \frac{d\Pi(\phi)}{dx}$$

### Osmotic Pressure



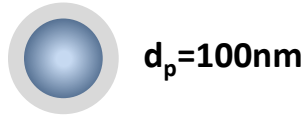
# Filtration modeling for colloids

- Theory: **deformable and porous colloid (casein micelles)**

## Permeability

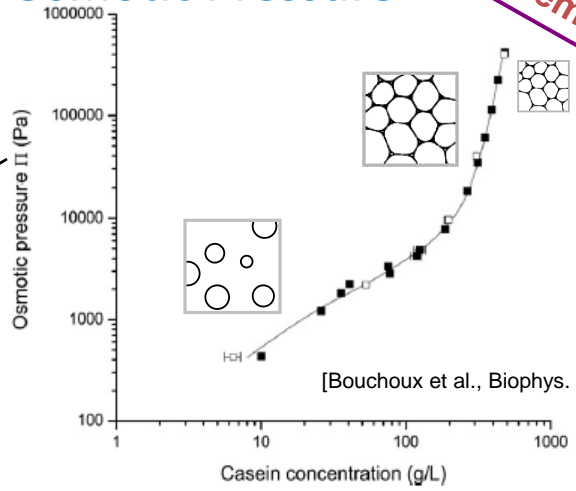


How to determine k for concentrated layers of casein micelles ?



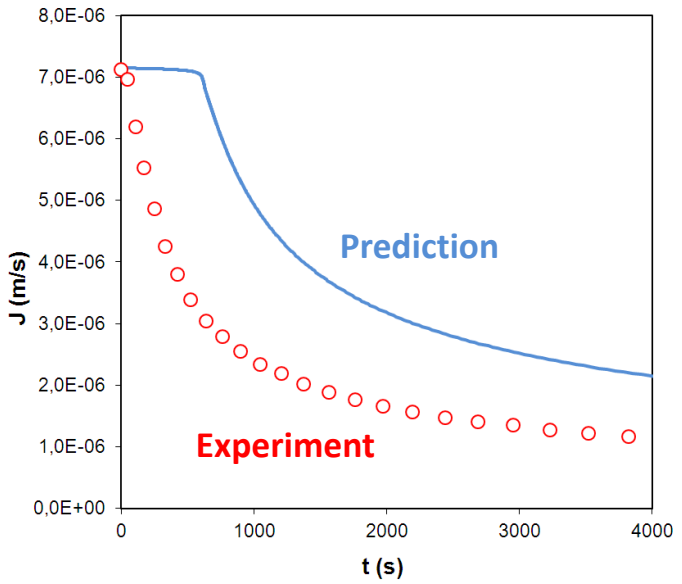
$$J = - \frac{k(\phi)}{\eta} \frac{d\Pi(\phi)}{dx}$$

## Osmotic Pressure



[Bouchoux et al., Biophys. J., 2009]

$\Pi$  : osmotic stress/ membrane osmometer

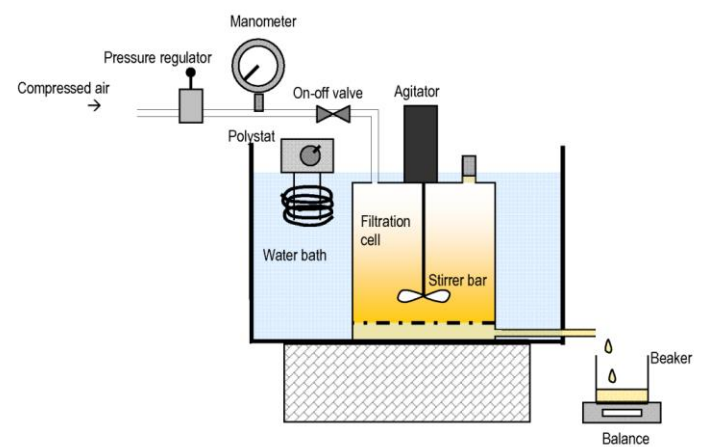
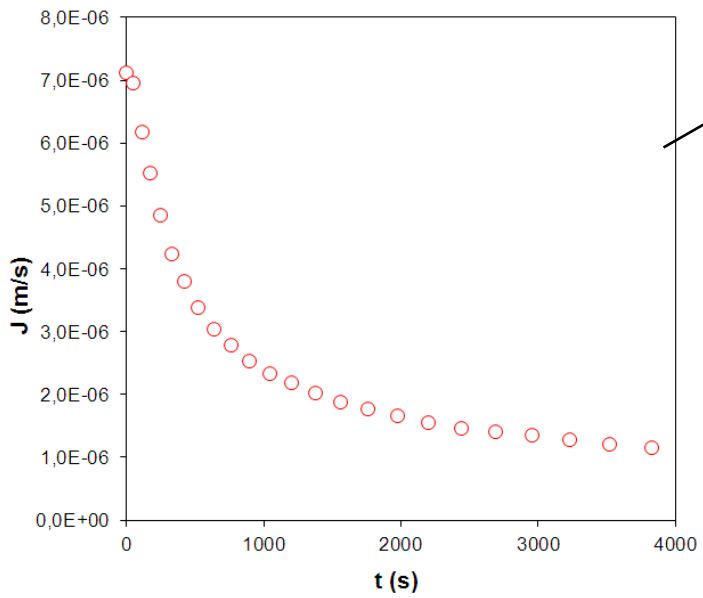
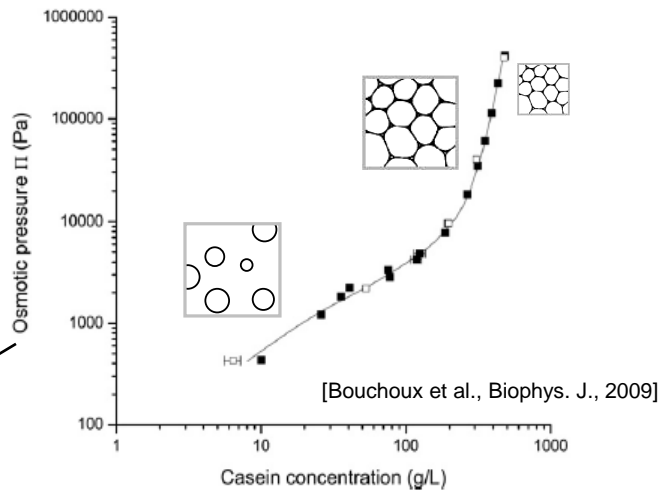


# Filtration modeling - Determination of k

## Strategy 1: Reverse-calculation approach [Bowen et Williams, J. Membrane Sci., 2001]

Permeability

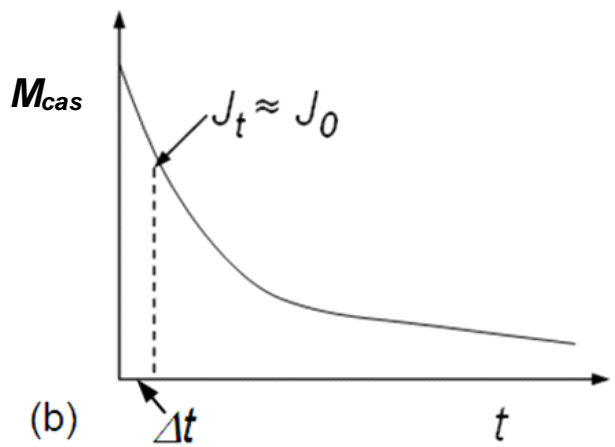
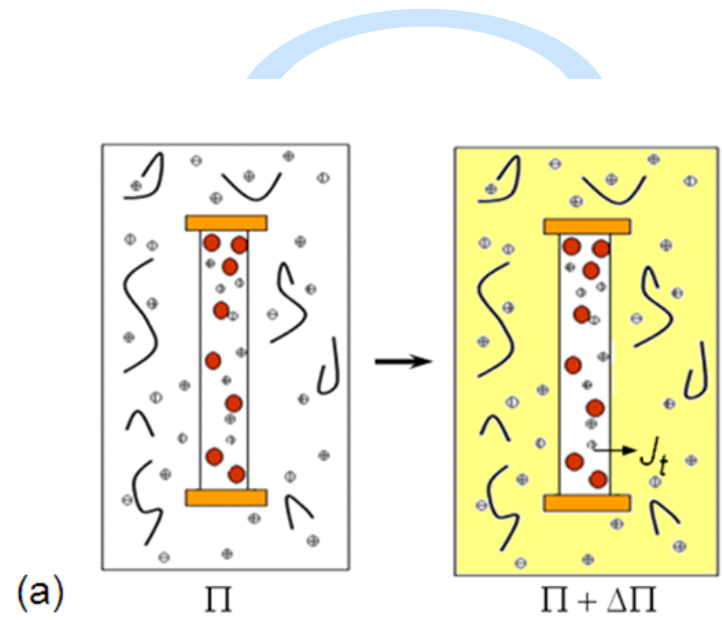
$$J = - \frac{k(\phi) d\Pi(\phi)}{\eta dx}$$



Dead-end filtration of native casein micelles, C 1g/L

# Filtration modeling - Determination of k

## Strategy 2: osmotic compression approach



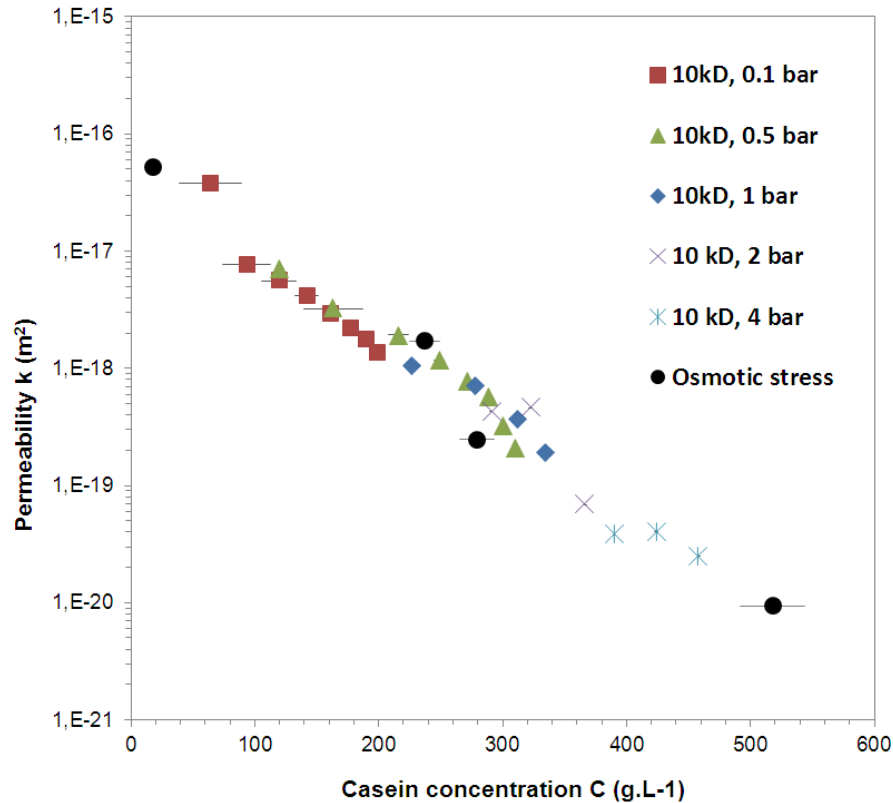
$$J_0 = \frac{k(C_{slice})}{\eta} \cdot \frac{\Delta\Pi}{e}$$

$$e = \frac{V_{bag}}{A_{bag}} = \frac{\rho_{cas} \cdot M_{cas}}{A_{bag}}$$

$e \rightarrow$  thickness of the slice



## Results: permeability



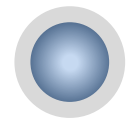
**The different approaches for the determination of k are coherent**

**Experimental values of k are distributed over one single curve**

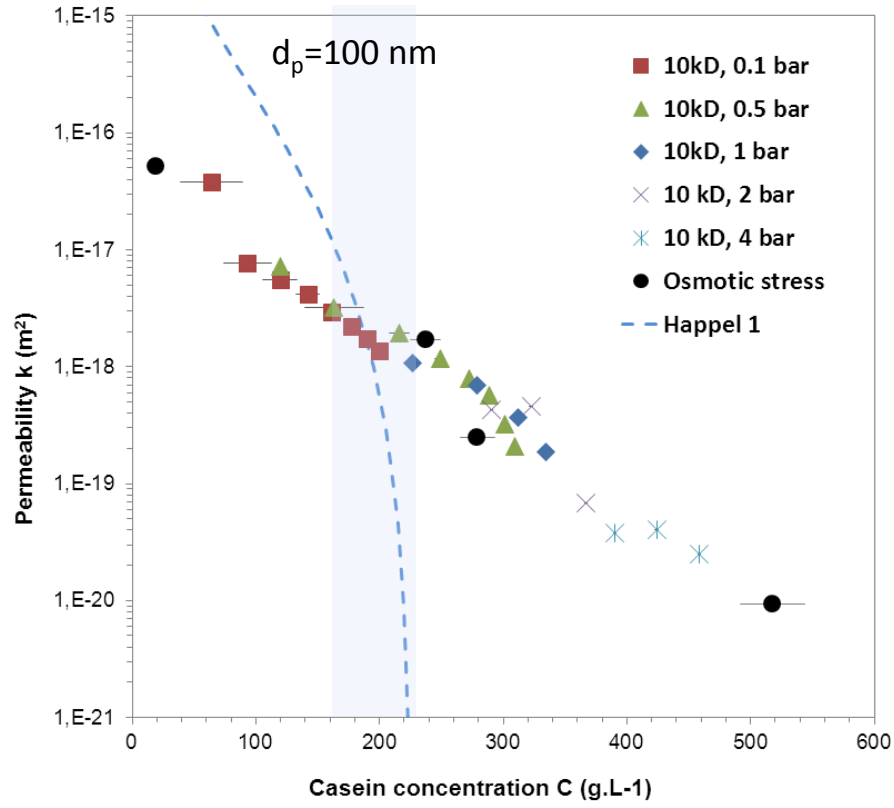
# Filtration modeling - Determination of k

## Results: permeability

$$k_{happel} = \frac{2r_p^2}{9\phi} \cdot \frac{3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2}{3 + 2\phi^{5/3}}$$



$d_p=100\text{nm}$



**Before close-packing:  $k$  micelles  $<$   $k_{happel}$  (hard spheres)**

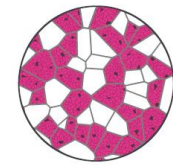
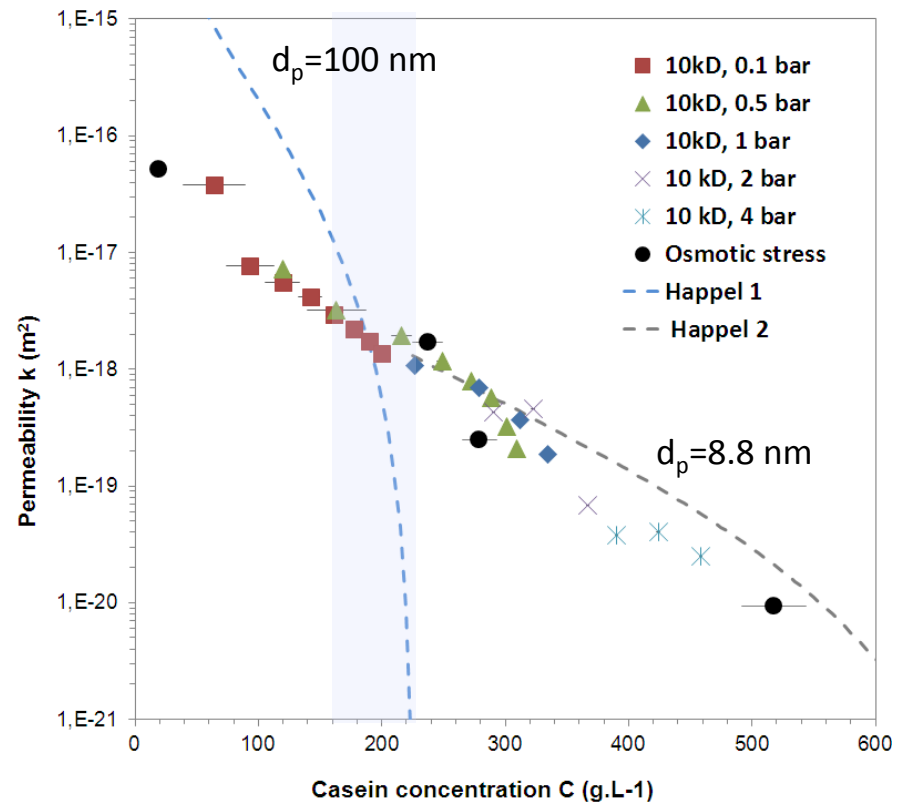
→ Polydispersity in size : unlikely [Li et Park, Ind. Eng. Chem. Res., 1998]

→ Impurities, degradation ?

# Filtration modeling - Determination of k

## Results: permeability

$$k_{happel} = \frac{2r_p^2}{9\phi} \cdot \frac{3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2}{3 + 2\phi^{5/3}}$$



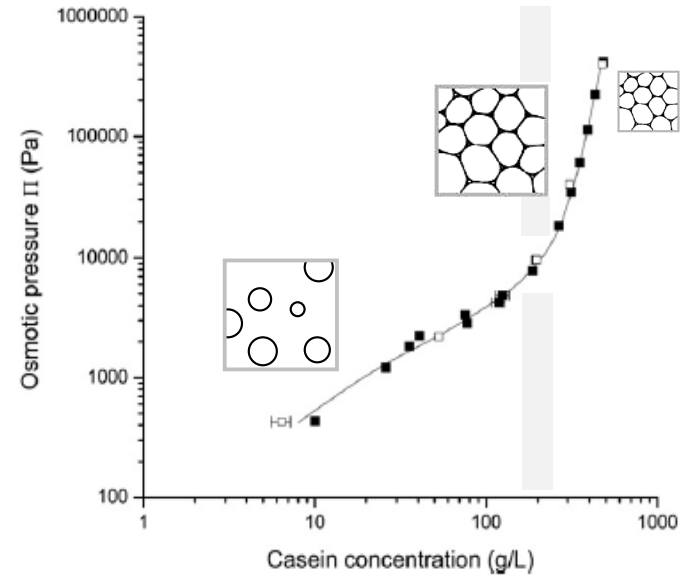
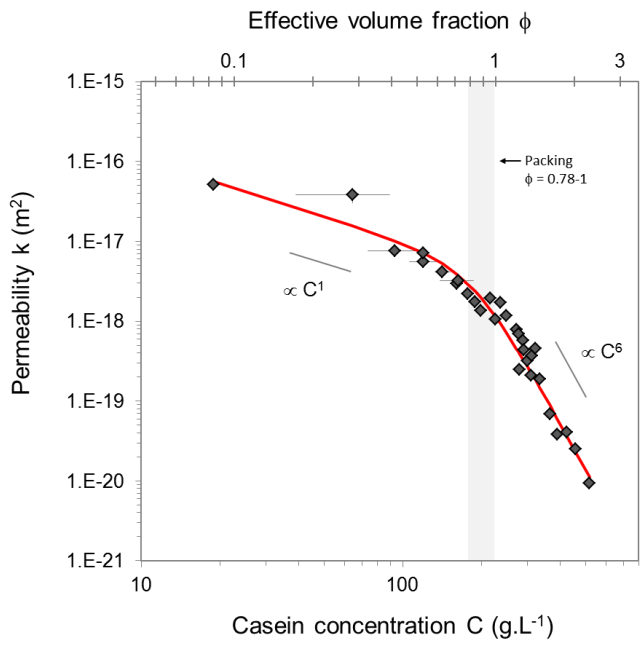
Casein micelle interior = collection of non connected hard spheres

$d_p=8.8$ nm

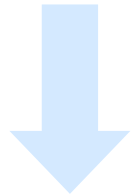
[Bouchoux et al., Biophys.J., 2010]

After close-packing:  $k \rightarrow$  internal organisation of casein micelle

## Results: modelling



[Bouchoux et al., Biophys. J., 2009]

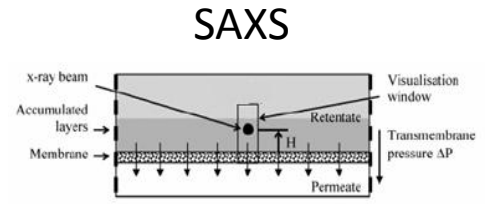
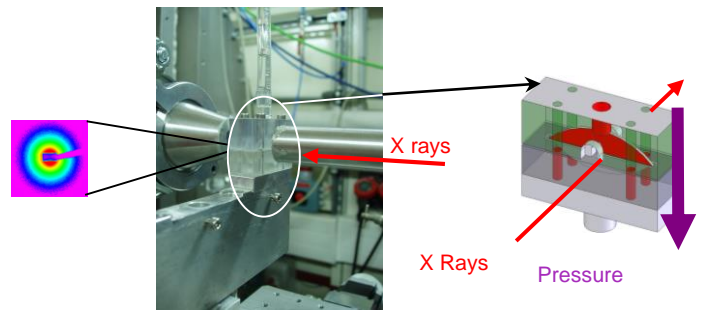


**Prediction is possible**

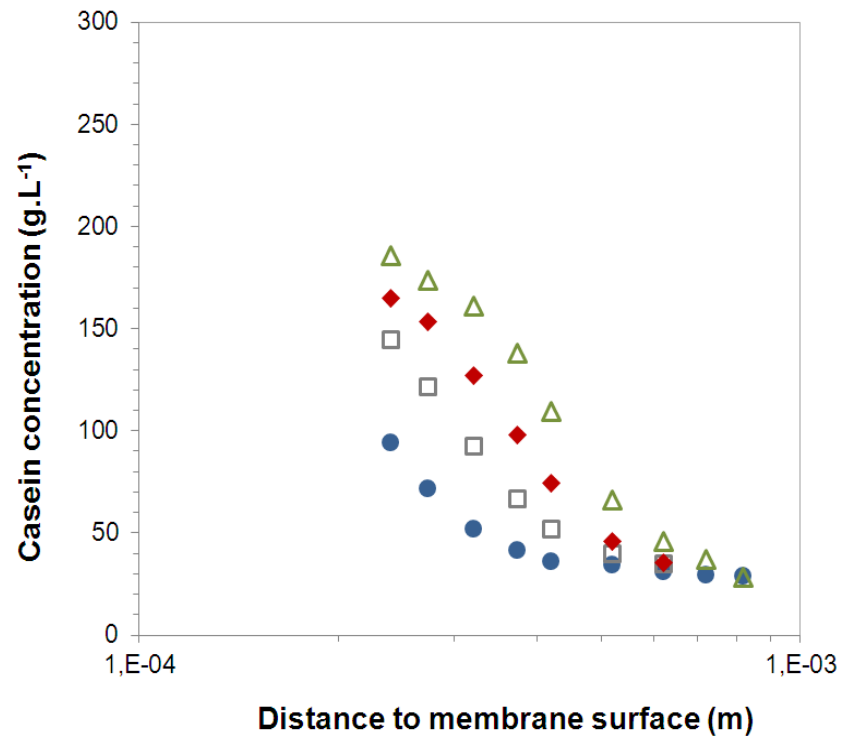
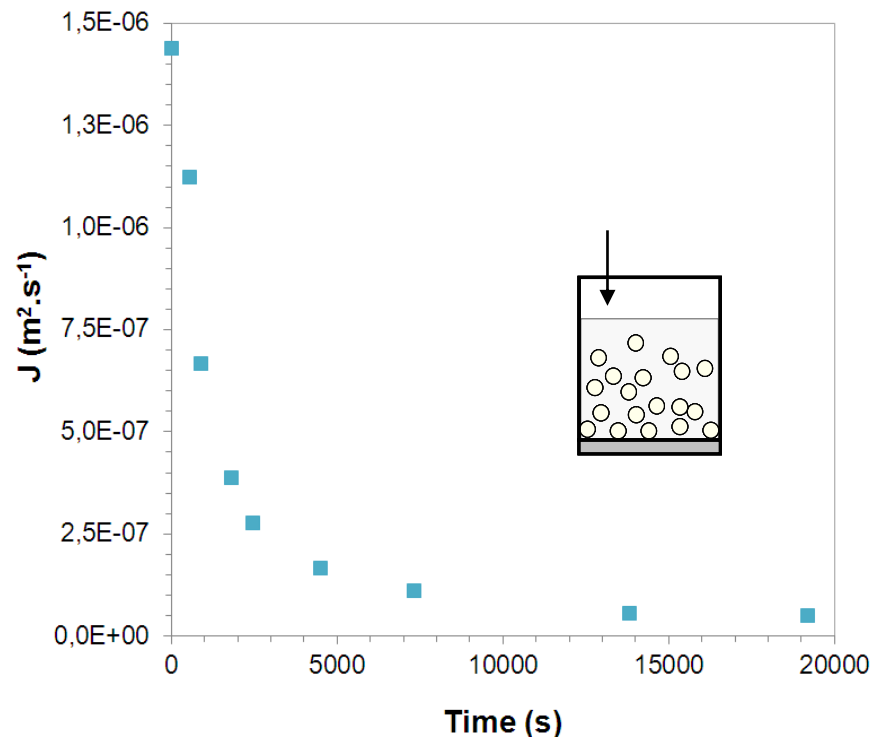
$$J = - \frac{k(C)}{\eta} \frac{d\Pi(C)}{dx}$$



# Filtration modeling - Model validation



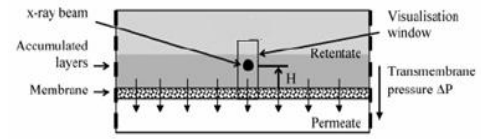
[David et al., Langmuir, 2008]



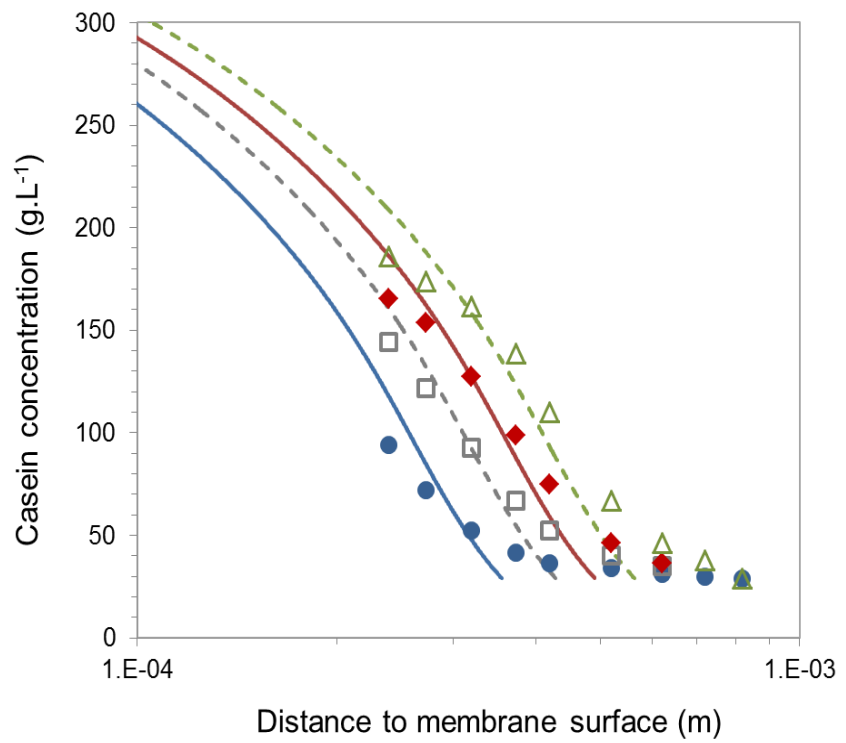
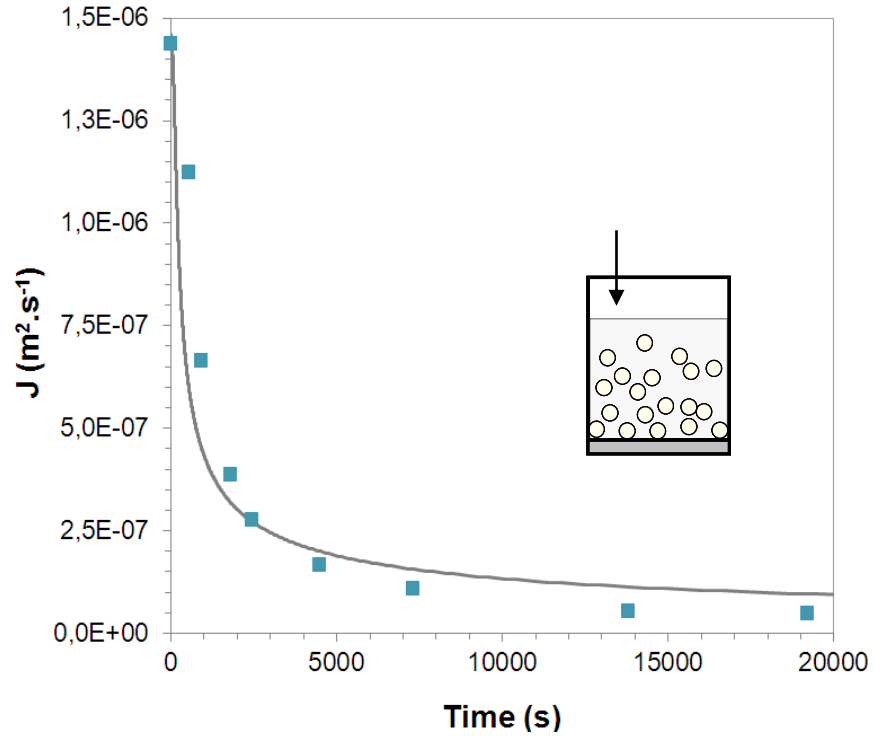
# Filtration modeling - Model validation



## SAXS



[David et al., Langmuir, 2008]



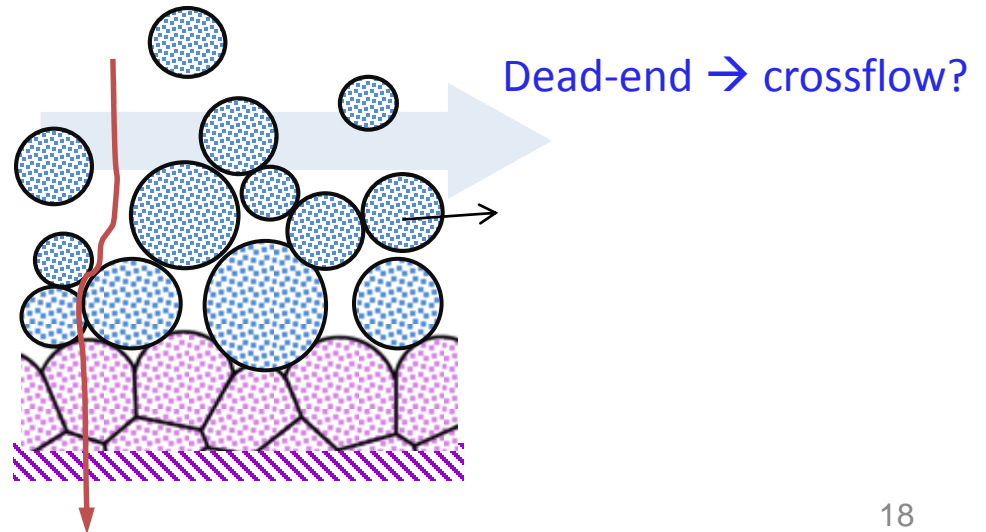
The results are satisfying

# Conclusion

- Proposal of a generic methodology for building a model able to predict the performance (J, C) of the filtration of soft and permeable colloids (casein micelles)
- Methodology based on
  - models developed for the filtration of hard spheres
  - experimental determinations of the colloidal osmotic pressure  $\Pi(C)$  and permeability  $k(C)$

Model ( $\Pi(C)$ ,  $k(C)$ )

## Perspectives



# Acknowledgments



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Région Bretagne & INRA



**Thank you for your attention !**

