Modeling the filtration of deformable and permeable colloidal particles: the case of casein micelles

Peng Qu, Antoine Bouchoux, Geneviève Gésan-Guiziou

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Agrocampus Ouest
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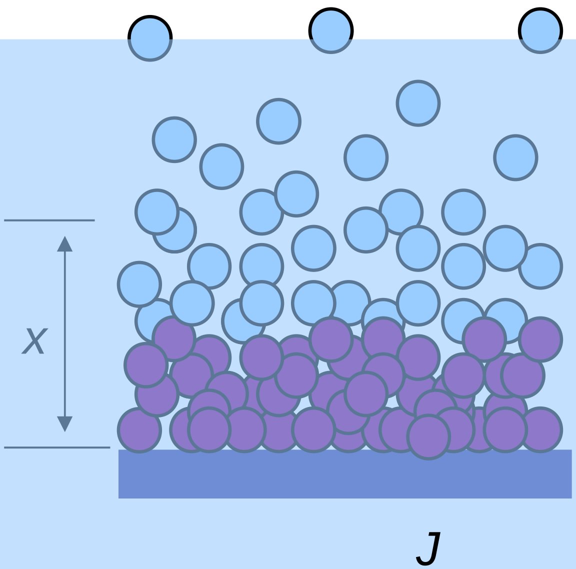
1. Context

- **Dead-end filtration of colloidal particles**

[Bacchin, Gordon Research Conference Membranes,2006]



Diffusion and convection in a polarised layer

$$J \cdot \phi - D(\phi) \cdot \frac{d\phi}{dx} = 0 \qquad \frac{D(\phi)}{D_0} = K(\phi) \cdot \frac{d\Pi}{d\phi}$$

Compression and permeation in a deposit

$$J = -\frac{k(\phi)}{\mu} \cdot \frac{dP_L}{dx} \qquad dP_L = -d\Pi$$

□ A single equation to describe concentration polarisation and deposit layers

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

With $\frac{k(\phi)}{\mu} = D_0 \frac{K(\phi)}{\phi}$

ϕ □ volume fraction

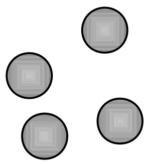
$D(\phi)$ □ collective diffusion coefficient
$D0$□ individual diffusion coefficient

$K(\phi)$□ sedimentation coefficient

$k(\phi)$ □ permeability

Π □ osmotic pressure

1. Context



- **Filtration model for non-interacting hard spheres**

Permeability

Happel equation

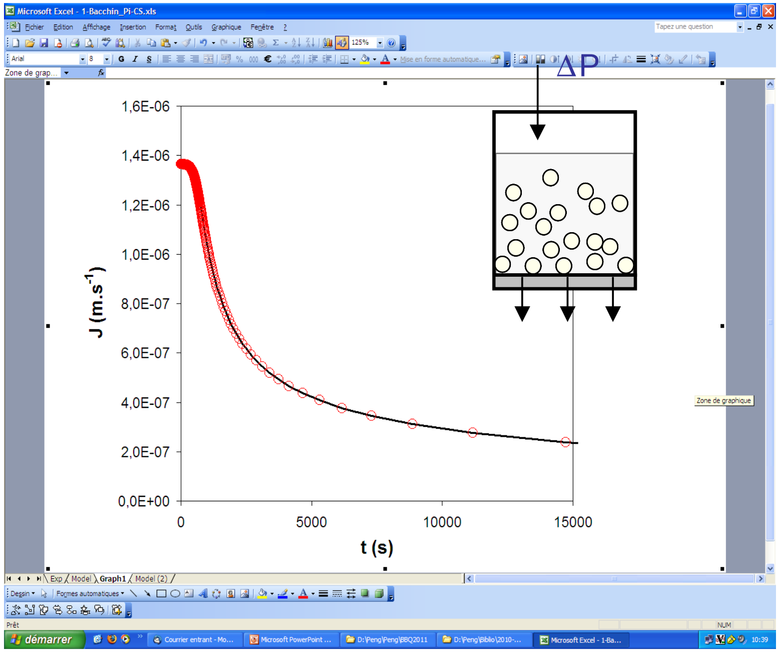
$$k_{happel} = \frac{2r_p^2}{9\phi} \cdot \frac{3 - 4.5\phi^{1/3} + 4.5\phi^{5/3} - 3\phi^2}{3 + 2\phi^{5/3}}$$

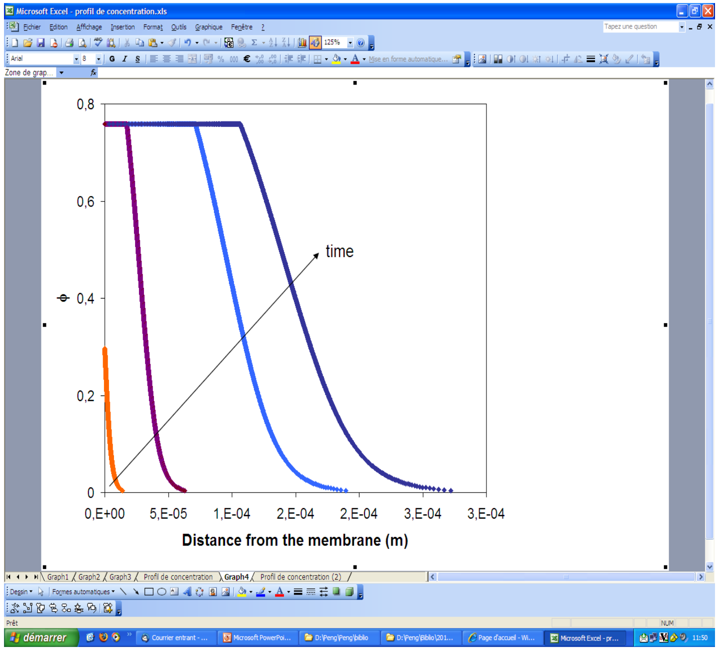
Osmotic pressure

Carnahan-Starling equation

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

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

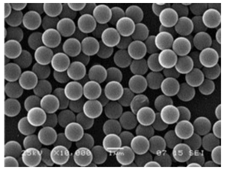




1. Context

- **Filtration model for charged hard spheres**

Experimental measurements



(Latex)

Permeability

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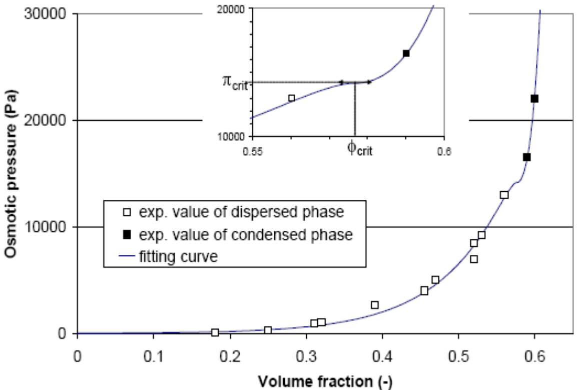
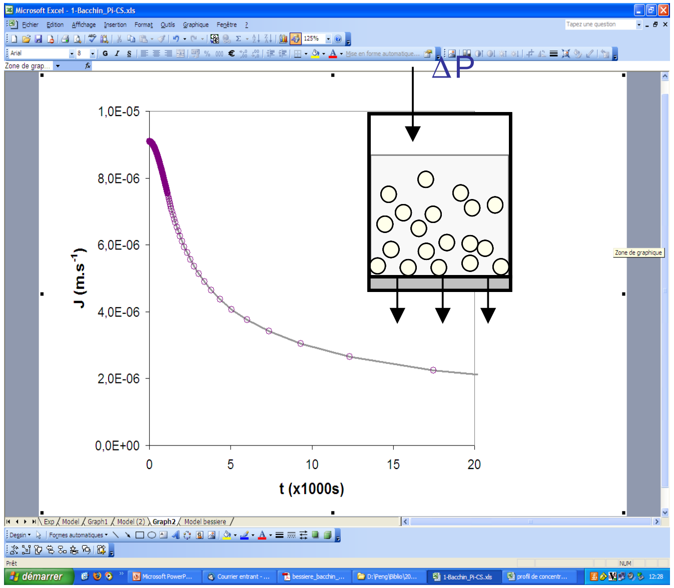
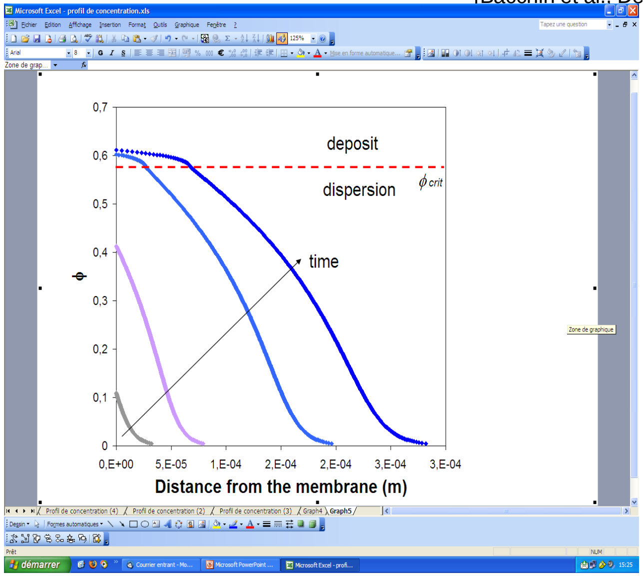
Osmotic pressure



[Bacchin et al., Desalination, 2006]

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

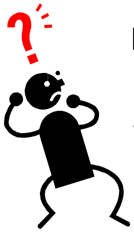




2. Research questions

- **Filtration model for compressible and/or permeable particles**

Permeability



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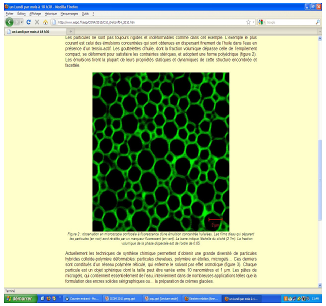
Osmotic pressure

$\boxed{\text{Experimental measurements}}$

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



Emulsion

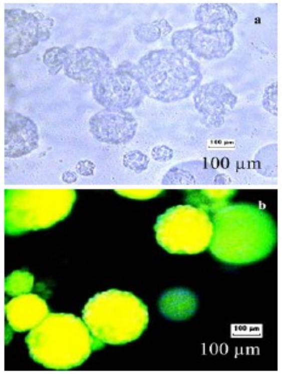


Fig. 4 The microscopy images of 0.5 % X AAm film containing 2 % X cationic microgel (hydrogel–hydrogel *semi*-IPN) under white light **a**, and **b** fluorescence microscopy image after absorption of fluorescein dye(FSS)

Micro-gels

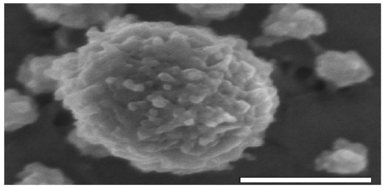


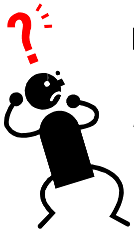
Fig. 2. Electron micrograph of an individual casein micelle, as for Fig. 1. Note the apparent connection between the main micelle and a subsidiary structure, which may be a part of the micelle being dissociated. Note the ring of smaller particles which may represent pieces dissociated from the micelle. Scale bar = 200 nm.

Casein micelles

2. Research questions

- **Filtration model for compressible and/or permeable particles**

Permeability



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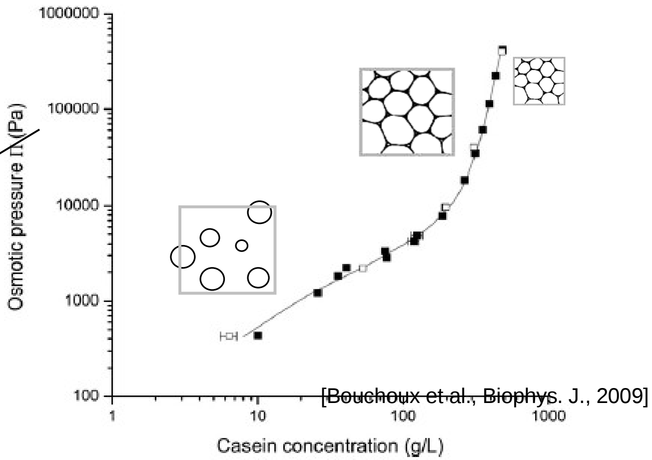
Osmotic pressure



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

~80% of the proteins in milk

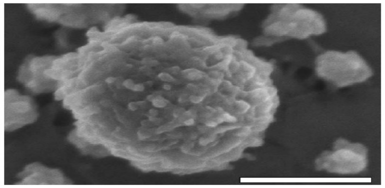
= Colloidal object (≈ sphere) :

Size distribution ~50-500nm

Water content 3.7g water/g proteins

Why milk filtration ?

Cheese production & proteins fractionation



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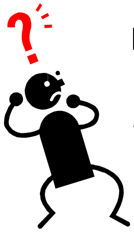

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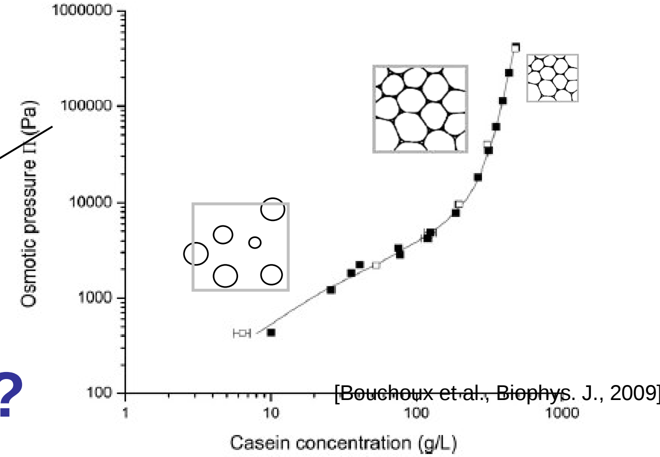
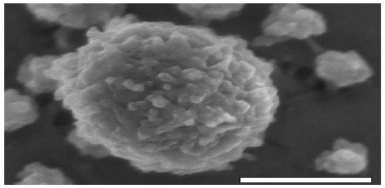
Osmotic pressure



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

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

- How to determine the permeability?



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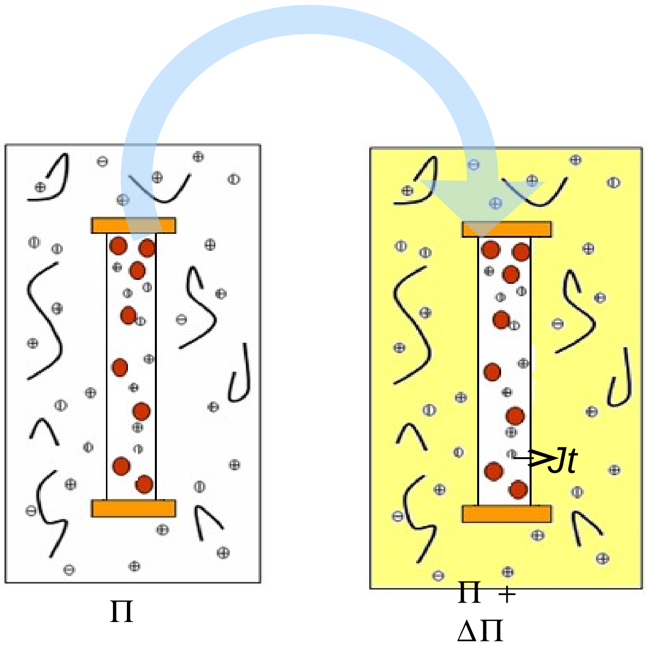
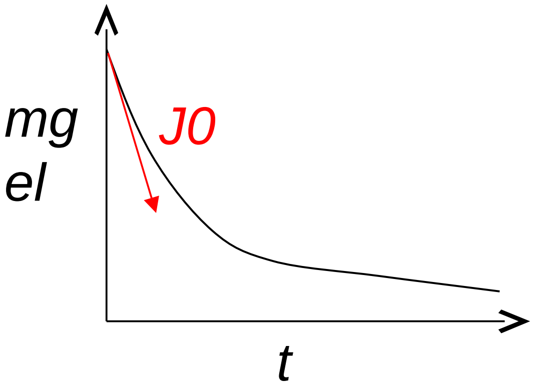
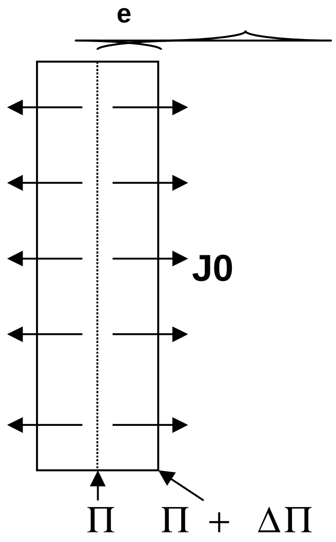
Casein micelles

3. Measurement of permeability: strategy 1

- **Using osmotic stress**







$$J_0 = \frac{k}{\mu} \cdot \frac{\Delta P}{e}$$

ΔP=ΔΠ
e=Vgel/Asac

3. Measurement of permeability: strategy 2

- **Using the model "reversely"** [Bowen et Williams, J. Coll. Int. Sci., 2001]

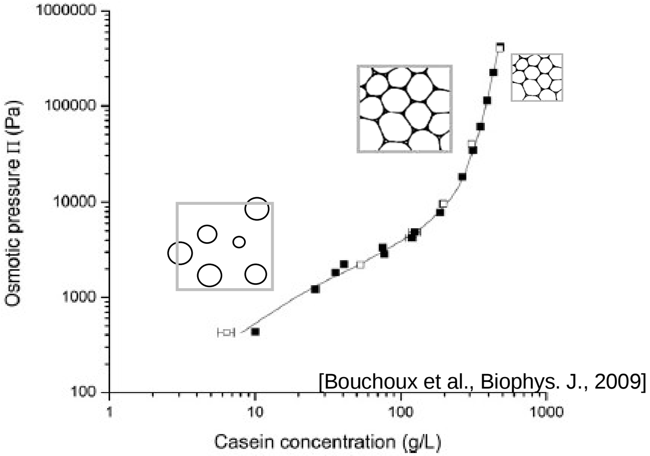
Permeability

Osmotic pressure

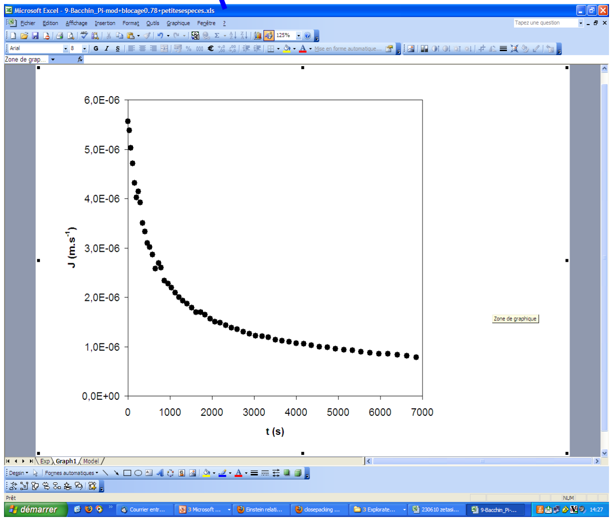
Model validation:

Can we use the results for the prediction of filtration in any other conditions?

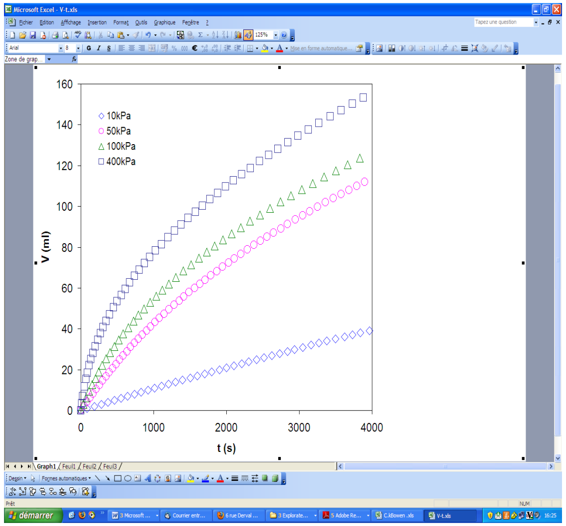
$$J = \frac{k(\phi)}{\mu}\frac{d\Pi}{dx}$$

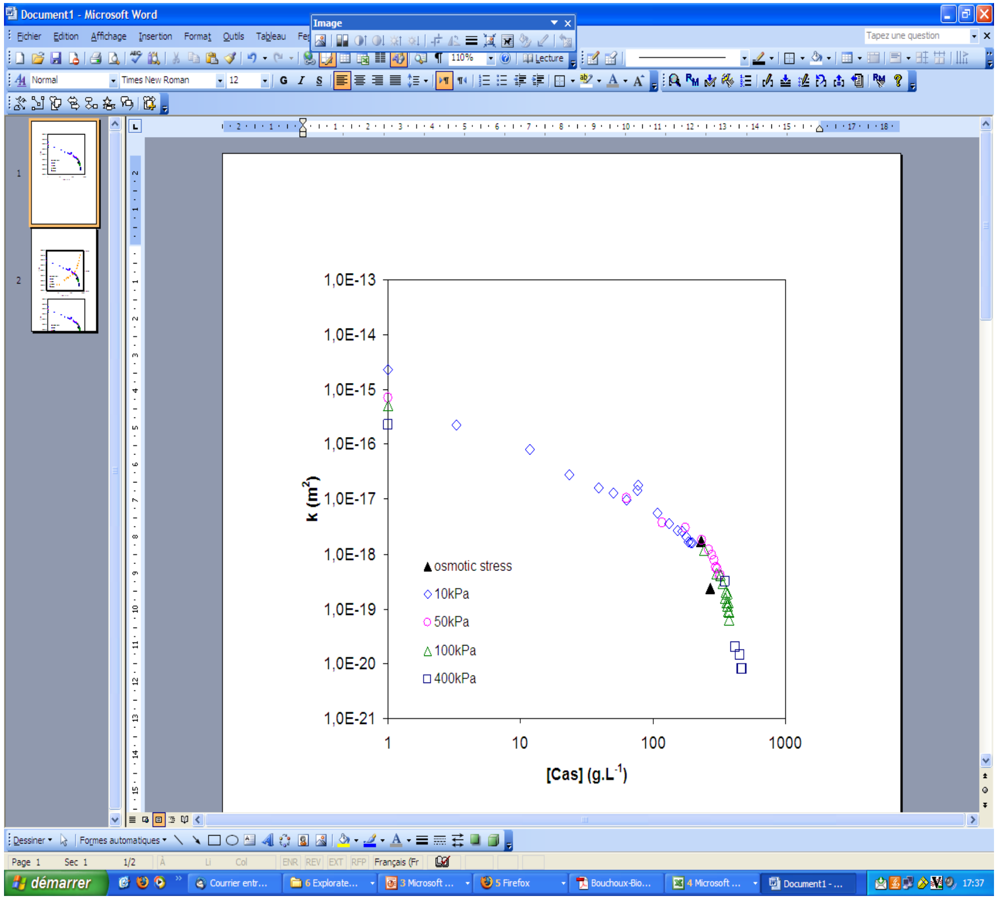


[Bouchoux et al., Biophys. J., 2009]



4. Permeability of casein micelles





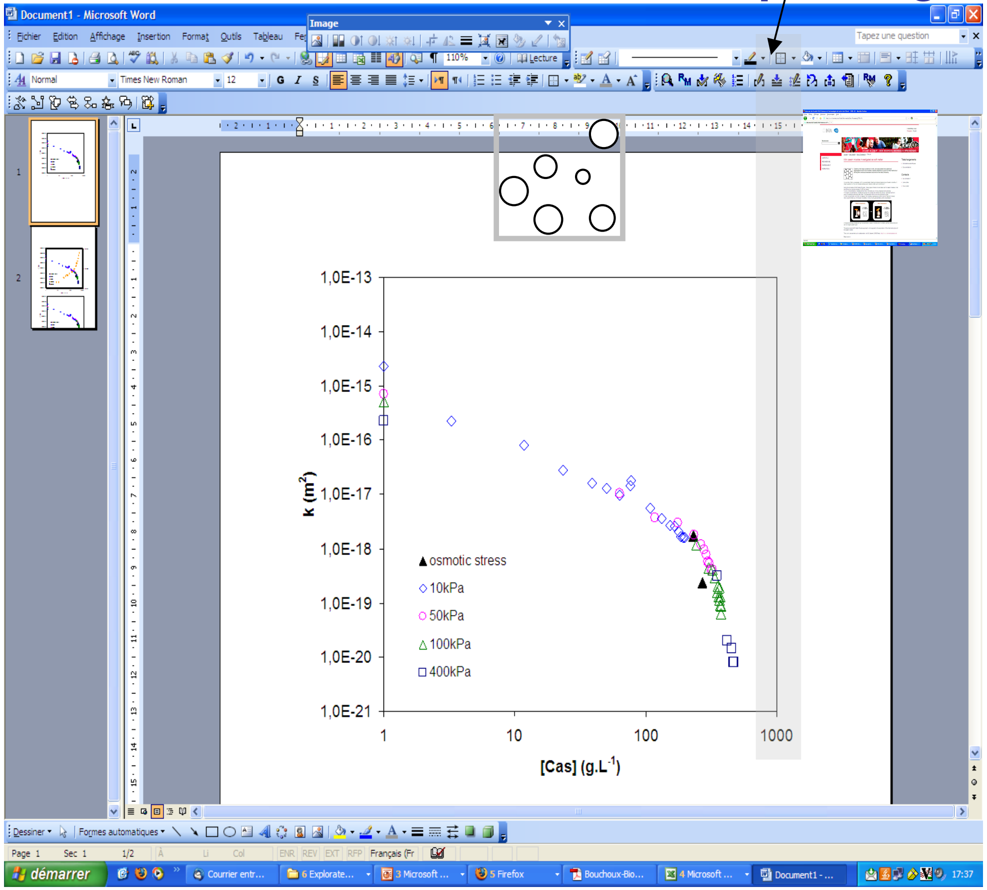
The results are continuous and homogeneous

The results determined by the two methods are similar

4. Permeability of casein micelles

- **Permeability values = 2 regimes**

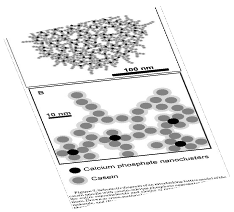
close packing

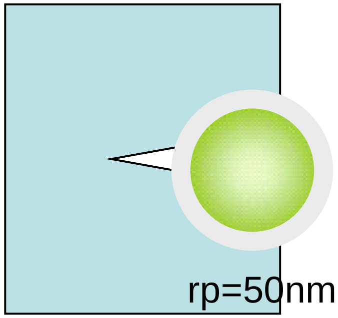


Phase transition (close packing) limits permeability

4. Permeability of casein micelles

- **Regime 1 - Before close packing**





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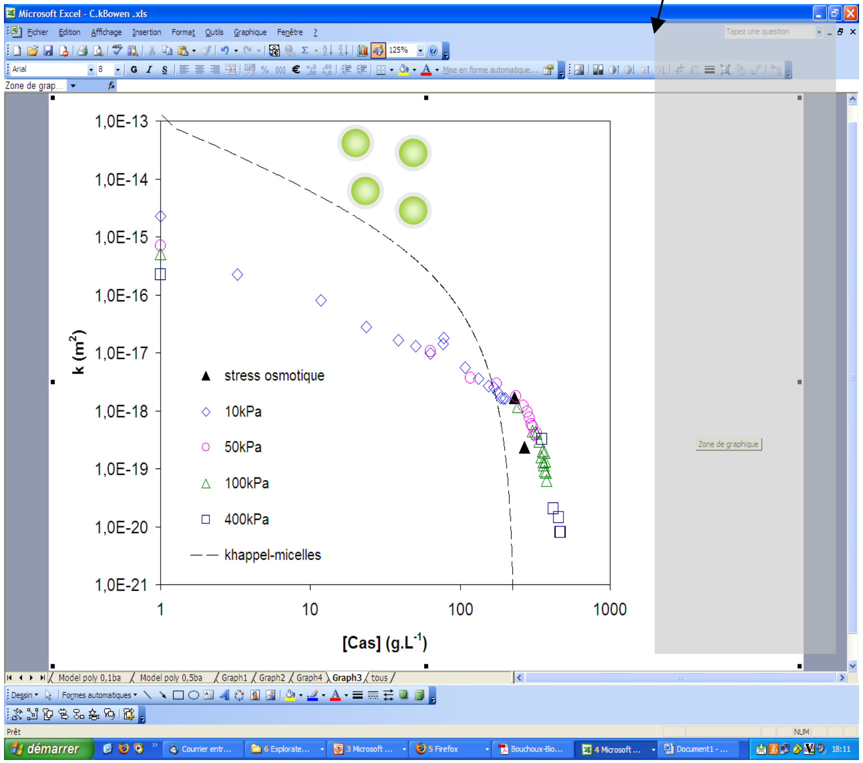
close packing

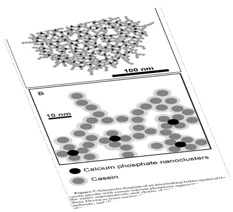


Very different from the "monodispersed hard spheres"

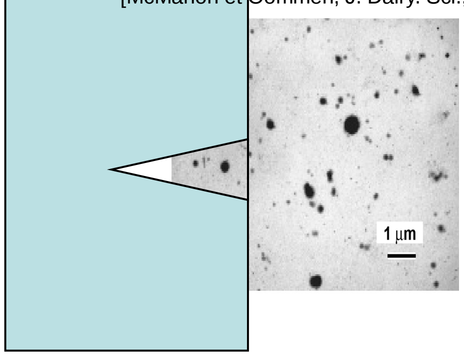
4. Permeability of casein micelles

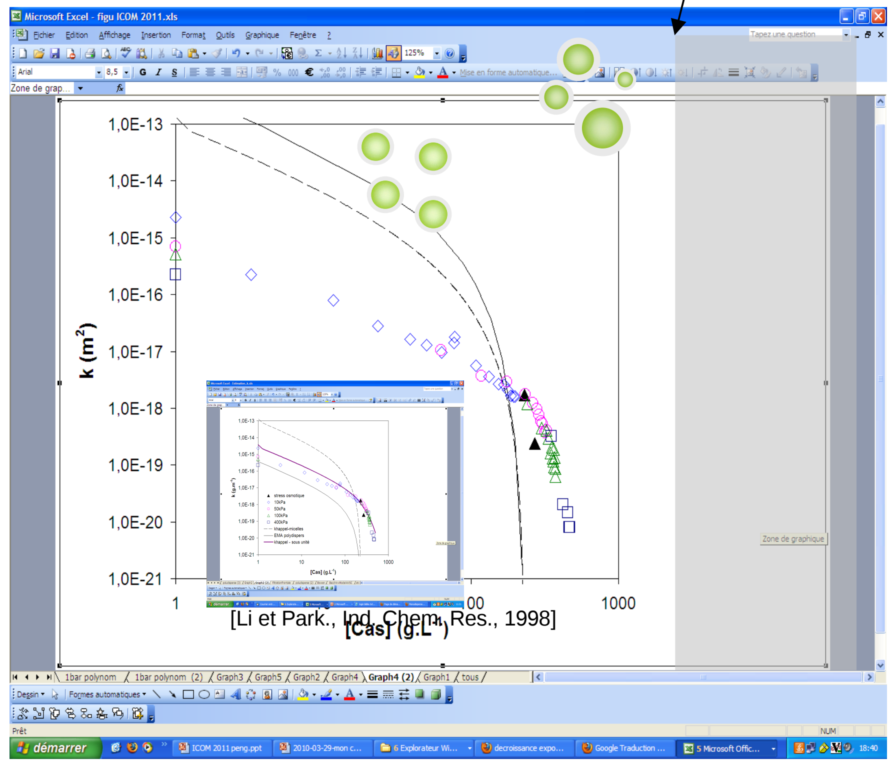
close packing

- **Regime 1 - Before close packing**



[McMahon et Oommen, J. Dairy. Sci., 2008]





[Li et Park., Ind. Chem. Res., 1998]

The difference is not due to the polydispersity

It should not be due to the porosity of micelles

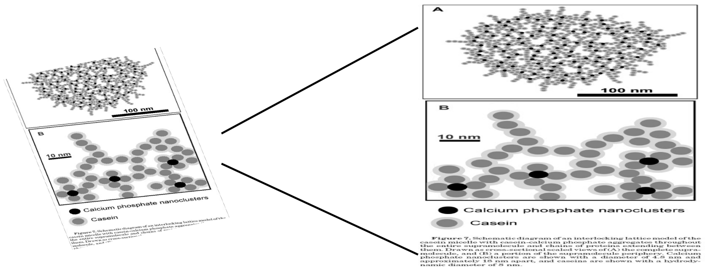
**** dispersions of porous particles are supposed to be more permeable than dispersions of hard particles** [Adade, JCP, 2010]

Other effects (proteins residual from proteolyses of micelles) affect the measurement? work in progress…

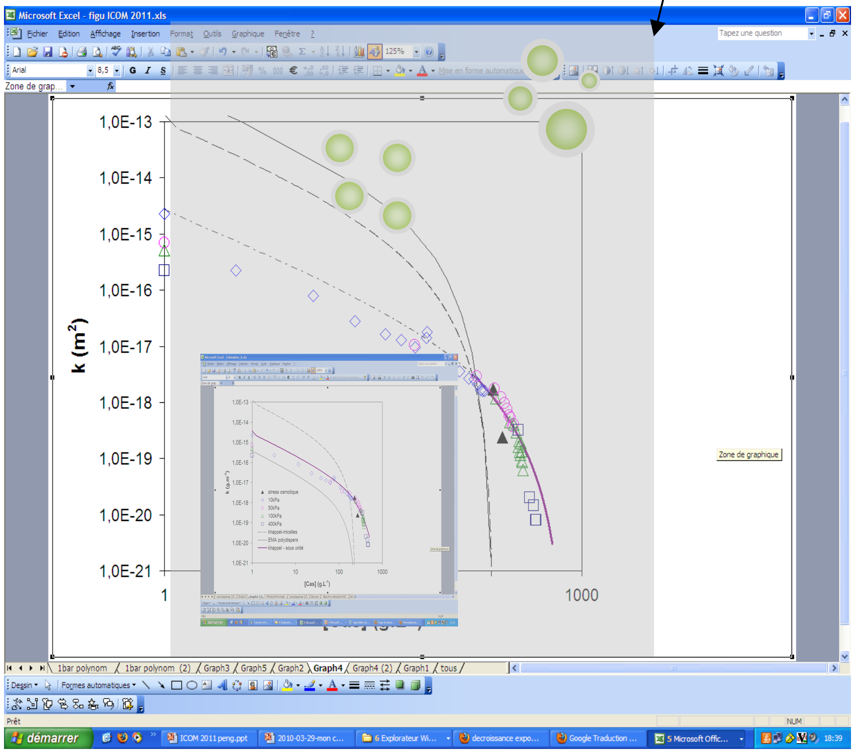
4. Permeability of casein micelles

- **Regime 2 - After close packing**

close packing



rp=4.5nm



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After close packing:

Casein micelles ≈ bags of small spheres

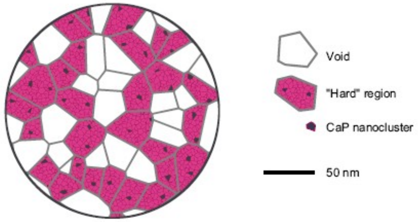
How does the internal organization of casein micelles affect the permeability ?

5. Permeability of modified casein micelles

- **Effect of NaCl 100mM**

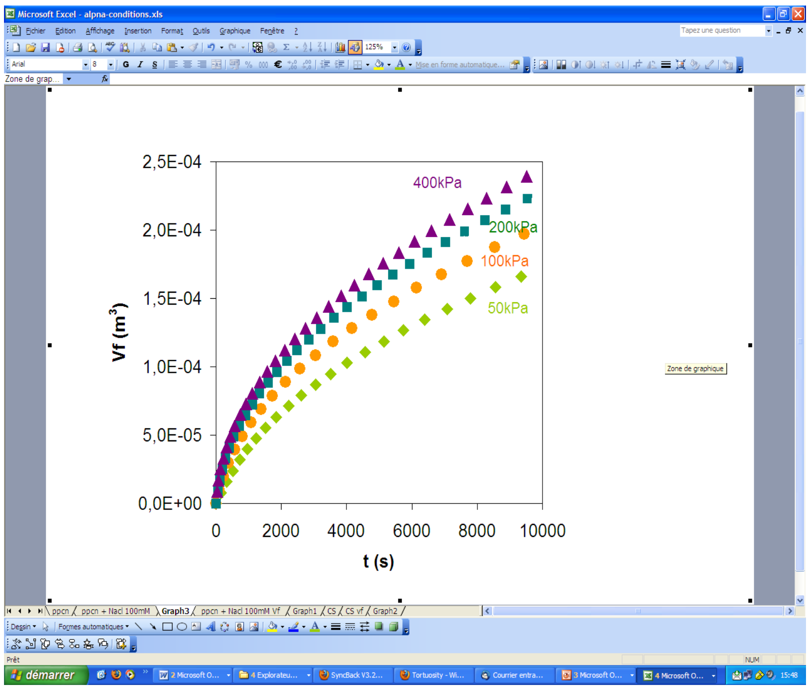
Ca2+ Na+

SA egion ↓

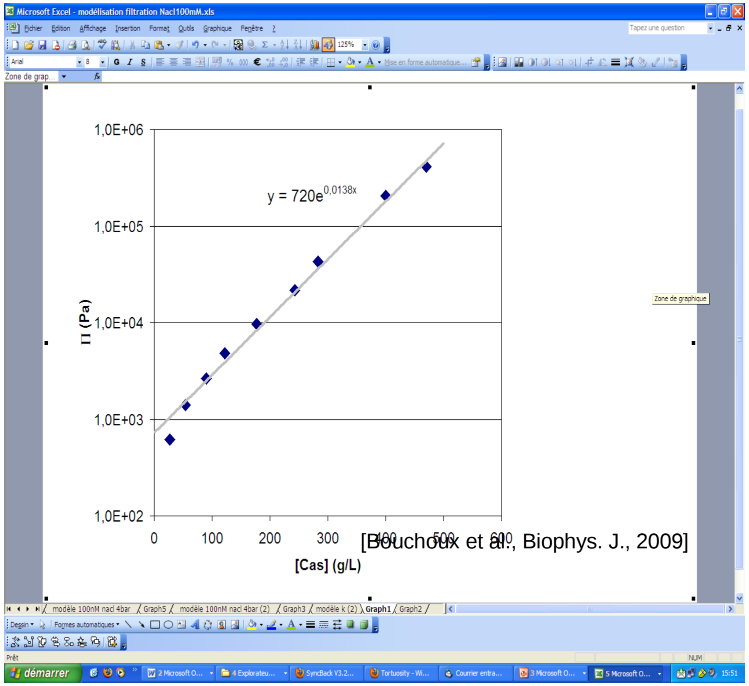


Casein micelles

Filtration experiments



Osmotic pressure

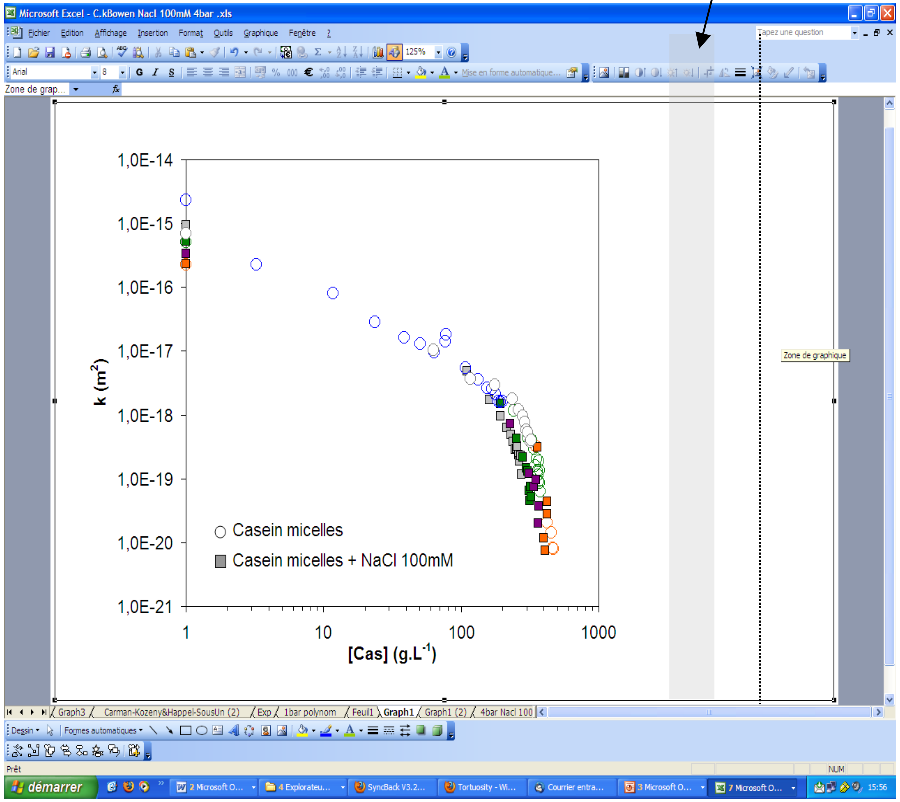


[Bouchoux et al., Biophys. J., 2009]

5. Permeability of modified casein micelles

- **Effect of NaCl 100mM**

close packing



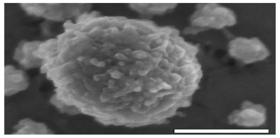
180-350 g/L, permeability is limited by the addition of 100mM NaCl

 More tortuous or less porous structure

>350 g/L, the permeabilities of the two dispersions become similar

5. Permeability of modified casein micelles

- **Sodium Caseinate**



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Casein micelles

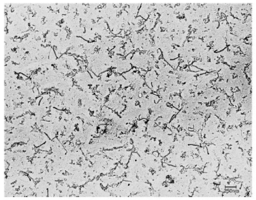
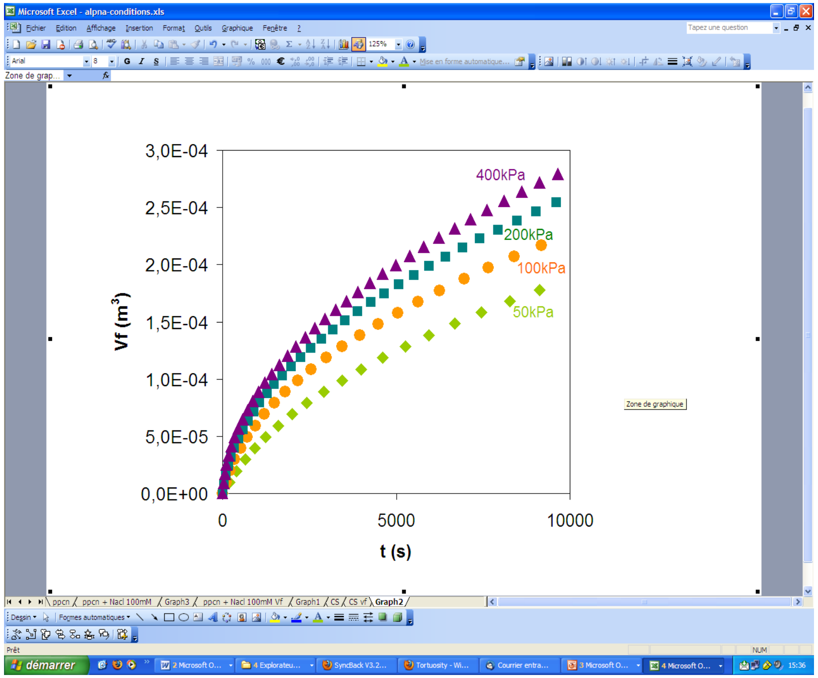


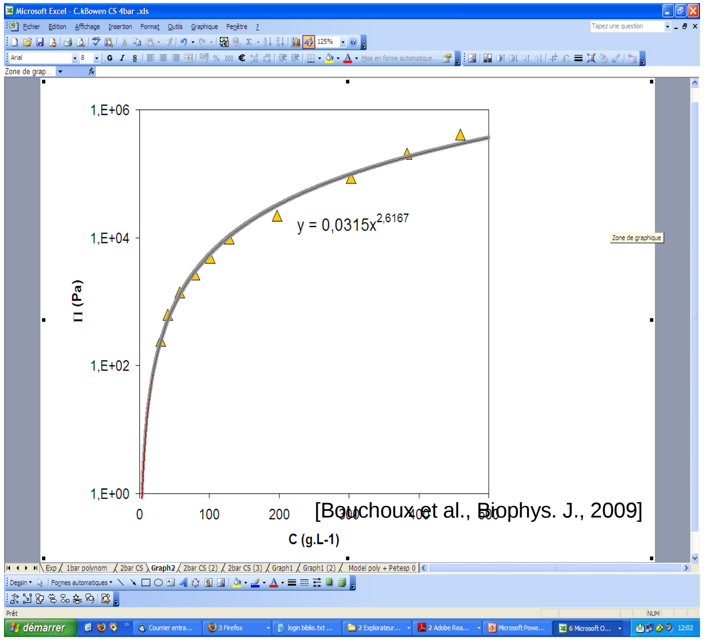
Fig. 4. Electron micrograph of 0.25% caseinate.

Sodium caseinate

Filtration experiments



Osmotic pressure

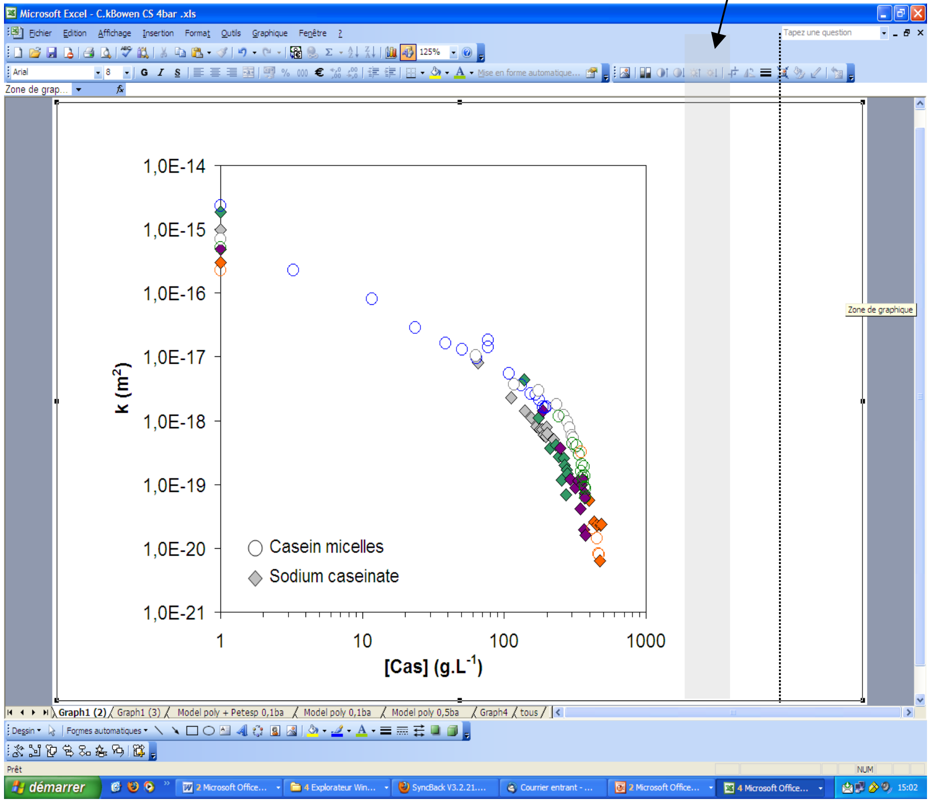


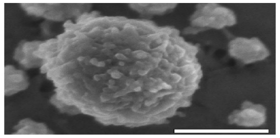
[Bouchoux et al., Biophys. J., 2009]

5. Permeability of modified casein micelles

- **Sodium Caseinate**

close packing





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Casein micelles

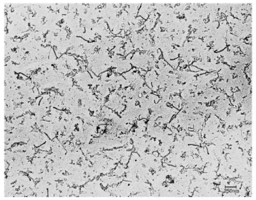


Fig. 4. Electron micrograph of 0.25% caseinate.

Sodium caseinate

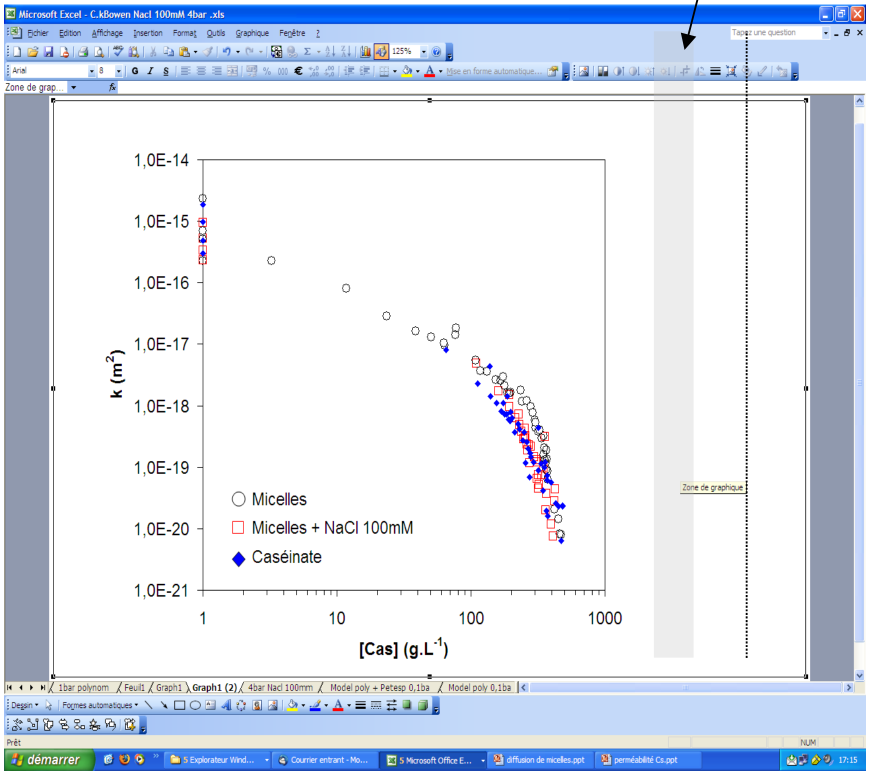
150-350 g/L, sodium caseinate dispersion is less permeable

 More tortuous or less porous structure

>350 g/L, the permeabilities of the two dispersions become similar

5. Permeability of modified casein micelles

close packing

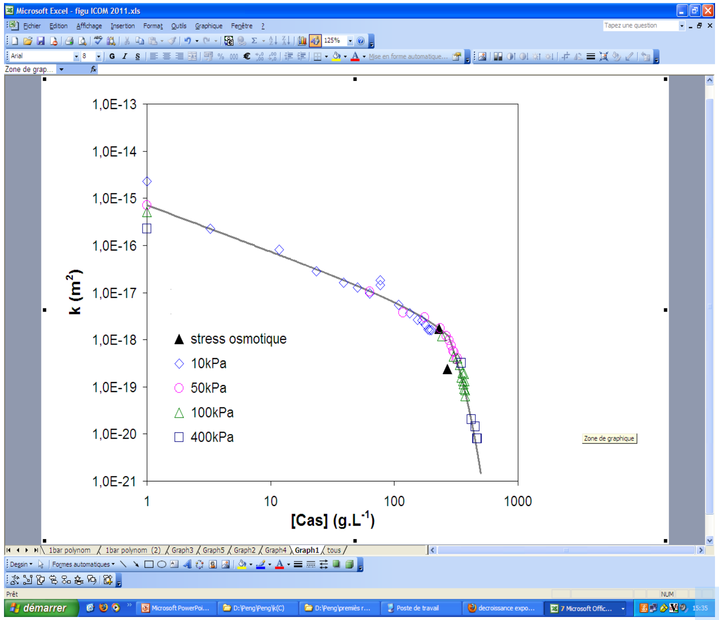


After close packing: the permeability is limited while the salt is added or the micelles are dissociate **More tortuous or less porous structure**

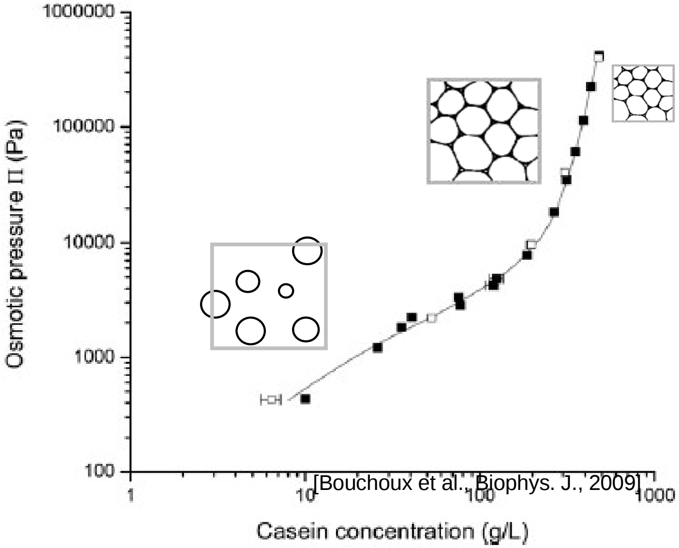
>350 g/L, the permeability is less dependent of the different conditions
 Whatever its initial structure, the system becomes homogeneous when it is highly packed

6. Model validation

Permeability



Osmotic pressure



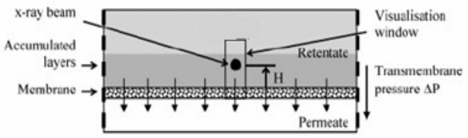
[Bouchoux et al., Biophys. J., 2009]

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

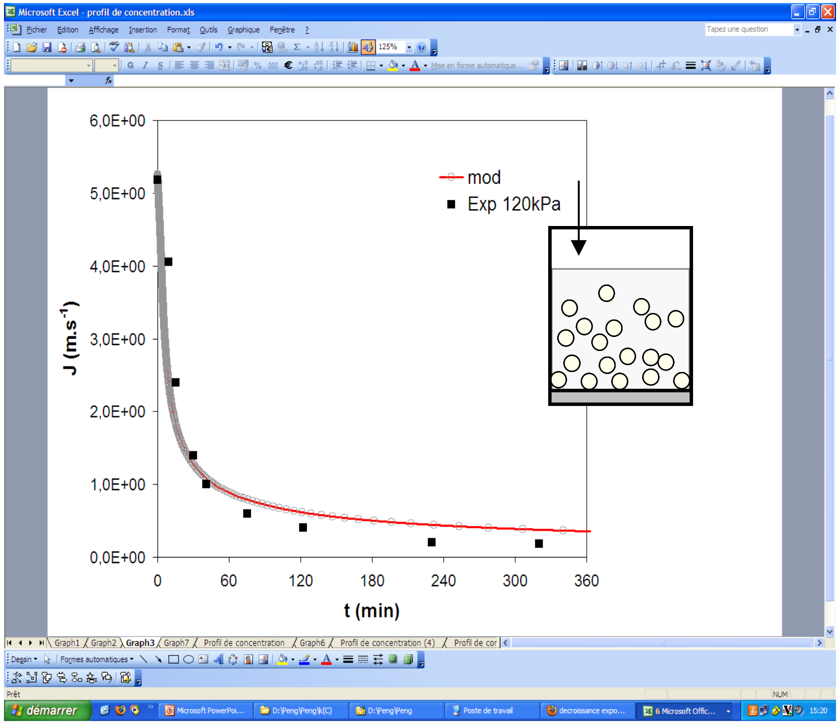
Prediction is possible

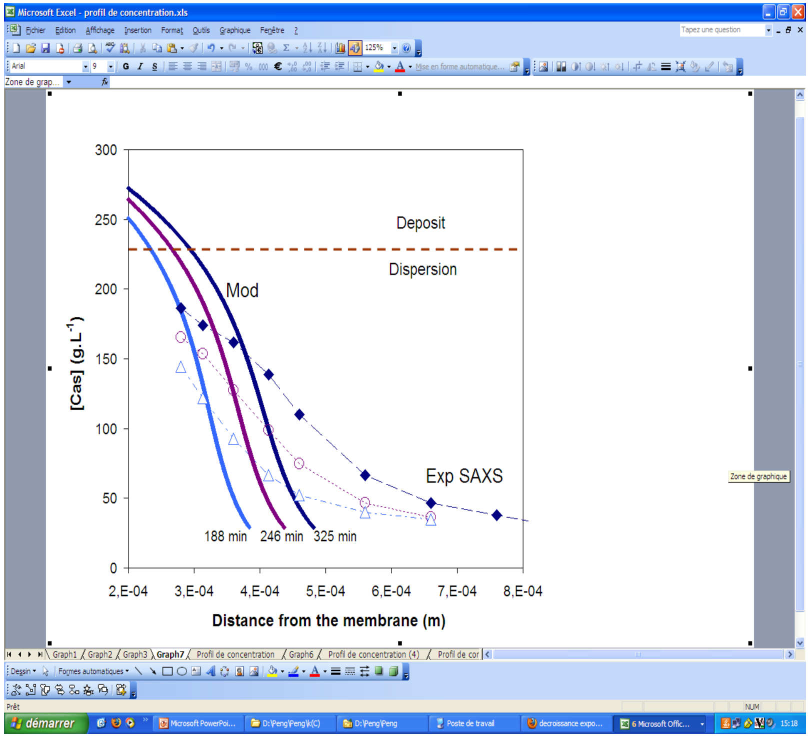
6. Model validation

- **Prediction vs. experimental results**



[David et al.,Langmuir, 2008]



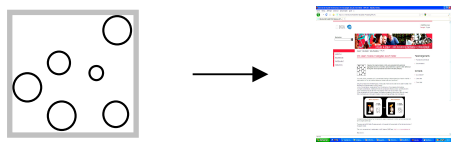


The results are satisfying and encouraging

7. Conclusion

1. We determined the **permeability of dispersions of permeable and compressible colloids**

2 regimes = before and after close-packing



2. Casein micelles are **individually permeable**, the permeability can be limited while the salt is added or the micelles are dissociated.

3. Able to **predict the filtration of soft objects** – General model for colloids

In the future…

Continue to understand how the permeability is affected by the organization of casein molecules in the micelles? What are the consequences on the filtration?

pH? Internal cross linking by enzyme?...

Thanks to Mr. Patrice Bacchin.

Thank you.