

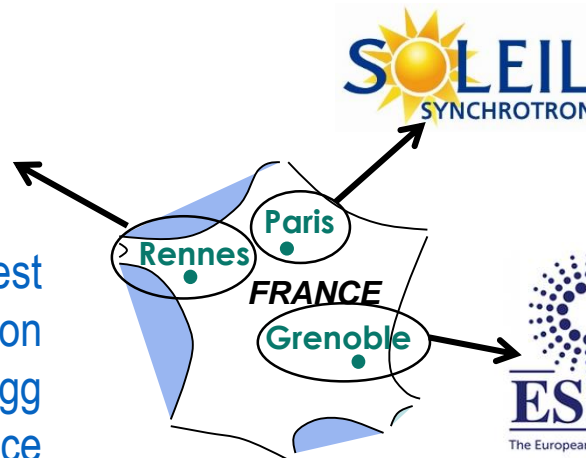
Structural organization of casein micelles concentrated layer during cross-flow ultrafiltration

Floriane Doudiès

M. Loginov, N. Hengl, F. Pignon, N. Leconte, F. Garnier-Lambrouin, J. Pérez, L. Sharpnack, M. Granger-Delacroix, M. Belna, G. Gésan-Guiziou

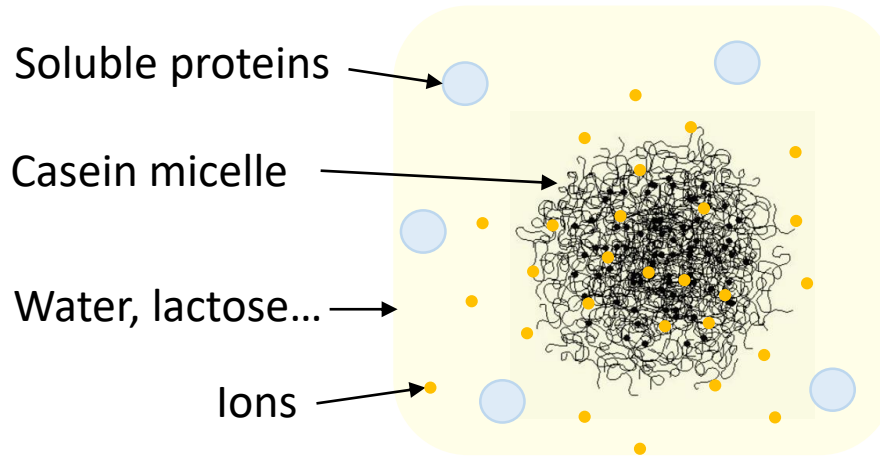


UMR 1253 STLO INRA-Agrocampus Ouest
Joint Research Unit on
Science & Technology of Milk & Egg
F-35000 Rennes, France



Laboratoire Rhéologie
et Procédés

Skimmed milk:



Casein micelles are large globular aggregates of caseins with calcium phosphate, they are **porous, deformable, compressible and dynamic particles (50-500nm)**

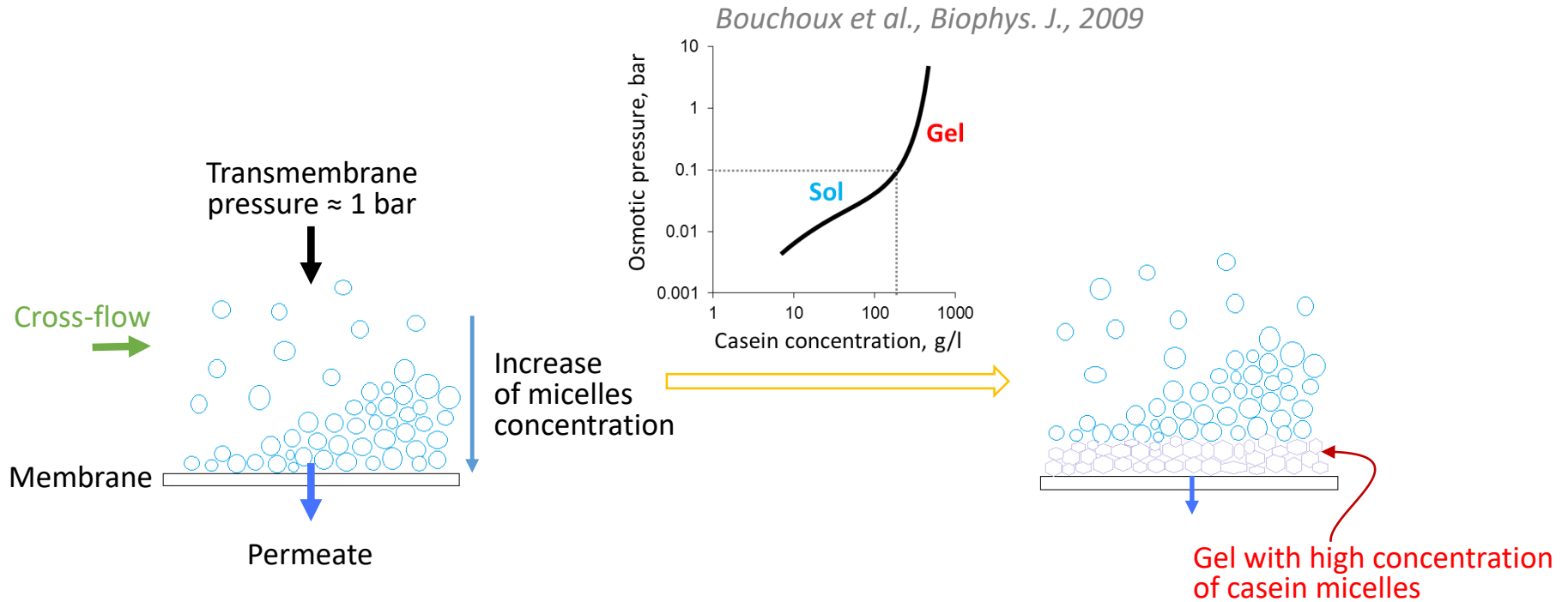
Micro- and ultrafiltration of skimmed milk are largely used in the dairy sector
 (≈ 40% of the membrane area installed in food sector)

ultrafiltration → **proteins concentration** (cheese manufacture, standardization)

microfiltration → **proteins fractionation** (high added value ingredients)



Membrane fouling by casein micelles



Formation of fouling gel layer:

- limitation of the filtration performance

reduces permeate flux, decreases permeate quality (low transmission of soluble proteins)

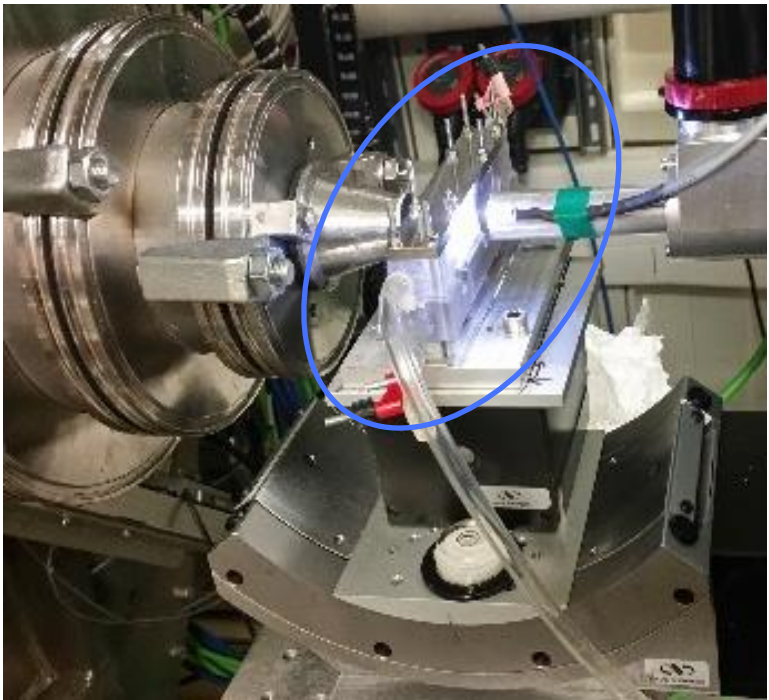
- difficulties of cleaning operation

large consumption of water, detergents and energy...

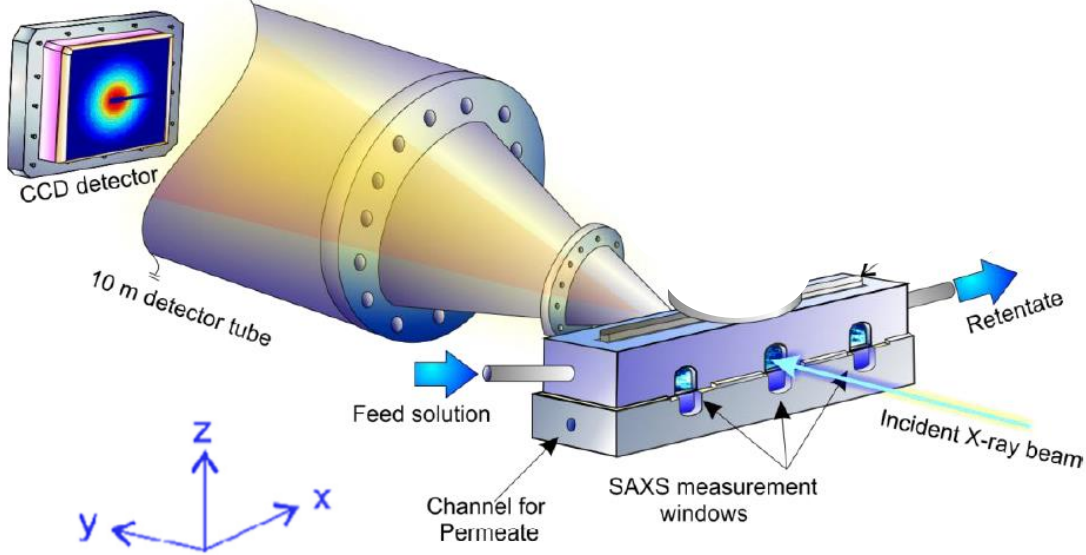
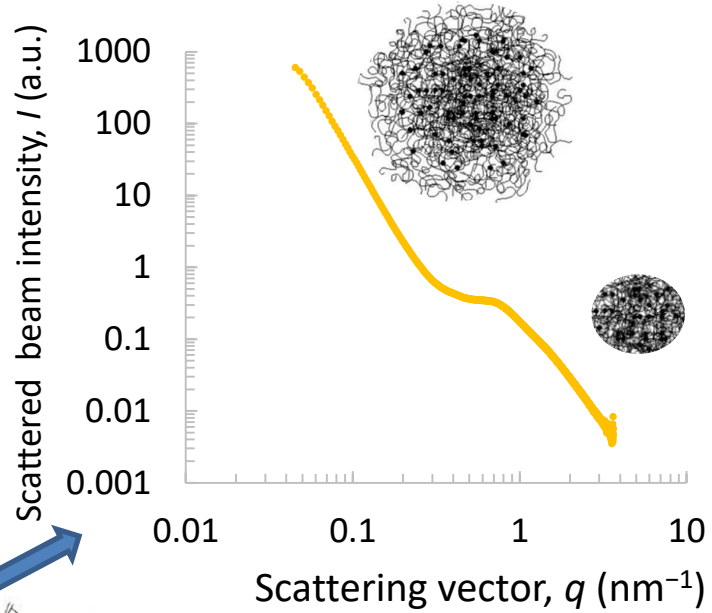
The structural organization and behaviour of concentrated casein micelles in fouling layer during cross-flow ultrafiltration

- to analyse fouling layer development during filtration step and redispersion during pressure relaxation step
- to focus on the effect of temperature
- to perform *in situ* Small-Angle X-ray Scattering (SAXS) cross-flow filtration

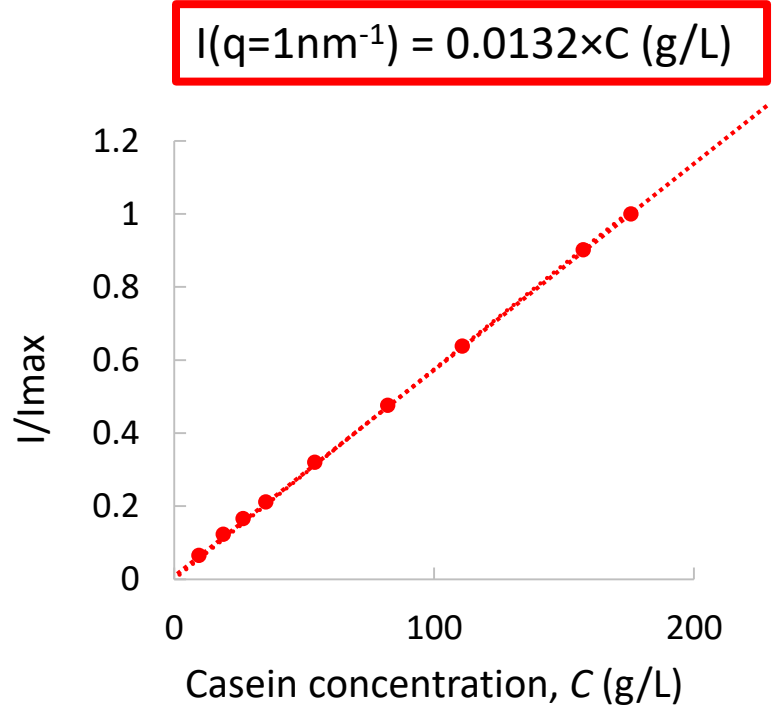
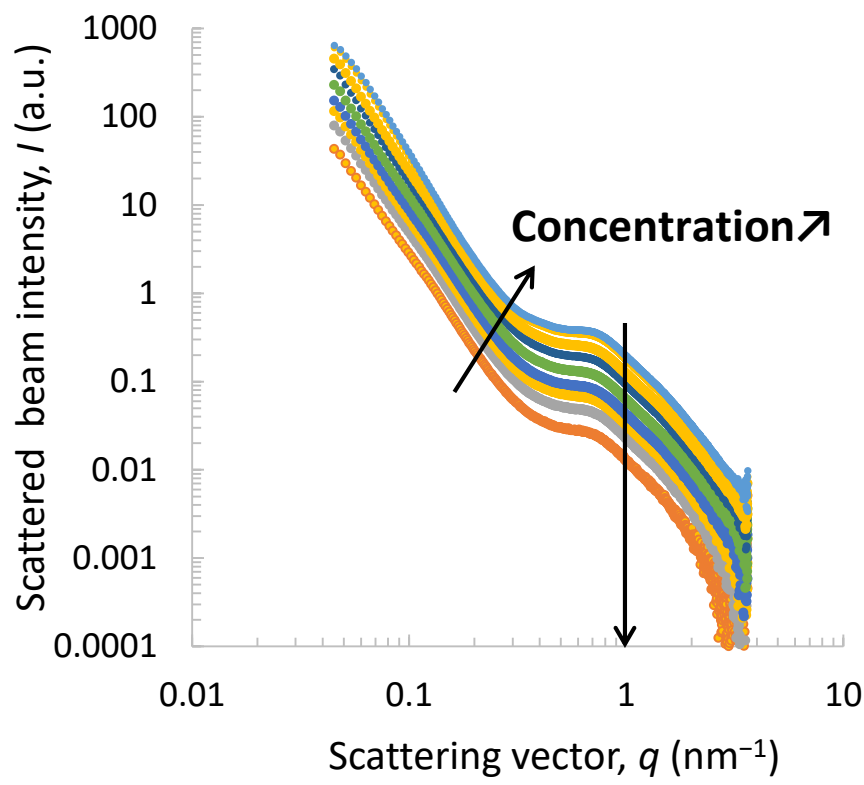
In-situ SAXS cross-flow filtration

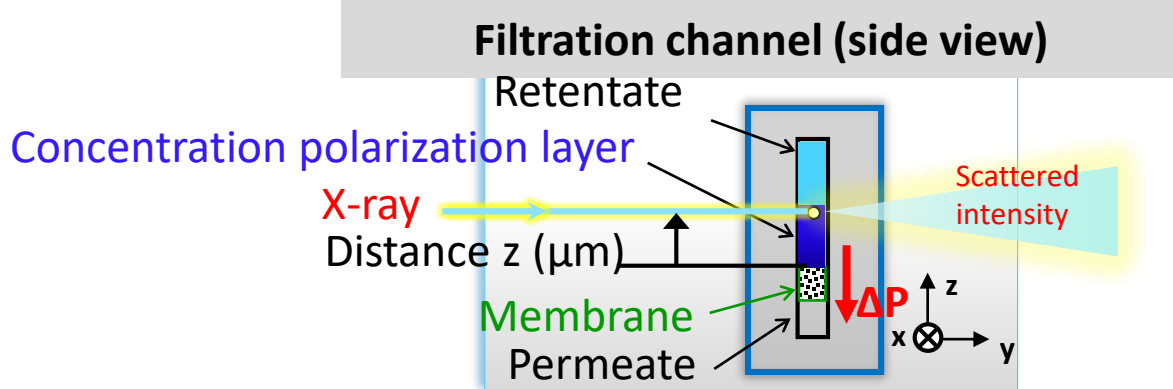
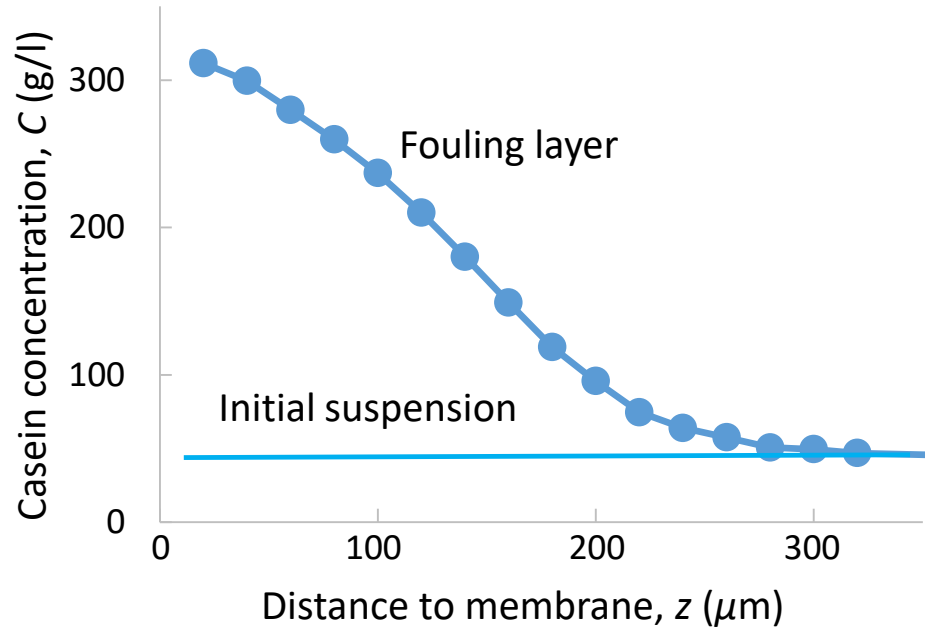
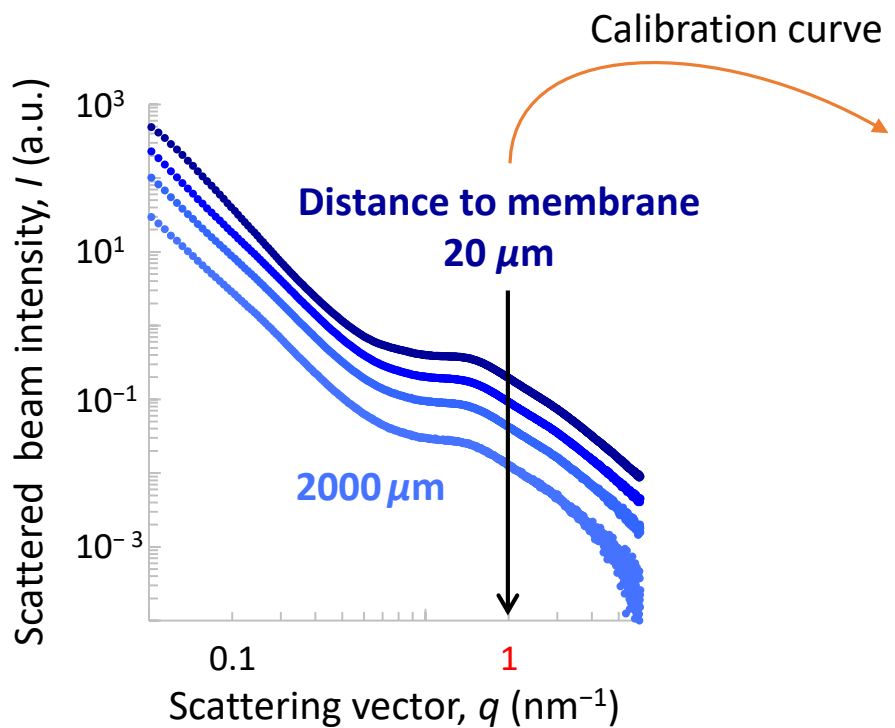


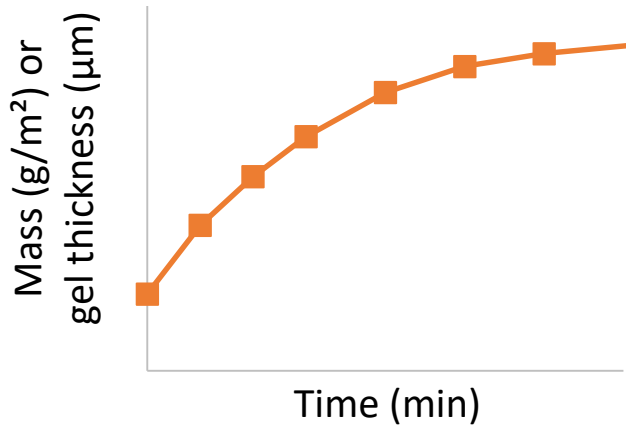
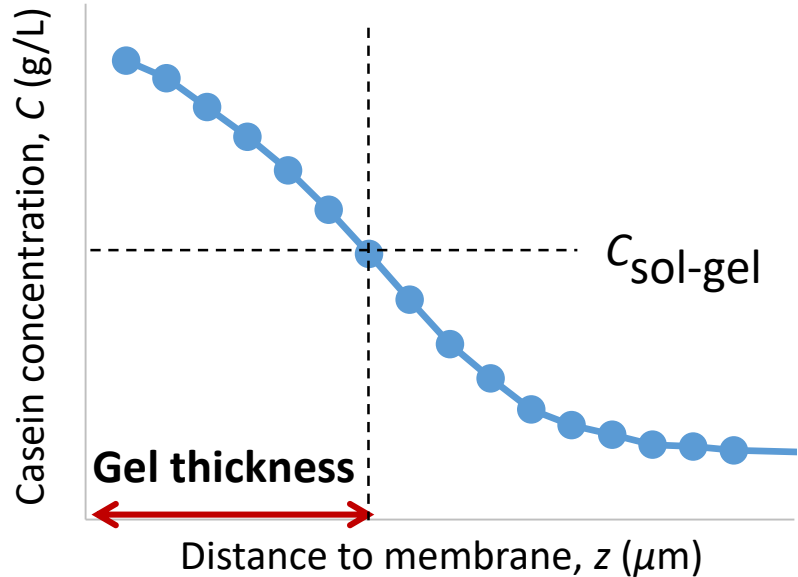
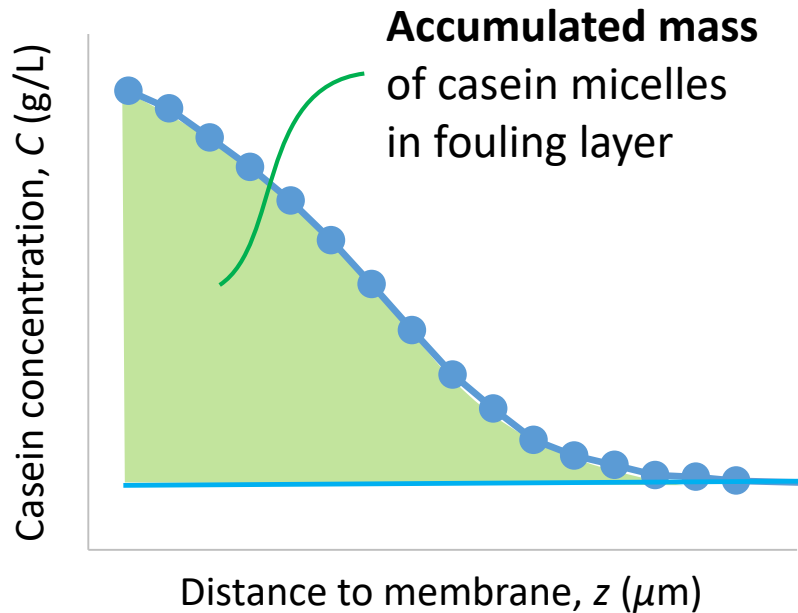
Spatial resolution 20 μm



Jin et al., J.Memb. Sci., 2014







Concentration of sol-gel transition:
12°C – 150 g/l
25°C – 174 g/l
42°C – 181 g/l
(from Nöbel et al., *Int. Dairy J.*, 2016)

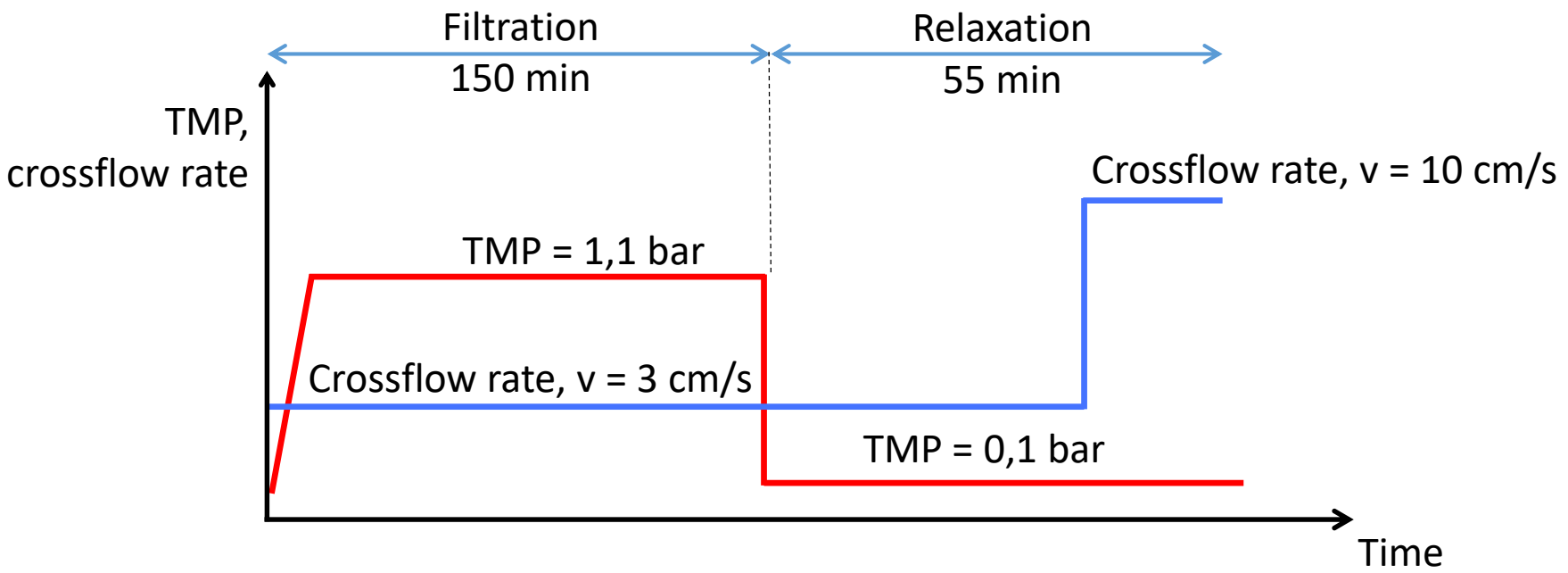
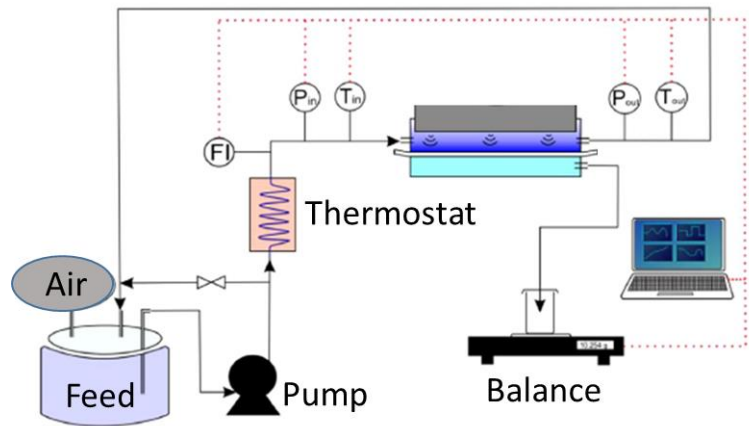
Filtration protocol

Suspension:

50 g/L of casein micelles in milk ultrafiltrate

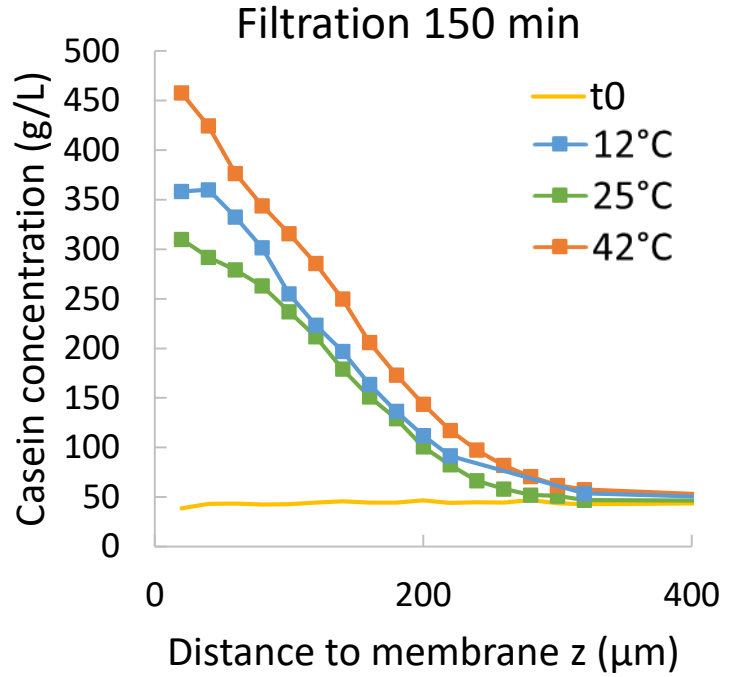
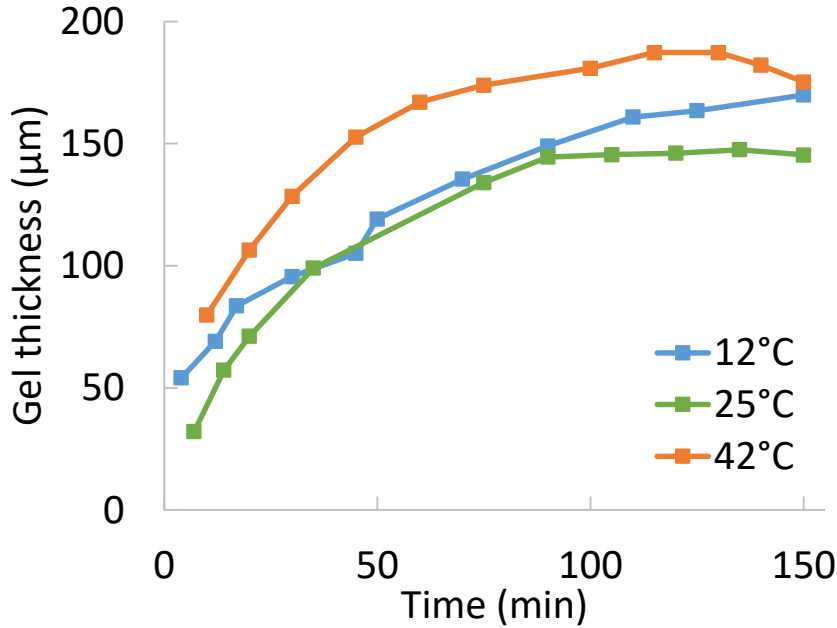
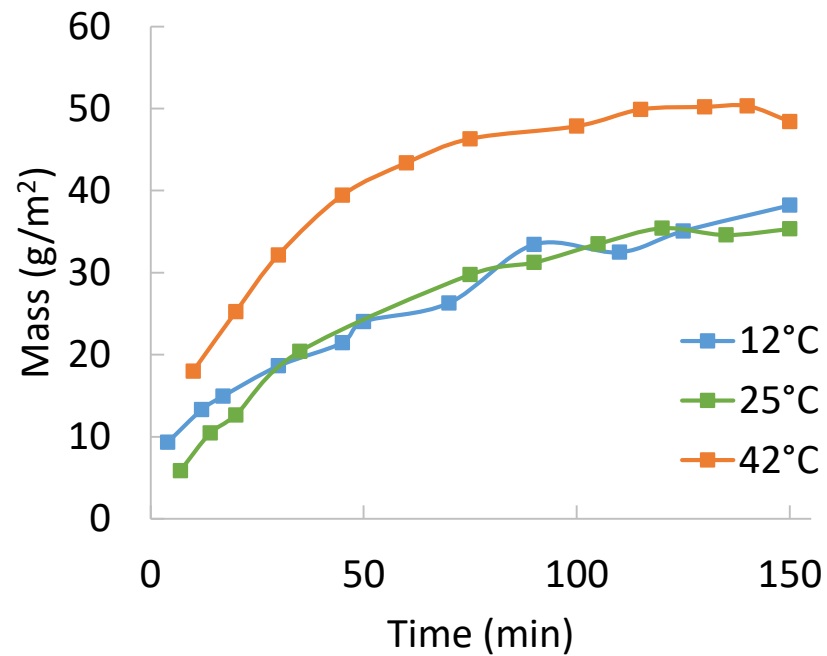
Temperature: 12, 25 or 42°C

Filtration cycle: 2 steps



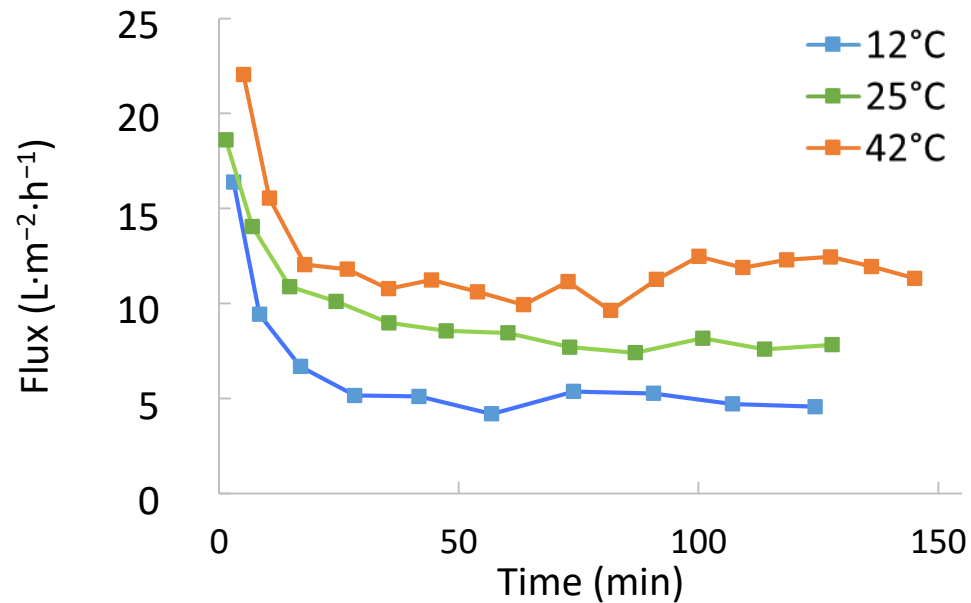
Filtration step

TMP = 1.1 bar
v = 3cm/s



Accumulated mass and gel thickness **rise over time**

At **42°C**, accumulation is **faster** and more **important**, gel is more **concentrated** and **thicker** than at 12 or 25°C



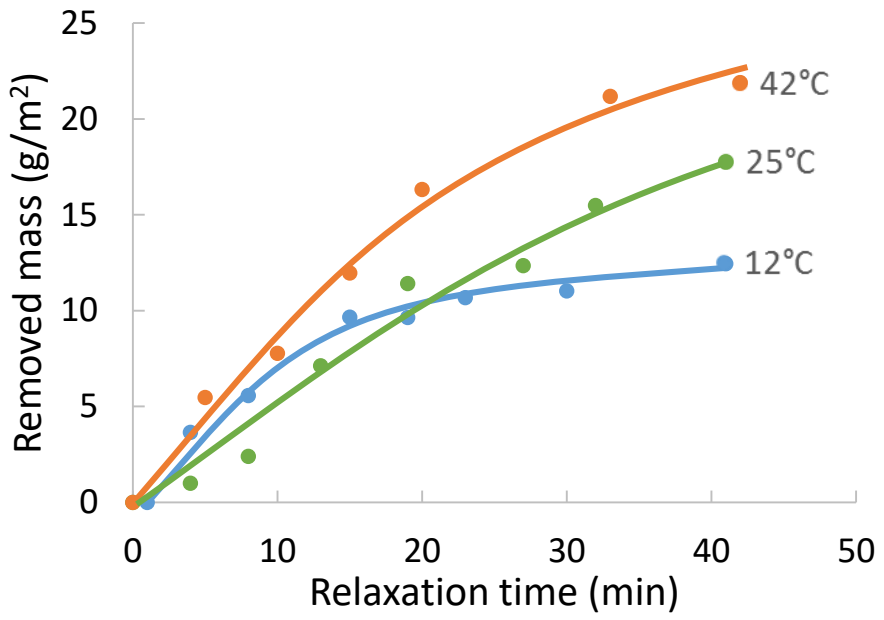
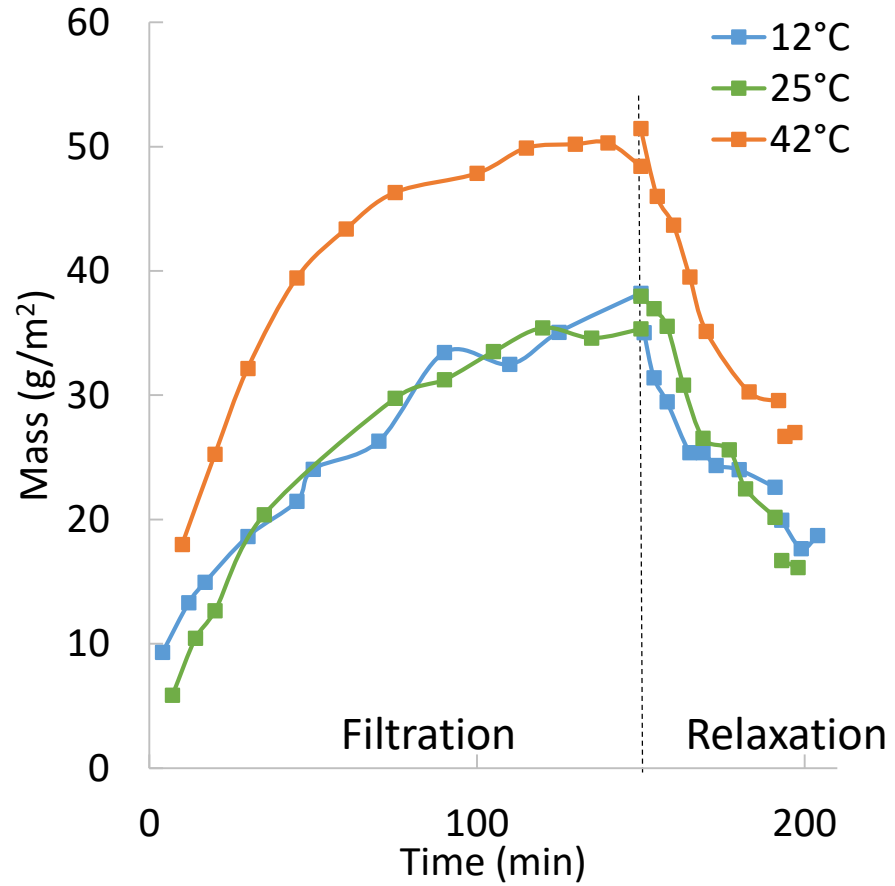
Permeate flux **decreases over time** for each temperature

With temperature **decreasing**, fouling layer **less permeable**

Fouling rate and intensity due to the **lower filtrate viscosity and higher filtrate flux**

Pressure relaxation step

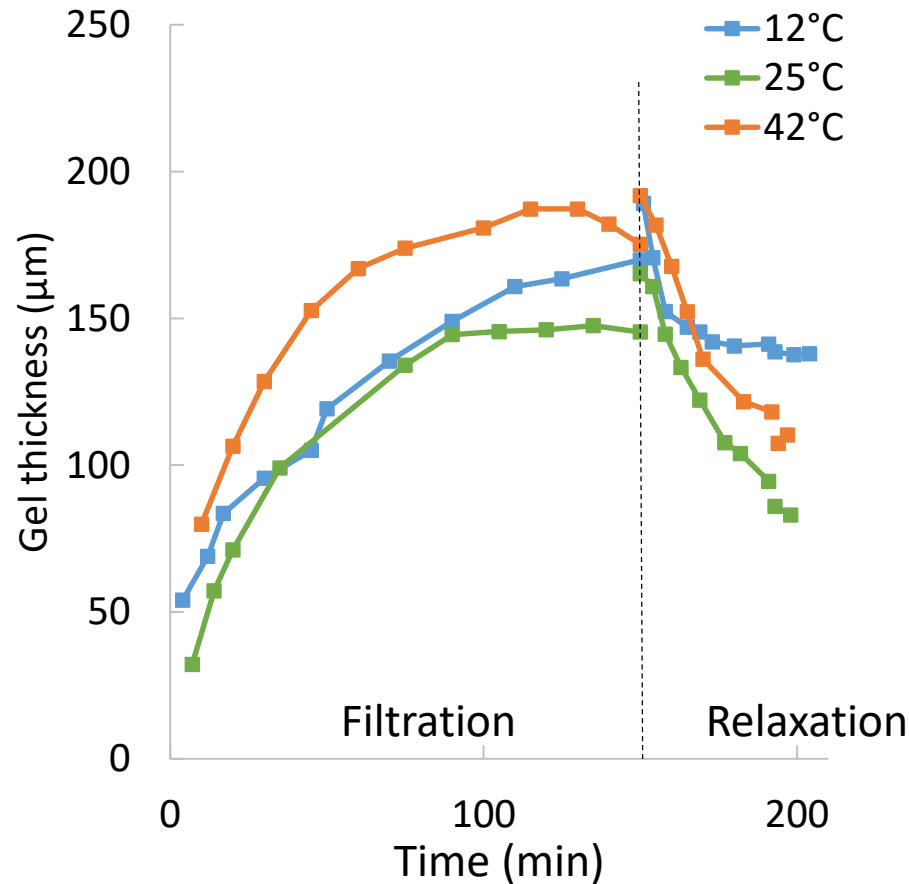
TMP = 0.1 bar
 v = 3cm/s and 10cm/s



Relaxation step allowed to remove a **part** of polarized layer **without using chemical products, ultrasound...**

But, relaxation time is comparable with accumulation time, relatively slow

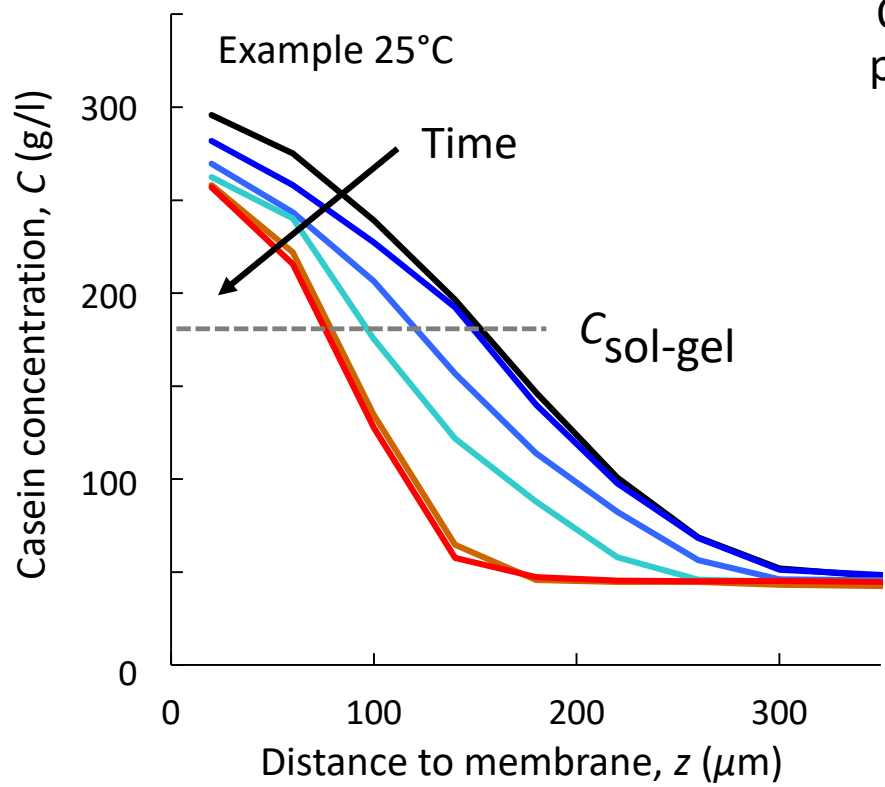
Removed mass **rises with temperature**



Gel removal follows same trend as total accumulated matter removal: starts simultaneously with pressure decrease, at the very beginning of relaxation step

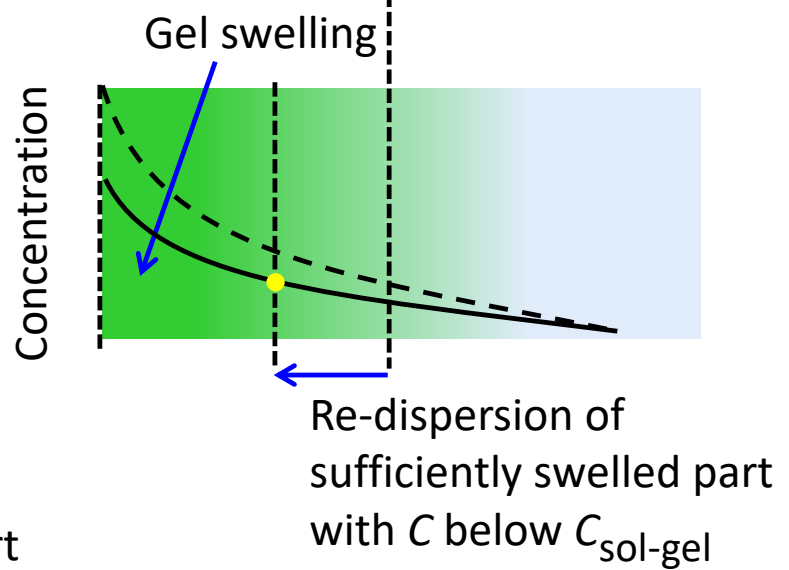
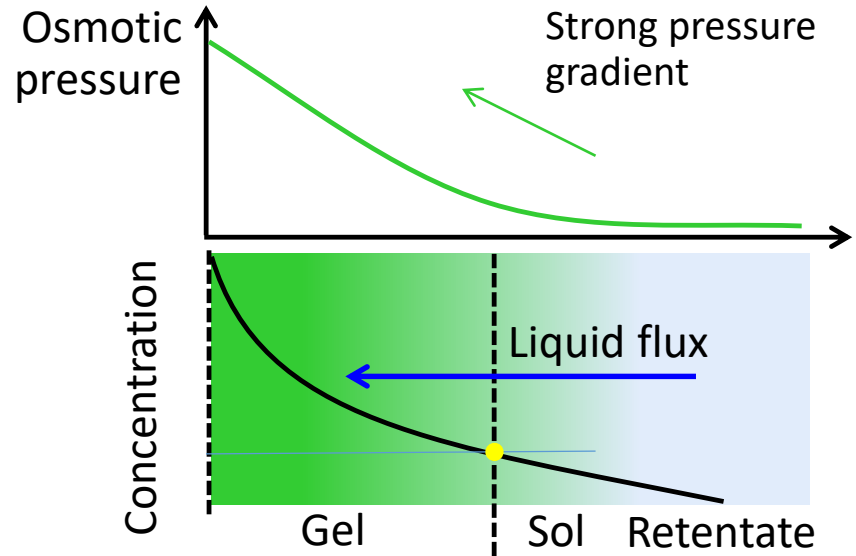
At 12°C, less accumulation than at 42°C but it is removed with **difficulty**

Gel behaviour after pressure release

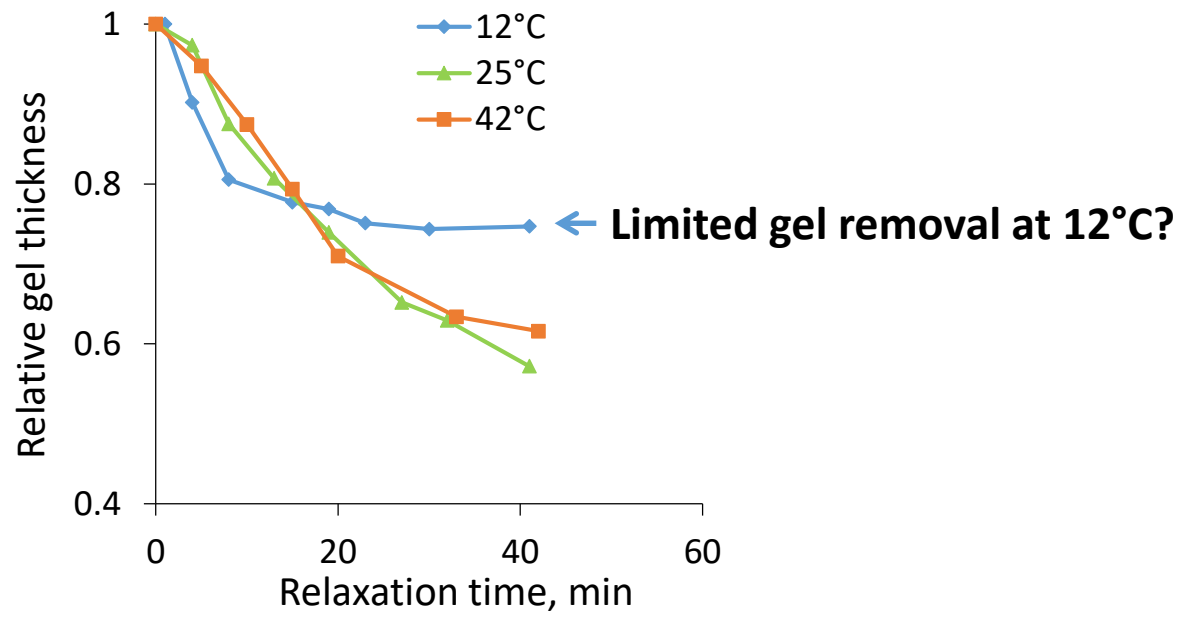


Simultaneous decreasing of gel thickness and concentration from beginning of relaxation

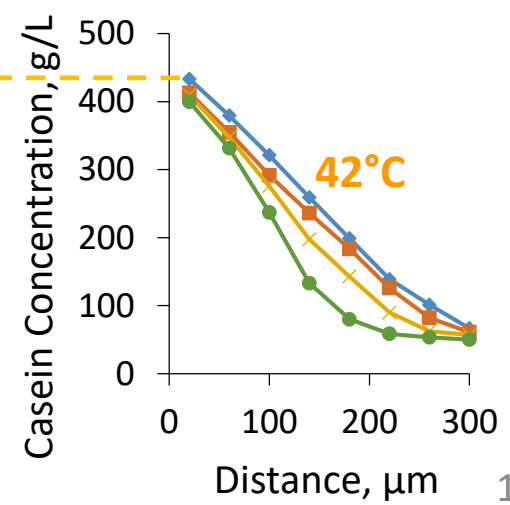
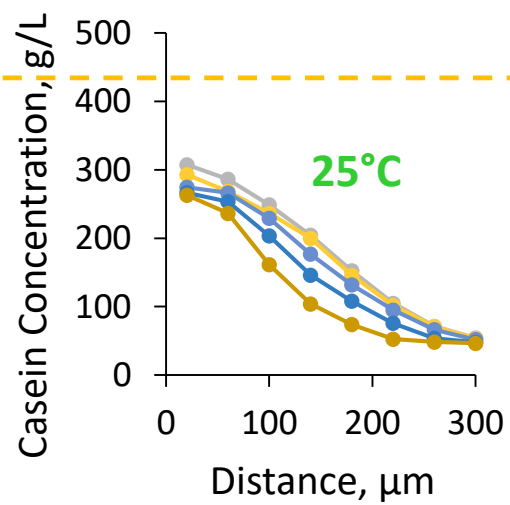
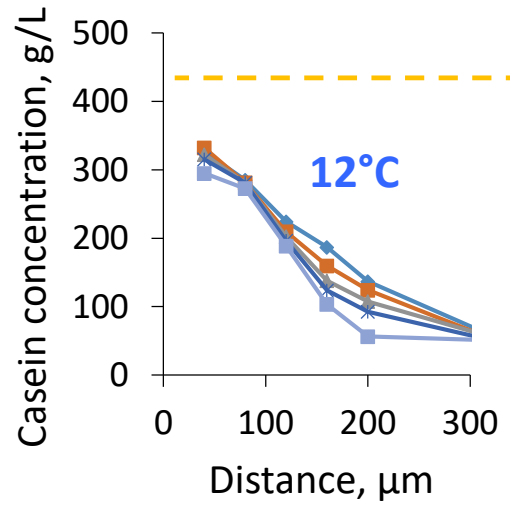
Fouling removal via gel swelling and re-dispersion of external swelled part



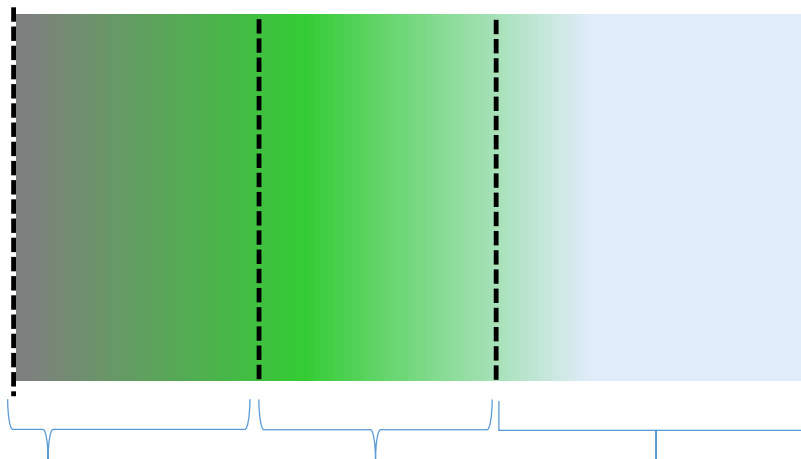
Impact of temperature on gel relaxation



Concentration profiles during relaxation at different temperatures (same Y-axis scale)



Schematic presentation of fouling layer

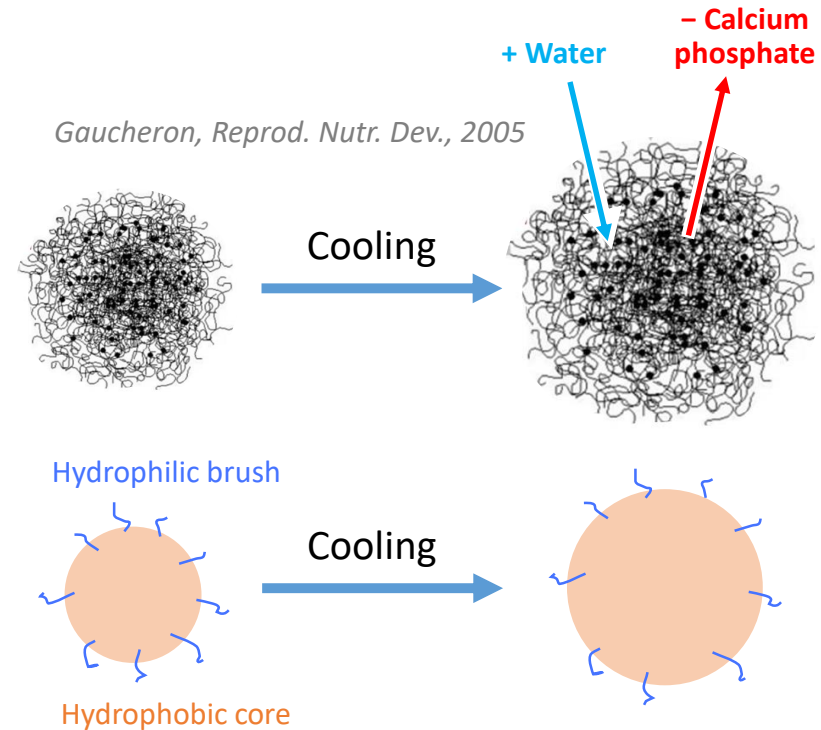


Gel that swells but doesn't re-disperse

Gel that re-disperses after swelling

Sol

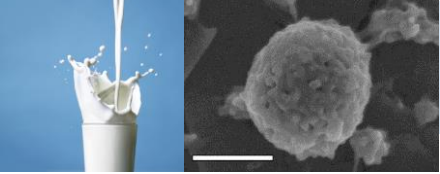
Observed at moderate gel concentration (12°C)
Not observed at highest concentration (42°C)
→ **Nature of fouling (repulsive gel/attractive gel) depends on temperature**



Gaucheron, Reprod. Nutr. Dev., 2005

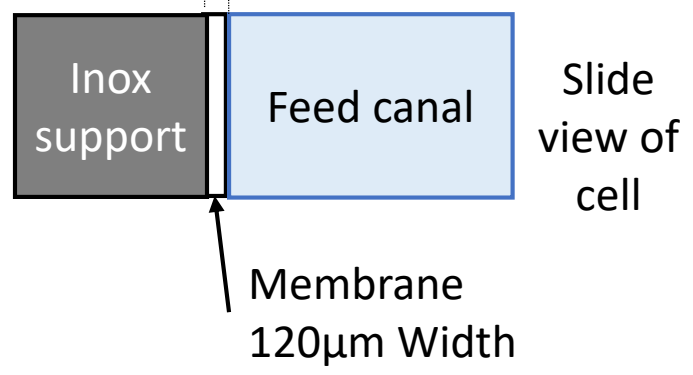
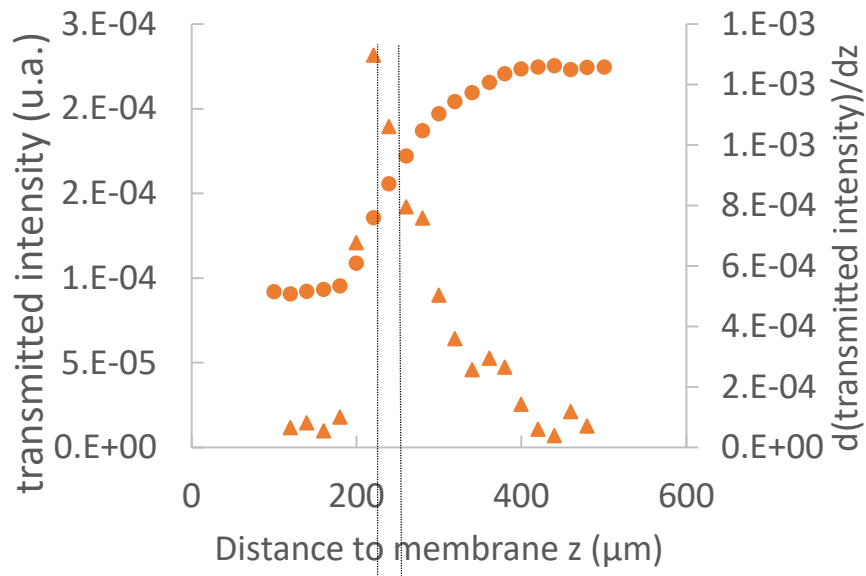
Lower steric barrier density – more open surface for interactions (gelling)?

- In-situ SAXS cross-flow filtration allowed analysis of casein micelles fouling layer with a unique resolution of 20 μ m during filtration step and relaxation step
- Fouling rate and fouling intensity (quantity of accumulated micelles and gel thickness) increase with temperature due to the lower filtrate viscosity and higher filtrate flux
- Important part of fouling can be reduced by simple pressure relaxation
- The fouling by casein micelles is removed through the swelling-dissolution mechanism
- A limited efficiency of pressure relaxation at 12°C can be explained by transformation of repulsive gel (swells and dissolves) into attractive gel (swells but does not dissolve)
- In the future:
 - 1) local microstructure
 - 2) rheological characterization of gels at different temperatures
 - 3) study of cross-flow, time and transmembrane pressure effects on gel properties in fouling layer

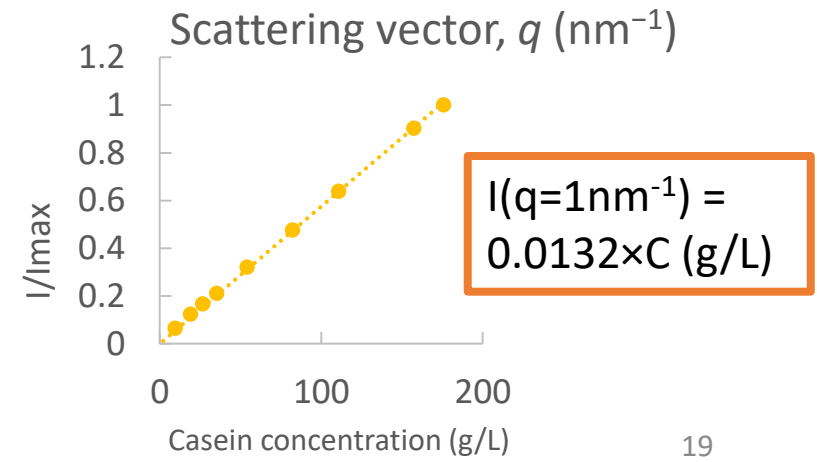
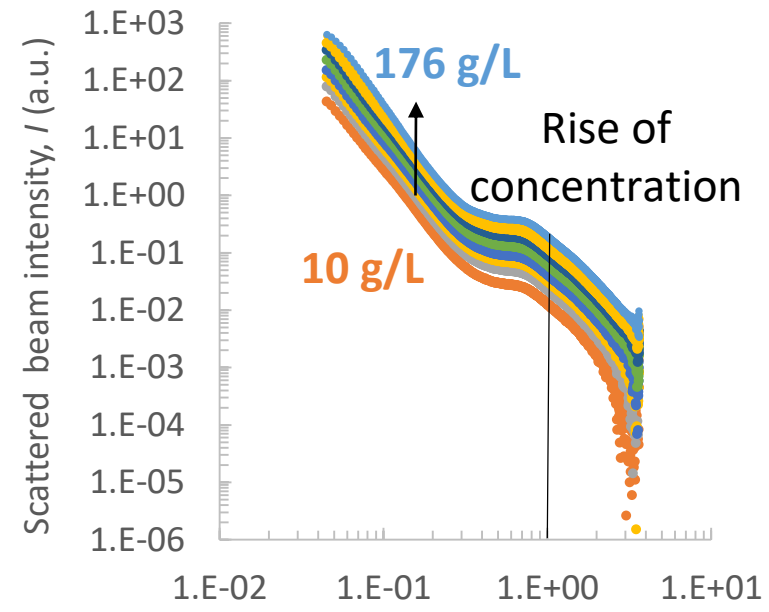


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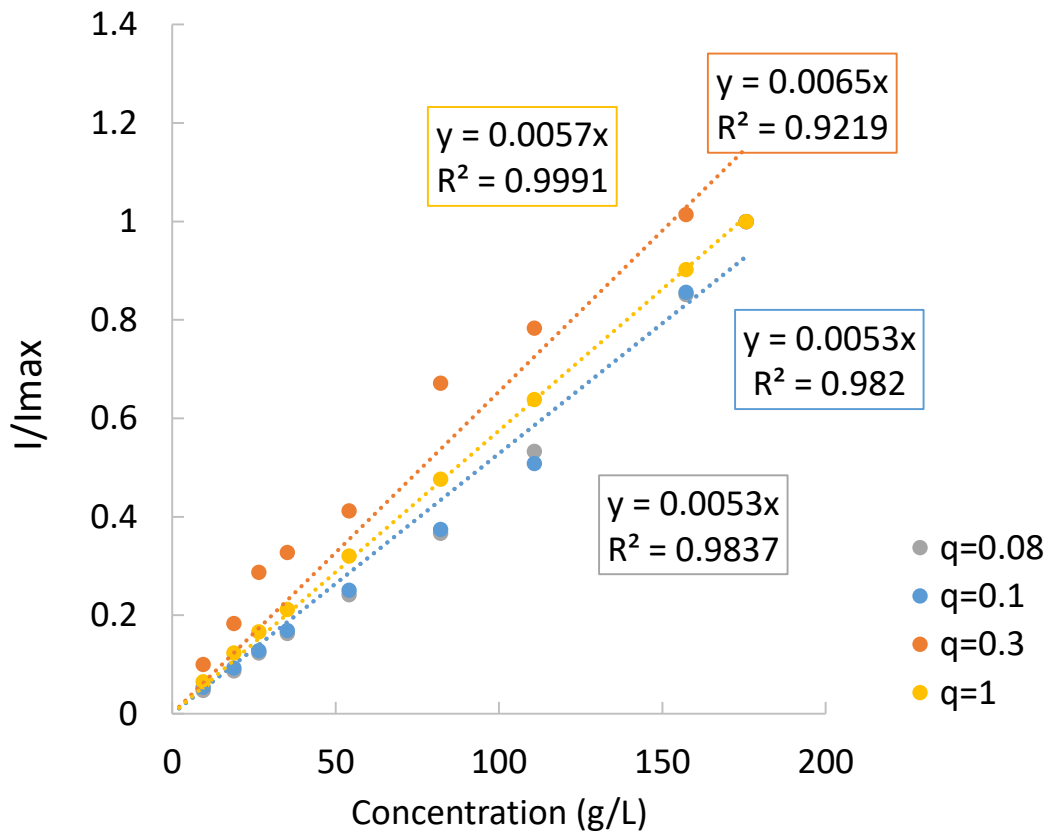
1) Zero membrane placement



2) Calibration in static

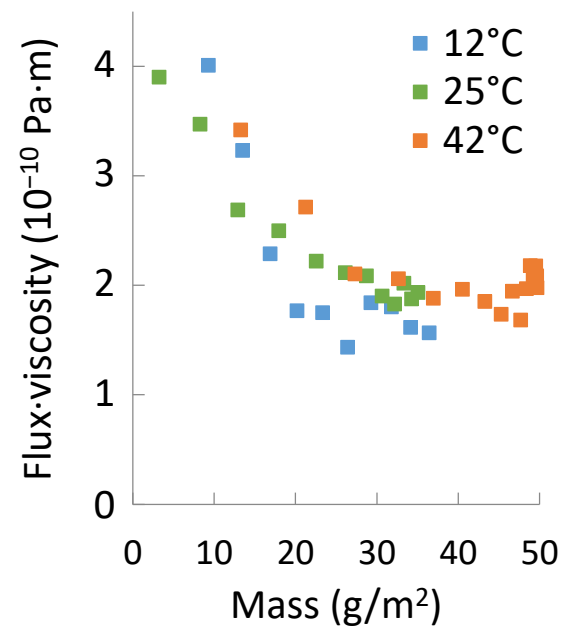
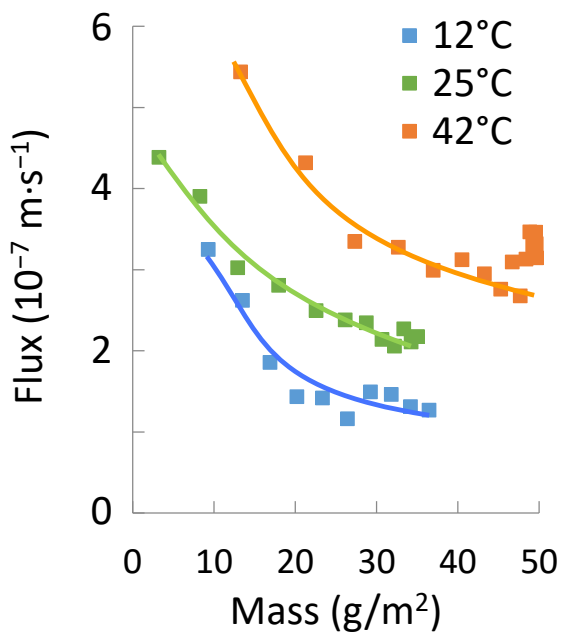
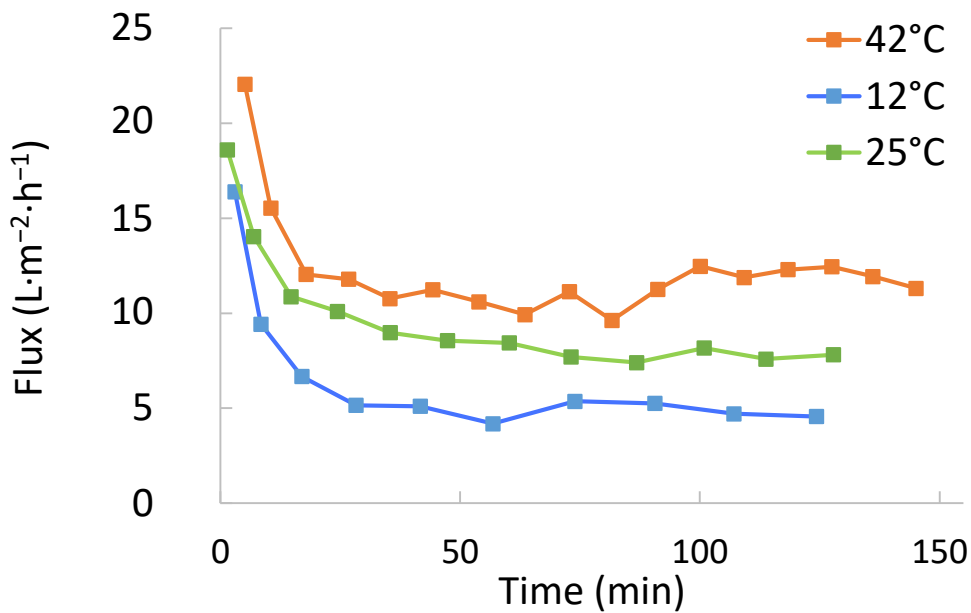


Calibration at different scattering vectors



Filtration kinetics

TMP = 1.1 bar
 $v = 3\text{cm/s}$



Accumulation mass **impacts** permeate flux

Viscosity corrects difference of flux observed for different temperatures