Nanoparticles at interfaces

D. Carrière

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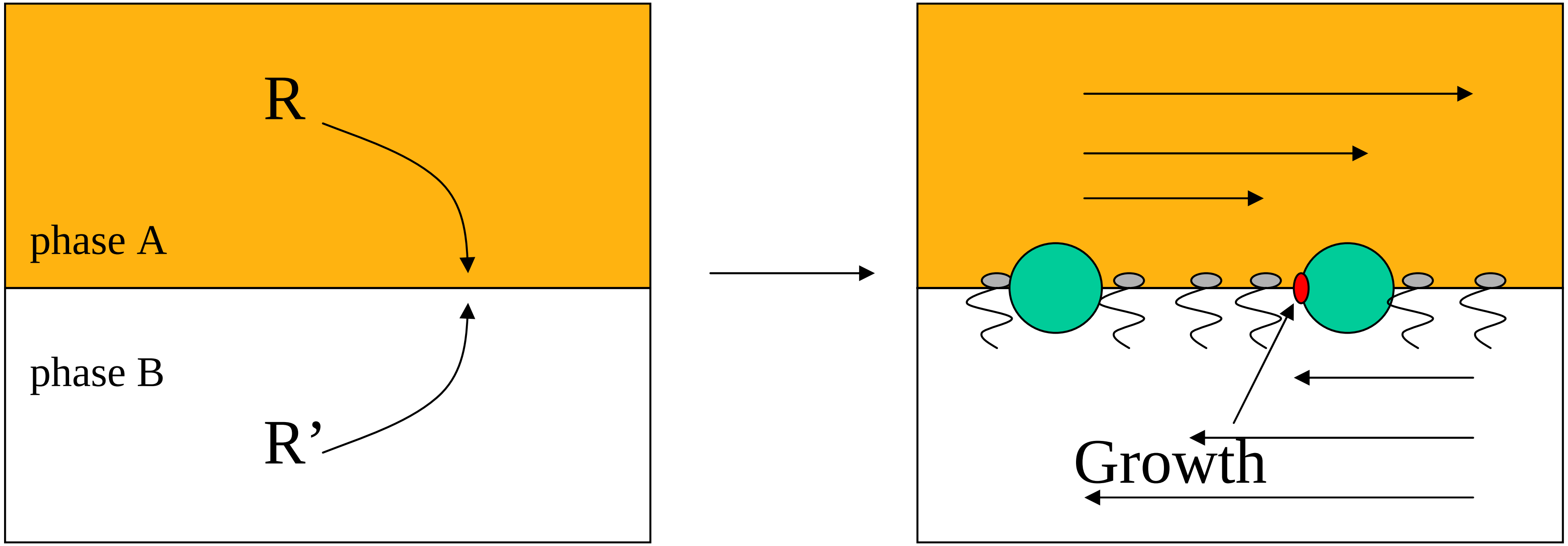
The principle



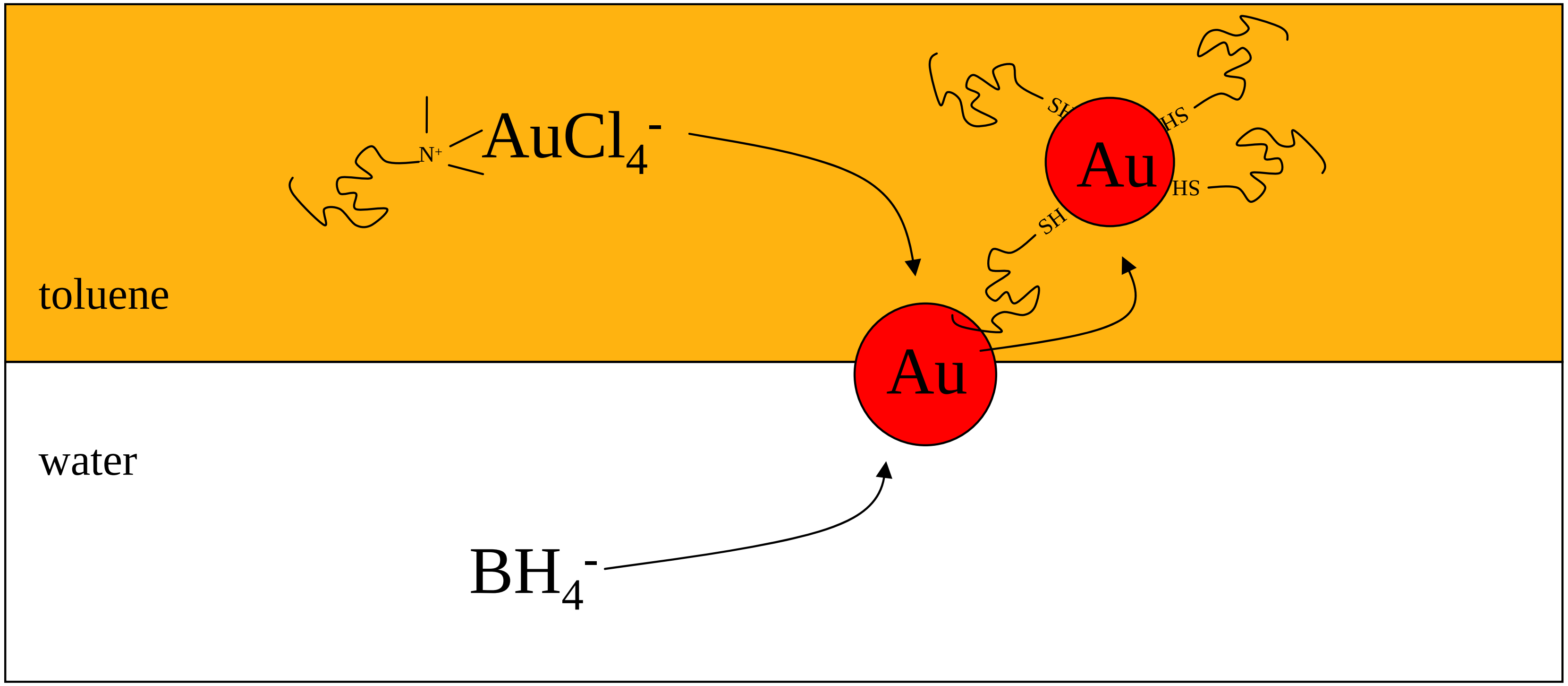
Two non-miscible reactive phases

Confinement of the reaction
Control by the interface

} Controlled growth of nanoparticles

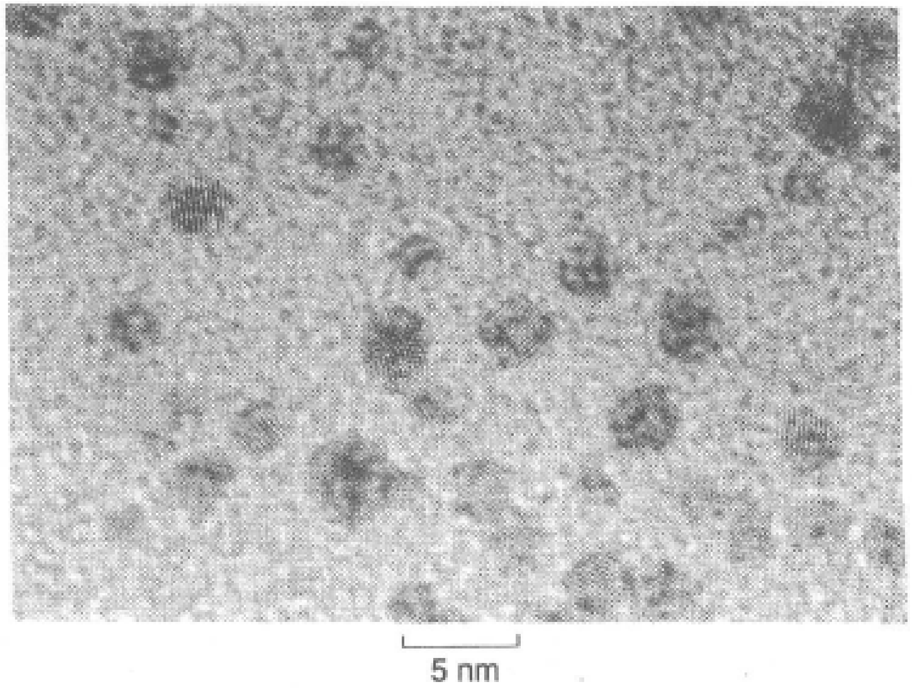
The context

Brust-Schiffrin « two phase » reaction



Brust1994

The context



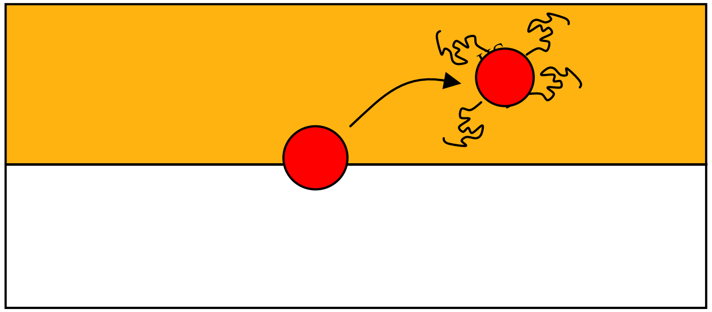
Works fine with metals but:

- limited success with chalcogenides
- no success with oxydes (> 20 nm)

Control

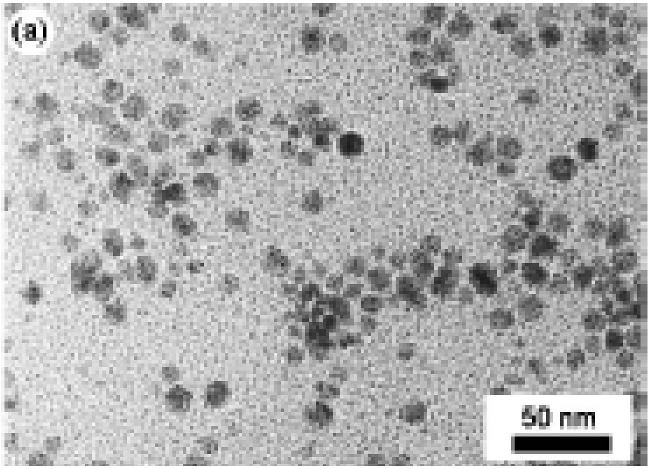
Pan2004&2007
Abu Bakar2007, Vorobyova2004

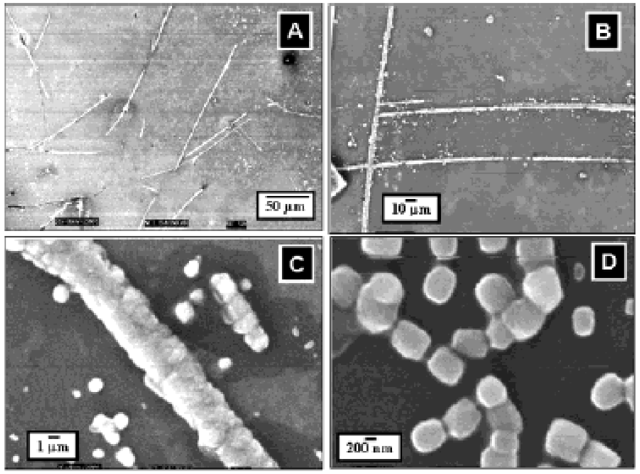
The context



Mechanism intellectually appealing but:

- film *vs* nanoparticle?
- contact angle *vs* “transfer agent”?
- shear?

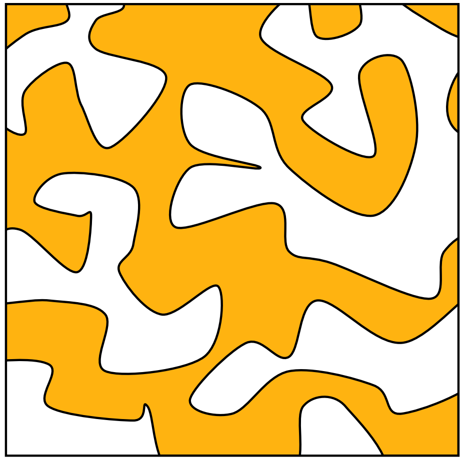




Patil2000, Rao2005, Fan2007, Sanyal2008

Rautaray2003

Our systems

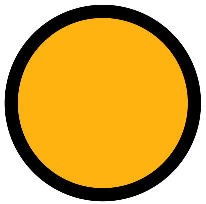


10 nm

Microemulsions
(Separate reactive phases!)

100 µm

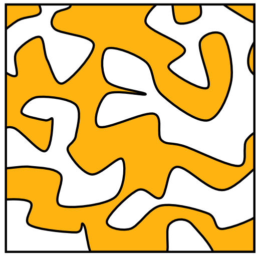
Dynamic interfaces
by microfluidics

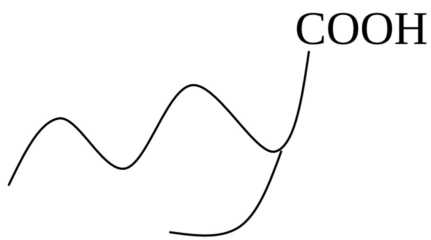


5 µm

Towards « smart »
surfactant vesicles

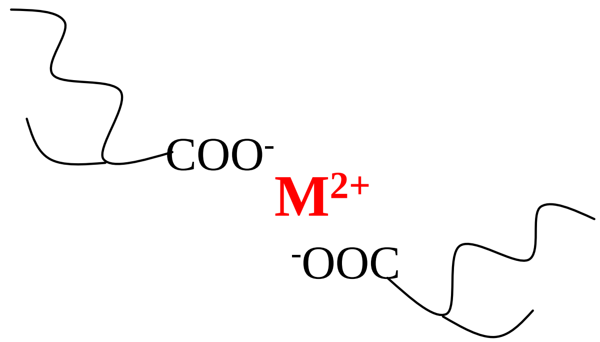
Reactive microemulsions





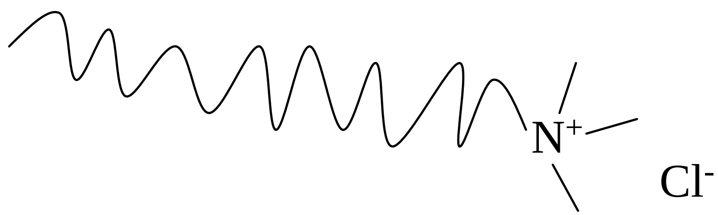
<u>Oil</u>: 2-ethyl hexanoic acid

very weak acid → hydrophobic



<u>Organic metal precursor</u>:

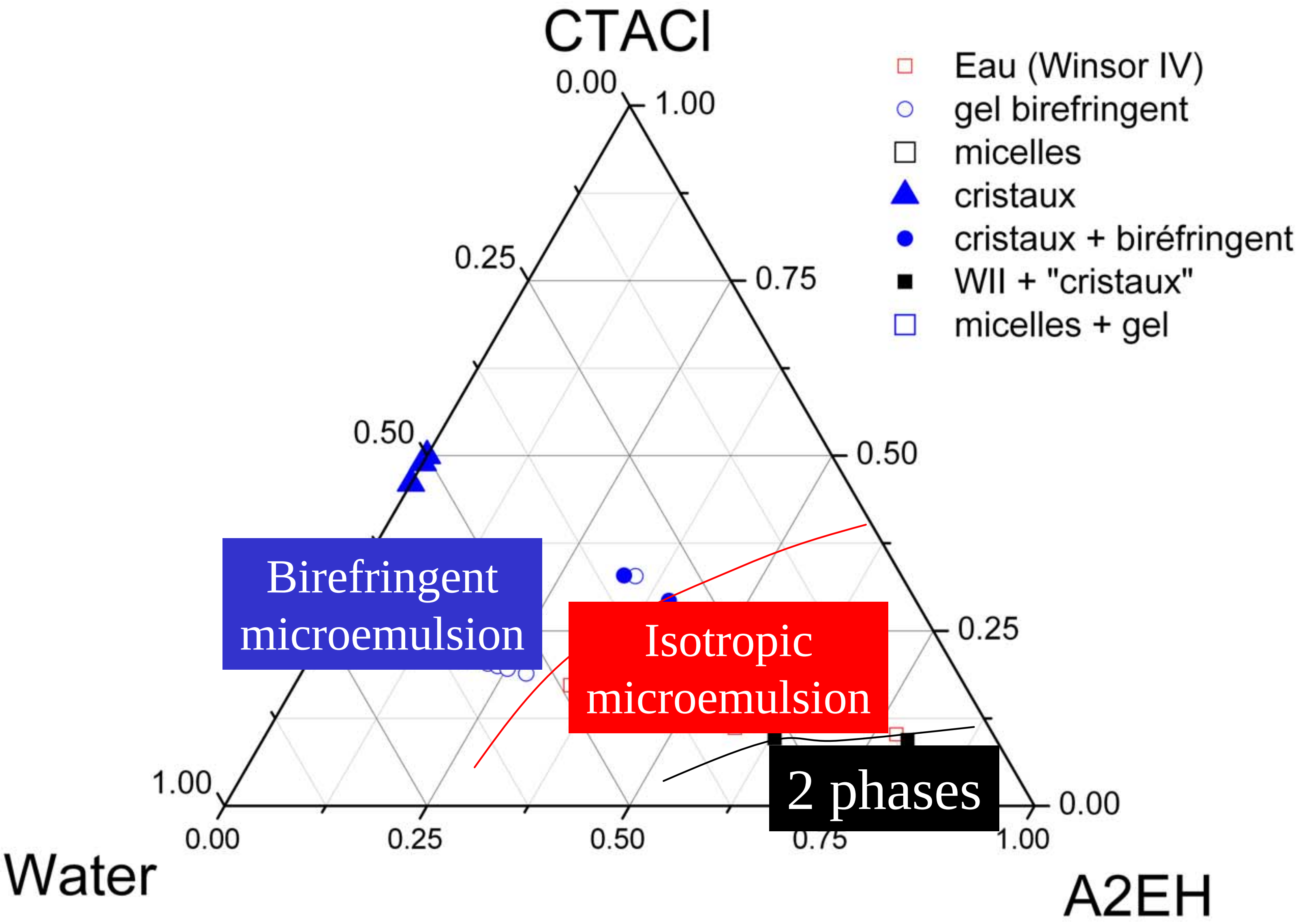
2-ethyl hexanoates → hydrophobic



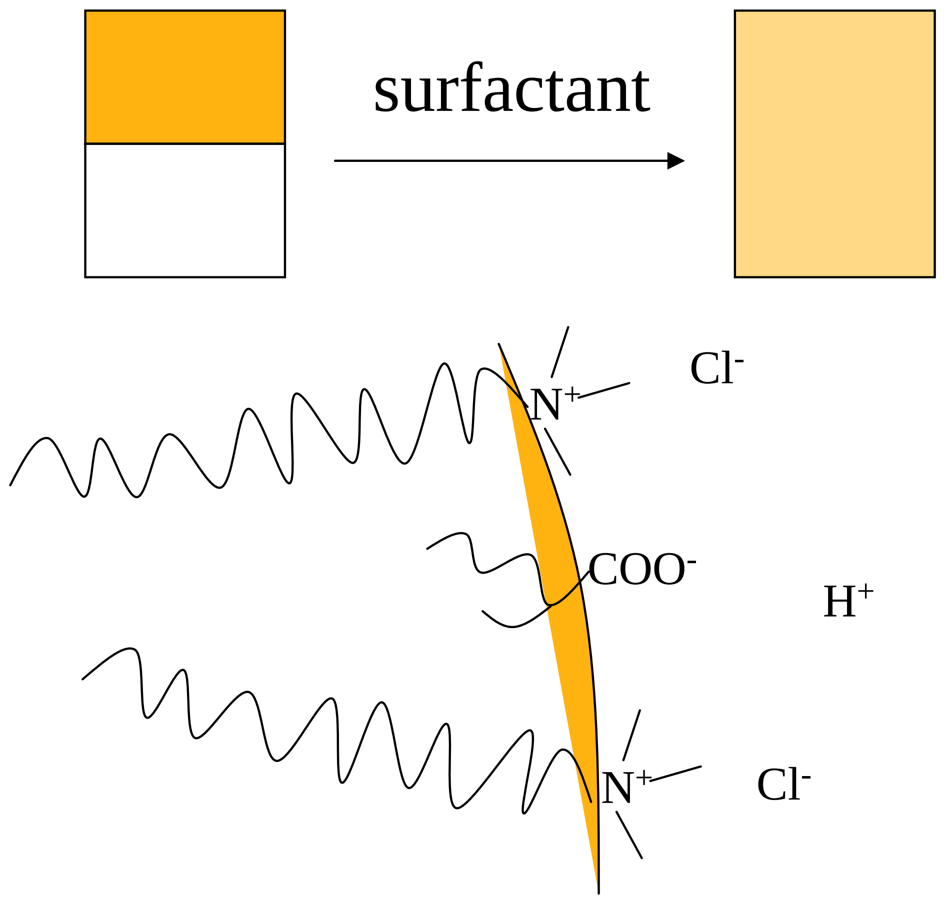
<u>Surfactant</u>:

CTACl

Phase diagram



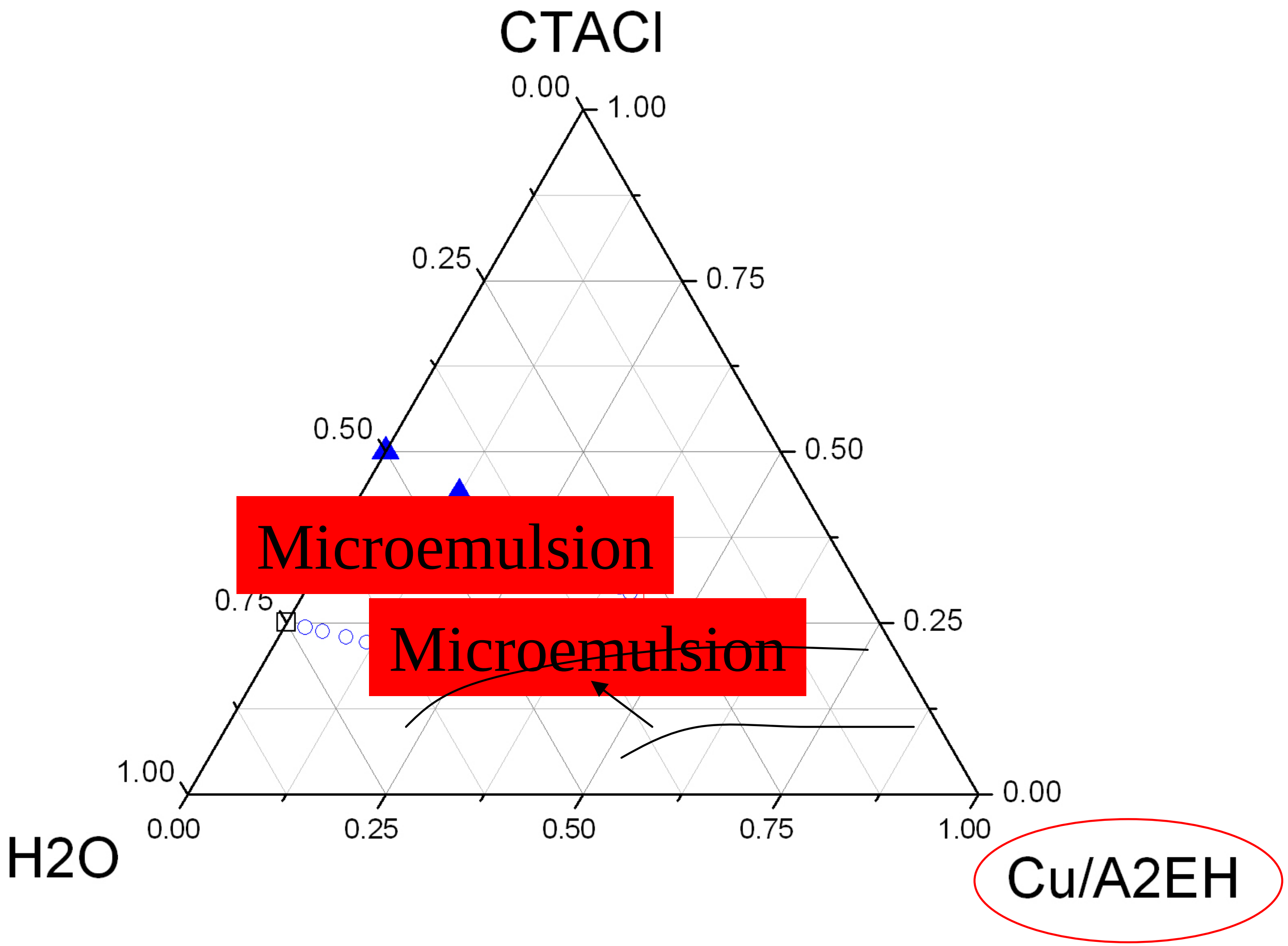
Stabilization mechanism



<u>Cosurfactant</u>: none!

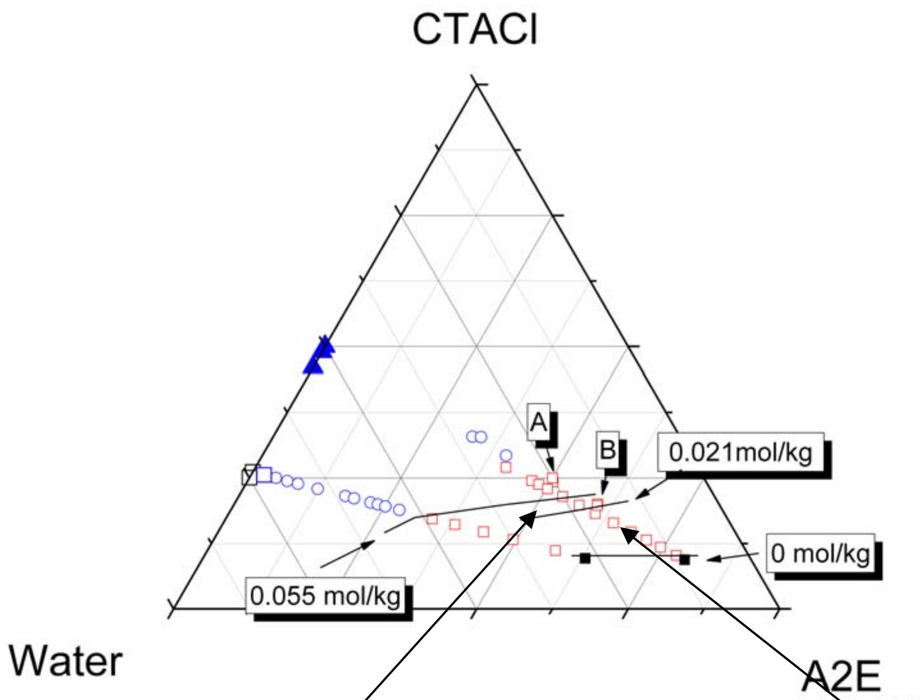
"Catanionic" film at the oil/water interface

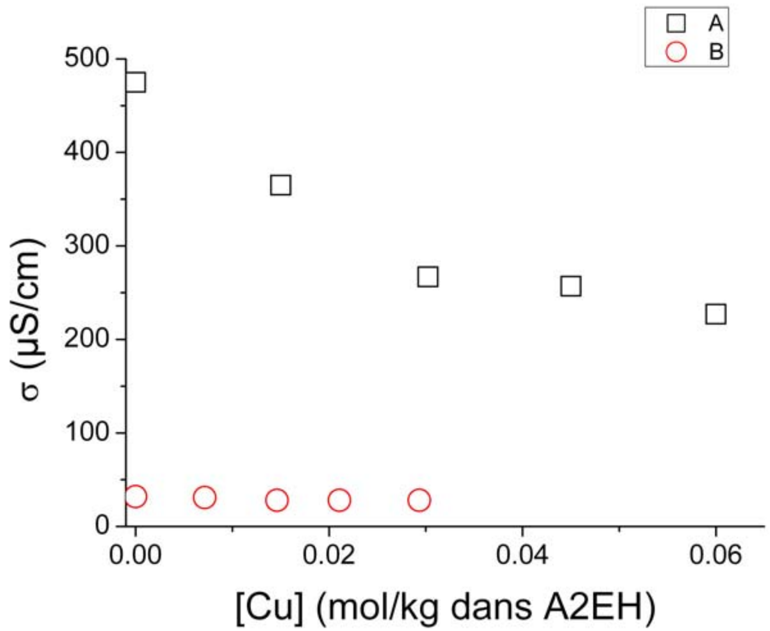
Effect of metal precursor



Metal precursor in oil phase:
Contraction of the microemulsion

Effect of metal precursor

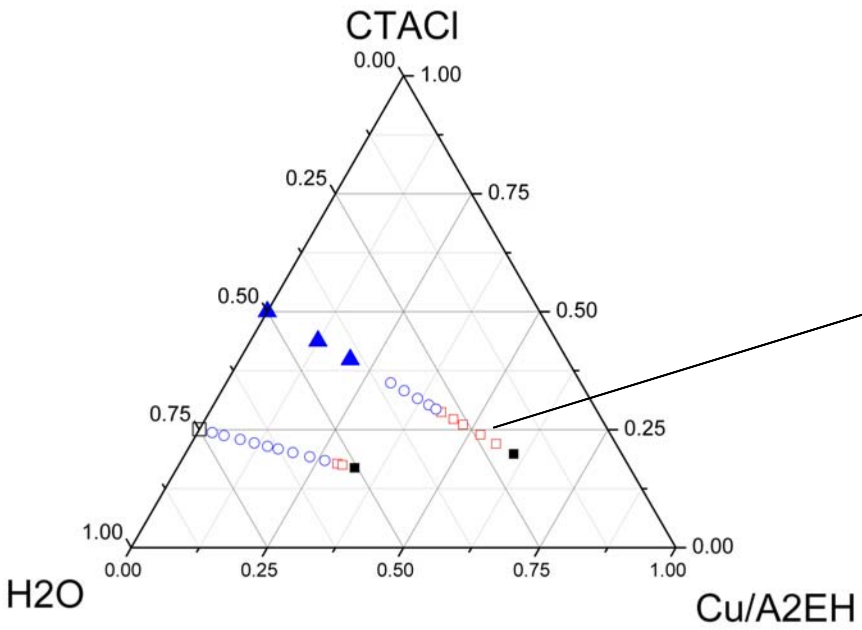


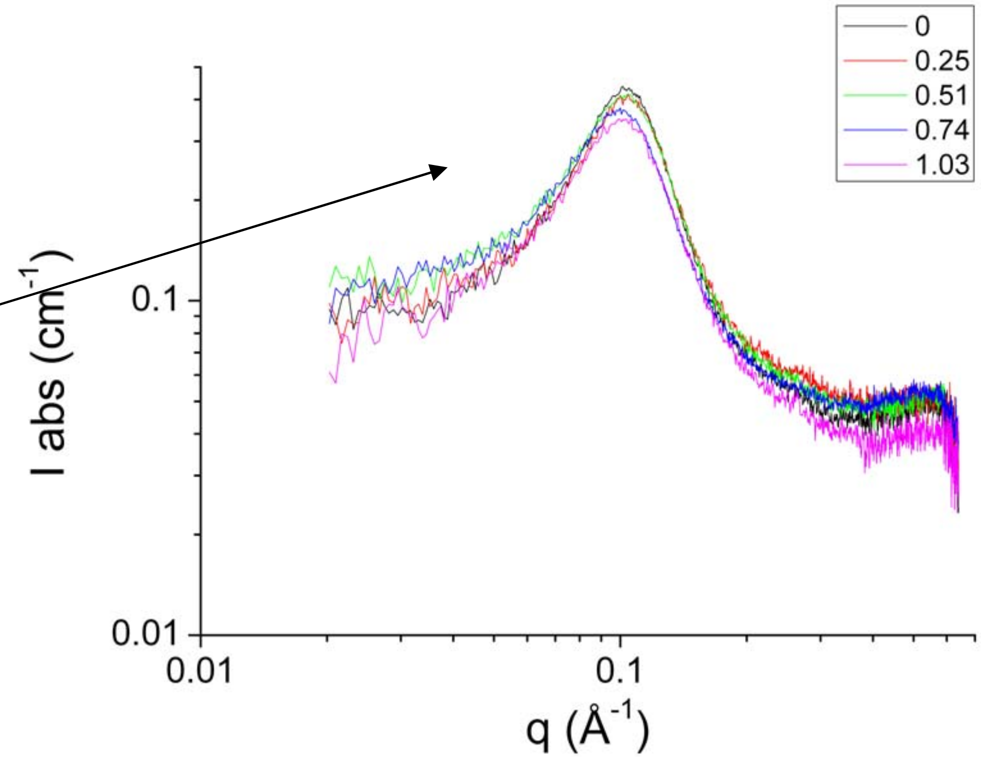


Bicontinuous emulsion?

Water-in-oil microemulsion

SAXS in W/O domain

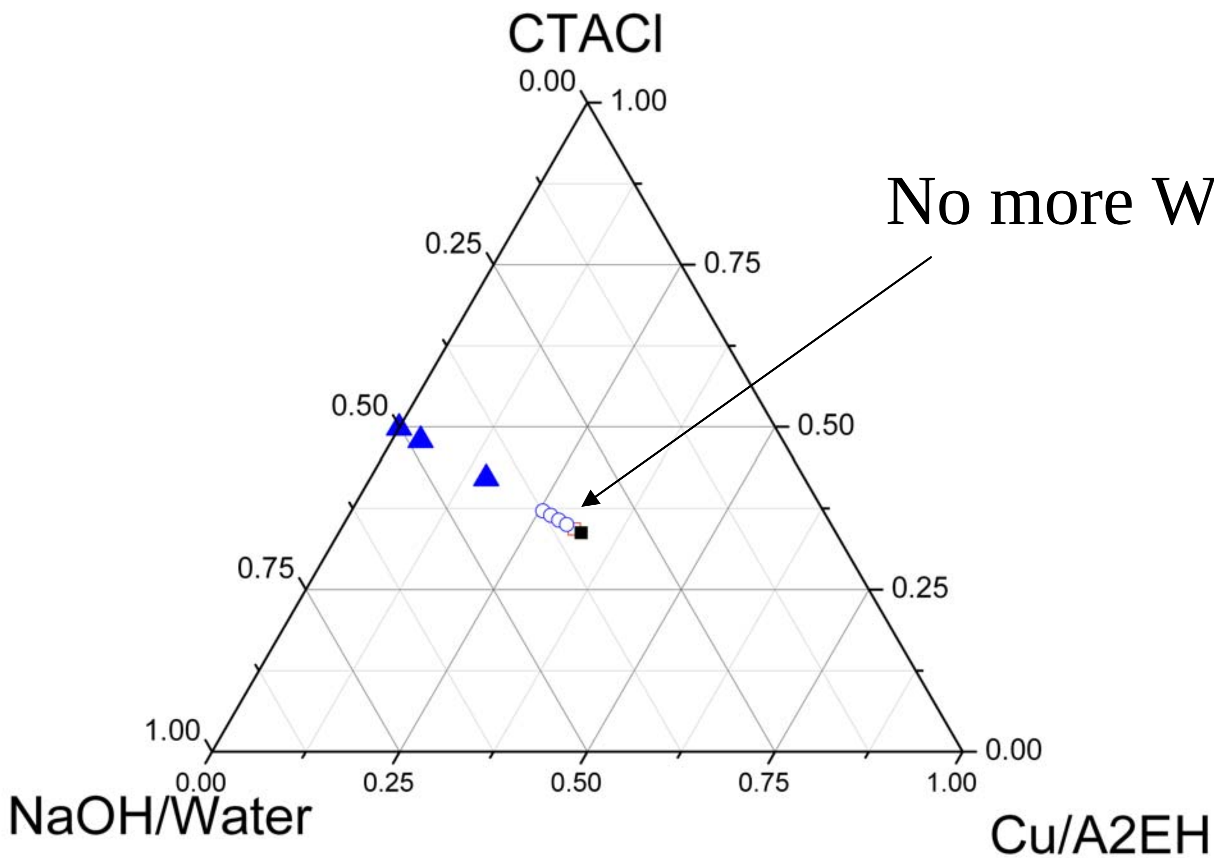




Water-in-oil ~ 6 nm independent on Cu concentration

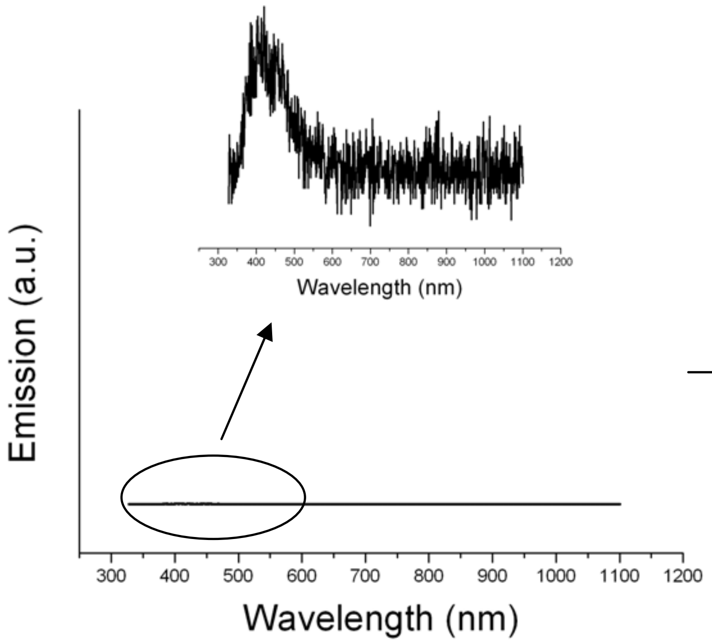
Reaction triggering (1)

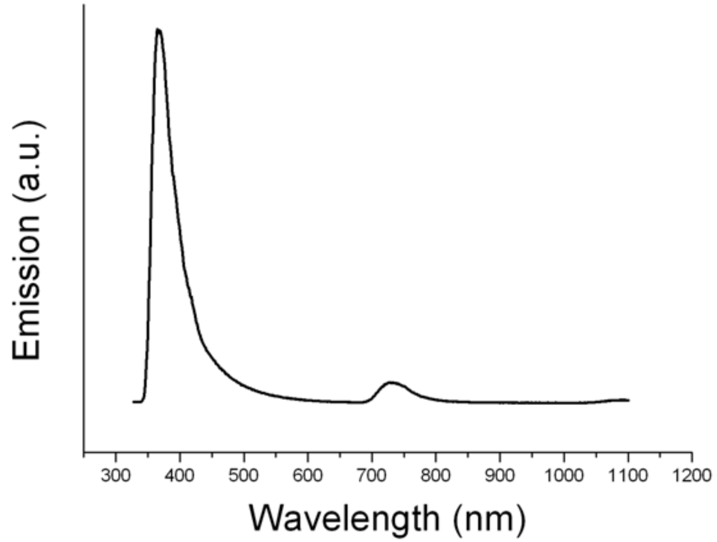
$$Cu^{2+}(L^-)_2 + 2\,OH^- \longrightarrow CuO + 2L^- + H_2O$$



No more W/O domain

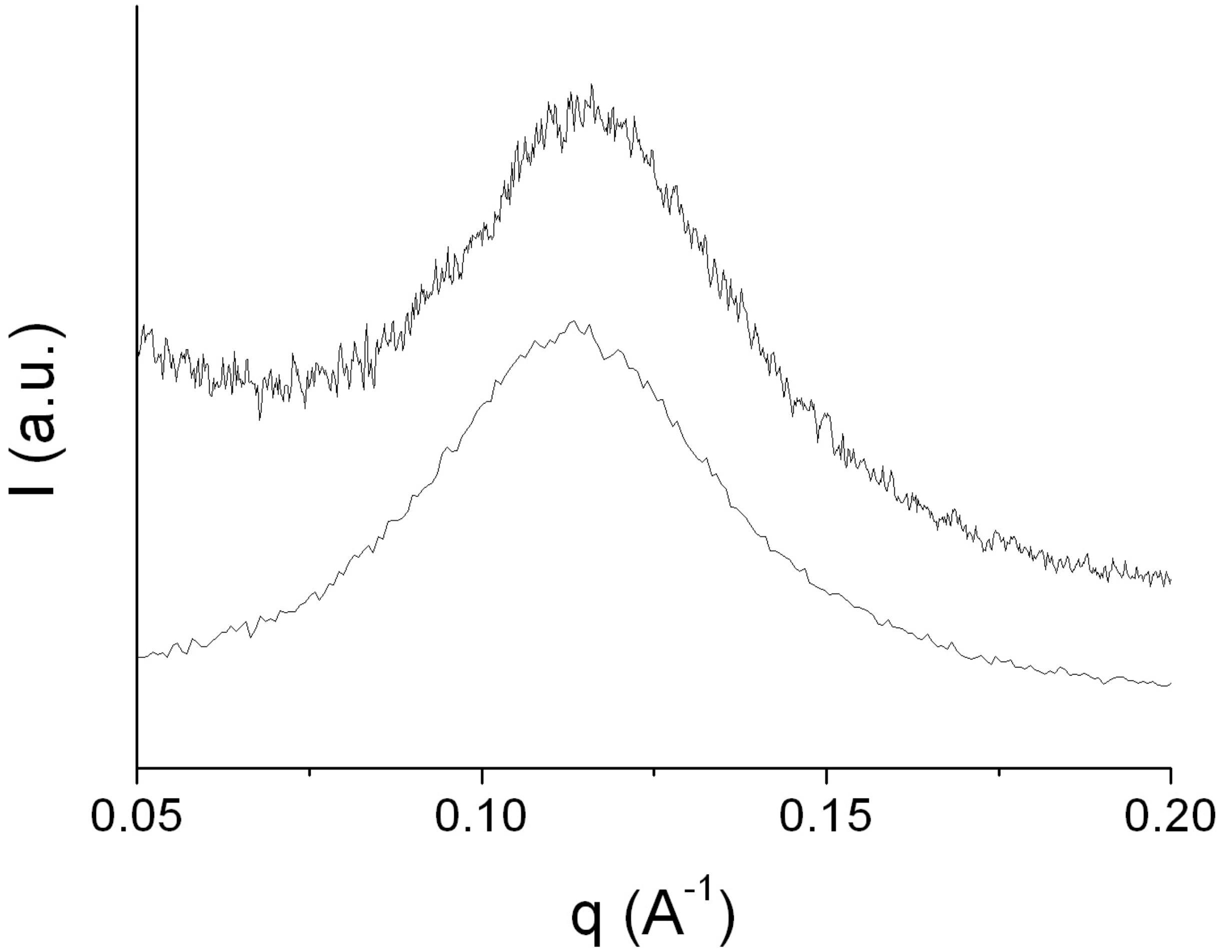
Reaction triggering (2)





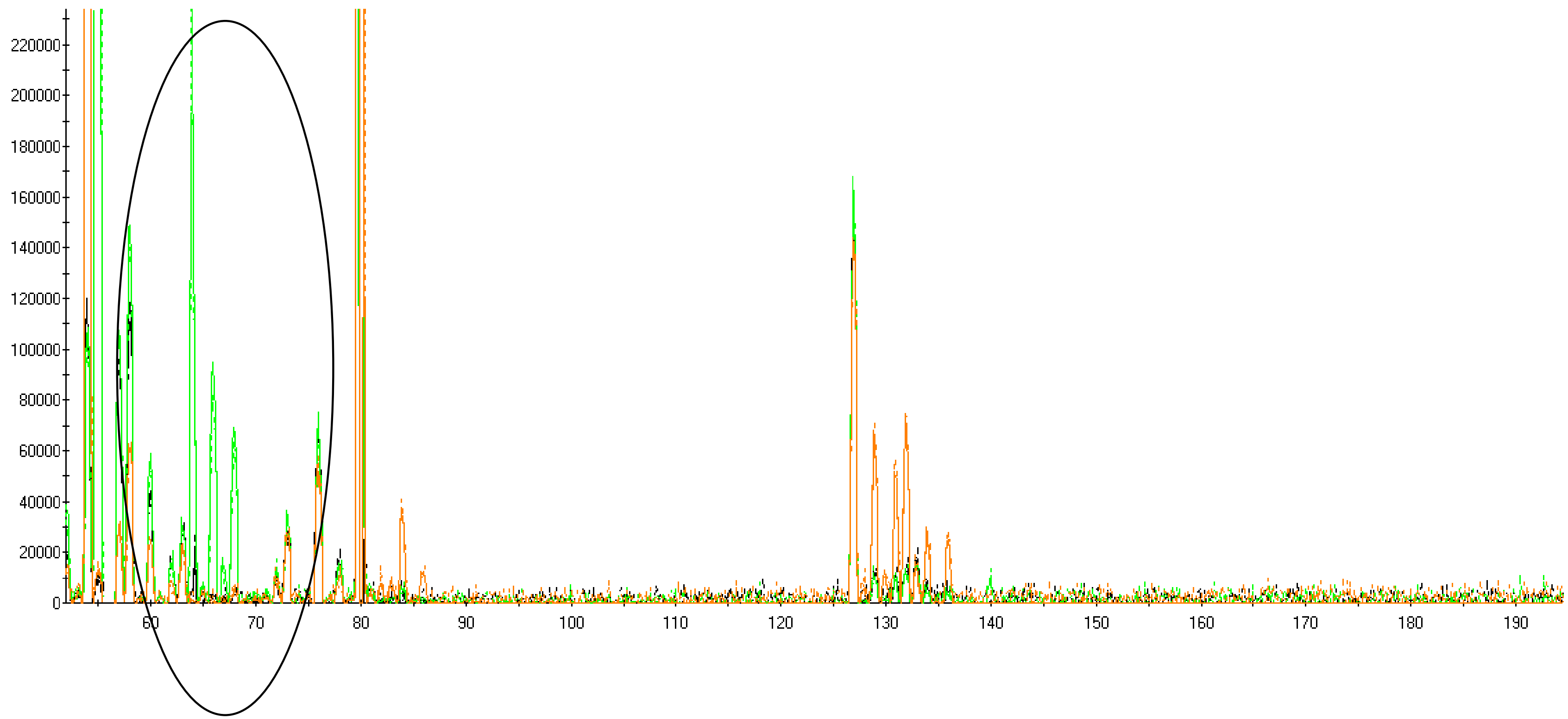
70°C : reaction triggering

SAXS



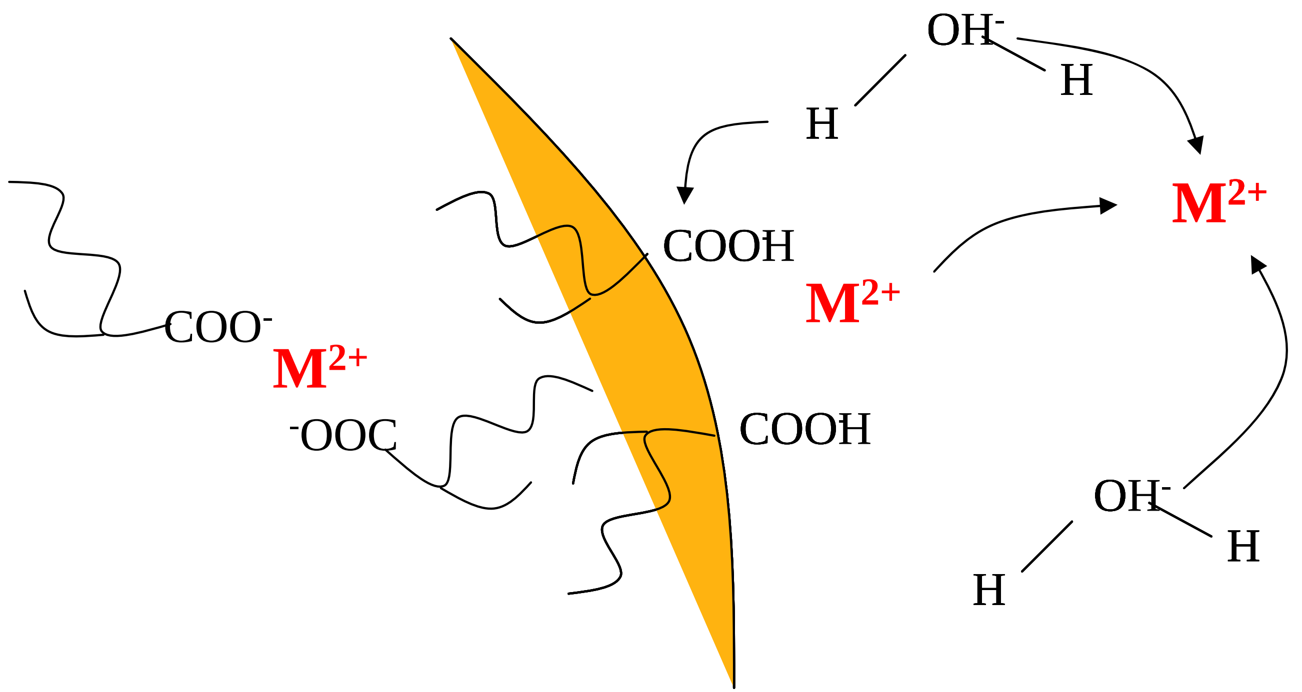
No structural change in the microemulsion upon reaction

ICPMS



Less low-Mw metal precursor
Mn reactivity > Cu reactivity
TEM: amorphous growth?

Mechanism



OH$^-$ generated in situ by heating?

Also works with NaCl addition: equilibrium $M^{2+} \leftrightarrow Na^+$

Conclusion

Original growth triggering (temperature, salt addition)

Mechanism to be clarified:

- Time-resolved ESR
- SAXS

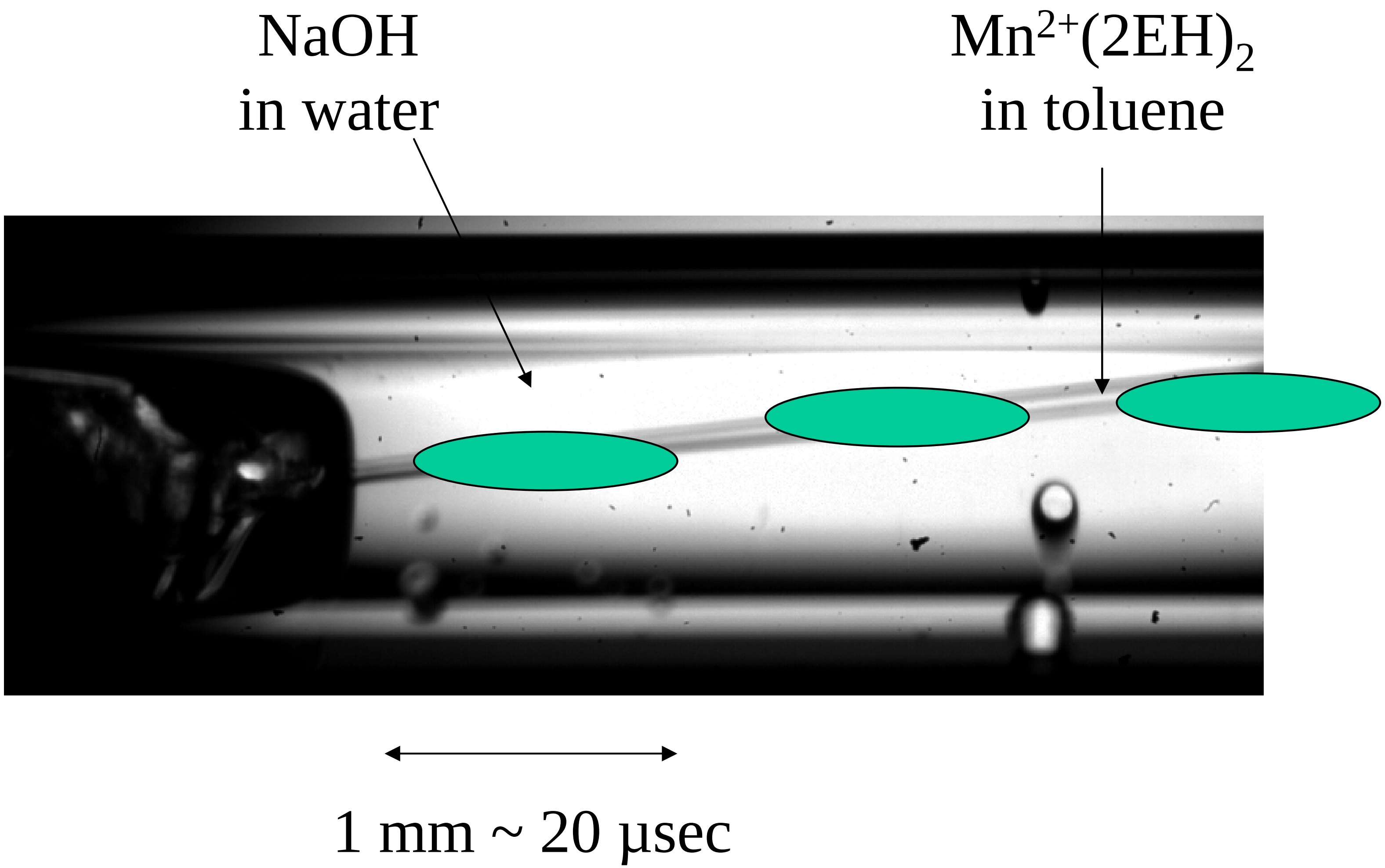
From amorphous to crystalline nanoparticles?

OK for materials, too complex for mechanism studies

→ simplification

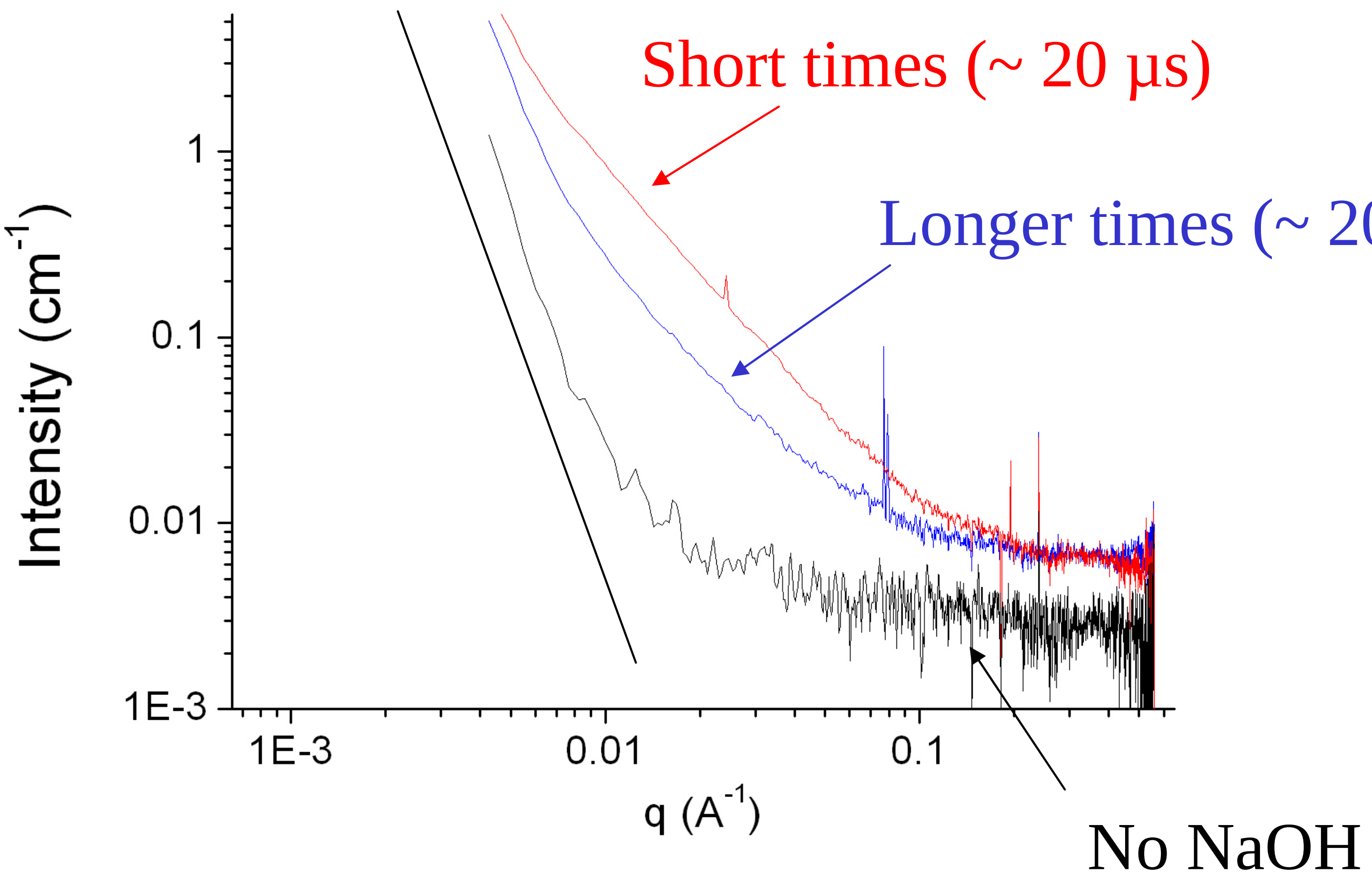
Dynamic interfaces
by microfluidics

Oil/Water dynamic interfaces



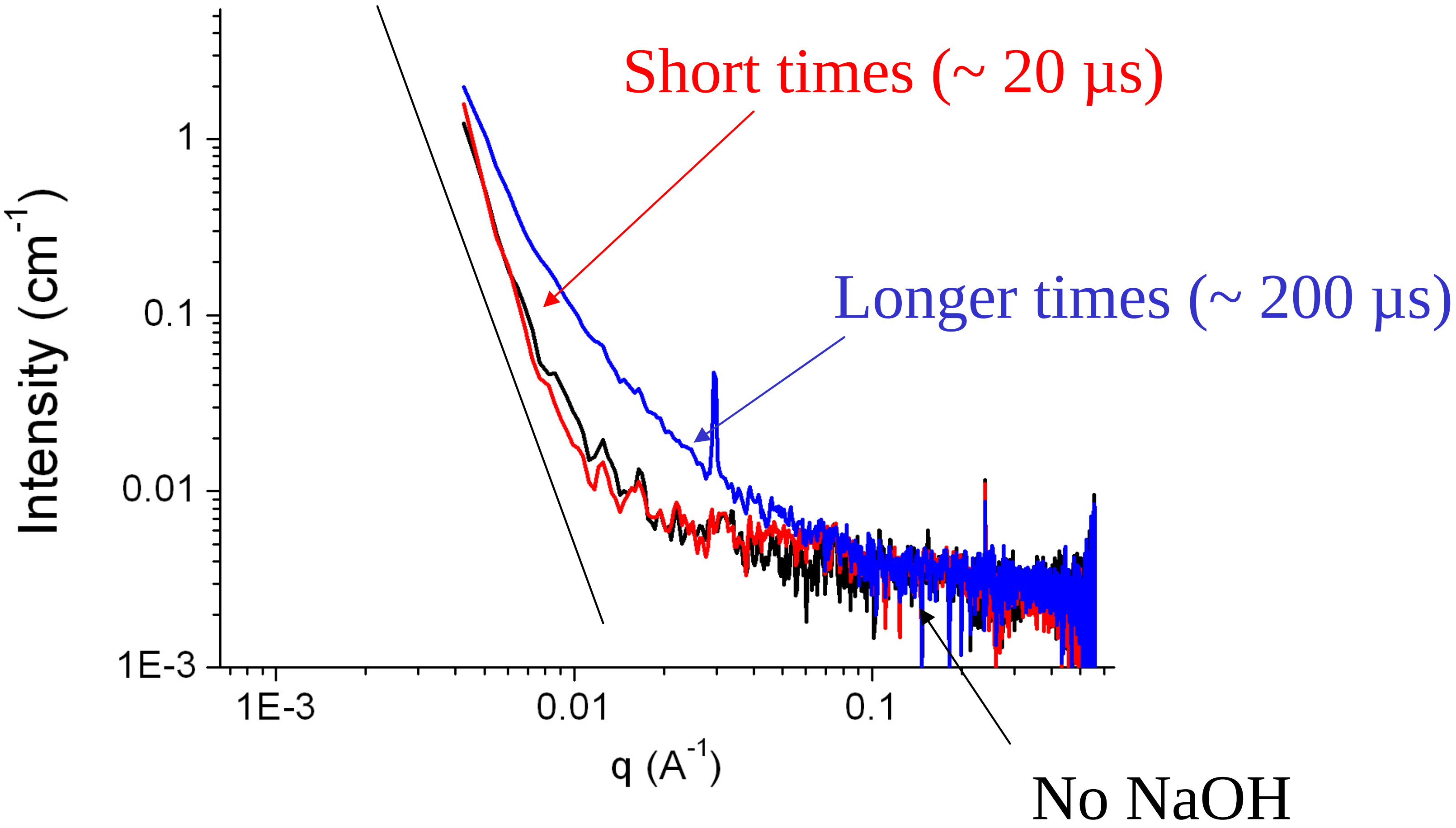
Time-resolved SAXS (Soleil, SWING)

NaOH = 0.1 mol/L^{-1}



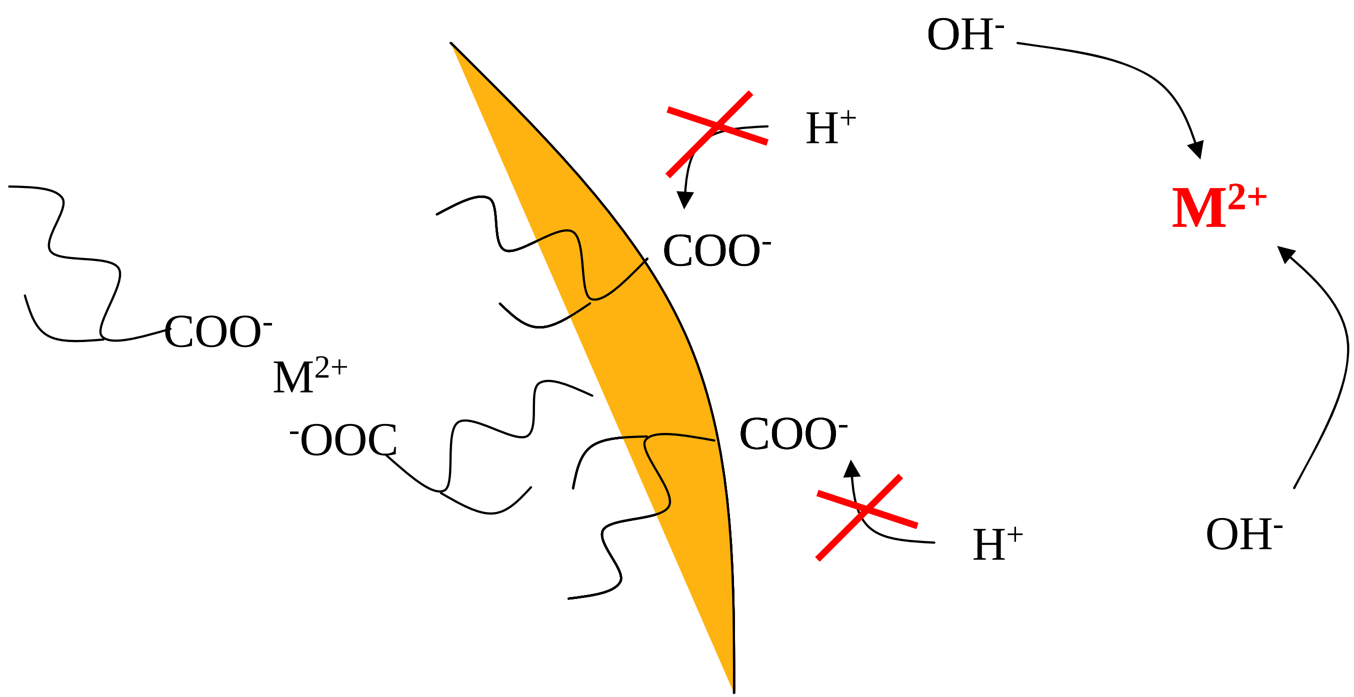
NaOH 0.1 M: increase then decrease
To be assigned to amorphous growth

NaOH = 1 mol/L^{-1}



NaOH 1 M: inhibition of the reaction at short times?

Mechanism



Cation reaction favorable at high NaOH
Ligand release/reprotonation not favorable

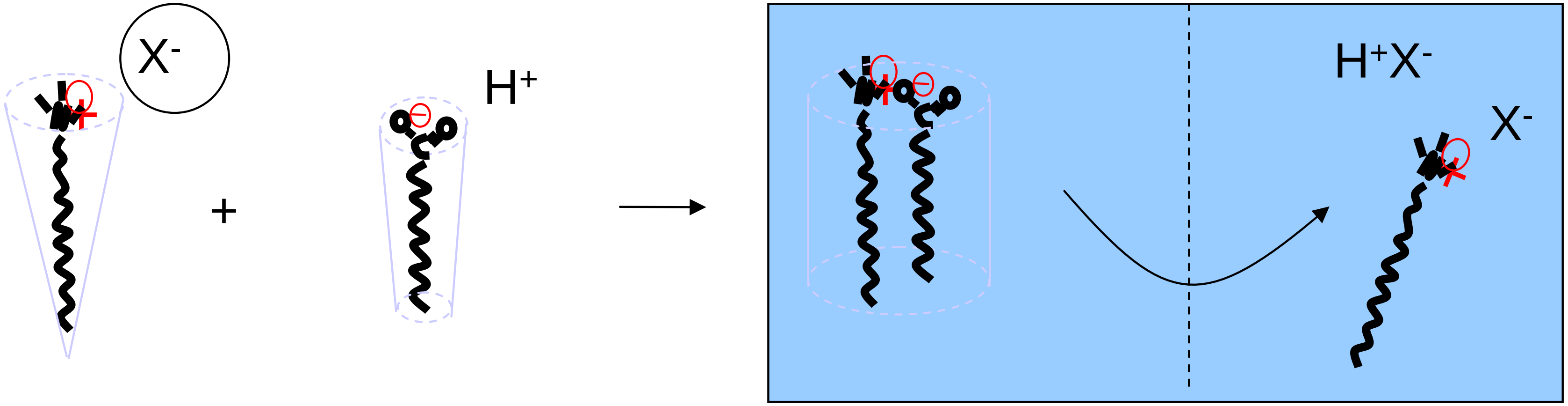
Conclusion

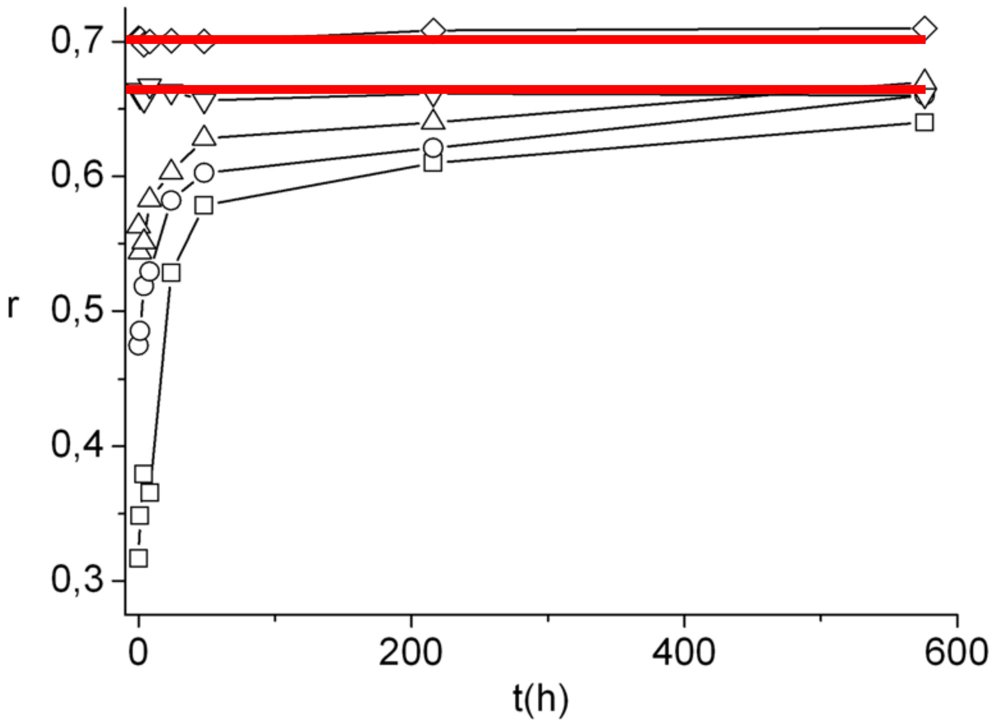
Microfluidics powerful tool for time-resolved SAXS (µs *vs* ms)

Inhibition of the reaction at short times despite expected higher reactivity

Towards « smart » surfactant vesicles

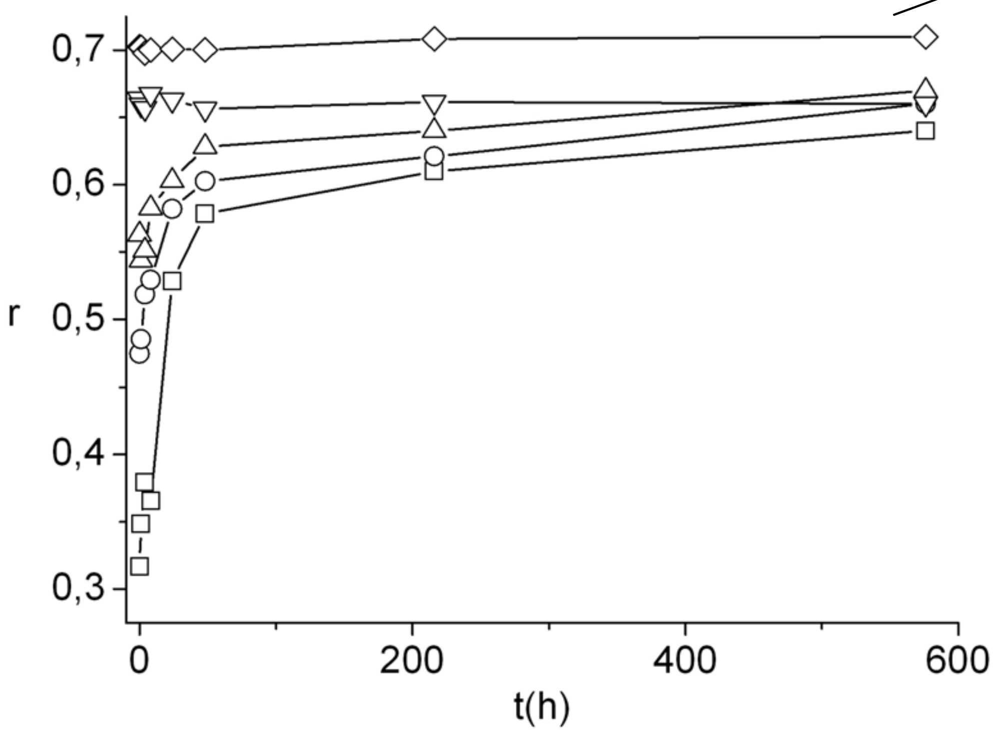
Catanionic mixtures

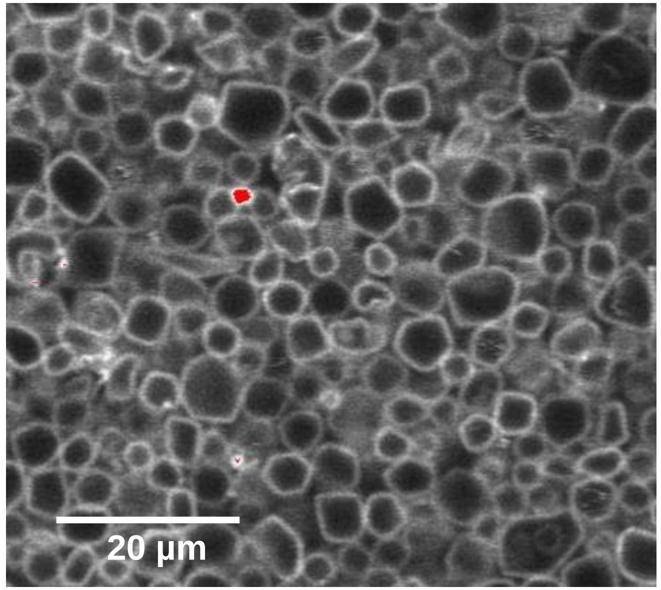




Critical molar fraction:
No surfactant extraction

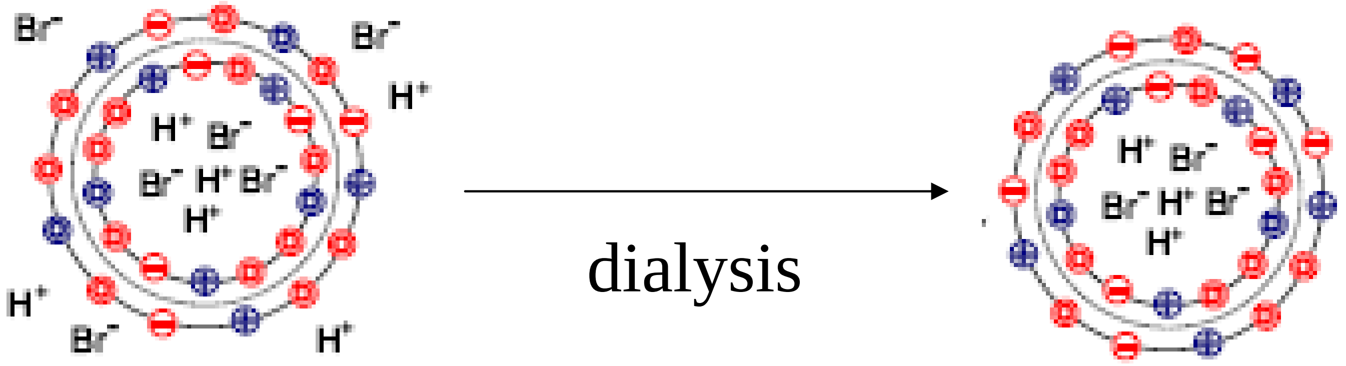
Catanionic vesicles

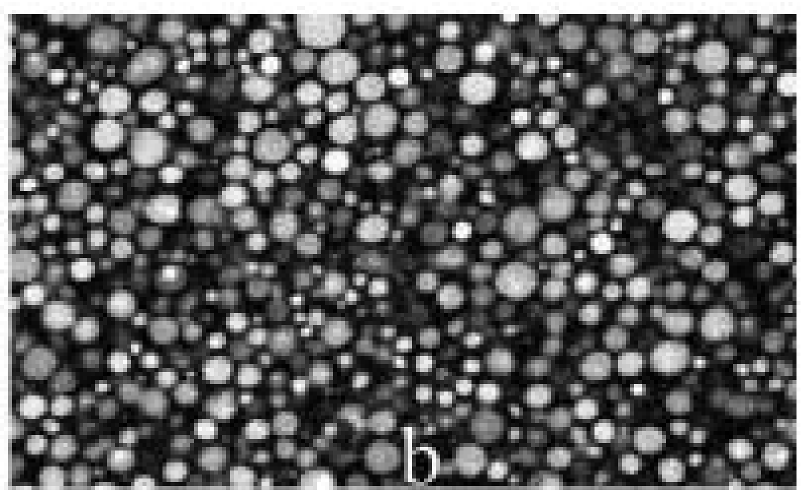


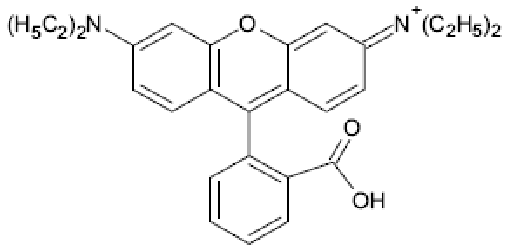


Vesicles at the critical molar fraction
Resistant to dialysis

pH measurement

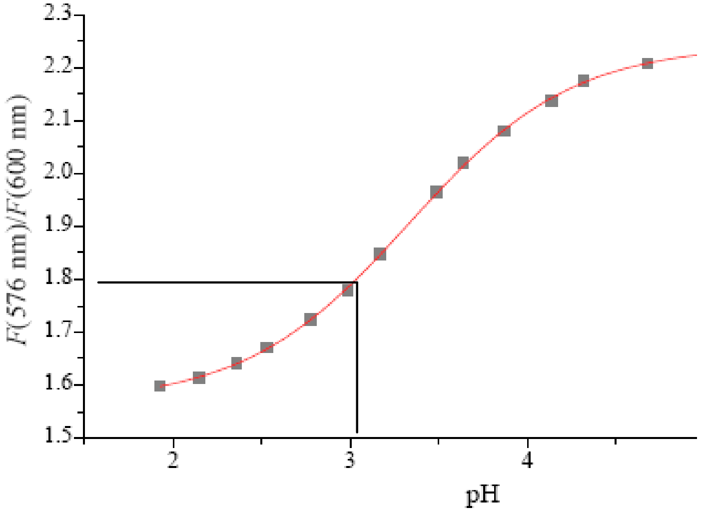


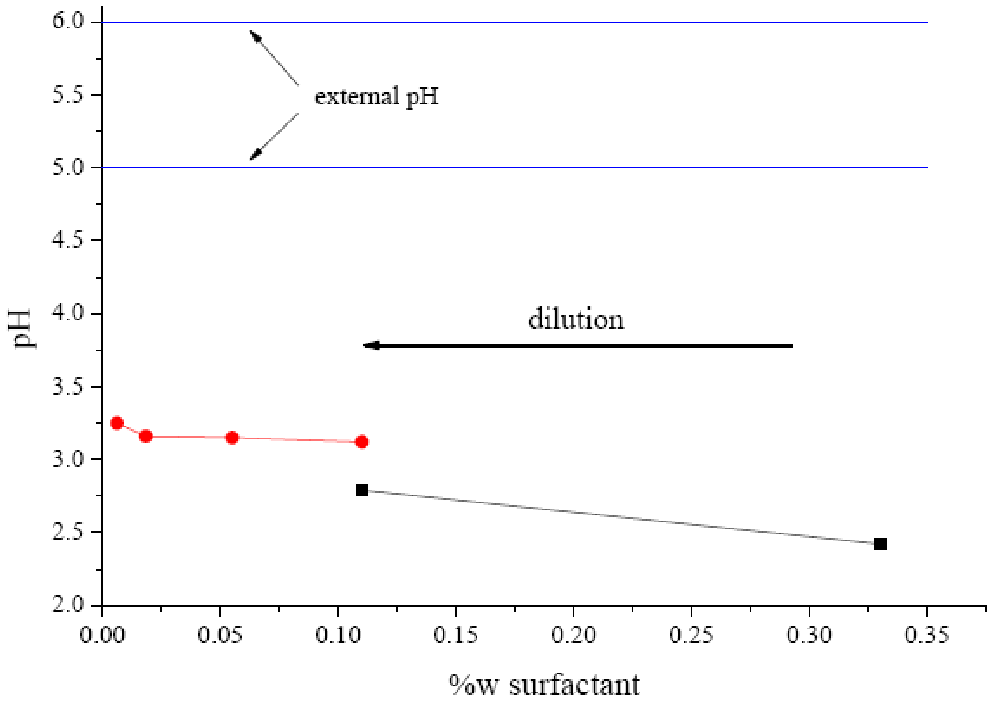




Encapsulation of a pH-sensitive probe

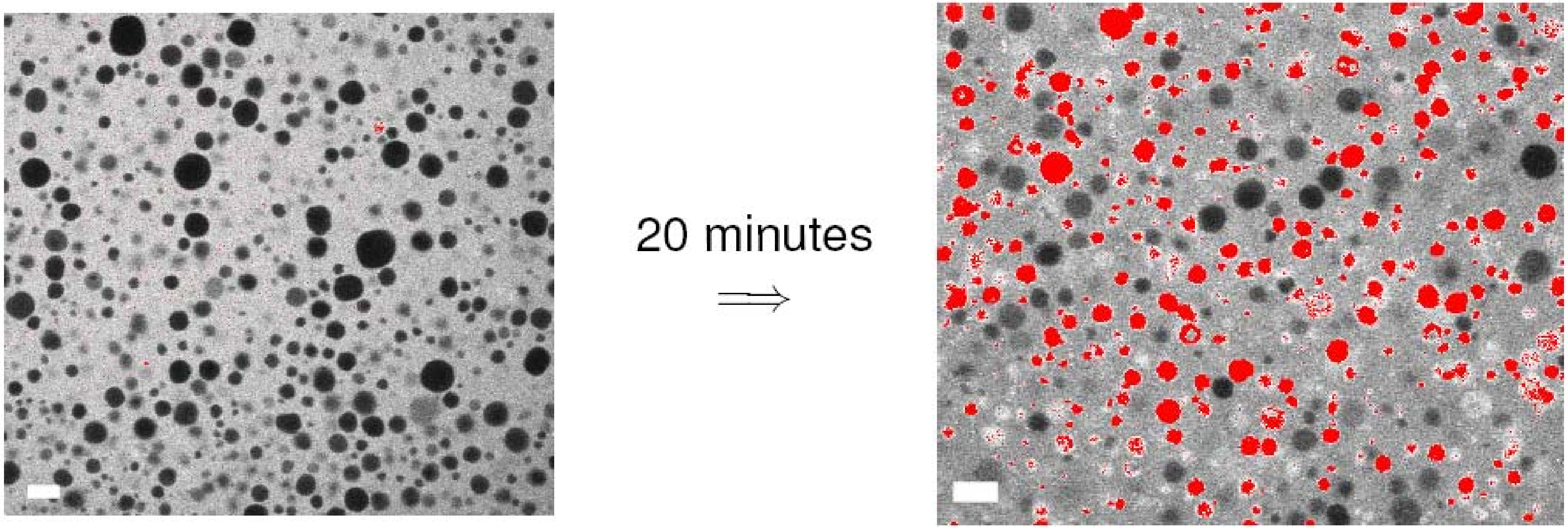
pH measurement





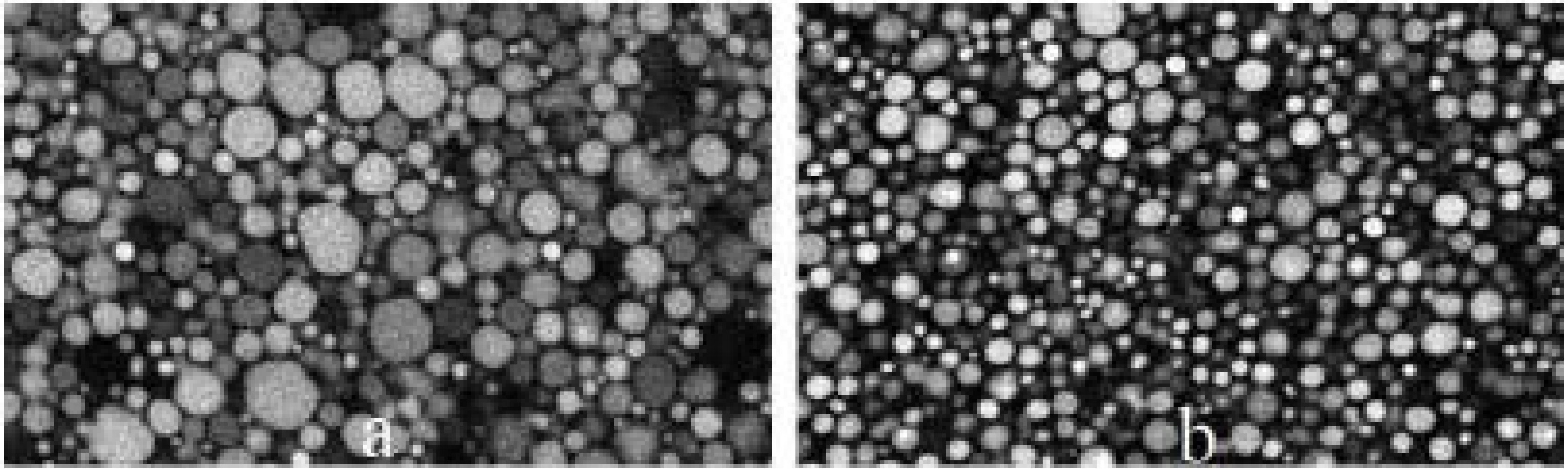
pH gradient accross the vesicle membrane

Spontaneous uptake



Spontaneous uptake of cations
Transmembrane potential (from permeabilities) ~ -33 mV

Size dependence



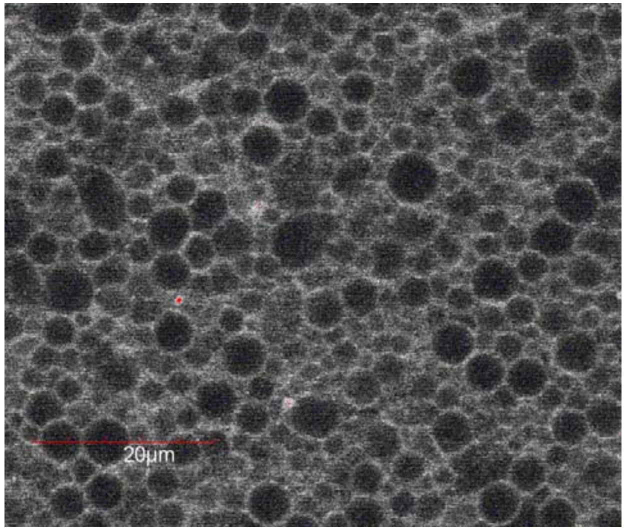
$Br^{-} = 0.74$ mM

$Br^{-} = 1.80$ mM

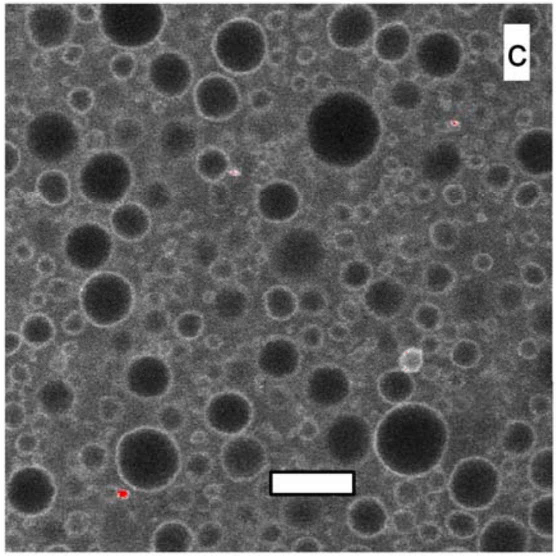
$$C \, \alpha \, S/V = 1/R$$

Control of the uptake and pH by the size of the vesicles

First attempts



+ $AgNO_3$ →



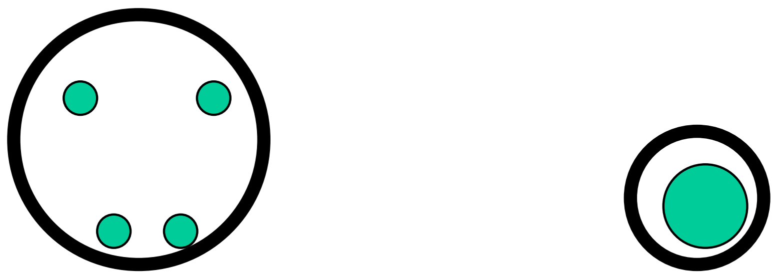
Uptake of Ag^+
Formation of [AgCl]
No vesicle destruction

Conclusion

More elaborate inorganic particles
Control of diffusion rates by the size of vesicles

↓

Sorting of the particle size by the vesicles



Three different soft-matter systems:

- microemulsions: original growth triggering
- microfluidics: mechanistic studies
- vesicles: selection of growth conditions

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P. Barboux (ENSCP): SER
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D. Kopetzki, Y. Michina (CEA, LIONS)
T. Gustavsson (CEA, LFP)
} Vesicles