Viscosity and structure of Hyaluronic acid/surfactant complexes

Philipp Buchold

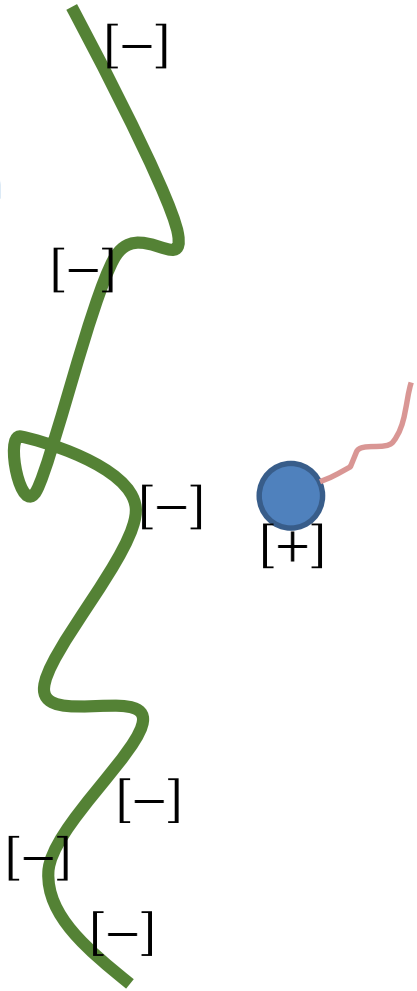
Ralf Schweins, Michael Gradzielski

Motivation

Eye fluid water like solution

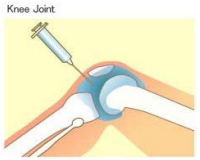
Shampoo viscous solution

Crèmes gel



Extracellular matrix various forms

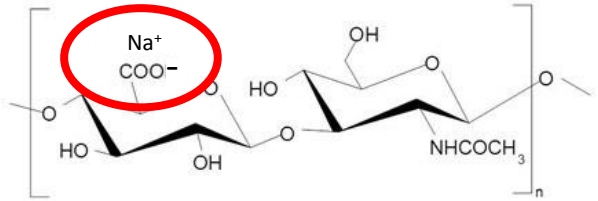
Skin injections viscous solution

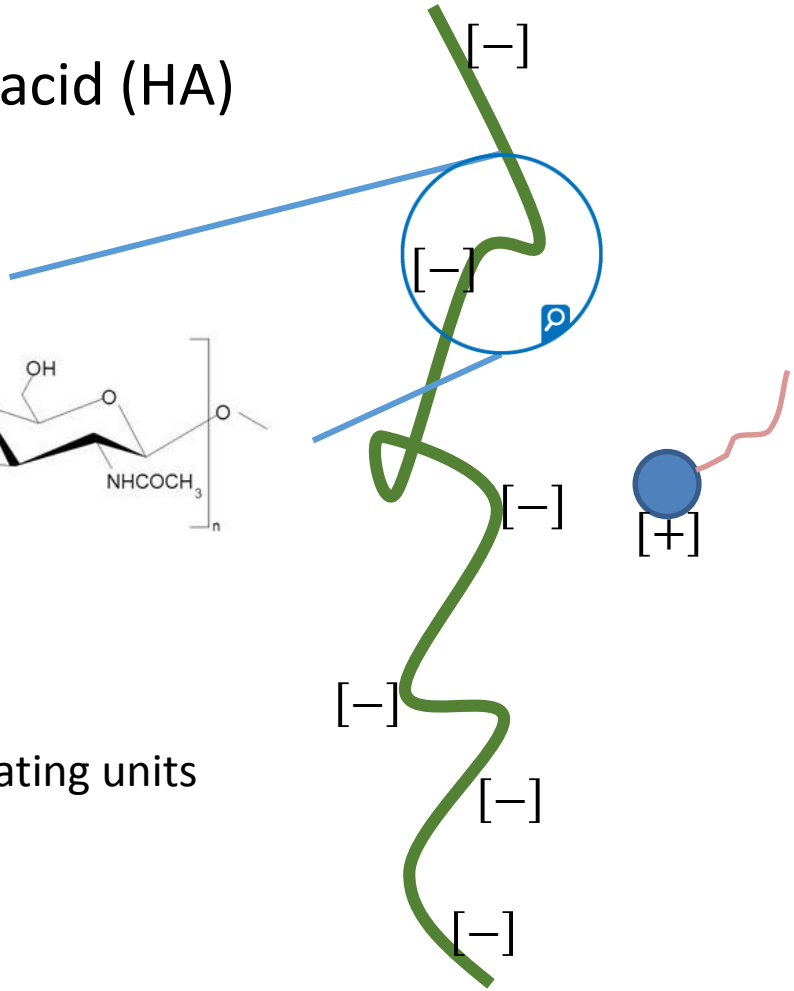


Knee injection gel

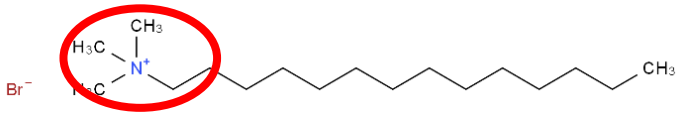
Ingredients

Hyaluronic acid (HA)

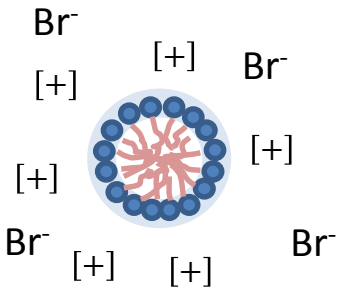




Tetradecyl trimethyl ammonium bromide (TTAB)



CMC: 0.34 mM (160 mM NaBr)



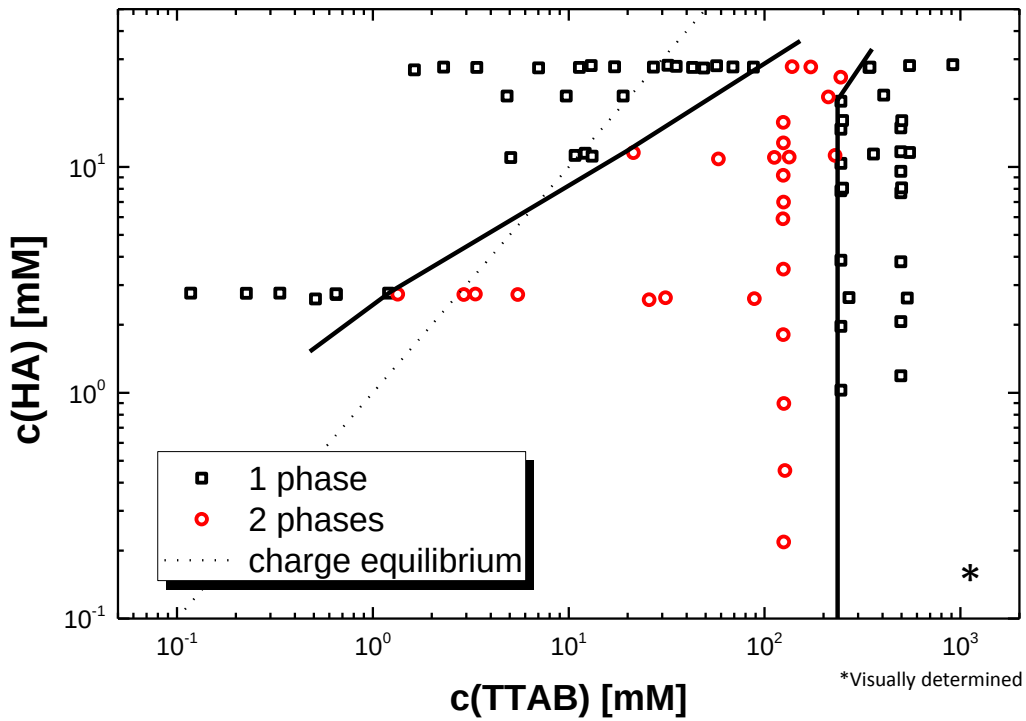
MW: 2 MDa
~ 5000 repeating units
pKa: 3.4
L_p: 9 nm
L_0: 1,02 nm

Solvent: 160 mM NaBr in D_2O

Project

Viscosity of the mixtures

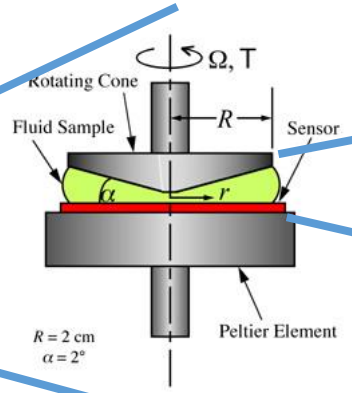
Structure of the formed complex

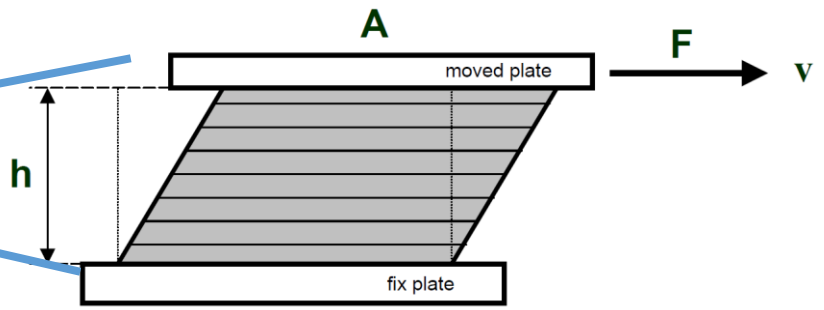


Dynamics of the solutions

Influence/control on the complex

Rheology

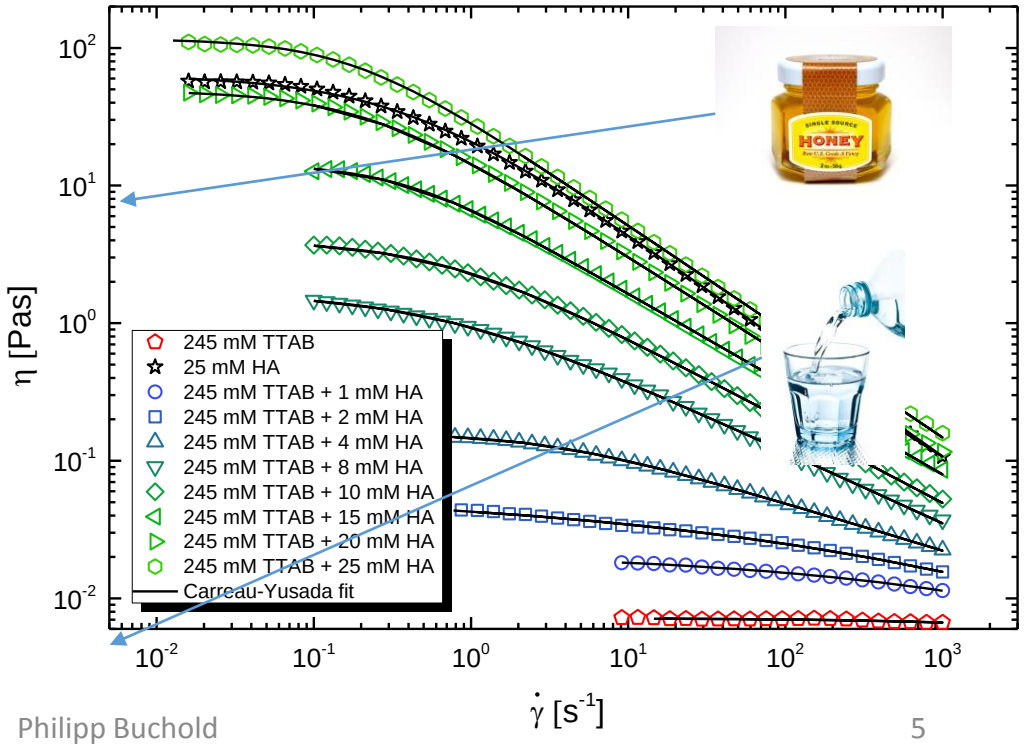




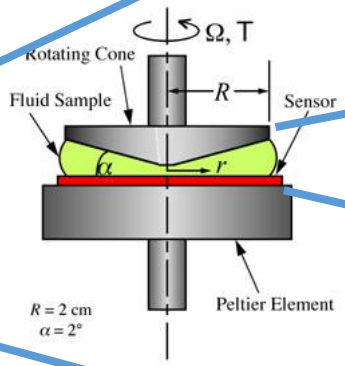
$$\text{shear stress} = \frac{\text{Force}}{\text{Area}} = \tau\ [\text{Pa}]$$

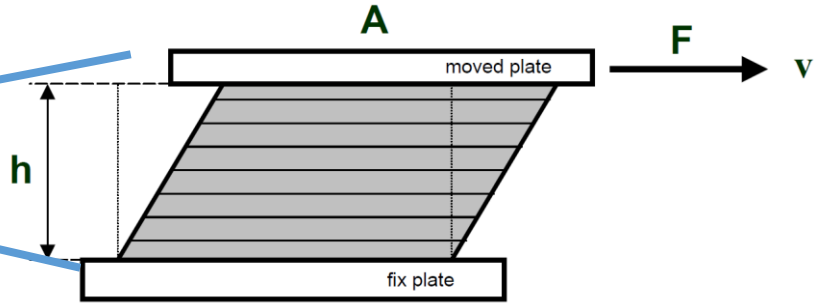
$$\text{shear rate} = \frac{\text{velocity}}{\text{disctance}} = \dot{\gamma}\ [s^{-1}]$$

$$\textbf{viscosity} = \frac{\textbf{shear stress}}{\textbf{shear rate}} = \boldsymbol{\eta}\ \textbf{[Pas]}$$



Rheology





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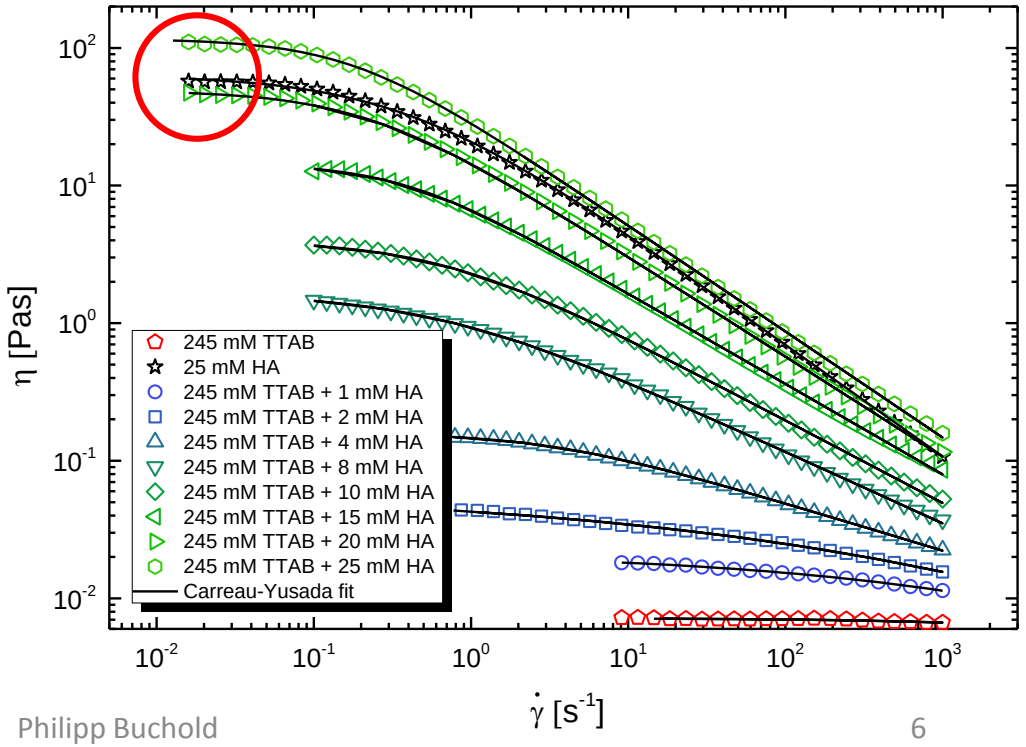
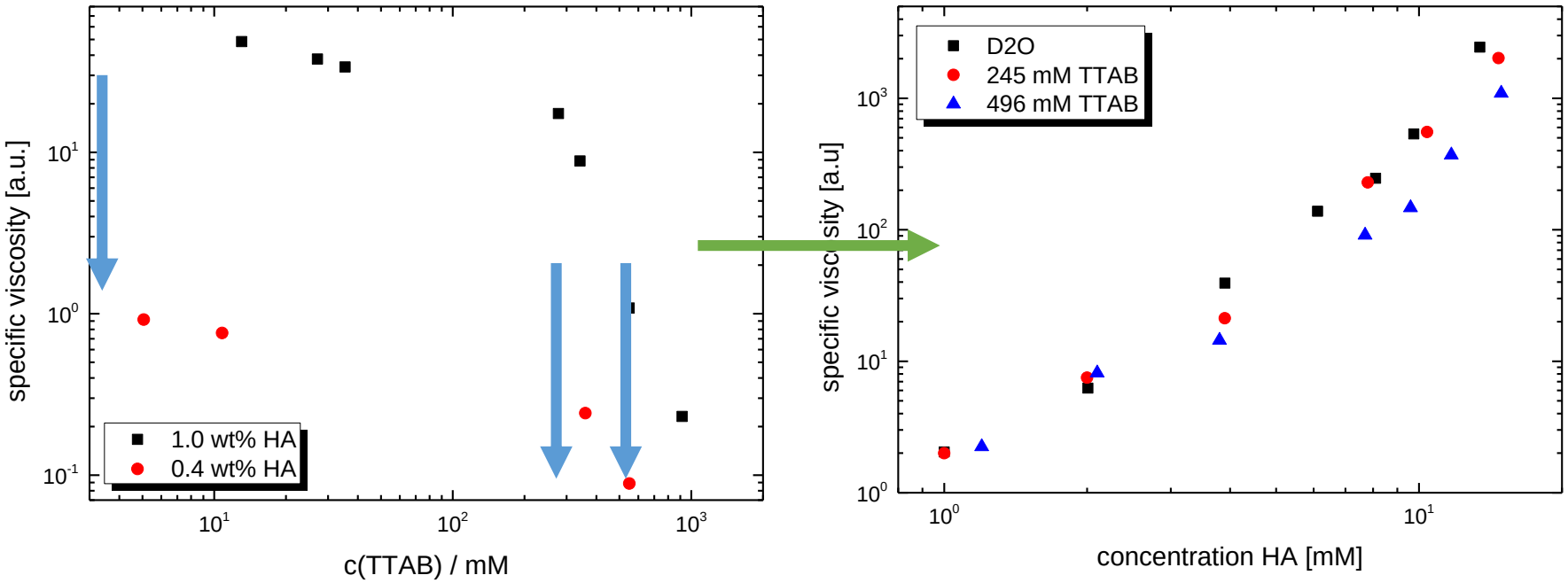
$$\eta_{sp} = \frac{\eta_{sample}}{\eta_{solvent}} - 1$$



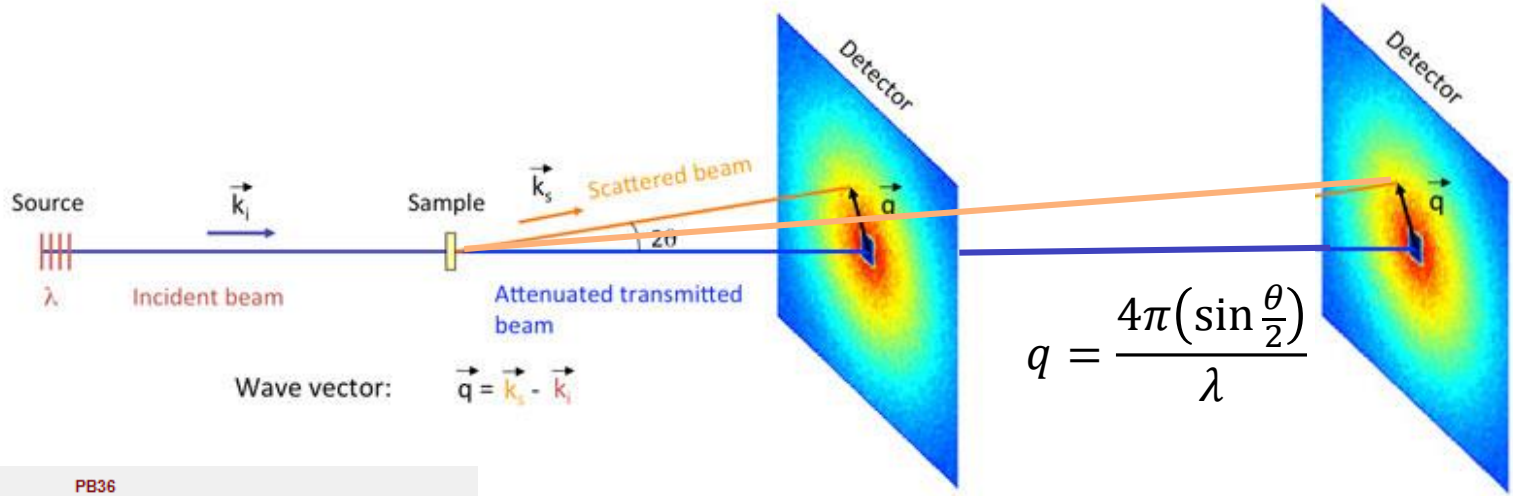
Viscosity of HA/TTAB mixtures

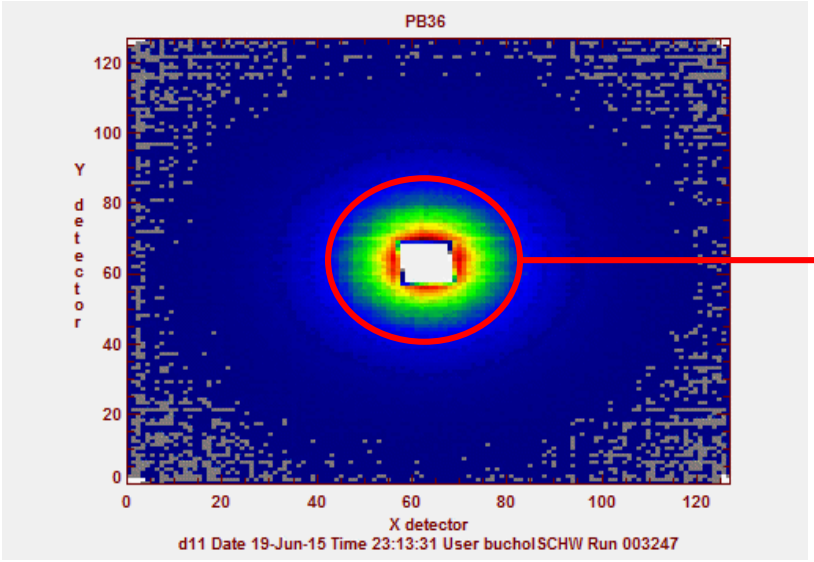


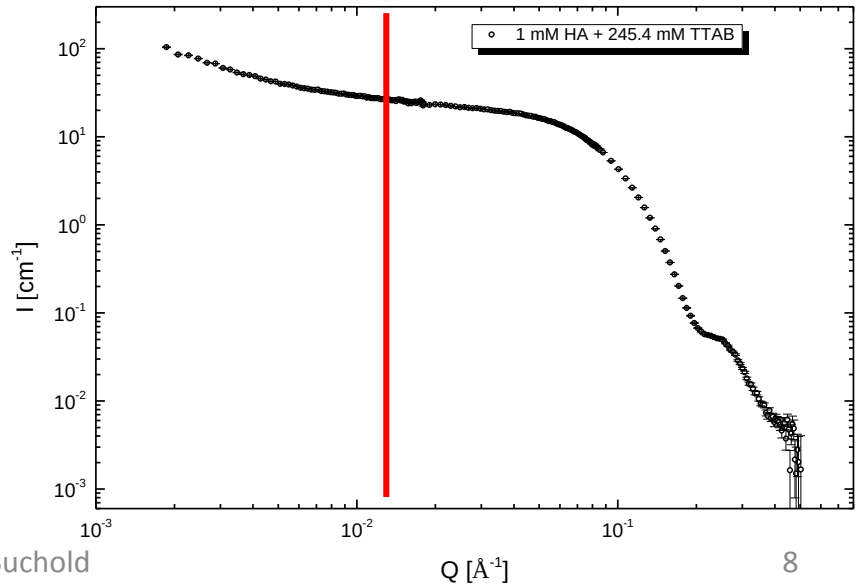
-> high viscosity of HA is not effected by
moderate addition of salt or high surfactant concentrations

-> Unusual: either precipitate,
or viscosity drop to surfactant

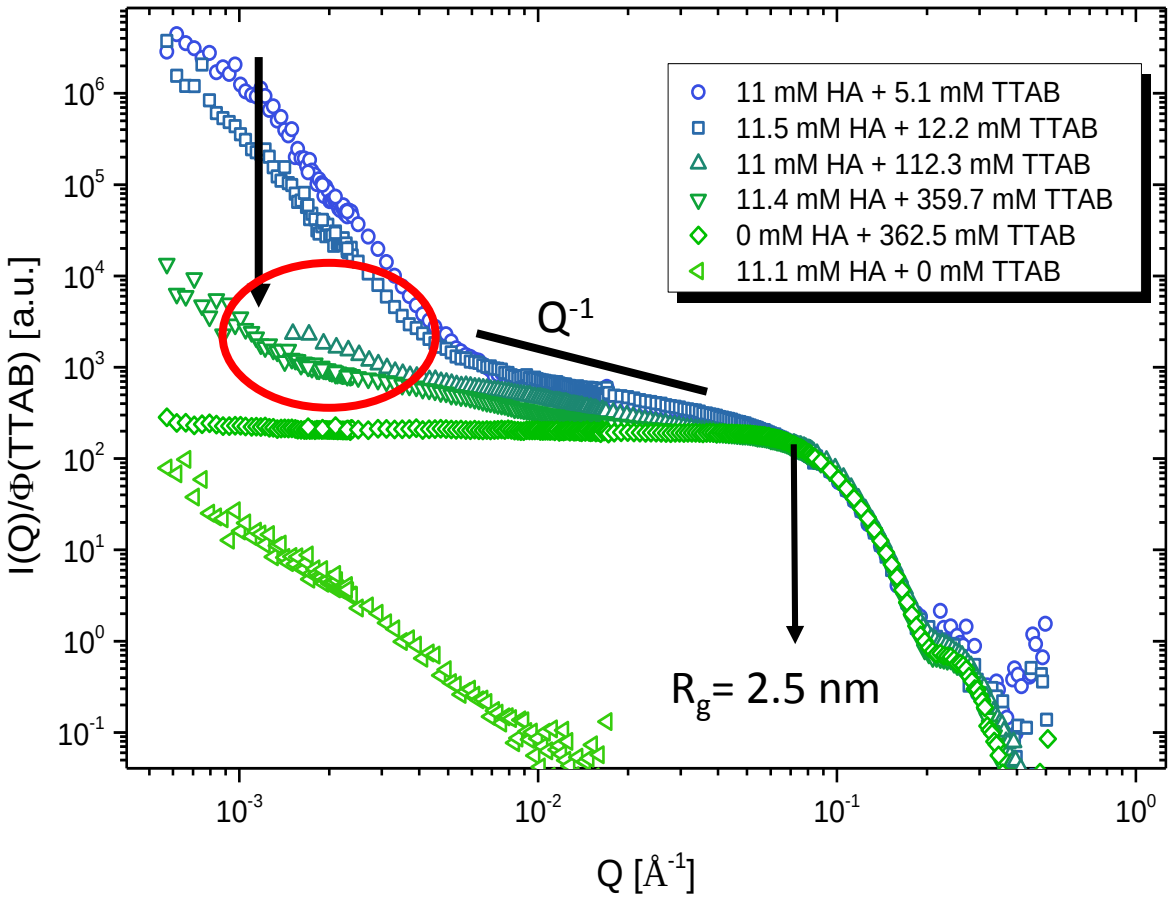
Small angle scattering

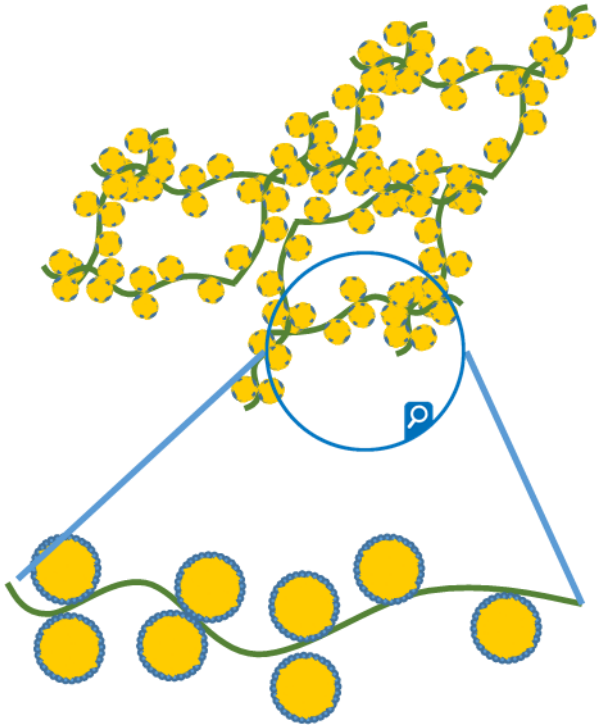




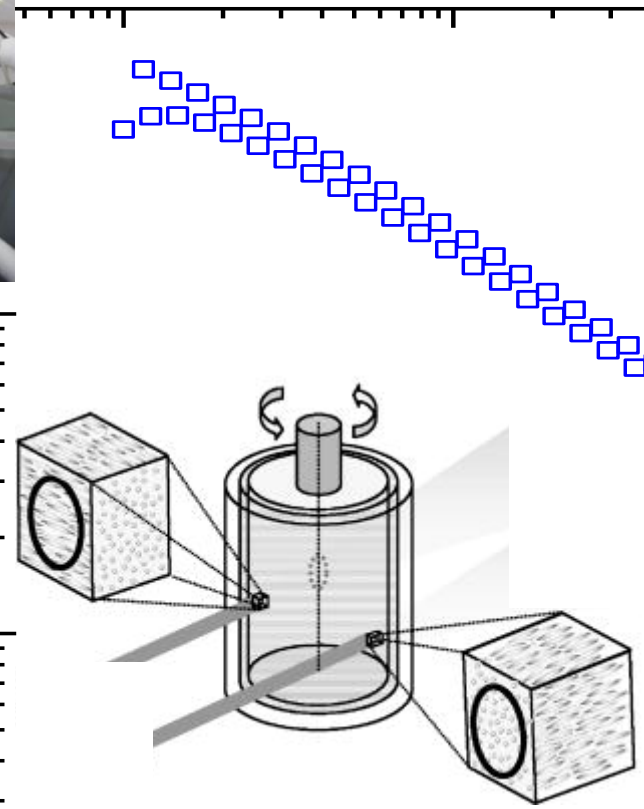


Structural arrangement





Alignment in shear flow



Mid q, 16 mM HA + 245 mM TTAB

FRM2-Data

viscosity [Pa s]

10^{1}

10^{0}

10^{-1}

0.1

1

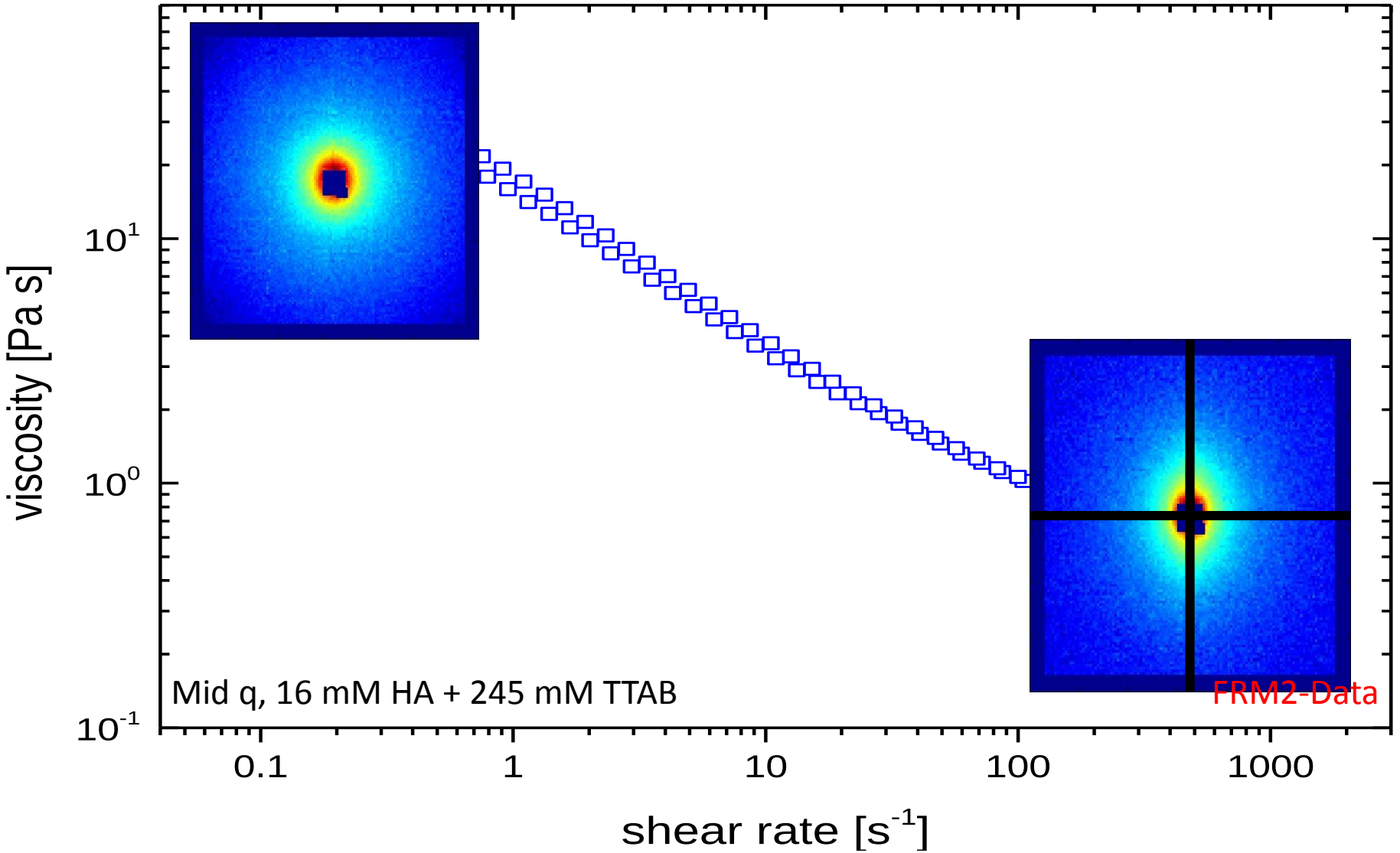
10

100

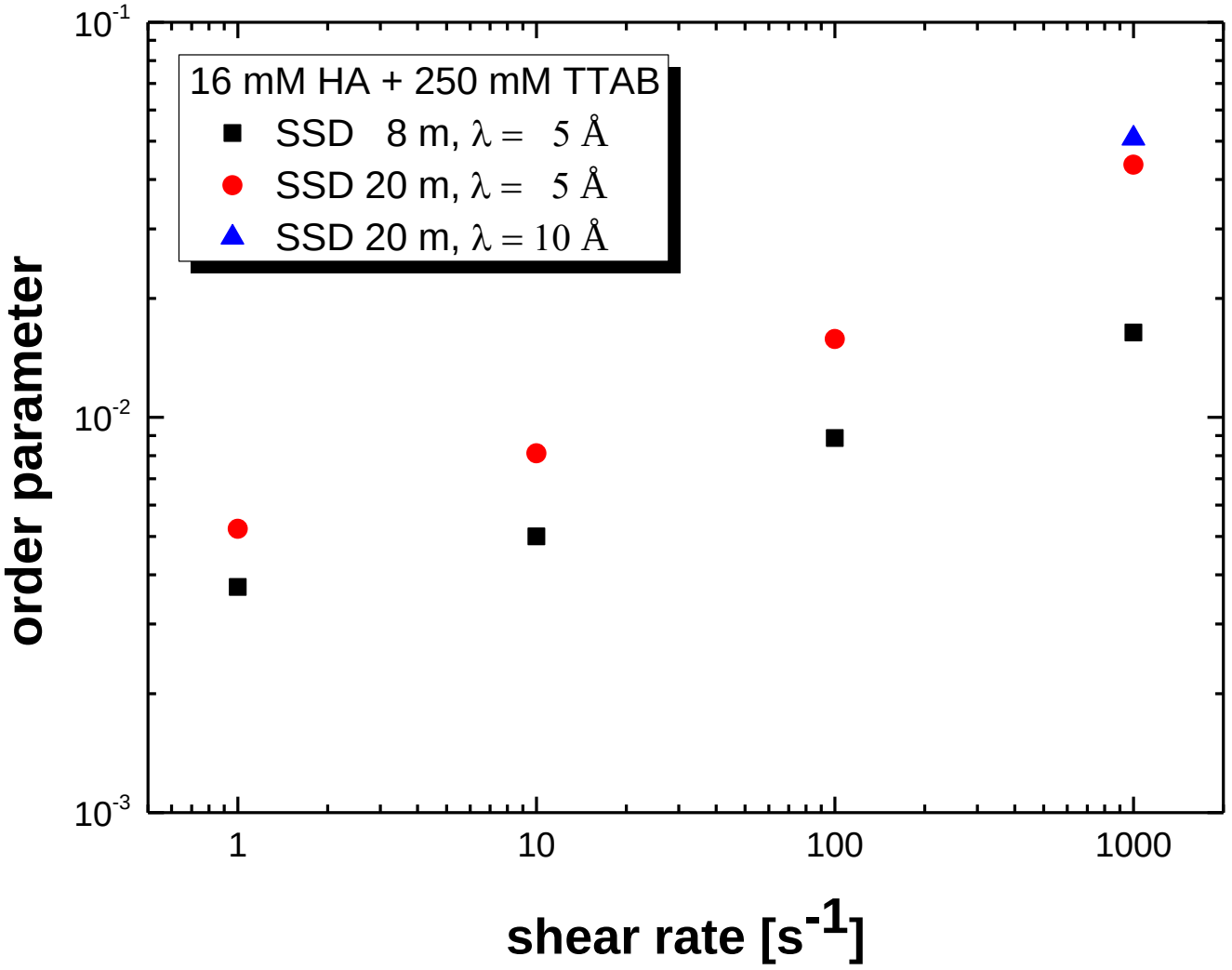
1000

shear rate [s^{-1}]

Alignment in shear flow



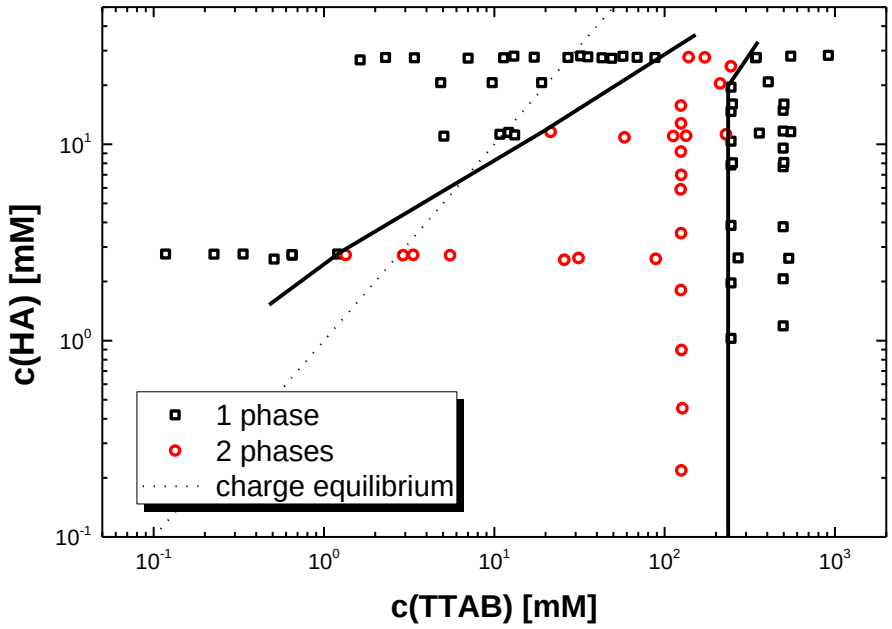
Order parameter SASET



Project

Viscosity of the mixtures

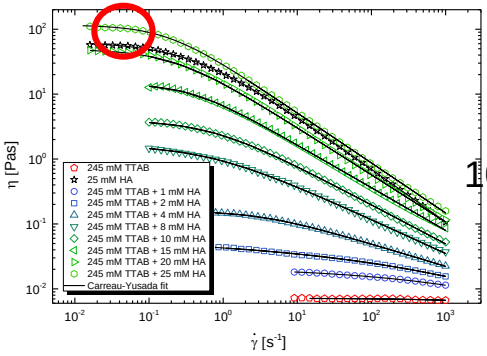
Structure of the formed complex

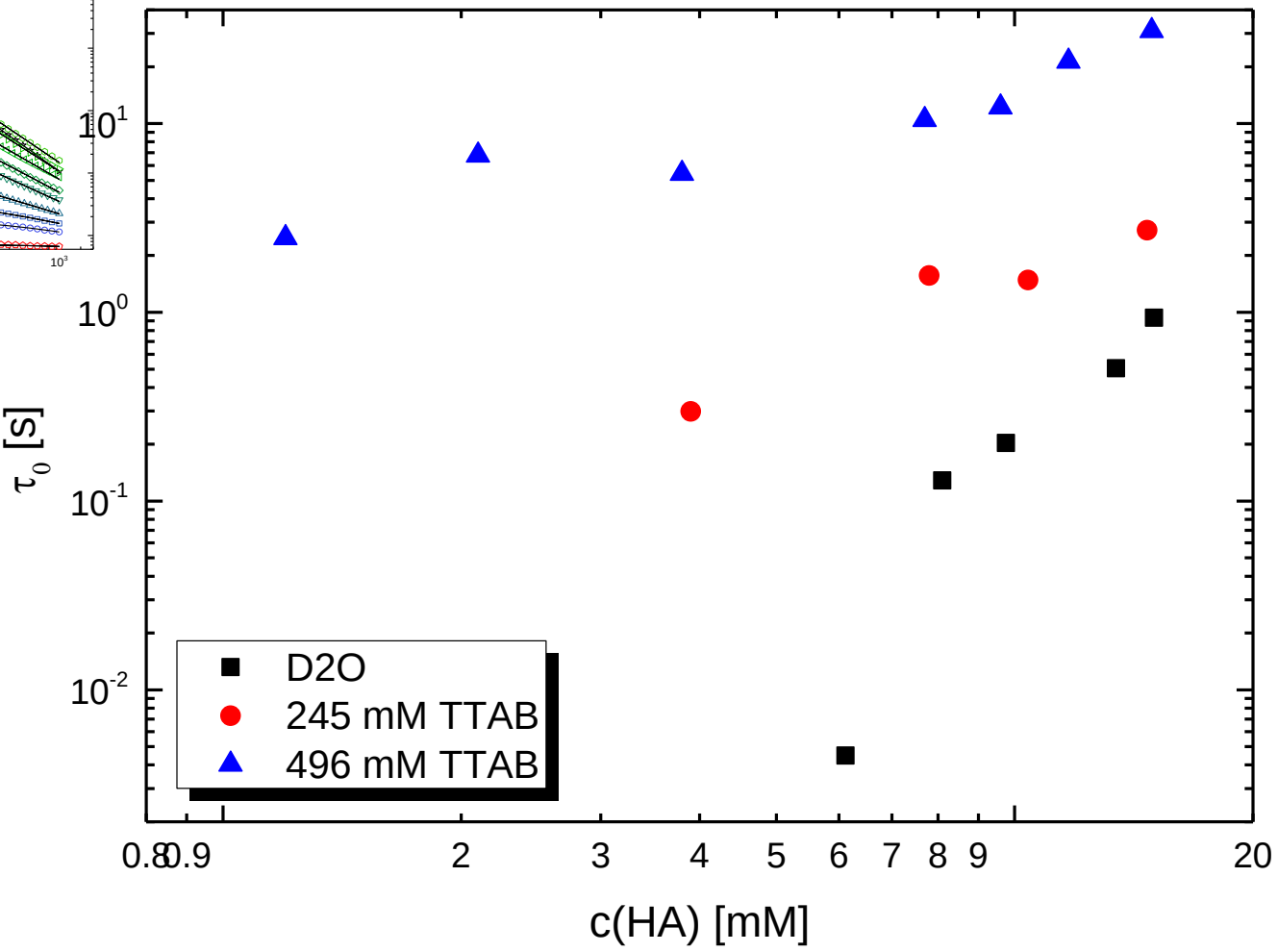


Dynamics of the solutions

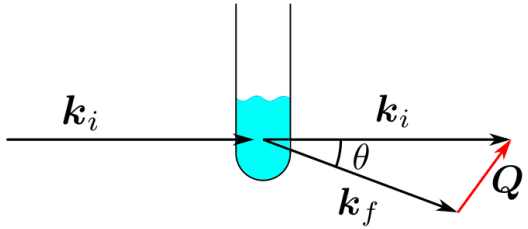
Influence/control on the complex

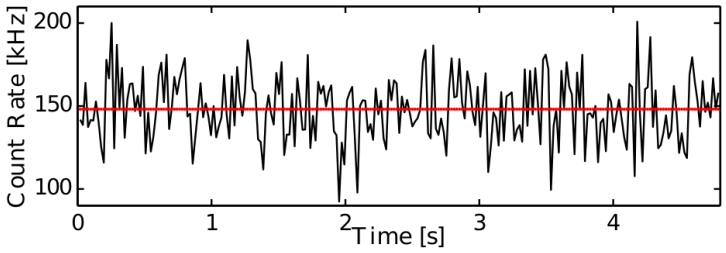
Macroscopic Relaxation time





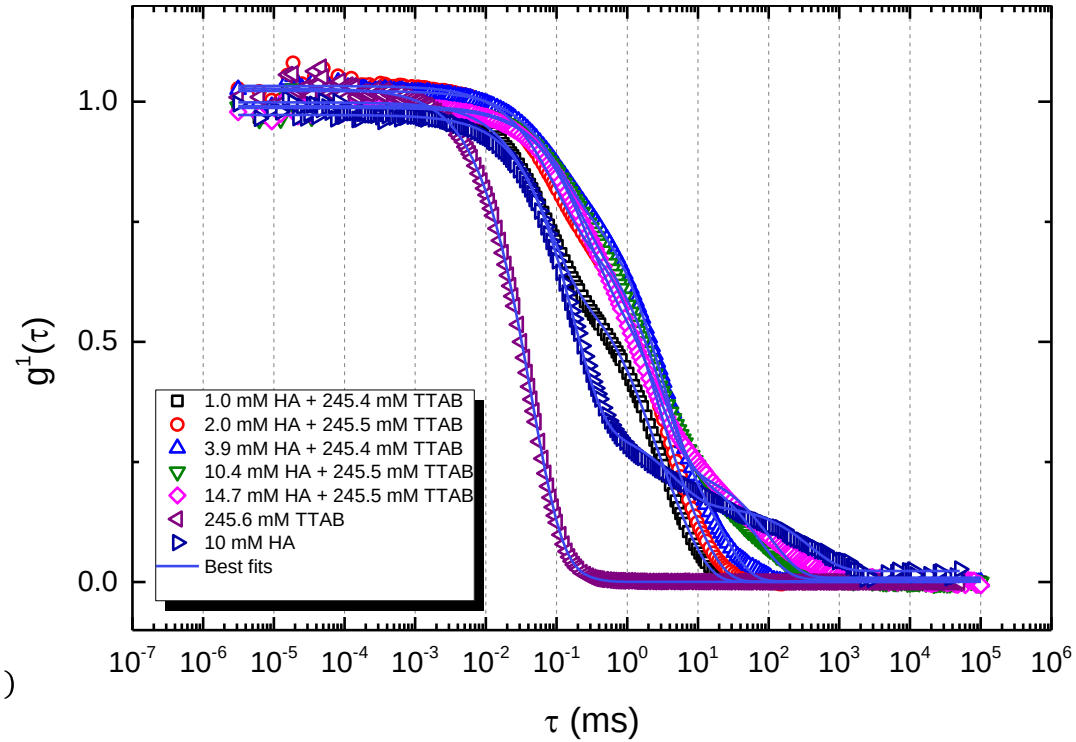
Dynamic light scattering





$$g(q,\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q)\rangle^2}$$

$$g(t) = A\,e^{(-t/\tau_3)} + B\,e^{(-t/\tau_3)} + C\,e^{(-t/\tau_3)}$$

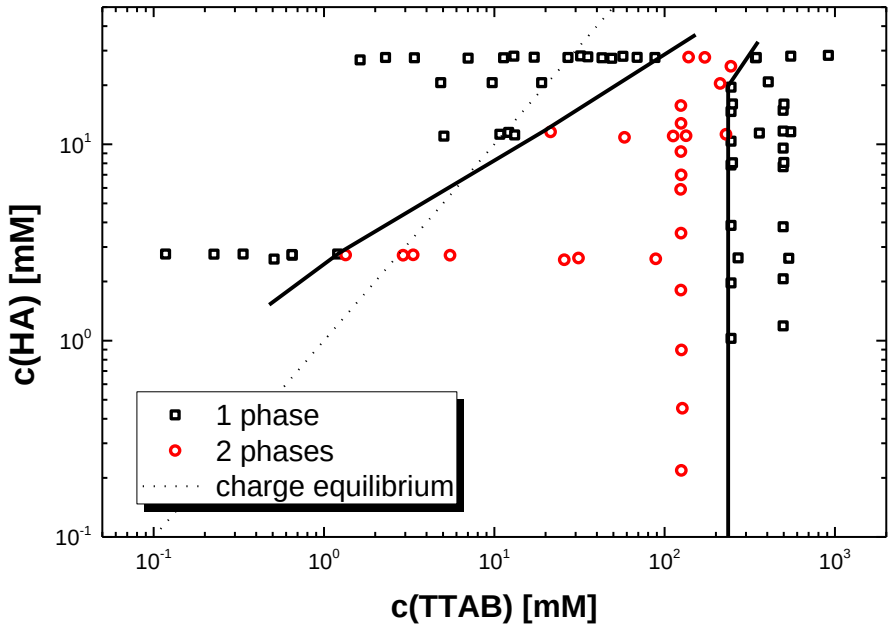


245 mM TTAB	R_h1 /nm	R_h2 /nm	R_h3 /nm
pure TTAB	2.5	8.5	0
+ 1 mM HA	4.3	75.6	327.5
+ 2 mM HA	4.8	111.6	516.5
+ 4 mM HA	6	152.6	1149.6
+ 10 mM HA	9.7	165.4	4014.6
+ 15 mM HA	12.5	156.6	5983.8

Conclusion

No breakdown of the viscosity

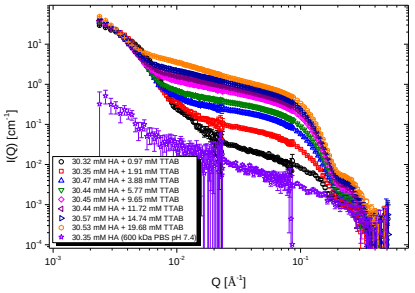
Elongated, cylinder like structure



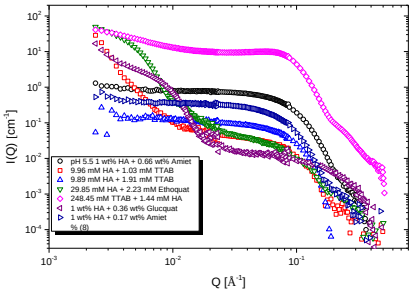
System diffuses slower than pure solutions

Simple mixing ratio changes the structure

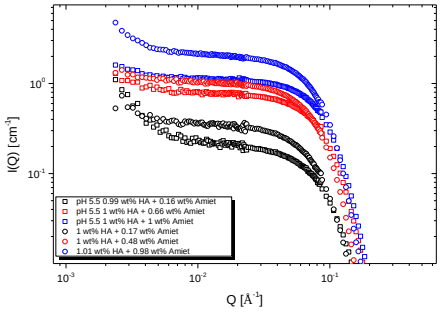
More details…



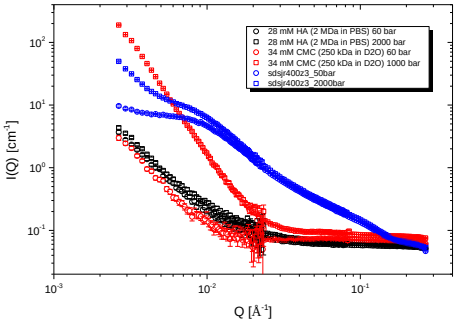
- Biological buffer (PBS) shows same behavior



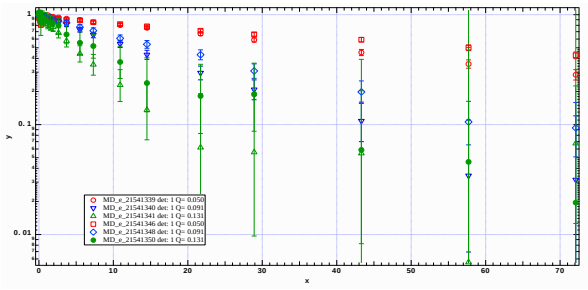
- Surfactant head-group plays important role



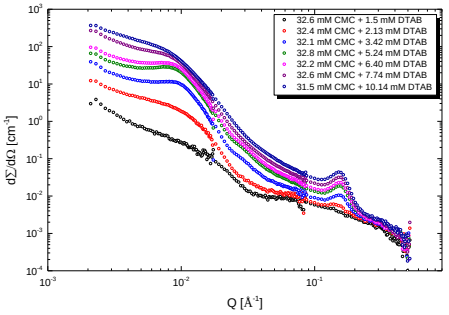
- Switching the charge on the surfactants on/off in/decreases the effect



- Complexes stable up to 2500 bar



- Spin-Echo - analysis ongoing
- Contras variation - analysis ongoing
- Reflectometry - analysis ongoing



- Different behavior for similar PE

Outlook

- Dynamics of the system:
  - Fluorescence Correlation Spectroscopy :
    “labeling the dynamics of the micelle”
  - Neutron Spin Echo
- Effects on the polymer network:
  - USANS experiment for lower q-range at KWS-3
- Cryo-TEM picture of the system

Acknowledgements

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Thank you for your attention.