Flow and phase transitions in micellar systems

Shear thickening & time-dependent rheology

Outline

- Basic shear thickening phenomena
- Wormlike micelles
- Experimental approach – light scattering microscopy
- Rheological & structural behavior

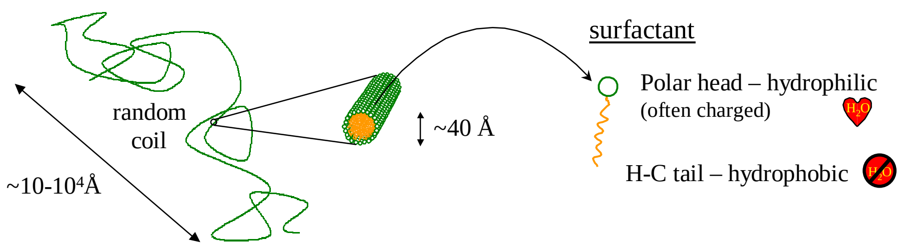
Collaborators

Chu-heng Liu (Xerox) – light scattering microscopy
Philippe Boltenhagen (Strasbourg) – rheo-scattering
Yuntao Hu (Unilever) – rheo-scattering
Jacqueline Goveas (Rice Univ.) – theory

1

Worm-like micellar solutions

(in water)



Concentration regimes

- critical micelle concentration (*cmc*)

  $c < cmc \rightarrow$ only free surfactant molecules
  $c > cmc \rightarrow$ micelles + free surfactant molecules

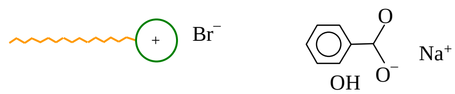
- overlap concentration (c^*)

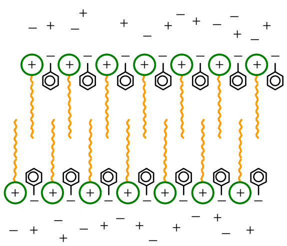
  micelles overlap each other above this concentration
  experimentally often defined by the concentration where
  solution viscosity = twice solvent viscosity

2

Shear-thickening worm-like micellar solutions

CTAB + NaSal + H_2O (cetyltrimethylamonium bromide + sodium salicylate + water)





- Sal^- ions are incorporated into micelles ~1:1 (NMR)

  (this is unusual – most charged micelles are not neutral!)

- c^* ~ a few millimolar

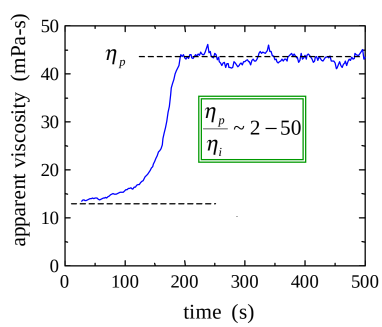
Most micellar systems which exhibit shear thickening are like this

3

Shear thickening in dilute worm-like micellar solutions

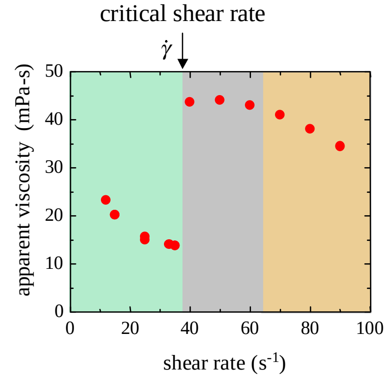
(basic rheology)

Response after turning on steady shear rate greater than some threshold



Note long latency time prior to shear thickening

critical shear rate



Shear thinning

Shear thickened state

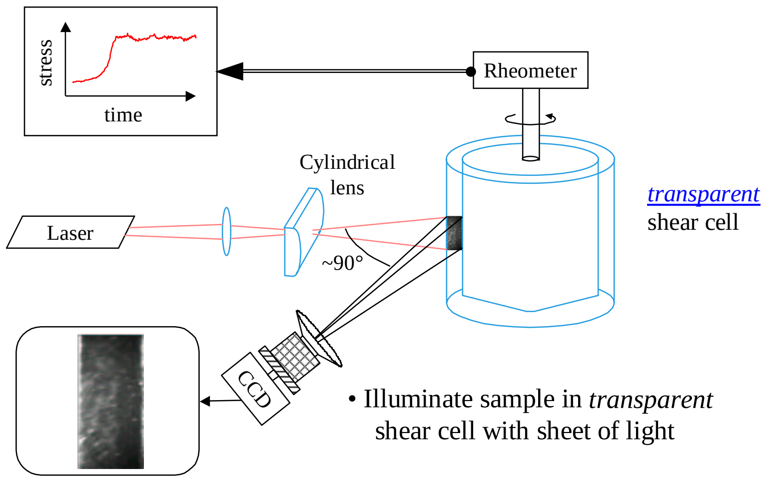
Shear thinning
(after shear thickening)

Concentrations for shear thickening: ~cmc < c < ~3-5 c^*

4

Experimental Approach

— simultaneous mechanical & structural measurements —



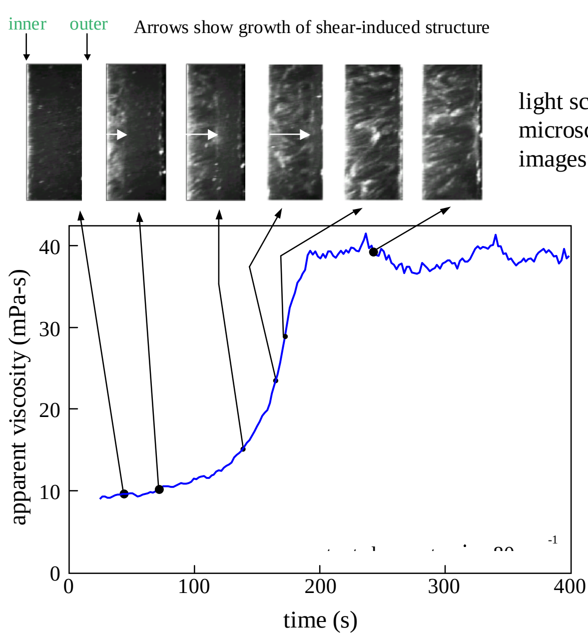
- Illuminate sample in *transparent* shear cell with sheet of light
- Collect light scattered by fluid structures with video camera

light scattering microscopy

(dark-field microscopy)

5

Time-dependent rheology & microscopy above the critical shear rate

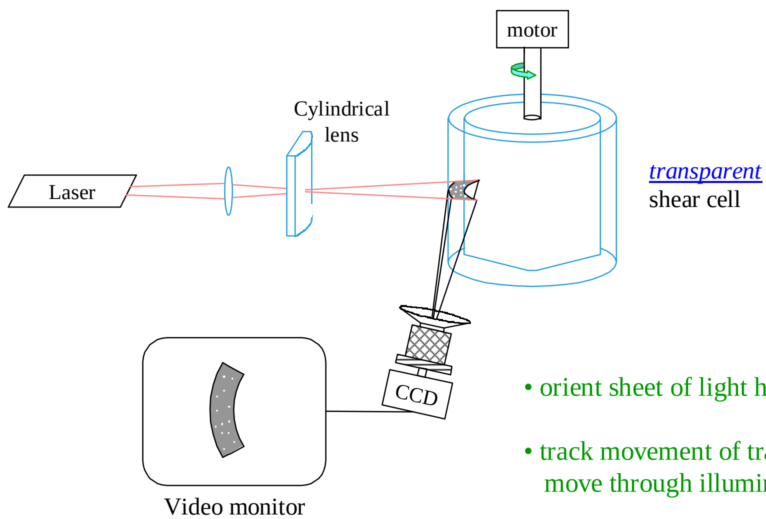


light scattering microscopy images

- inner cylinder at left
  outer cylinder at right
- a white structure starts growing from inner cylinder (left) after about 1 minute
- growth of white structure associated with increase in apparent viscosity
  ⇒ white structure is very viscous or even gel-like

6

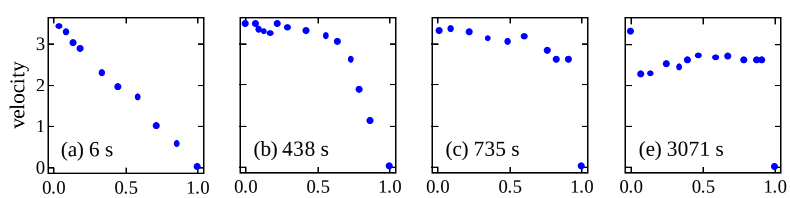
Measuring velocity profile

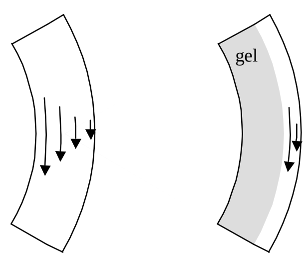


- orient sheet of light horizontally
- track movement of tracer particles move through illuminated sheet

7

Velocity profiles during shear thickening experiment





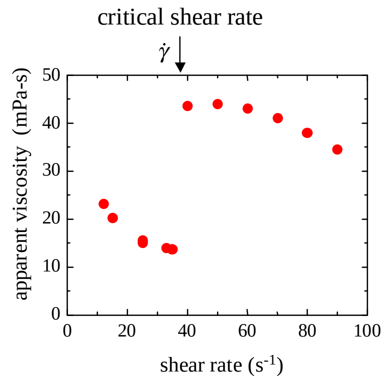
There is little or no flow within the “white” phase

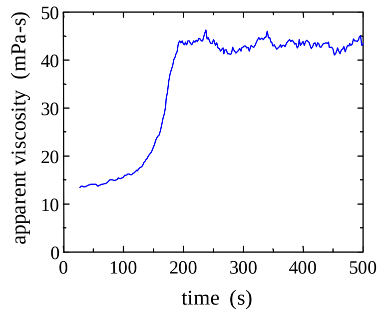
⇒ we can call it a ~gel

Note: shearing a gel causes it to scatter more light

8

Why the steady state gel thickness & apparent viscosity increase discontinuously ...





(1) When $\dot{\gamma} > \dot{\gamma}_c$, "gel" begins to grow from inner cylinder

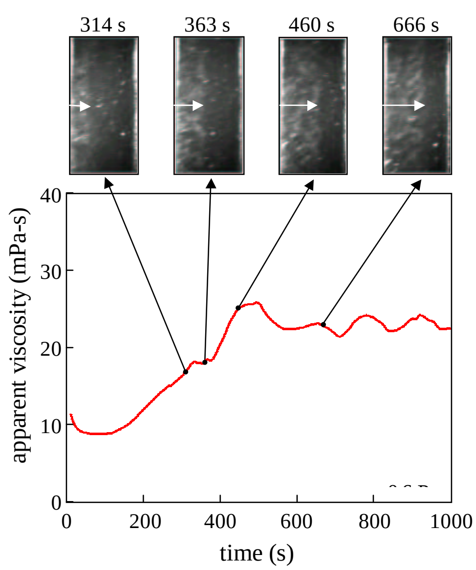
(2) Since the gel doesn't flow, the shear rate and stress in the remaining fluid increase

(3) This causes more gel to form and further increases the shear rate & stress

(4) This process continues until there are no more micelles available to attach to gel

9

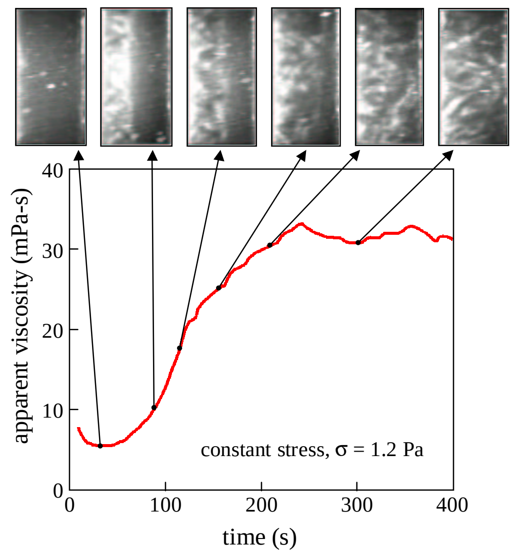
Time-dependent rheology & microscopy for controlled stress



- inner cylinder at left
  outer cylinder at right
- a white structure starts growing from inner cylinder after about 120 s
- growth of white structure associated with increase in apparent viscosity
  ⇒ white structure is very viscous or even gel-like
- gel-like structure continues to grow outward until reaching a steady-state thickness of about 5/8 of the cell gap width

10

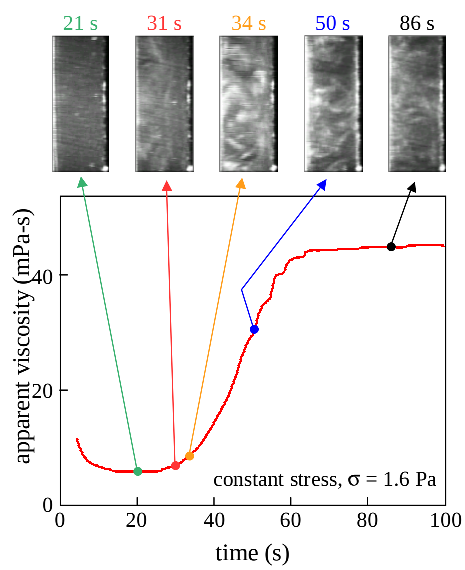
Increase the stress …



- at higher level of stress, gel seems to nearly fill the gap
- there continues to be a close correspondence between the apparent viscosity and the thickness of the gel-like structure

11

BUT ... sometimes the correspondence between gel thickness & apparent viscosity breaks down ...



- at 21 s, there is no gel
- at 31 s, the gel is barely visible but can be seen nearly throughout the gap
- at 34 s, the gel is clearly visible & fills gap

BUT ...

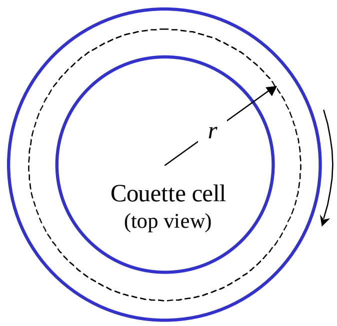
- the apparent viscosity does not rise significantly until ~10 s later

What is happening ?

HOMOGENEOUS NUCLEATION

12

Nucleation and stability of gel phase



Mechanical equilibrium ⇒ $\sigma \propto \frac{1}{r^2}$
(balance torque at r)

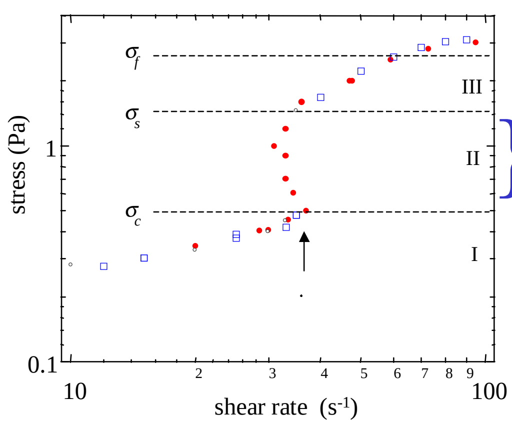
⇒ Stress is greatest near inner cylinder

- when stress or shear rate is increased incrementally, gel nucleates only at the inner cylinder
- when stress or shear rate is increased such that $\sigma >> \sigma_c$, gel nucleates everywhere in the cell where $\sigma >> \sigma_c$

HOMOGENEOUS NUCLEATION

13

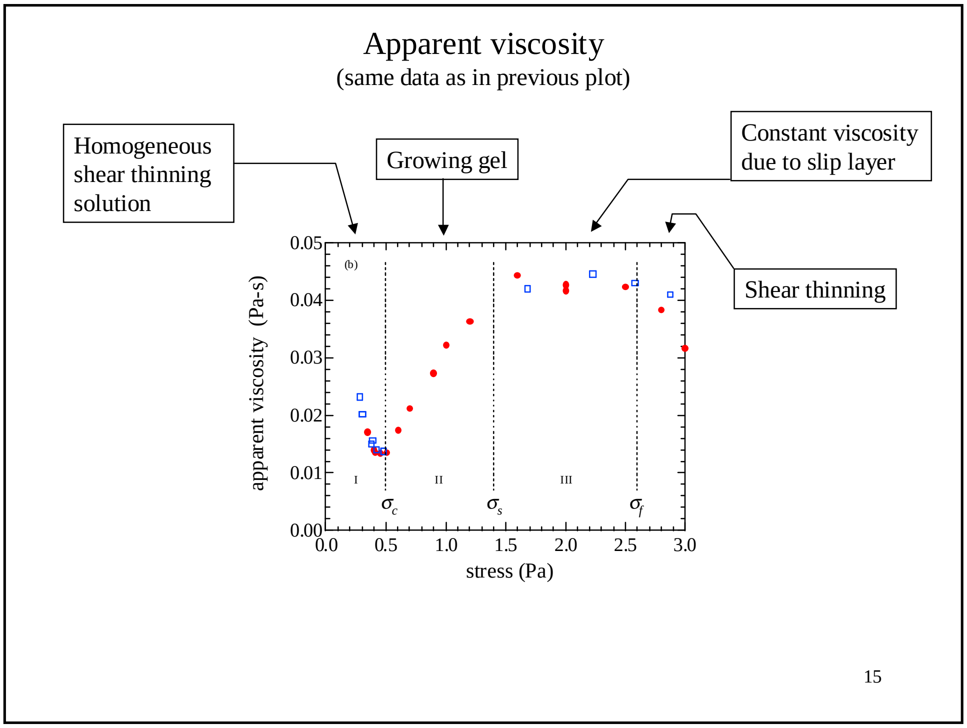
Role of stress and shear rate

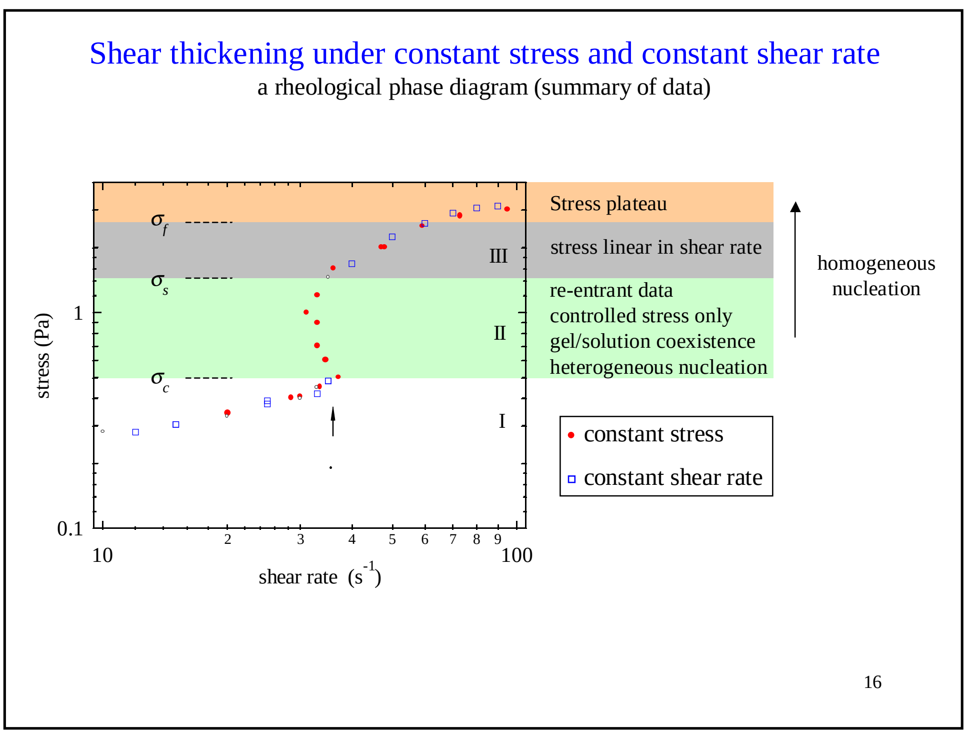


- In region II, $\dot{\gamma} < \dot{\gamma}_c$, but gel remains under controlled stress
- Shear rate in gel phase is nearly zero but gel phase persists for $\sigma > \sigma_c$
- Gel phase is observed iff $\sigma > \sigma_c$

⇒ stress (and not shear rate) controls the formation of gel

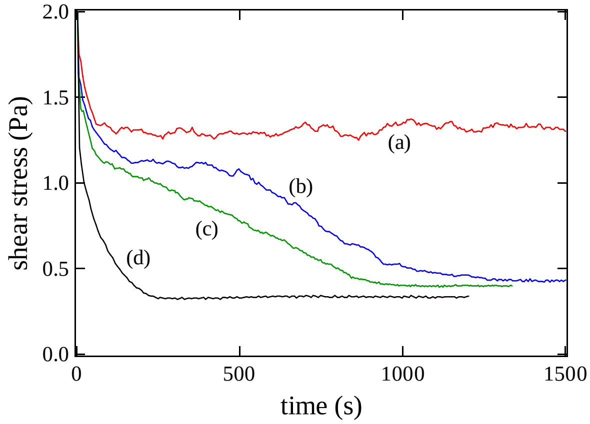
14

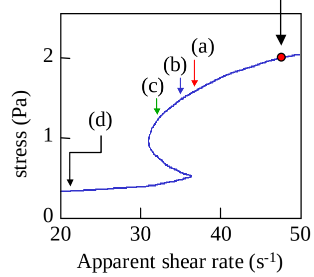

Apparent viscosity
(same data as in previous plot)
Homogeneous shear thinning solution
Growing gel
Constant viscosity due to slip layer
Shear thinning
apparent viscosity (Pa-s)
stress (Pa)
I
II
III
σc
σs
σf
15


Shear thickening under constant stress and constant shear rate
a rheological phase diagram (summary of data)
Stress plateau
stress linear in shear rate
re-entrant data
controlled stress only
gel/solution coexistence
heterogeneous nucleation
homogeneous nucleation
constant stress
constant shear rate
stress (Pa)
shear rate (s-1)
σf
σs
σc
I
II
III
16

Quenching from gelled state to lower shear rate

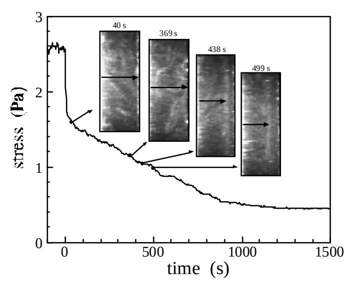
Quench experiment
(1) prepare system in high shear fully gelled state
(2) reduce shear rate & follow evolution of stress





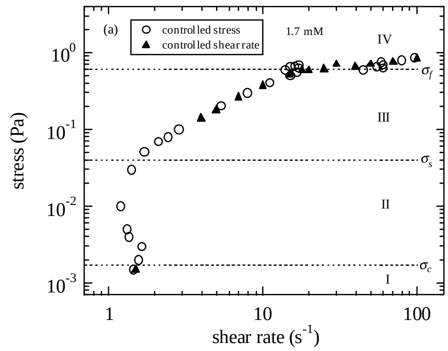
17

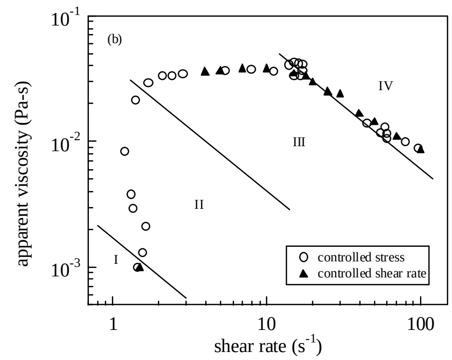
"Melting" of gel



18

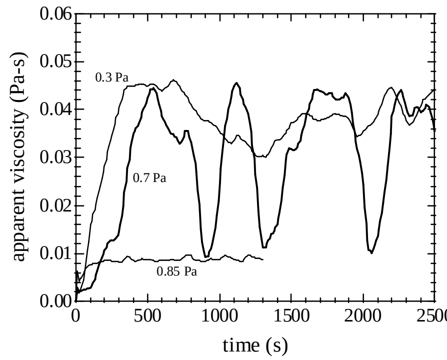
Shear thickening (II) and shear thinning (IV)

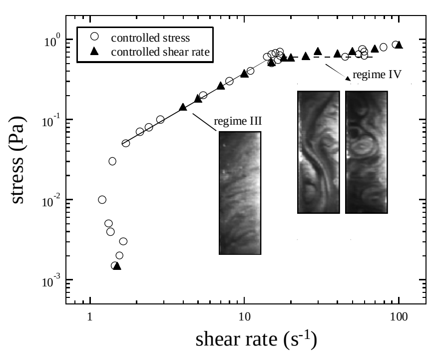




19

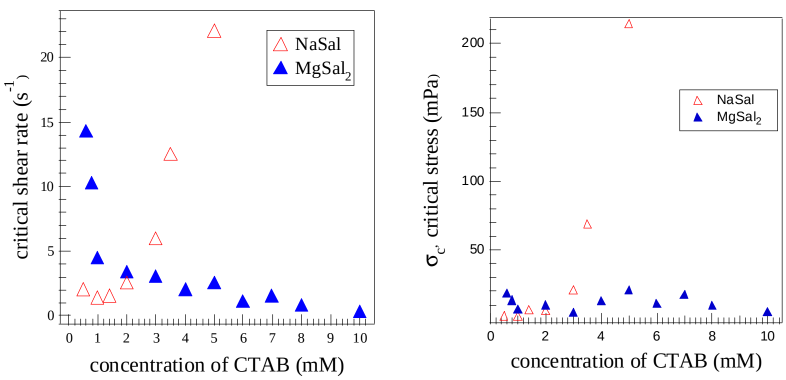
Behavior in shear thinning region





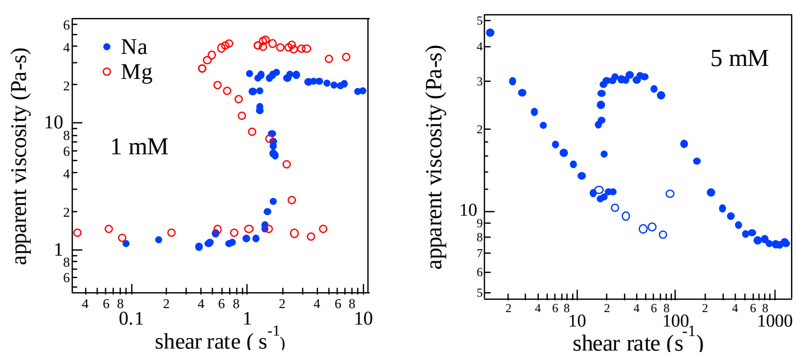
20

Effect of counterion valence on critical shear rate & stress



21

More rheology …



22