T1

Rheology of Wormlike Micelles

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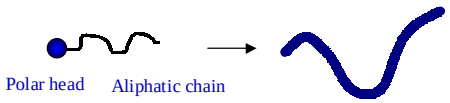
Wormlike micelles

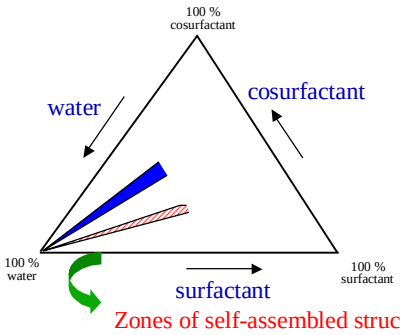
Long polymer-like chains resulting from the association of surfactant



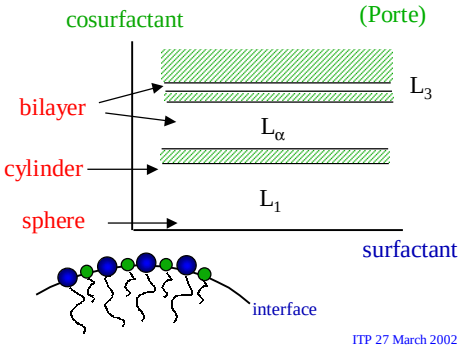
Usually :
C16-surfactants and cationic

Phase Behavior

Cylindrical aggregates are intermediate in terms of curvature of the surfactant film between spheres and bilayers



Zones of self-assembled structures



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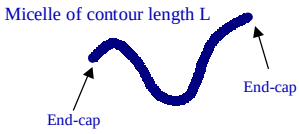
Growth of cylindrical micelles (Israelachvili 1976)



The end-cap enery E drives
the unidimensional growth of the aggregates

E ~ 20 k_BT (~ 1 k_BT per surfactant in the endcap)

Number density c(n) of micelles of aggregation number n :

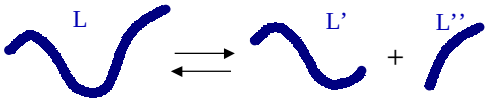
$$c(n) = \frac{c}{\bar{n}^2}\exp(-\frac{n}{\bar{n}})$$

c is the concentration
$\bar{n}$ is the average aggregation number

$$\bar{n} = \sqrt{c \times \exp(E / k_B T)}$$

Predictions are that micelles are broadly distributed in size, polydispersity index 2
Experimentally : 100 Å in length correspond to 200 molecules

Dynamic of breaking/recombination (Cates 1987)



Equilibrium properties are based on curvature of the surfactant film (or packing of surfactants)

Probability of breakage ~ $c_1 \times L$
(c_1 and L are thermally activated)

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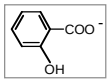
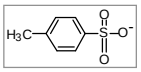
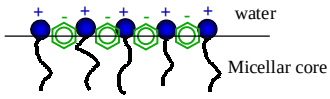
Experiments : How to make micelles grow ?

1. Add cosurfactant — as in CPCl/Hexanol/water (Porte)
2. Add salt (to screen electrostatics) — as in CTAB/KBr (Lequeux, Candau)
3. **Add strongly binding counterions** — **Rehage, Hoffmann and others**
4. …. — Gemini surfactant (In, Zana); Cationic-anionic mixtures (Kaler)

Salicylate 

Tosylate 

Salicilate etc… are not simple salt : they are incorporated to the body of the micelles
(Estimation from the effective charge per unit lenth : 90 % are in the micelles)



With strongly binding counterions

Strongly viscoelasticity in entangled state
The viscoelasticity is Maxwellian

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Illustrations of a Maxwellian behavior

CPCl-NaSal-H_2O

Rehage and Hoffmann (88)

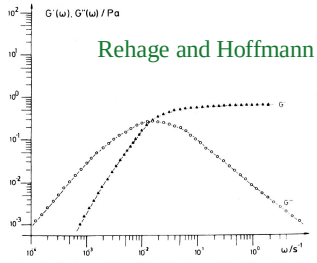
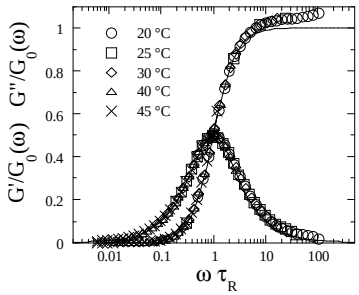


Figure 10. Storage modulus G' and the loss modulus G'' as a function of the angular frequency ω for a solution of 15 mmol CPyCl and 12.5 mmol NaSal at $T = 20$ °C.

CPCl-NaSal-H_2O (0.5 M NaCl)



Viscoelasticity arises from entangled network

Cates Model (1987)

1. Unicity of relaxation time is explained by the combination of reptation and breaking
2. Scaling laws for viscoelastic parameters *versus* concentration $\eta_0 \sim c^{7/2}$ and $G_0 \sim c^{9/4}$

1 is almost always observed, 2 not always !

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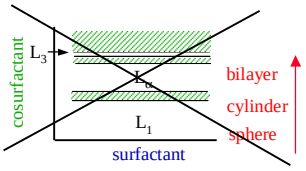
Specificity of the strongly binding counterions

1 - With increasing counterions concentration
No change of morphology
(Except from sphere to worms)

2 - Rehage and Hoffmann (88)



Static viscosity

Maxwellian behavior

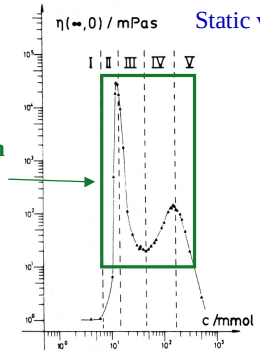


Figure 8. Zero shear viscosity $\eta(\infty,0)$ as a function of the NaSal concentration for solutions of 15 mmol CPyCl at $T = 20$ °C.

Not all Maxwellian fluids are equivalent (shear thinning, shear tickening, or both)

Theoretical predictions (growth law, scaling) might not apply

There is a specificity for micelles made with counterions, especially for the dynamics of the network ?

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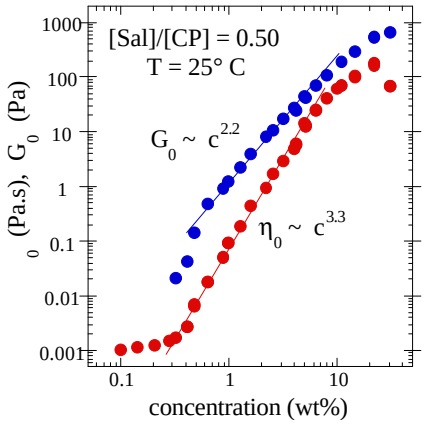
Rheology of Wormlike Micelles

System investigated : CPCl, NaSal
Requirements : 1 - Fix the ratio counterion /surfactant (here 0.5)
2 - Saturate the solutions with salt (screening electrostatics)



Scaling in agreement with Cates Model

Changing counterion/surfactant ratio and the agreement is less good

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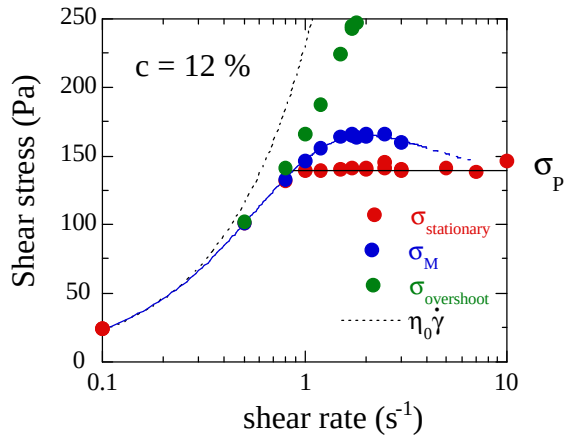
General Flow curve

Micellar system : CPCl-NaSal-H_2O (0.5 M NaCl)
Experiments made at stationary state



At the stationary state, the stress shows a plateau (above γ_1). The stress plateau is robust

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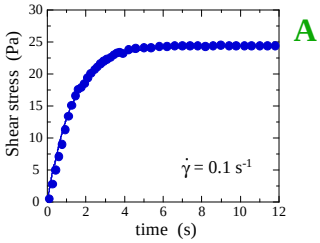
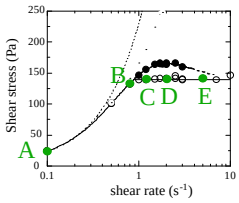
Transient rheology of Wormlike Micelles

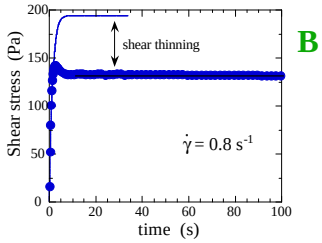
Before the plateau

Linear regime :
in agreement with stress relaxation function



$G_0 = 240$ Pa, $\tau = 1$ s



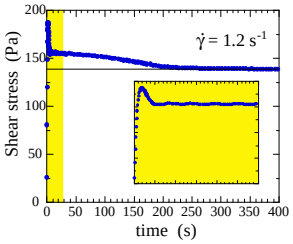


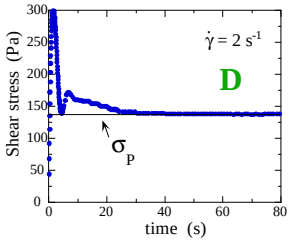
Nonlinear regime : overshoot

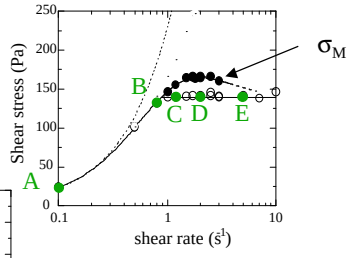
TT9

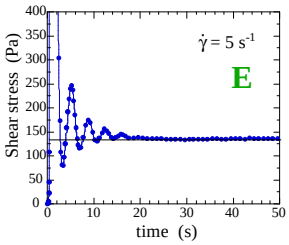
Transient rheology of Wormlike Micelles

At the stress plateau









- Long-time relaxations
- Oscillations
- σ_M : « mechanical » stress

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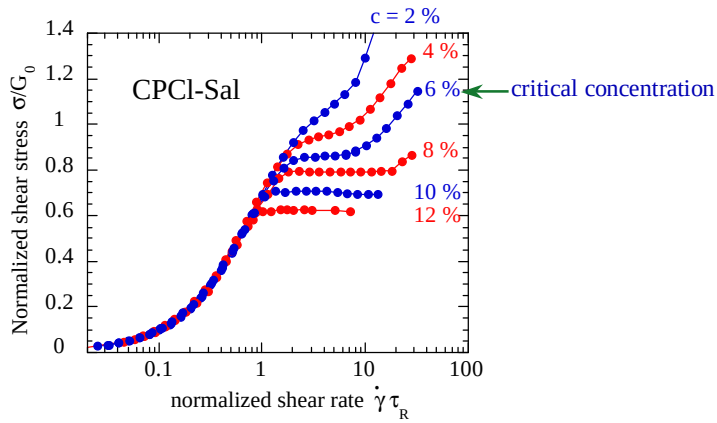
General Flow Phase diagram

Playing with concentration and temperature



Stress plateaus are robust
Strong analogy with phase transition
In this case : isotropic-to-nematic induced by shear

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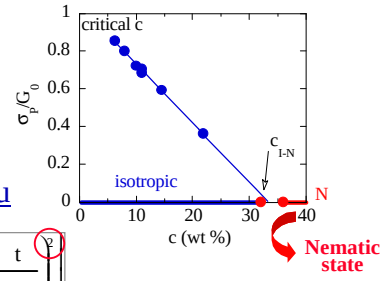
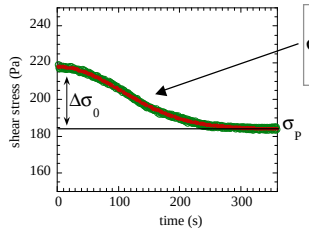
Arguments in favor of the I-N transition (1994)

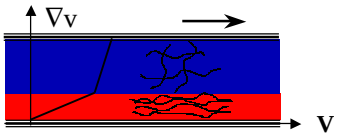
1 - σ_P/G_0 extrapolates at 0 for $c = c_{I\text{-}N}$
(found in two different systems)



2 - Kinetics at the onset of stress plateau



$$\sigma(t) = \sigma_P + \Delta\sigma_0 \exp\left[-\left(\frac{t}{\tau_{I-N}}\right)^2\right]$$



- The stress decrease coincides with the nucleation and growth of the aligned (nematic) state
- The exponent 2 is related to a one-dimension mechanism
- Strongly aligned phase is the high shear rate band

SANS and FB
Inconclusive !

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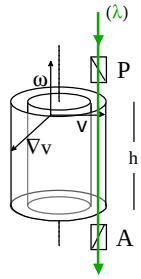
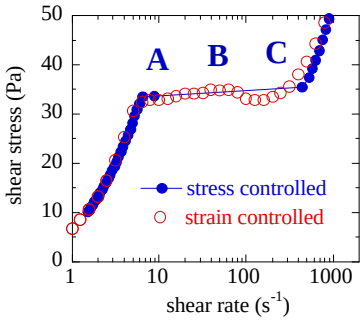
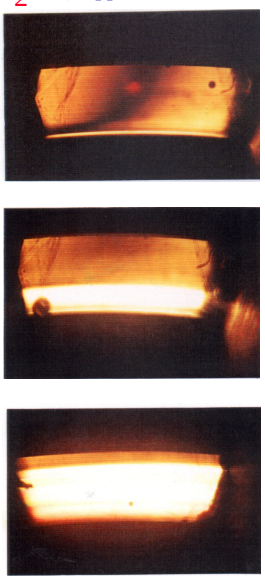
The «ideal » example : CTAB/$D_2$0 (Cappelaere et al. 1997)

- Rheology
  (rate and stress controlled)
- SANS
- Flow birefringence
  (J.P. Decruppe)







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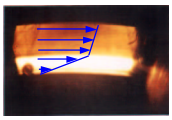
New results (1) : Fisher and Callaghan (2000)

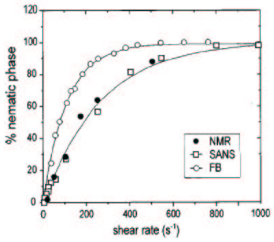
NMR measurements

Does the highly birefringent band correspond to a high shear rate band ?



Micellar system : CTAB-D_2O

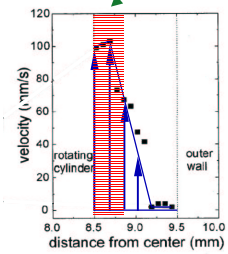
Proportion of nematic phase



The agreement between SANS and NMR is excellent

Velocity profile

Birefringent band



The highly birefrigent phase is not the high shear rate band

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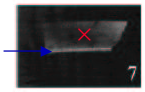
New results (2) : Lerouge et al. (2000)

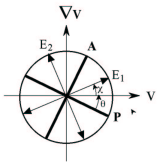
Transient flow birefringence

Micellar system : CTAB-$NaNO_3$

Rheology identical to CPCl-NaSal

Appearence of a thin band

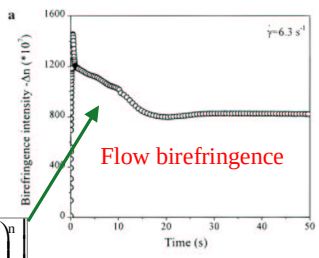


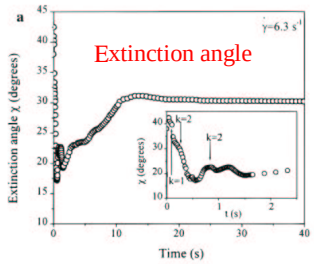


$$I(t) \sim \sin^2\frac{\phi(t)}{2}\sin^2(2\chi(t)-\theta)$$

$$\Delta n = \frac{\lambda\phi}{2\pi h}$$

ϕ : phase shift
χ : extinction angle
θ : angle between polarizer and V
Δn : birefringence
h : height of the Couette cell





$$\sim \exp\left[-\left(\frac{t}{\tau}\right)^n\right]$$

The long-time kinetics in FB coincides precisely with the kinetics seen in transient rheology

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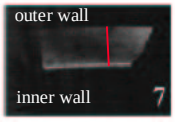
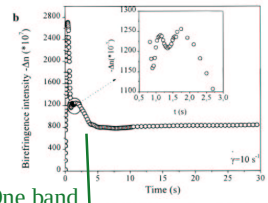
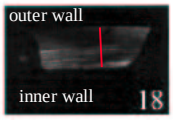
Transient birefringence



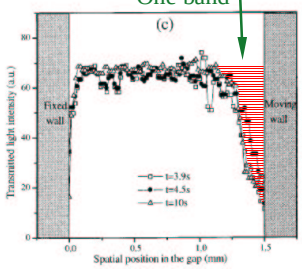


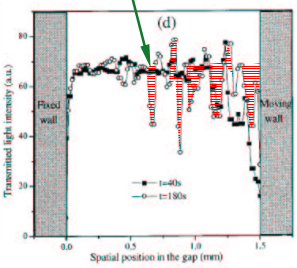


One band

multibands

Short time





Long time

Evidence of multibanded flow / the stress remains constant

Final bands are 100 µm broad and not stationary

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conclusions

1. In entangled state, wormlike micelles are Maxwellian fluids
2. The nonlinear rheology of wormlike micelles show stress plateaus
3. Stress plateaus are associated to shear banding (flow birefringence)
4. The picture of an isotropic-to-nematic transition is not appropriate
5. A description in terms of a mechanical instability related to the existence of a non monotonic constitutive equation is plausible

Possible routes :
Determine experimentally the non-monotonic constitutive equation for wormlike micelles (?)
Investigate simultaneously the temporal and spatial (at the micron length scale) responses of the sheared fluids using FB, NMR, scattering

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