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Rheology and phase behavior of dense casein micelle dispersions

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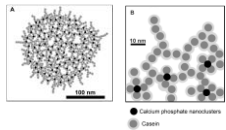
Our questions...

Dairy concentration and drying operations

→ dense dispersions of casein micelles

- What is the **behavior** of "native" casein micelles upon **concentration** ?
- How the **rheological properties** of the dispersions change with **casein concentration** [Cas] ?
- How these properties are linked to the peculiar **structure and properties** of the casein micelle ?

[McMahon, JDS, 2008]

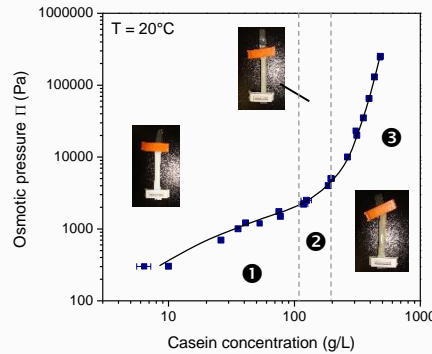


Casein micelle =

- . Large (r~100nm) globular aggregates of caseins + calcium phosphate
- . Soft and "dynamic" colloid
- . Highly porous / hydrated (voluminosity = 4.4 mL/g)

What we know from Osmotic Stress experiments

[Bouchoux, Biophys.J., 2009]



The osmotic pressure profile of casein micelle dispersions

→ Dramatic changes in "observed" properties : **textural, optical**

→ **3 compression regimes**

1 Dilute regime

Liquid-like behavior
Turbid

2 Transition regime

Liquid-like → Soft-solid
Turbid → Yellowish

3 Concentrated regime

Solid-like
Translucent

Methods

Materials

- Native casein micelles → Native PhosphoCaseinate (NPC)
- "Unorganized" caseins (no CaP clusters) → Sodium caseinate (SC)

Sample preparation

- . [Cas] < 150 g/L = Dilution / [Cas] > 150 g/L = Osmotic compression (with PEG)
- . Solvent = "native" environment → milk ultrafiltration permeate (UF)

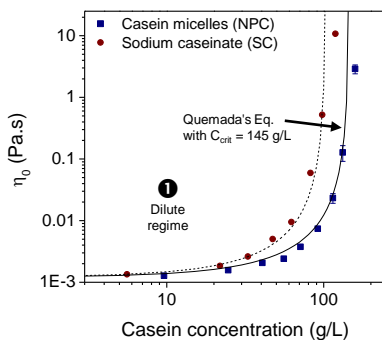
Rheology

- . AR2000 rheometer / T = 20°C
- . Geometries : Couette / Cone-Plate / Plate-plate
- . 3 types of experiments

- a - Steady shear flow → zero-shear viscosity VS [Cas]
- b - Oscillatory → G' & G'' VS [Cas] & frequency
- (c - Creep / Recovery → in progress / results not shown)

Results

a - Zero-shear viscosity η_0



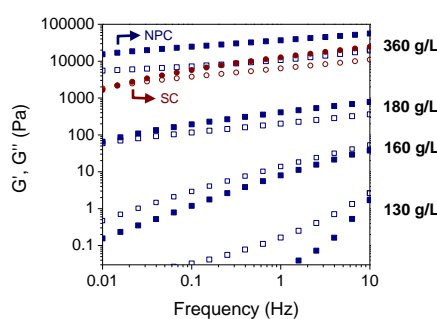
- η_0 for NPC follows the Quemada's eq. for non-interacting hard-spheres :

$$\eta_0 = \eta_{\text{solvent}} \left[1 - \frac{C}{C_{\text{crit}}} \right]^{-2}$$

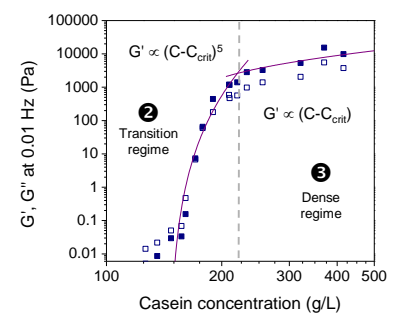
with $C_{\text{crit}} = 145 \text{ g/L} \rightarrow \phi = 0.64$ random close packing fraction

- $\eta_{0,SC}$ (unorganized) $\gg \eta_{0,NPC}$ (structured)

b - Viscoelastic shear moduli G' (solid symbols) / G'' (open symbols)



- Clear transition from a liquid-like behavior to a behavior close to a viscoelastic solid (gel ?) (360 g/L = G' & G'' almost freq. independent)
- In contrast, the SC dispersion clearly behaves as a viscoelastic liquid at 360 g/L
- Strong increase in G' from $C_{\text{crit}} = 145 \text{ g/L}$



- From 145 g/L to ~220 g/L ($\phi \sim 1$)
 - . $G' \propto (C - C_{\text{crit}})^5 \rightarrow$ percolation model
 - . Casein micelles get into contact and deform
 - . Connections are established ? (\rightarrow gel ?)
- From ~220 g/L to ~400 g/L
 - . $G' \propto (C - C_{\text{crit}})$
 - . Casein micelles are into contact and deswell

Summary

- Upon concentration, the rheological behavior of casein micelle dispersions is in line with the peculiar nature and structure of this object (while SC dispersions mostly behave as typical polymer solutions...)

1 Dilute regime

The casein micelles are independent and behave as hard spheres

2 Transition regime

The casein micelles get in contact and deform
G' increases dramatically

3 Concentrated regime

The casein micelles are in contact and deswell
G' increases linearly with [Cas]

→ Still some questions...

- . Can we really call the dispersions a "gel" in the dense regime ?
- . What forces are involved in the cohesion of this "gel" ?