Exploring the nature and kinetic of establishment of molecular interactions in aqueous solution: the example of polysaccharide systems

Unité de Recherche en Chimie Organique et Macromoléculaire

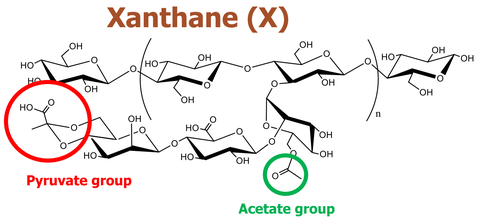
Normandie Univ, UNIHAVRE, FR 3038 CNRS, URCOM, 76600 Le Havre, France

Alexandre Cordinier[a], Nicolas Hucher[a] and Michel Grisel[a]

Alexandre.cordinier@univ-lehavre.fr

Context

Xanthane (X)



- Synthesized by bacteria
- Used as **rheological modifier** and **stabilizer**

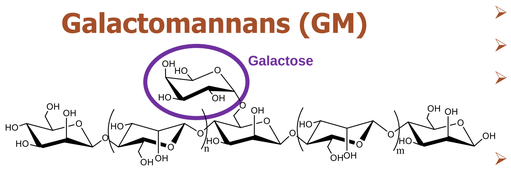
Chemical variability:

- Fermentation conditions => Variability of degrees of substitution of **pyruvate** (DS_{Py}) and **acetate** (DS_{Ac}) groups

Structural variability:



Galactomannans (GM)



≠ type of GM:

- Locust Bean Gum (LBG)
- Guar Gum (GG)
- Tara Gum (TG)
- etc…

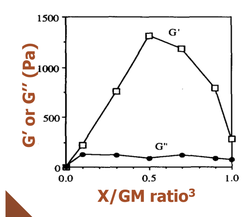
- Extracted from plant seeds
- Used mainly as **rheological modifier**
- Main chain = Mannose units (M) substituted by galactose residues (G)

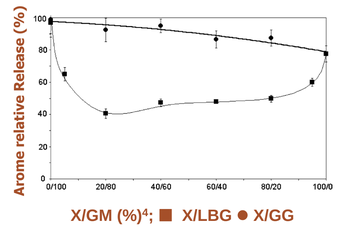
Structural variability:

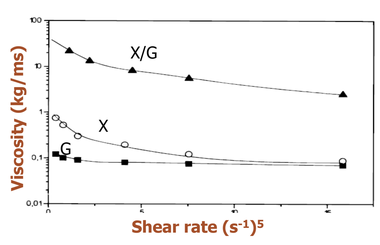
- ≠ varieties of seeds:
  - ✓ Variation of the **M/G ratio**
  - ✓ Distribution of G:
    - ⇨ Degree of blockiness[1,2] (DB)



Synergy X/GM







- Mixed in **specific conditions** ⇨ **POSITIVE SYNERGY** between X and GM
- Over the past 50 years, several interaction models have been proposed:
  - ✓ Dea & Morris' model[6] based on **polarimetric measurements**
  - ✓ Tako's model[7] based on **rheological measurements**
  - ✓ Cairns' model[8] based on **X-ray diffraction measurements**

3 ≠ models based on **3 ≠** techniques

≠ Conformations or **≠** chemical structures of X

On the ground of the observations done at the macroscopic scale, why one model would be more accurate than another ?

⇨ **Check what happen at microscopic scale !**

Objectives

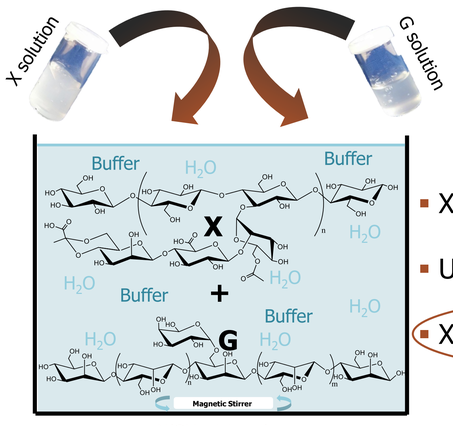
⇨ **Develop an universal analytical tool to study the interactions at the molecular level**

The aim of this project is to characterize the interactions at the molecular scale between polymers in solution

Characterization of interactions at the molecular scale ? ⇨ **FLUORESCENCE SPECTROSCOPY**

Results

At the macroscopique scale



X/GM mixing phase

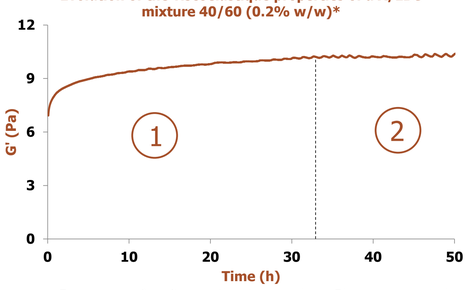
X/GM mixtures preparation

- X/GM mixtures at 0.2% (w/w)
- Use of a phosphate buffer at pH 7.4
- X/GM mixture stirred during ~ ½ h

High shear rates !

Use of a Discovery Hybrid Rheometer to follow viscoelastic properties of our X/GM mixtures with time

Evolution of the viscoélastique properties of a X/LBG mixture 40/60 (0.2% w/w)*



*For reasons of clarity only the stock modulus G' was represented

- Stabilization of viscoelastic propoerties is not happening suddenly
- **2 ≠ phases**:
  - ✓ **1** ⇨ Structuration phase
  - ✓ **2** ⇨ Stabilized system
- The period of the structuration phase is depending on the composition of X/GM mixture
- The period of the structuration phase is depending also of the mixture preparation conditions
- Few studies have been made about this structuration step[11,5]

At the molecular scale

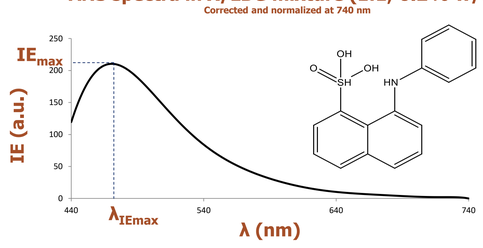
⇨ Use of 2 molecular specific probes

⇨ Same mixing process between X and GM as at the macroscopic scale

⇨ Injection of 1 of the 2 selected **fluorescence probes**: 8-anilino-1-naphtalen sulfonic acid **(ANS)** or 2-benzofuryl-3-hydroxy-4(1H)-quinolone **(3HQ-Bf)** in small quantities

ANS spectra in X/LBG mixture (1:1; 0.2% w/w)

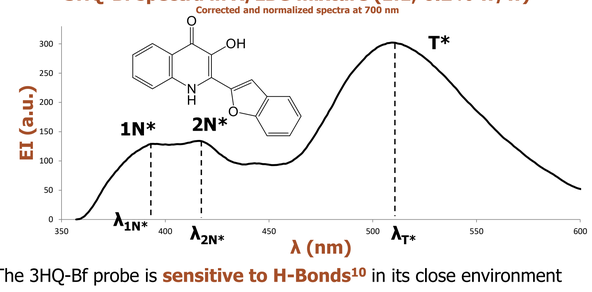
Corrected and normalized at 740 nm



- The ANS probe is **sensitive to Hydrophobic interactions**[9] (EI)
- **H_2O** is a **quencher** to the fluorescence of ANS probe
- The ANS probe is also sensitive to the **polarity** of the medium (λ)
- ANS is t available commercially

3HQ-Bf spectra in X/LBG mixture (1:1; 0.2% w/w)

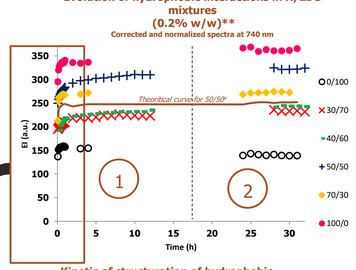
Corrected and normalized spectra at 700 nm



- The 3HQ-Bf probe is **sensitive to H-Bonds**[10] in its close environment
- 3HQ-Bf is not available commercially, it has to be **synthesized**
- 3HQ-Bf is a **ratiometric** probe
- Ratio EI_{N*}/EI_{T*} ≈ **Strength** of the **H-bond network**

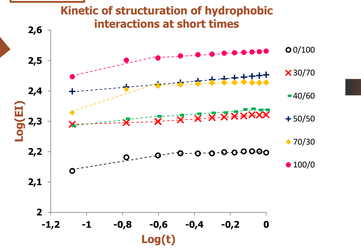
Evolution of hydrophobic interactions in X/LBG mixtures (0.2% w/w)**

Corrected and normalized spectra at 740 nm



Representation « log-log »

Kinetic of structuration of hydrophobic interactions at short times



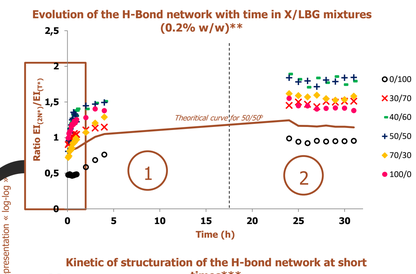
- **2 ≠ phases**:
  - ✓ **1** ⇨ Structuration phase
  - ✓ **2** ⇨ Stabilized interactions

[a] Calculated as follow: $EI_{50/50theo}=0.5xEI_{100/0exp}+0.5xEI_{0/100exp}$

[b] Calculated as follow: $[EI_{(2N*)}/EI_{(T*)}]_{50/50theo} = 0.5x[EI_{(2N*)}/EI_{(T*)}]_{100/0} + 0.5x[EI_{(2N*)}/EI_{(T*)}]_{0/100}$

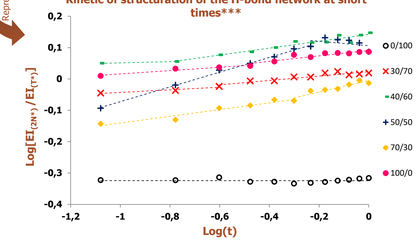
- **Interaction strucuration** depends on the **composition** of X/GM mixture

Evolution of the H-Bond network with time in X/LBG mixtures (0.2% w/w)**



Representation « log-log »

Kinetic of structuration of the H-bond network at short times***



**For reasons of clarity standard deviations were not represented

***Dotted lines only help to read the graphs

Conclusions

- Before any **stabilization** of X/GM mixtures, both molecular interactions (**hydrophobic interactions** and **H-bonds**) need a period of time which depend on the preparation conditions and of the composition of the X/GM mixture
- **Structuration phases** can be observed **at both scales**, macroscopic and molecular
- **Structuration phases** are strongly **dependent** of the **composition** of X/GM mixtures and dependent of the **preparation conditions**

References

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