CHARACTERIZATION OF OPAQUE AND CONCENTRATED EMULSIONS: A CHALLENGE FOR LIQUID/LIQUID SEPARATION

CARACTÉRISATION DES ÉMULSIONS OPAQUES ET CONCENTRÉES: UN CHALLENGE POUR LA SÉPARATION LIQUIDE/LIQUIDE

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AFCAT

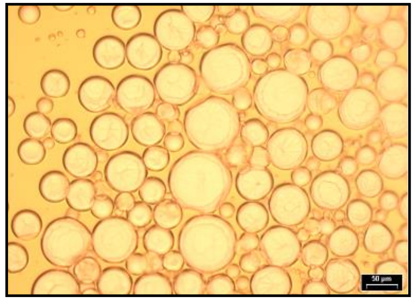
JCAT53, PALAISEAU – 22-24 MAI 2023

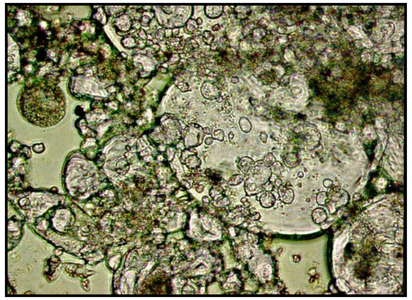
IFP Energies nouvelles

CONTEXT

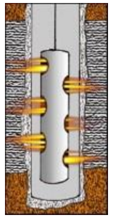
- Liquid/Liquid separation processes
  - Oil dehydration
  - Deoiling of waste waters
  - Breaking of « chocolate mousse » after an oil spill
  - …..

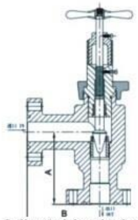
LIQUID/LIQUID SEPARATION: EMULSION ISSUES





DURING PRODUCTION, EMULSIONS ARE FORMED:





Adjustable choke valve

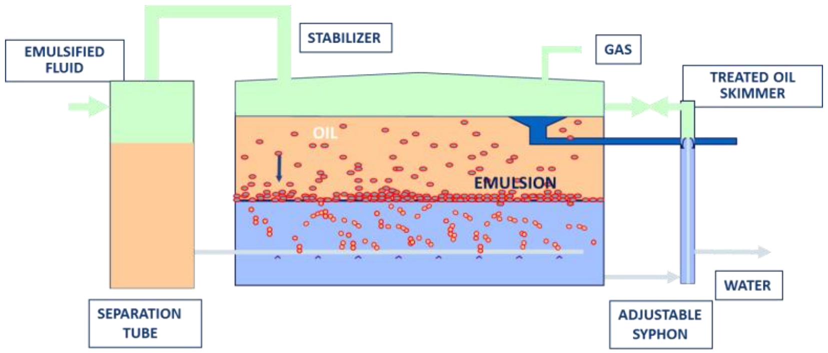
- Through perforations (comingled oil/water/gas)
- Through choke valves
- By turbulence (multiphase lines)

Everywhere when a sufficient amount of energy is transferred to the system

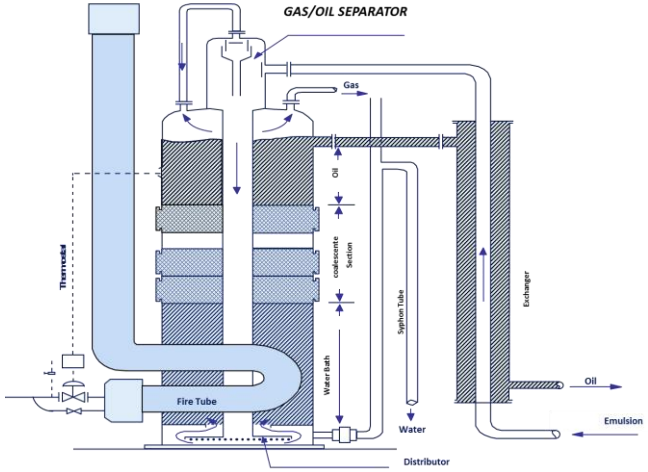
- With some chemicals (surfactants, emulsifying agents) or solid particles (sand, silt, clay....)

Study of droplet breakup through a calibrated orifice

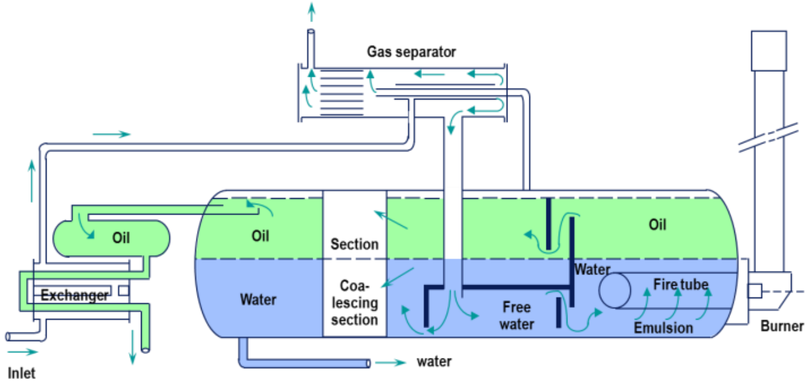
OIL DEHYDRATION: CLASSICAL TREATMENTS



Wash Tank

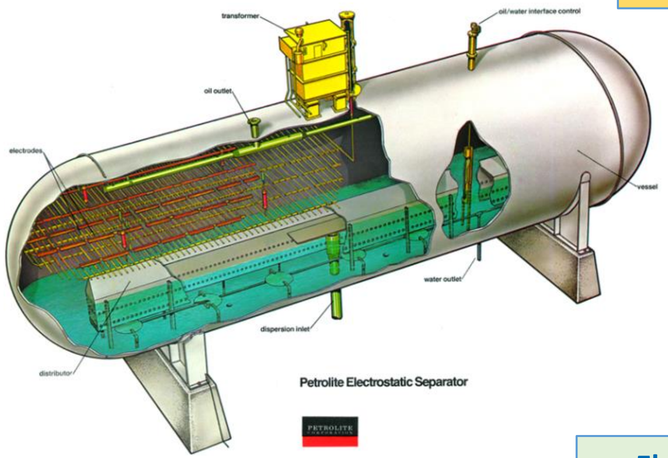


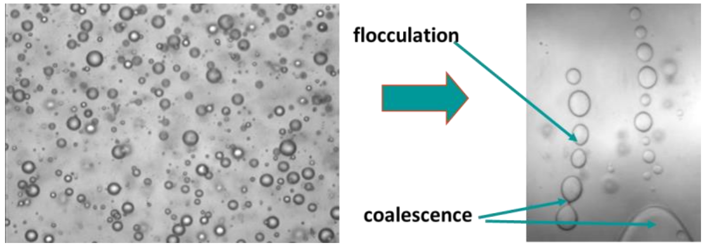
Vertical Heater Treater



Horizontal Heater Treater

Gravitational Separation / Heating / Electrocoalescence / Demulsifiers

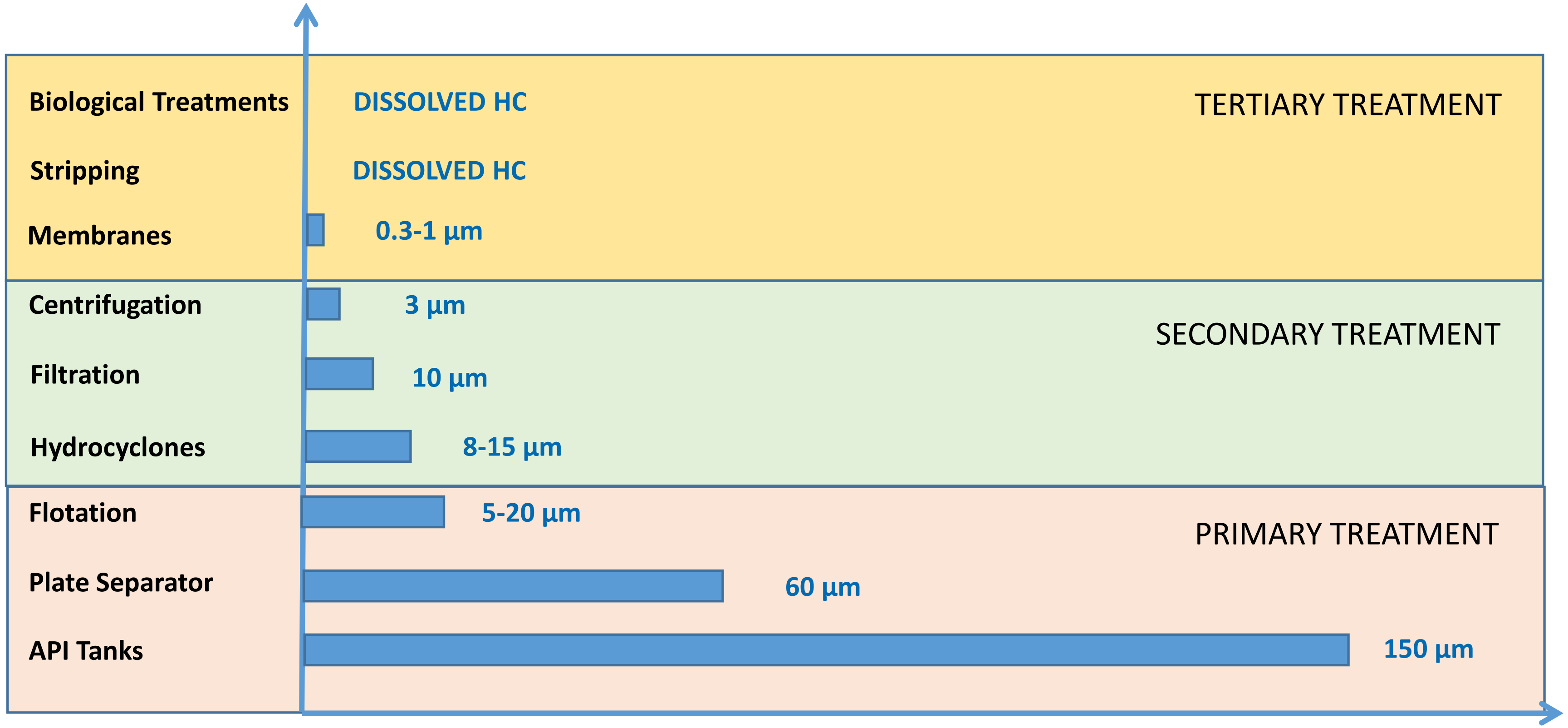




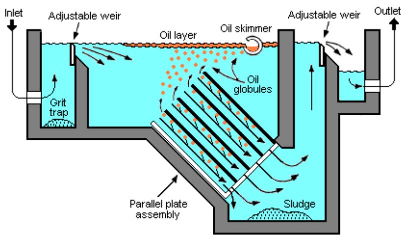
Electrostatic dehydrator or desalter

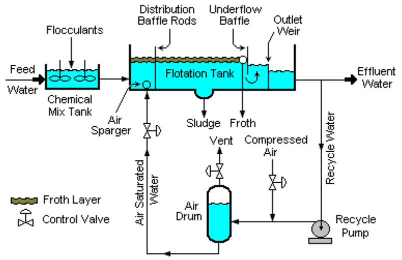
Chemical Demulsifier

WATER DEOILING: CLASSICAL TREATMENTS

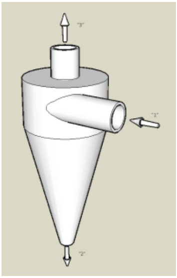


Source: Alfa Laval



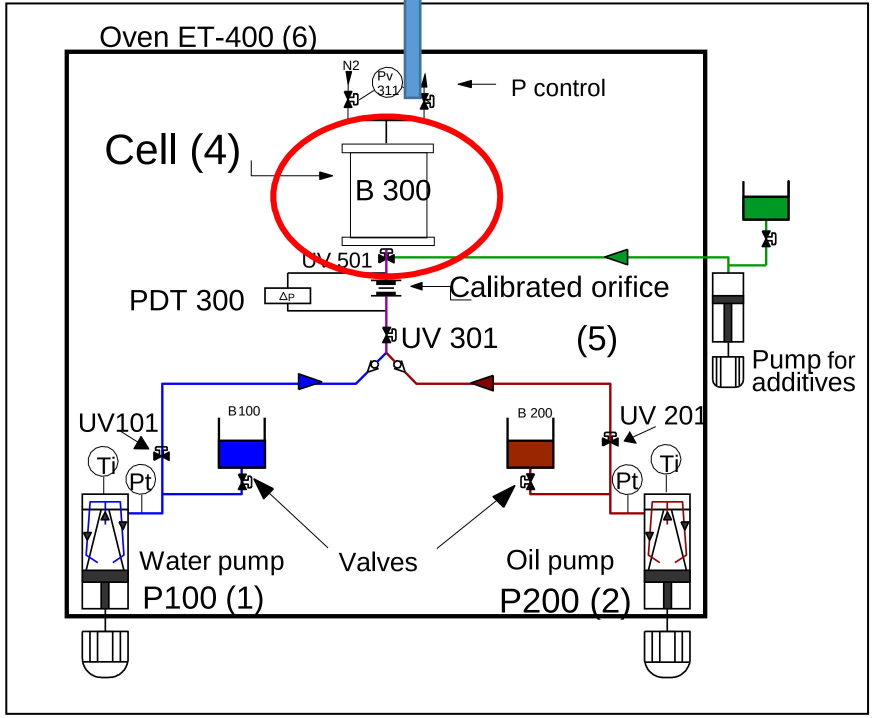


Source: Wikipedia



OIL PARTICLE DIAMETER (µm)

GENERATION OF REPRESENTATIVE EMULSIONS

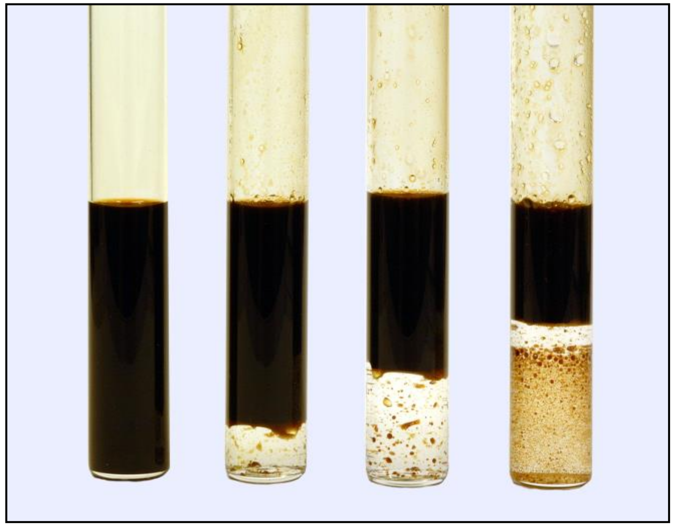


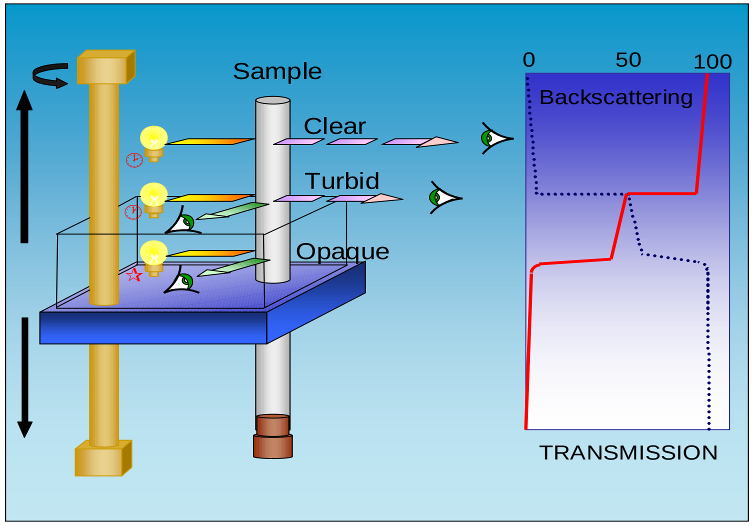
IFPEN DISPERSION RIG WITH INSTRUMENTED SEPARATOR

Janssen, Noïk and Dalmazzone (2001), SPE n°71473

CHARACTERIZATION OF EMULSIONS - STABILITY

CLASSICAL BOTTLE TESTS IN THE LAB





Source: Formulaction

Particularly suitable for the study of concentrated and opaque crude oil emulsions

Kinetics of emulsion separation

Mode of action of demulsifiers

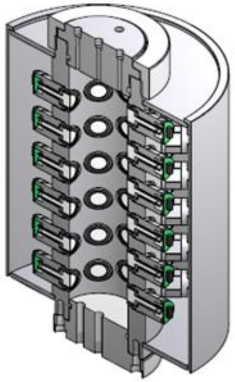
Clarity of separated water

Thickness of the o/w interface

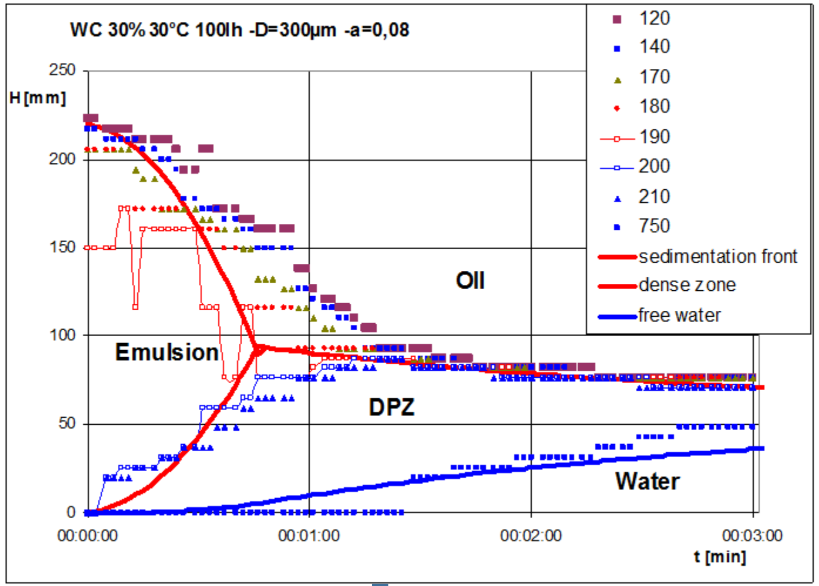
Monitoring of the evolution of phase separation by using transmitted and backscattered light (Turbiscan™)

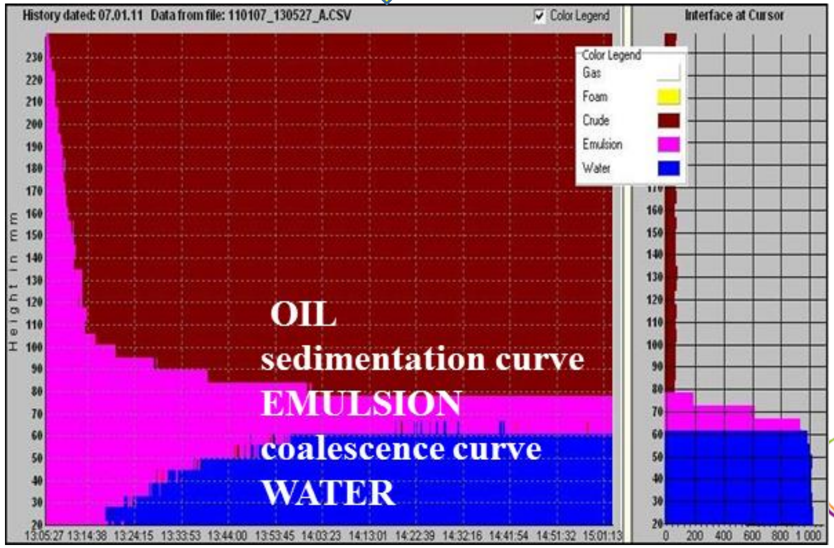
Dalmazzone and Noïk (2001), Development of New "green" Demulsifiers for Oil Production, SPE n°65041

CHARACTERIZATION OF EMULSIONS - STABILITY



Instrumented cell with capacitance sensors





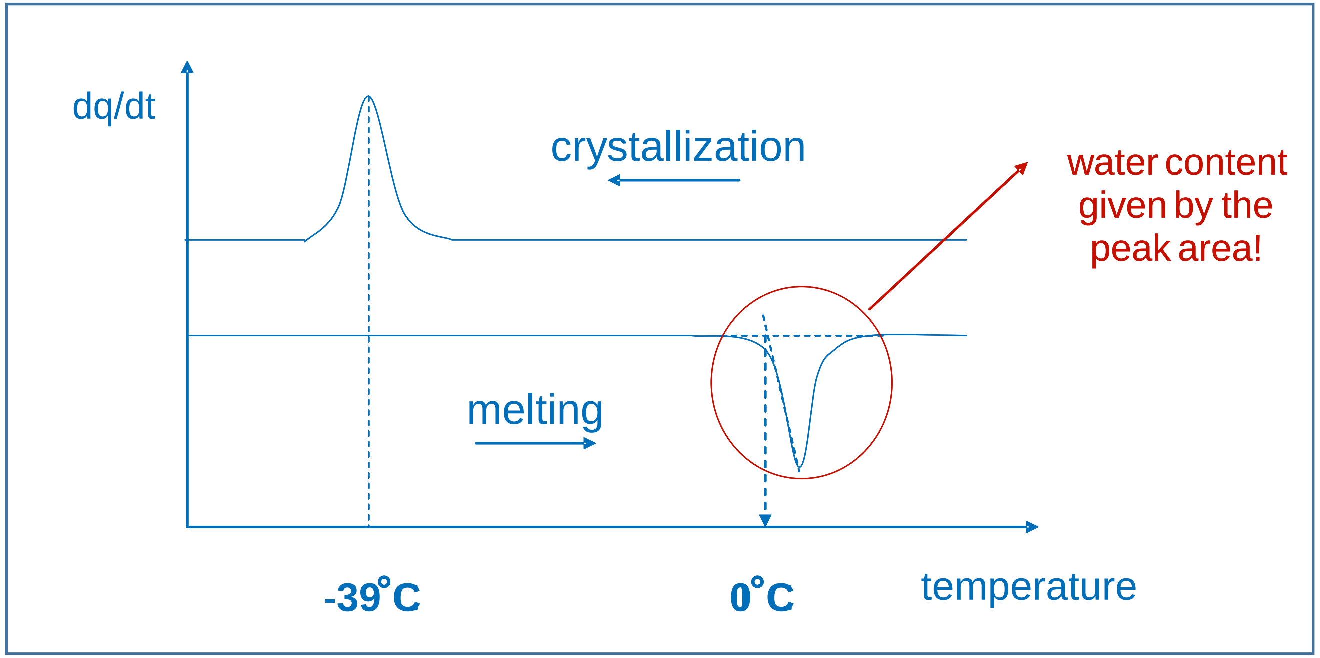
Noïk, Palermo and Dalmazzone (2013), *Journal of Dispersion Science and Technology* **34**, 1029.

CHARACTERIZATION OF EMULSIONS – STABILITY - DSC

Differential Scanning Calorimetry (DSC) may be advantageously used to characterize complex water-in-oil (w/o) emulsions.

Peaks of crystallization: the lower the temperature of ice crystallization, the smaller the droplets

Peaks of melting: the peak area gives the water content

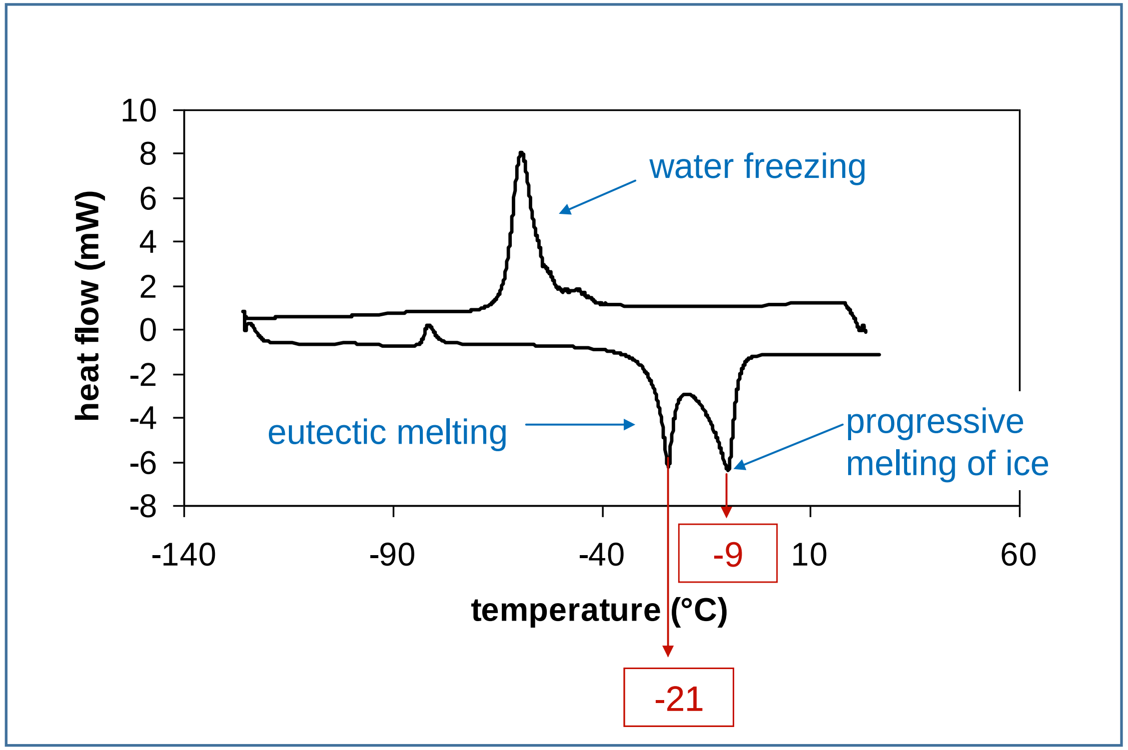


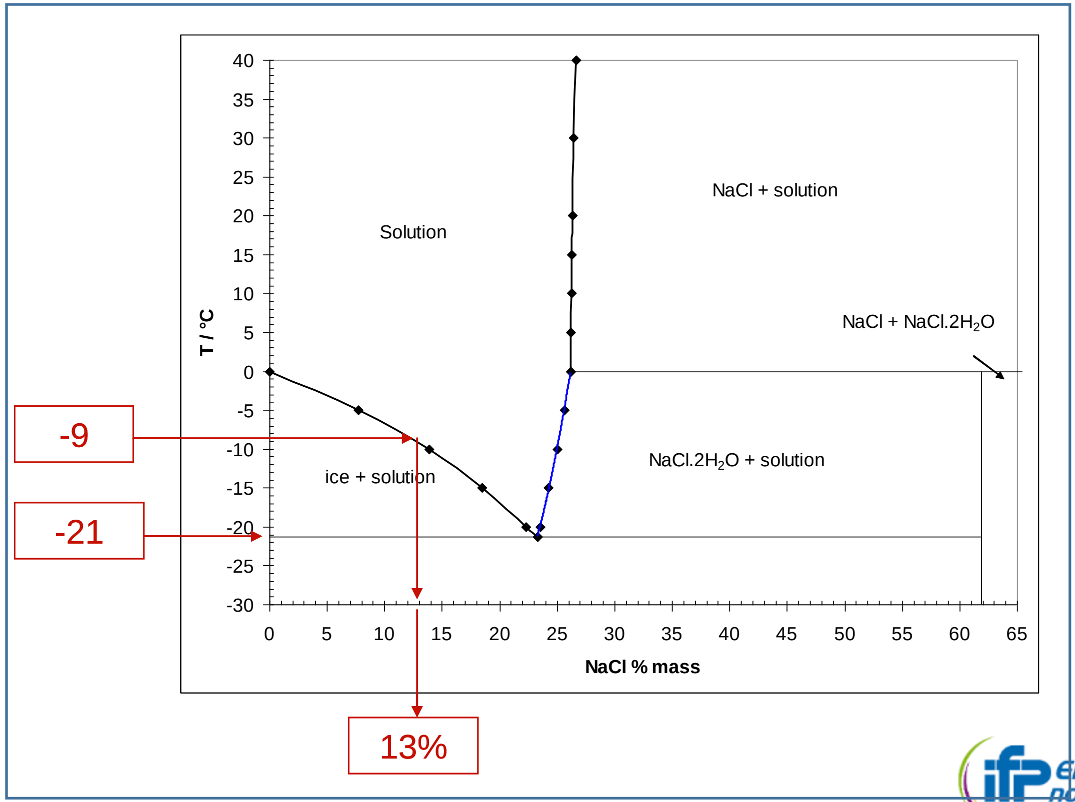
Dalmazzone, Noïk and Clausse (2009), Application of DSC for Emulsified System Characterization, *Oil & Gas Science and Technology* **64**(5), 543.

CHARACTERIZATION OF EMULSIONS – STABILITY - DSC

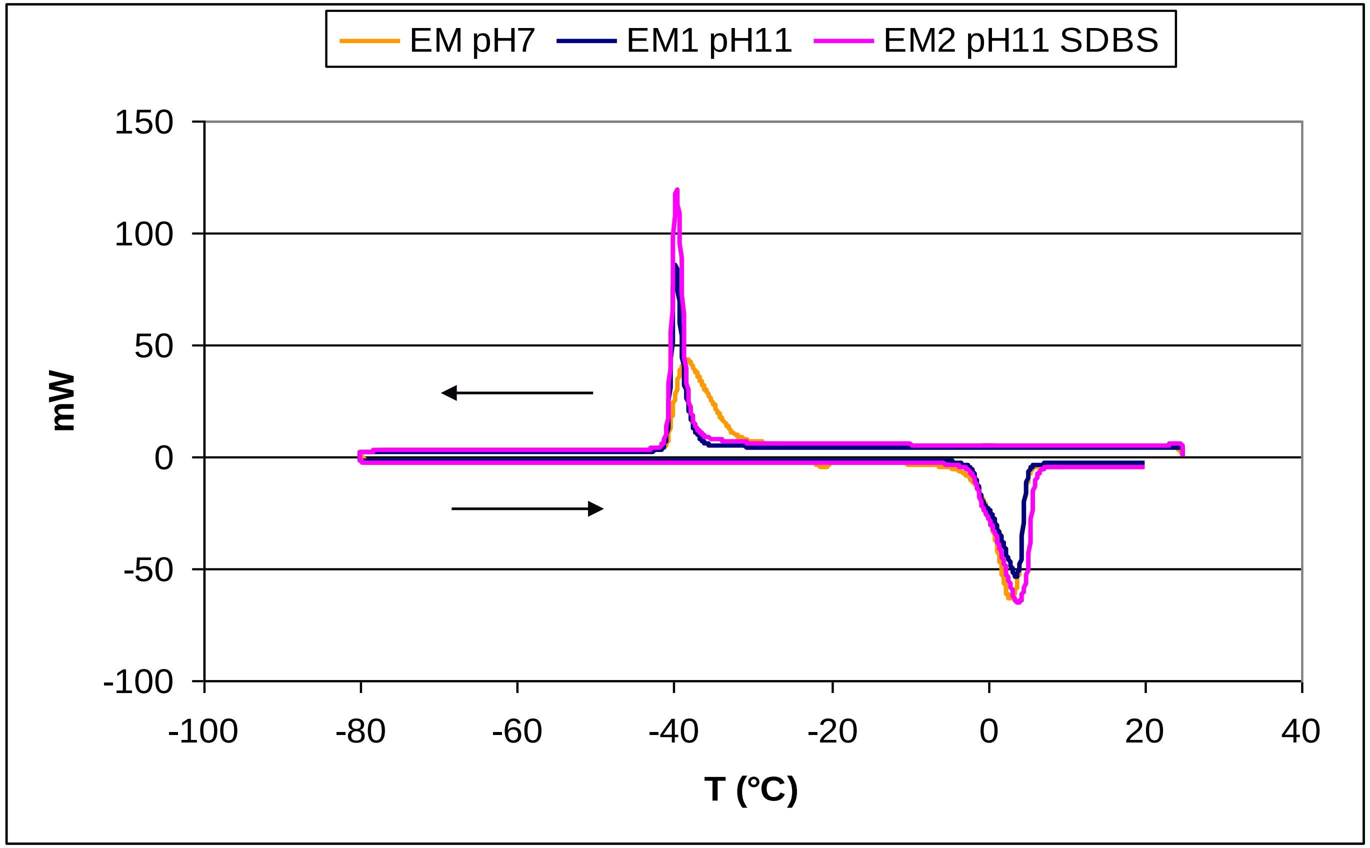
In the case of brine-in-oil emulsions:

- the temperature of end of ice melting gives the composition of the aqueous phase for a binary mixture water+solute (salt for example)
- for salts like NaCl, the binary phase diagram may be used to determine the composition from DSC thermograms





CHARACTERIZATION OF EMULSIONS – STABILITY - DSC



EM: Emulsion pH7,

5 g/L NaCl

EM1: Emulsion pH11,

10 g/L Na_2CO_3

EM2: Emulsion pH11,

10 g/L Na_2CO_3,

0.1% SDBS (sodium dodecylbenzene sulfonate)

Comparison of Water-in-Heavy Oil Emulsions

Dalmazzone *et al.* (2012), *Energy & Fuels* **26**, 3462.

CHARACTERIZATION OF EMULSIONS – DROPLETS SIZE

Encapsulation of the droplets in order to avoid coalescence

Interfacial polymerization

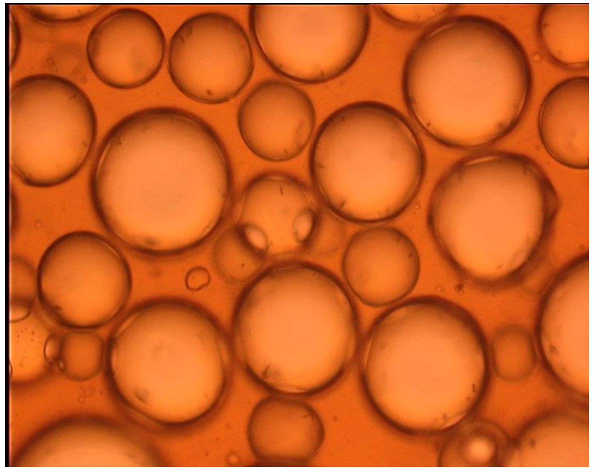
hydrophilic reagent: triethylene tetramine

hydrophobic reagent: terephthaloyl dichloride

Optical Microscopy

+

Image Analysis

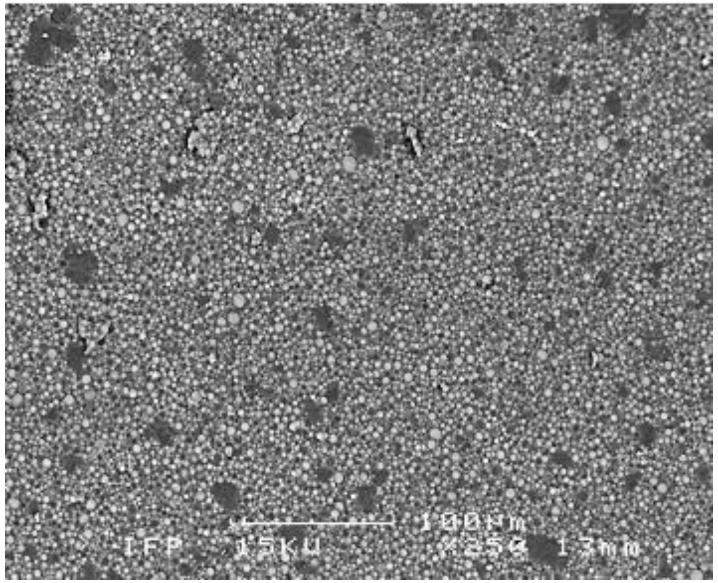


Noïk *et al.* (2004), *Oil & Gas Science and Technology* **59**(5), 535.

CHARACTERIZATION OF EMULSIONS – DROPLETS SIZE

CRYO-SEM: SEM fitted with a cold stage unit

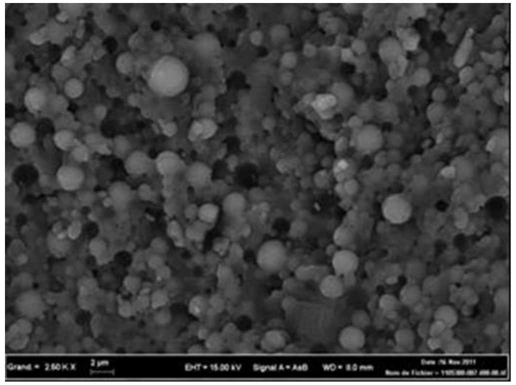
- Freezing of emulsion in a nitrogen slush at -200°C
- Transfer in a cryo lock chamber at -170°C
- Fracturation and metallization with Cr
- Transfer to the microscope chamber at -180°C

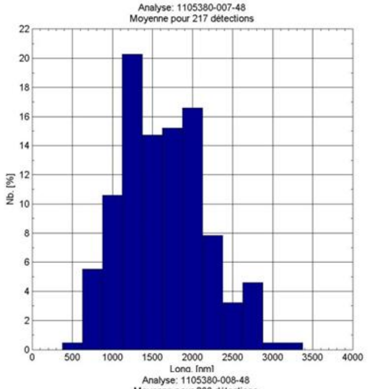


Water-in-Crude Oil Emulsions

Determination of droplet size distribution in the emulsion

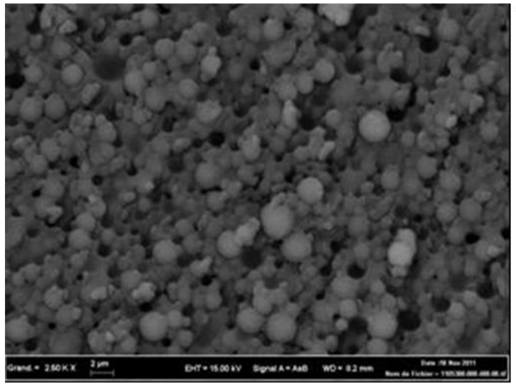
- Image analysis software

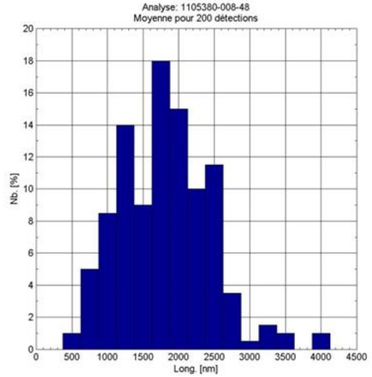




EM1

Average Diameter 1.6 µm





EM2

Average Diameter 1.8 µm

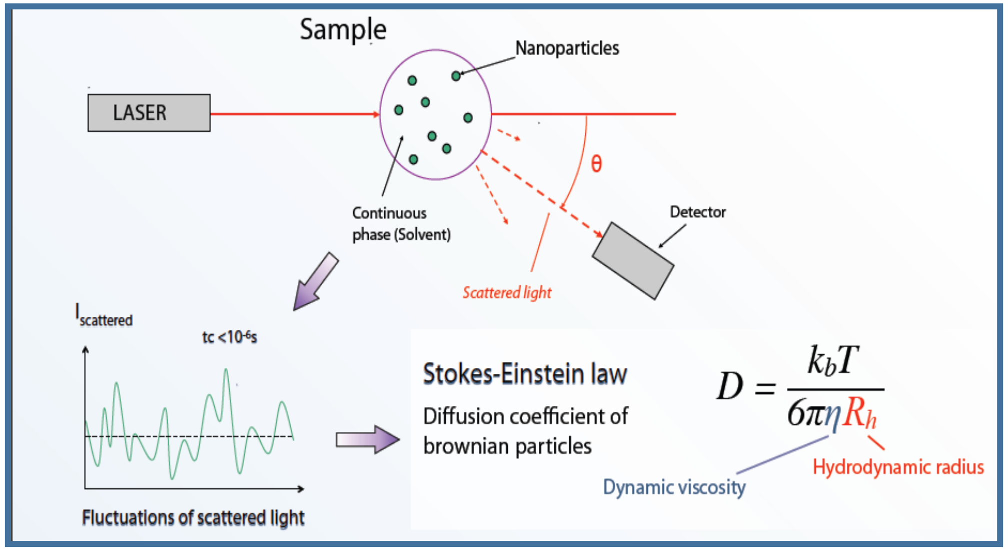
Limit of Detection: 400 nm!!!

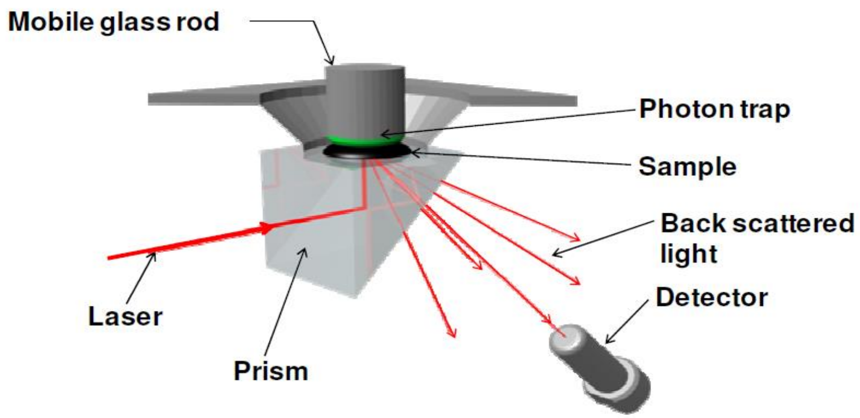
Al Ghamdi *et al.* (2009), *SPE Journal* **14**(4), 595.

CHARACTERIZATION OF EMULSIONS – DROPLETS SIZE

Dynamic Light Scattering (DLS): powerful technique to characterize diluted and transparent dispersions of particles from the **nanometer up to a few microns** through the analysis of scattered light fluctuations caused by the Brownian motion of particles.

To overcome the DLS limitations, IFPEN has developed an original optical design of the sample cell. The bottom of the measuring cell is formed by the upper surface of a glass prism guiding the laser beam while a mobile glass rod allows an accurate control of the sample thickness (down to a few tens of microns thickness).



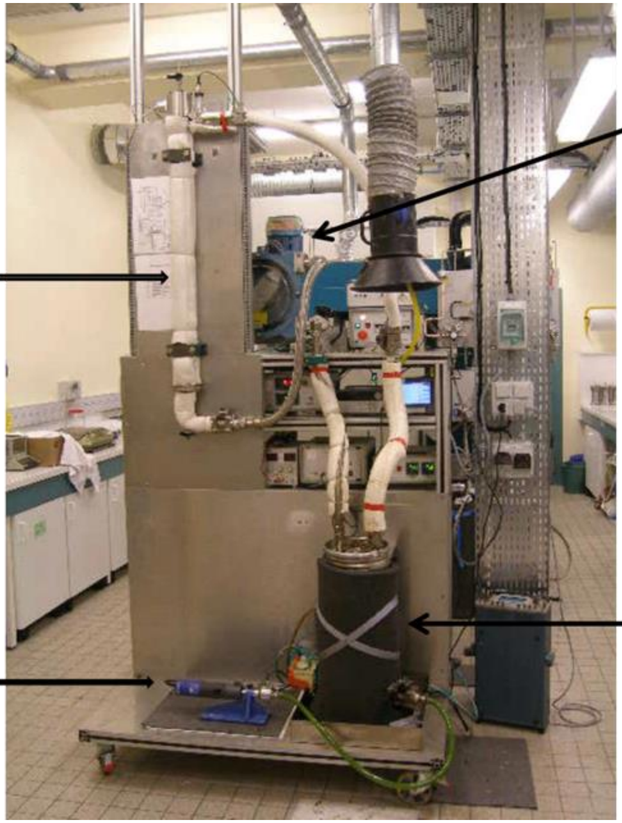


Vasco DLS instrument (Cordouan Technologies)

Yudin et al. (1998), *Journal of Petroleum Science and Engineering* **20**, 297.

CHARACTERIZATION OF EMULSIONS – ELECTRICAL STABILITY

Dalmazzone *et al.* (2010), *SPE Journal* **15**, 726.



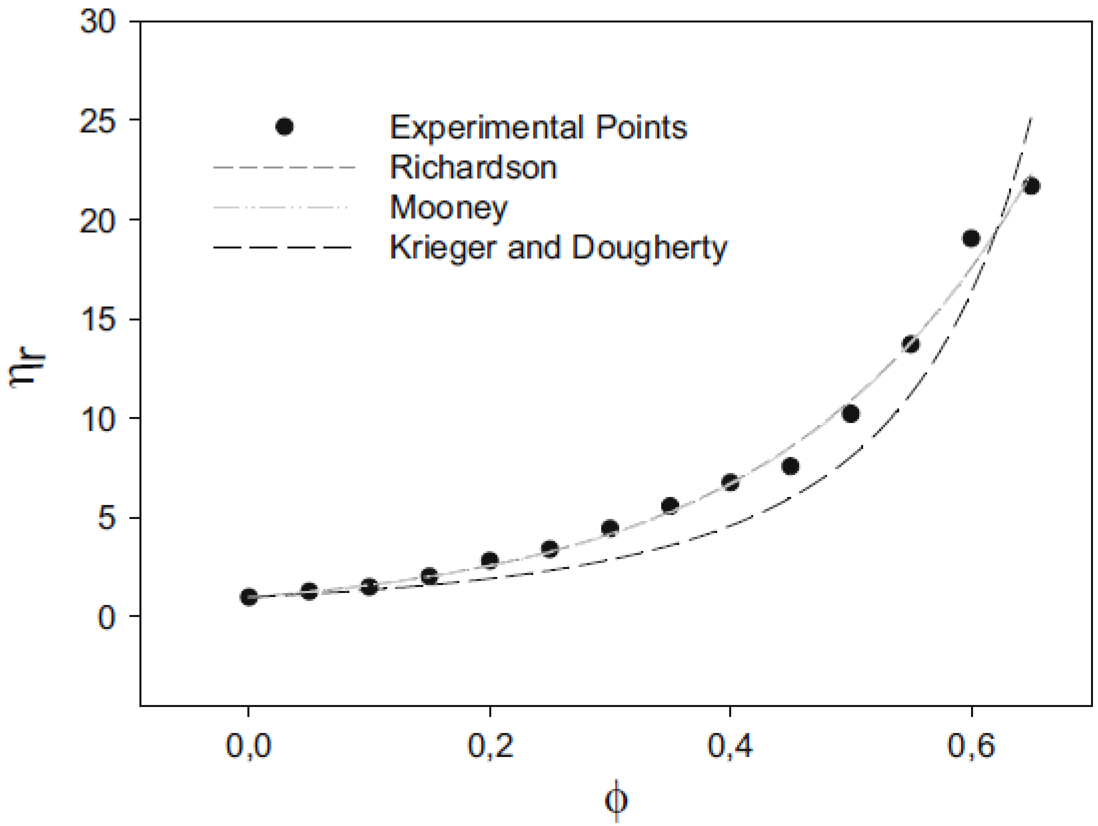
Electrical Stability Tester EST

Method and electrical apparatus used for oil-based drilling mud stability control (API 13B-2)
Simple electrode, AC Voltage @ 340 Hz
Progressive increase of voltage @ 150 V/s up to 12.9 kV/cm
Critical Electrical Voltage measured at 61 µA (short-circuiting)
Method: Tests on reconstituted emulsions
After EST test, monitoring of the volume of separated free water after 24 hours

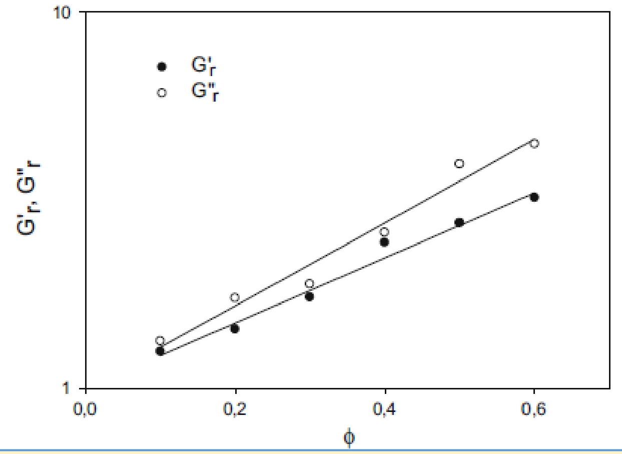
IFPEN Electrocoalescence set-up

Fluid injection into the annular between 2 concentric tubes as electrodes
AC field: high voltage/high frequency 50Hz – 2 kHz
Flow rate 0.1 – 1.2 m^3/h - T from ambient to 60°C

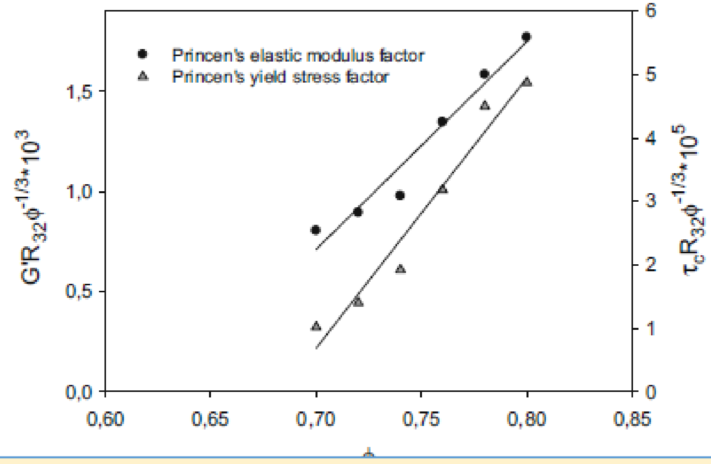
CHARACTERIZATION OF EMULSIONS – RHEOLOGY



Comparative plot of different viscosity models (relative viscosity versus dispersed volume fraction) – 30°C



G' and G'' vs volume fraction, 20°C, 1 Hz

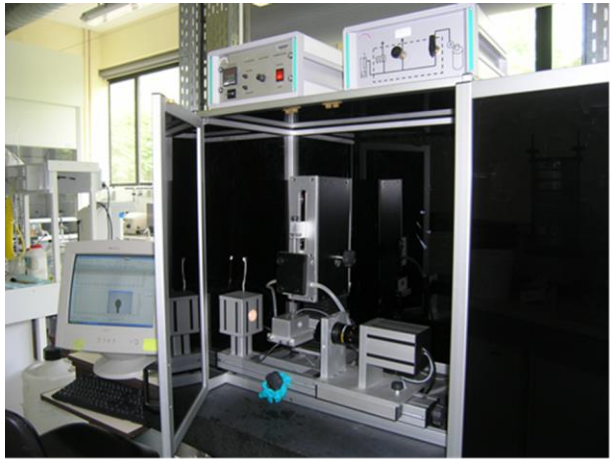


Princen parameters for G' vs volume fraction, 20°C

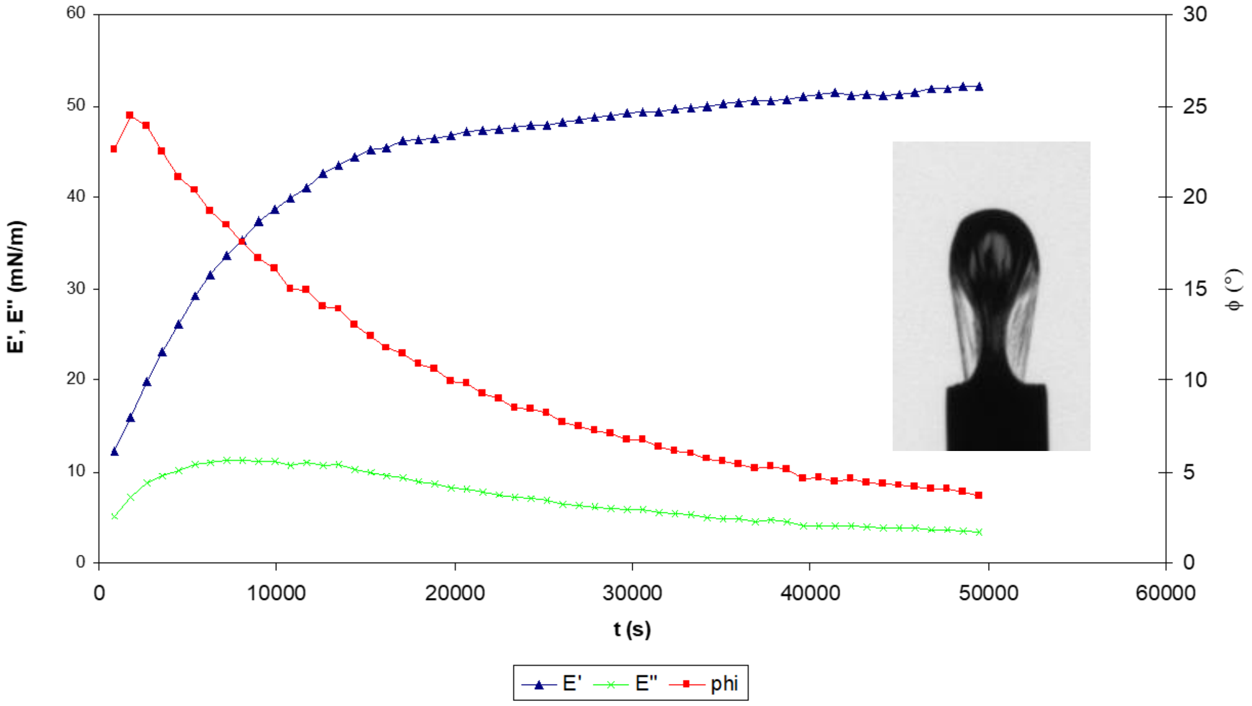
Quintero, Noïk, Dalmazzone and Grossiord (2008), *Rheol Acta* **47**, 417.

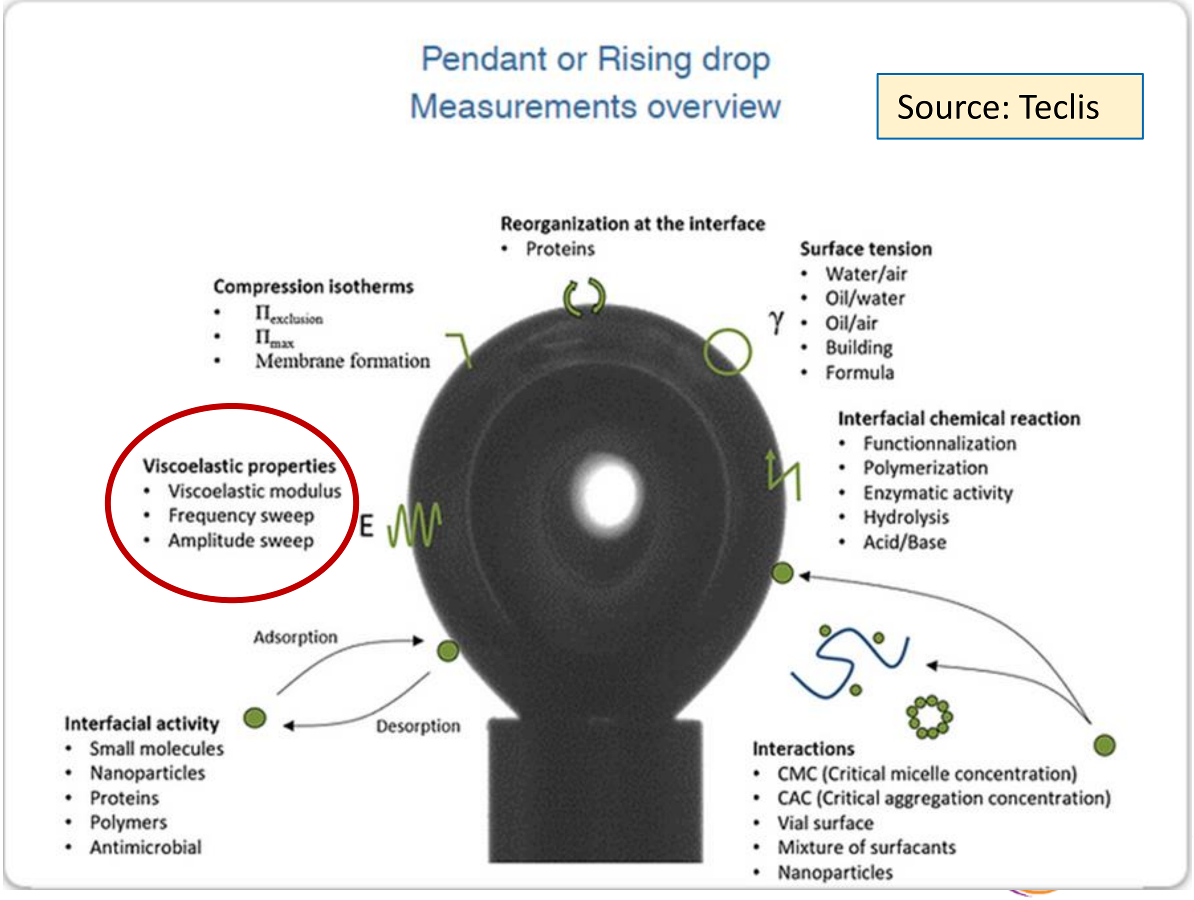
CHARACTERIZATION OF EMULSIONS – INTERFACIAL RHEOLOGY

Tracker (TECLIS) for interfacial rheology



Evolution of E', E'' and ϕ with time (crude C, 0.1 Hz, 30°C)





Quintero, Noïk, Dalmazzone and Grossiord (2009), *OGST-Rev. IFP* **64**, 607.

CONCLUSION

- The step of characterization is essential at the lab and semi-industrial scale
  - To develop flexible and efficient technologies
  - To develop specific additives (emulsion breakers, flocculant, clarifiers…)

- Combination of several methods to characterize opaque and concentrated emulsions
  - Stability
  - Droplets size
  - Rheological behavior

Acknowledgments: C. Noïk, A. Mouret, L. Podesta-Foley, P. Thoral, C. Burnichon, D. Frot, I. Hénaut ....

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