

# STUDY OF AGGLOMERATION OF ICE PARTICLES AND OF TRICHLOROFLUOROMETHANE HYDRATE PARTICLES SUSPENDED IN A HYDROCARBON PHASE

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## ABSTRACT

This work deals with the problem of pipeline plugging by gas hydrates during oil production. Gas hydrates are crystals resulting from water and gas molecules association under high pressure and low temperature conditions. Such thermodynamical conditions are generally encountered during oil production and transport, particularly in deep offshore fields or in cold areas. Due to an agglomeration process which is still debated, hydrate occurrence can lead to plug formation.

This study aims at improving the understanding in this mechanism process, in the case of water-in-oil emulsions. Therefore, ice or hydrate particle agglomeration is compared. Ice or trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ) hydrate particles dispersed in xylene with asphaltenes as surfactant is chosen as a model system. As  $\text{CCl}_3\text{F}$  hydrates are stable under atmospheric pressure, it allows us to apply different techniques without being limited by high pressure conditions. The Nuclear Magnetic Resonance (NMR) technique is used. The very different relaxation rate for solids or liquids is used to monitor *in situ* the ratio between solid and total hydrogen or fluorine as a function of time with controlled shearing conditions. Thus, a kinetic study is realized, that enabled to know the amount of ice formed. The apparent viscosity of the system, during crystallization and plugging, is also followed with rheometry in order to characterize agglomeration.

This experimental approach allows us to highlight that physico-chemistry of interface water/oil has an important role in agglomeration. It enables us to discuss different mechanisms of agglomeration of ice and hydrate particles in a hydrocarbon phase.

**Key Words:** Hydrates, Freon, Ice, Emulsion, Crystallization, Agglomeration, NMR, Rheometry

## NOMENCLATURE

$a$  Primary Particle Radius [ $\mu\text{m}$ ]

$B_0$  Magnetic Field at Thermodynamic Equilibrium  
[T]

$D$  Fractal Dimension

$\Delta t$  Crystallization Time [min]

$F$  Force of Adhesion [N]

$\dot{\gamma}$  Shear Rate [ $\text{s}^{-1}$ ]

$k_B$  Boltzmann Constant [ $\text{J.K}^{-1}$ ]

$m$  coefficient which represents breakage  
mechanism

$M_0$  Initial Magnetization [a.u]

$M_{\text{liq}}$  Liquid Magnetization [a.u]

$M_{\text{tot}}$  Total Magnetization [a.u]

$M_y$  Magnetization in the (x,y) plan on y axis [a.u]

$\mu$  Suspension Viscosity [Pa.s]

$\mu_0$  Continuous Phase Viscosity [Pa.s]

$N$  Molecule Number per Volume Unit [ $\text{m}^{-3}$ ]

$\Phi$  Volume Fraction

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$\Phi_{\text{eff}}$  Effective Volume Fraction  
 $\Phi_{\text{max}}$  Maximum Volume Fraction  
 $R$  Aggregate Radius [ $\mu\text{m}$ ]  
 $\sigma$  Energy of Adhesion per Area Unit [ $\text{J.m}^{-2}$ ]  
 $t$  Time [min]  
 $t_L$  Induction Time [min]  
 $T$  Temperature [K]  
 $T_2$  Transversal Relaxation Time [ms]  
 $T_2^*$  Characteristic relaxation Time of Transversal Magnetization [ms]  
 $T_2^+$  Relaxation Time due to Field Inhomogeneities [ms]  
 $\tau$  Shear Stress [Pa]  
 $\tau_0$  Critical Shear Stress [Pa]

## INTRODUCTION

Gas hydrates are crystalline compounds which may lead to pipeline blockage during offshore oil production. These compounds form at high pressure and low temperature when water and gas molecules are in contact. These conditions may be encountered during oil production in deep offshore where gas molecules (methane for example) are in contact with water droplets of water in oil emulsions. These hydrate particles, by an agglomeration mechanism, progressively tend to form a blockage in pipelines and impair production.

This work aims at trying to understand agglomeration mechanism of gas hydrate particles in water in oil emulsions. To study this mechanism, a model system is chosen: a model emulsion water in xylene/asphaltene and a hydrate model: Freon hydrate. This system illustrates what it happens in pipelines as produced water with oil is often dispersed by surfactants naturally present in oil phase. Moreover, Freon well models methane behavior because both methane and Freon are soluble in oil and insoluble in water. It enables to mimic a transfer phenomenon between oil and water phase during hydrate formation. As Freon hydrate forms at atmospheric pressure and low temperature, there is no need of pressurized systems in the experimental techniques used. Freon boiling point is 297K, so it is very volatile at ambient temperature. So it was necessary to find solutions to keep installations airtight. To better understand particle agglomeration process in pipeline, two kinds of particles are studied: ice and Freon hydrate particles in the same oil phase. Rheology is the main characterization method used for this. It is

completed by NMR to study agglomeration kinetics and quantify amount of formed crystals.

## EXPERIMENTAL METHODS

### Model system: a model oil and a model hydrate

Hydrate agglomeration properties in emulsion are studied thanks to a model emulsion. It is composed of oil phase (continuous phase), deionised water (dispersed phase) and asphaltenes (surfactant) coming from SINCOR crude oil, insoluble in heptan. Different oil phases are studied. For ice system, two oil phases are used: orthoxylene (named XA below) and dodecane + orthoxylene (named XDA below). For hydrate the oil phase is constituted of orthoxylene + freon.

Orthoxylene is a dispersing agent of asphaltenes whereas dodecane or freon precipitate asphaltenes. Dodecane is added to xylene for ice in order to be close to the flocculation onset of asphaltenes. In these conditions, asphaltenes is a good surfactant; emulsion is better stabilized [1]. Flocculation conditions are determined by microscopy and refractive index measurements.

### Asphaltenes as surfactant

Asphaltenes are the most polar and highest molecular weight compounds in crude oils.

It is not possible to associate a single chemical formula to all asphaltenes present in a crude oil and so impossible to generalize a formula for all origins of crude oil. There is a wide polydispersity in the same crude oil too. However, asphaltene molar mass is estimated between 500 and 1,000  $\text{g.mol}^{-1}$  while micelles molar mass is about 10,000  $\text{g.mol}^{-1}$ . Carbon and hydrogen are the two main constituents of asphaltenes. Their atomic ratio H/C is estimated between 0.9 and 1.2. They are represented by an opened structure with aromatic nucleus linked by alkyl (figure 1)

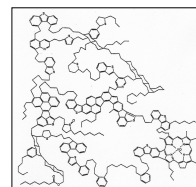


Figure 1: Example of schematic representation of asphaltene molecule

The asphaltene structure give them amphiphilic properties. Indeed, carbon and hydrogen are non polar and heteroatoms are polar so asphaltenes have surfactant properties. Asphaltenes adsorb

themselves naturally to the water/oil interface such away the heteroatoms are in contact with water phase and hydrocarbon components with the oil phase. Moreover, emulsion stability is linked to asphaltenes capacity to form aggregates and so thick layer in interface water/oil. Crude oil are constituted by asphaltenes (insoluble in heptan (371K) but soluble in toluene), maltenes (components Saturated, Aromatic and Resins). Asphaltenes are by definition insoluble in heptan. This properties is used to precipitate them and separate of liquid fraction (maltenes + heptan) by filtration. This method is named SARA separation. This separation processus is defined by AFNOR NF T60-115 standard.

#### Elaboration of emulsion

A model emulsion is used for this study in order to simplify the system. Indeed, a petroleum emulsion, containing crude oil and water, has a very complex composition with numerous different components in oil phase. Here, the oil is Xylene, Xylene + Dodecane or Xylene + Freon and surfactant is asphaltenes. They are extracted from the Venezuelan crude oil SINCOR. Asphaltene extraction is realized with heptan so asphaltenes are named SINCOR I7 (insoluble in heptan). To prepare emulsion, asphaltenes are dissolved in xylene  $C_8H_{10}$  which is a good solvent of asphaltenes. Emulsions are prepared with a Ultra Turrax of 8 mm diameter at 13500 rpm during a minute. Deionised water is added drop by drop in oil + asphaltene phase;

#### Freon hydrate: Model hydrate

Studied hydrates are Freon 11 hydrates. Freon 11, named trichlorofluoromethane too, has for chemical formula  $CCl_3F$ . Freon hydrate forms at atmospheric pressure which enables us to use numerous characterization techniques without needing to use pressure systems. Moreover, Freon well models methane action because, as itself, it is soluble in oil and insoluble in water. It enables to mimic a transfer phenomenon between oil and water phase during hydrate formation. By contrast, Freon inconvenient is its volatility. Indeed, Freon boiling point is 297K, so it is very volatile at ambient temperature. So it was necessary to find solutions to keep installations airtight.

Freon molecule has a radius of gyration of  $3.3\text{\AA}$  which predicts a hydrate structure type II (figure 2). Crystalline network of structure II is diamond

type, cubic, parameter mesh  $17.2\text{\AA}$  and given composition  $16M_1.8M_2.136H_2O$  [2].

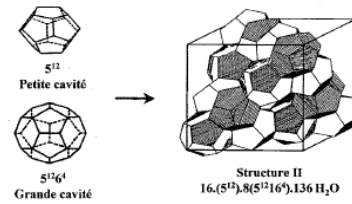


Figure 2: Type II hydrate structure

With the size of Freon molecule, only wide cage are full which predict a composition  $8M_2.136H_2O$ . We can write:



#### **Rheology**

Agglomeration of hydrate particles is studied by rheology. The comprehension of rheological results is based on Mill's theory [3] and R. Camargo's results [4]. Hydrate crystals are expected to form at the water-oil interface. Thus, a solid shell forms around water droplet making them to behave as solid particles. In the following, hydrate particles will be assumed to be spherical, with an identical diameter as water droplet.

Considering that the final size of hydrate particle aggregates is controlled by shear rate [5], we have:

$$\frac{R}{a} = \left( \frac{\tau_0}{\mu \dot{\gamma}} \right)^m \geq 1 \quad (2)$$

where  $R$  and  $a$  are respectively the aggregate radius and the primary particle radius which is the average radius of a water droplet,  $\mu$  the apparent viscosity of the suspension,  $\dot{\gamma}$  the shear rate,  $\tau_0$  the critical shear stress below which aggregates can form and  $m$  an exponent which represents breakage mechanism of aggregate and generally reported around 0.5 in the literature [6].

The critical shear stress is related to the force of adhesion  $F$  between particles as:

$$\tau_0 \alpha \frac{F}{a^2} = \frac{\sigma}{a} \quad (3)$$

where  $\sigma = \frac{F}{a}$  is the energy of adhesion per area unit and depends only on the physico-chemical properties of the system.

The effective volume fraction  $\Phi_{\text{eff}}$  scales with the actual volume fraction  $\Phi$ , which represents water cut, as:

$$\phi_{\text{eff}} = \left(\frac{R}{a}\right)^{3-D} \phi = \left(\frac{\tau_0}{\mu\dot{\gamma}}\right)^{(3-D)m} \phi \quad (4)$$

D represents fractal dimension.

Moreover, effective volume fraction  $\Phi_{\text{eff}}$  and viscosity of hydrate suspension  $\mu$  are linked by (5)

$$\mu = \mu_0 \frac{1 - \phi_{\text{eff}}}{\left(1 - \frac{\phi_{\text{eff}}}{\phi_{\text{max}}}\right)^2}; \phi_{\text{max}} = 4/7 \quad (5)$$

with  $\mu_0$  the oil viscosity and  $\Phi_{\text{max}}$  the maximum packing.

This equation is verified for  $\Phi_{\text{eff}} < \Phi_{\text{max}} = 4/7$  and

$$\tau > \tau_0 \left(\frac{\phi}{\phi_{\text{max}}}\right)^{\frac{1}{(3-D)m}}. \text{ If this condition is not fulfilled, blockage appears.}$$

### NMR Nuclear Magnetic Resonance

NMR has been often used in hydrate studies to determine their structure by spectroscopy but relaxation properties hasn't much been used [8]. Study of relaxation time in NMR allows us to determine ice or hydrate solid fraction as function as time.

All these informations come from 2 measurement sequences:

- Carr-Purcell and Meiboom-Gill spin echo sequence (CPMG)
- Free Induction Decay measurement (FID)

One of the advantages of this technique is its non destructive character and its ability to measure high solid concentrations.

#### NMR notions [9]

NMR relaxometry is based on radiofrequency field application on atoms nuclear spins in order to manipulate them. A spin population is considered at thermodynamic equilibrium in a magnetic field  $\mathbf{B}_0$ . So spins are manipulated in applying a radiofrequency field named pulse. The process of relaxation involve with the particle which comes back to its original energy state by loss of achieved energy. Relaxation occurs through exchange of energy between the particle and its environment according to two processes: longitudinal relaxation

(or spin-network) and transverse relaxation (spin-spin). In our studies, transverse relaxation is considered.

The transverse relaxation insures the return of the particle in its fundamental state, causing the decrease of the magnetization  $M_y$  in the (x, y) plan. The effects that tend to reduce the magnetization in the plan (x, y) is the spin-spin relaxation and non uniform field. The spin-spin relaxation is described according to Bloch by:

$$M_y = M_0 \exp(-t/T_2) \quad (6)$$

The time constant  $T_2$  is called transverse relaxation time. The spin-spin relaxation is due to the presence within the molecule many other nuclei, all at their own precession Larmor frequency. They can provide additional varying magnetic fields quickly and regularly, which may interact with the molecule. The result is a loss of phase coherence between the particles at resonance which induces a decrease in  $M_y$ .

The magnitude of the magnetization  $M_0$  of an NMR signal is proportional to the number of elements detected by the probe according to the law of Curie (for a spin  $I = 1/2$ ):

$$M_0 = N \frac{\gamma^2 \hbar^2 B_0}{4k_B T} \quad (7)$$

#### Relaxation time measurement $T_2$ : Measurement of liquid species in sample

A spin population in an inhomogeneous field after a  $\pi/2$  pulse has his Larmor frequency distribution which widens out. So, inhomogeneity field induces a delay for some spins and an lead for others. If spins can move during a time  $\tau$  after a  $\pi/2$  pulse then a  $\pi$  pulse is them applied in comparison with the same phase, so there is a symmetrical spin turning which will evolve in opposite direction during time  $\tau$ . So spins will come back in their initial configuration which will bring about a spin echo (figure 3):

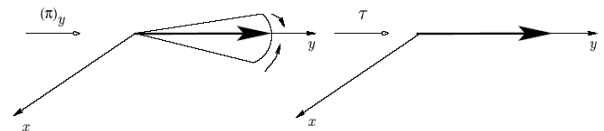


Figure 3: Spin echo

### Carr-Purcell and Meiboom-Gill CPMG method

This method consists in an echo succession. Diffusion effects are corrected by inter echo time.

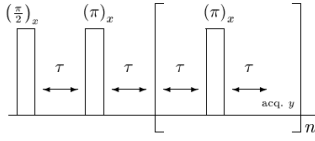


Figure 4: CPMG sequence

This sequence (figure 4) enables to know number of entities presents in liquid phase and relaxation times  $T_2$  of liquid entities presents in sample. Signal is a decreasing exponential which, with its extrapolation, enables to know liquid amplitude and so know number of entities presents in liquid phase (figure 5).

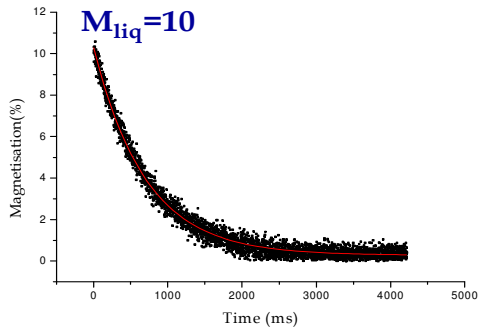


Figure 5 : Example of  $T_2$  cpmg measurement

### FID measurement: Measurement of all species of sample

This is the simplest measurement. Pulse sequence of FID measurement is an impulsation application  $(\pi/2)_x$  and an acquisition on  $O_y$  axis (figure 6).

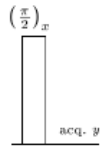


Figure 6: Free Induction Decay sequence

This sequence enables characteristic time of transversal magnetization disappearance  $T_2^*$  established by the relation (8) to be measured:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2^+} \approx \frac{1}{T_2^+} \quad (8)$$

$T_2^+$  is the characteristic time of the transversal magnetization disappearance due to other effects that the spin-spin coupling effects including mainly inhomogeneity field. The order of

magnitude  $T_2^+$ , which can be seen mainly as an apparatus characteristic is few milliseconds. By contrast,  $T_2$  is governed by dipolar relaxation and depends on entities environments.

The number of protons is measured by the hydrogen probe (and the number of fluorine by the fluorine probe in the case of measurements relating to hydrate Freon). This sequence has the advantage of not neglecting the too short relaxation time entities. So if the NMR signal is calibrated on a sample quantity of protons (for the hydrogen probe) is known, it is possible to determine the amount of protons present in any sample. A solid relaxes quickly:  $T_2 \approx 10 \mu s$ . A liquid has a longer  $T_2$  (10 to 3000ms). An example of hydrate suspension in emulsion is shown (figure 7). In this system, the  $T_2$  relaxation time of Freon hydrate particles is very short (a few  $\mu s$ ) compared to that of Freon (about 1000ms). That is why we find the two behaviors and the two environments fluorine in Figure 7. In addition, the relative values of the amplitudes are proportional to the relative quantities of fluorine of each species which will enable measure quantitatively the number of fluorine present in the sample.

This technique is used to detect the quantity of solid and liquid within the same sample.

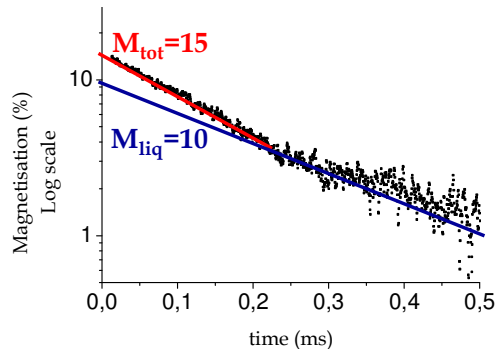


Figure 7: FID echo solid signal of Freon hydrate

So when solid echo FID and CPMG sequences are coupled, one can access to total and liquid entities number and know solid concentrations in sample:

$$\text{solidfraction} = \frac{N_{\text{solid}}}{N_{\text{solid}} + N_{\text{liquid}}} = \frac{M_{\text{tot}} - M_{\text{liq}}}{M_{\text{tot}}} \quad (9)$$

This methodology enables us to measure ice and hydrate concentration in our sample. To simplify measurement and after verifying that  $M_{\text{liq}}$  found

from an linear extrapolation with FID (figure 7) and from an exponential extrapolation with  $T_2$  CPMG measurement (figure 5) are the same:  $M_{liq} = 10$ , we just show and use results obtained from FID.

#### NMR experimental system

Used equipment is the Brüker minispec mq-serie 2001. Field is at 19.65 MHz frequency (permanent magnet). Probes which are used for our experiments are a temperature hydrogen probe and a temperature Fluor probe. They are controlled by a BVT 3000 which can be used from 173K to 473K. Temperature is regulated with liquid nitrogen, gaz nitrogen and a PID.

#### **Experiments under shear rate**

Study of ice and hydrate agglomeration is done under controlled shear rate. To avoid particles sedimentation, an helix mobile is used. The Couette analogy described by Ait-Kadi *et. al.* [7] is used to access the true shear rate. A schematic description of the helix mobile is shown on figure 8.

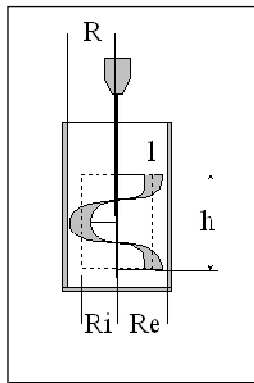


Figure 8: Helix and cylinder geometry dimensions

$h = 34 \text{ mm}$ ;  $R_e = 18.35 \text{ mm}$ ;  $R = 16.5 \text{ mm}$ ;  $R_i = 13.95 \text{ mm}$ ;  $l = 8 \text{ mm}$

To complete rheological measurements, particularly for kinetics study, and to evaluate the amount of crystals formed, NMR measurements are done under the same shear rate conditions than in rheology measurements. Indeed, an helix (a in figure 9) located at the bottom of an NMR tube (b) and centered by stoppers (c), is connected to a motor (d) which enables rotation at controlled speed. This helix has been calibrated using the same procedure used for the previous device.

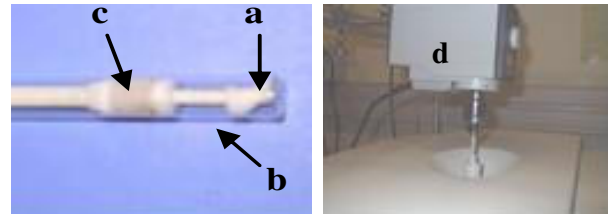


Figure 9: NMR Helix and assembly on NMR equipment.

Thus, comparison of induction times and crystallization times can be done with these two experimental techniques. For ice particles, an helix made of Teflon is used and for hydrate particles an helix in PEEK (PolyEthylEtherKetone) is used.

## **EXPERIMENTAL RESULTS AND DISCUSSION**

Ice and hydrate suspensions are studied by rheometry and NMR. In these 2 cases, samples undergo the same program:

- Cooling to 266K
- Two rheograms (only in rheometry)
- An isotherm at 266K under a constant shear rate during crystallization
- Two rheograms after crystallization (only in rheometry)
- Dissociation of crystals

Crystallization and agglomeration are observed and so studied during isotherm stage. Viscosity evolution is a consequence of agglomeration of crystals in the suspension. Moreover, NMR measurements give information on kinetics of crystals formation and conversion from water to crystals over time.

#### **Ice suspensions**

Two different oils are studied for ice case. The first is Xylene (named XA below) and the second is Xylene + Dodecane (named XDA below), with Asphaltenes as surfactant in these 2 cases. For these two different emulsions four water cuts (2%, 5%, 10% and 15%) and three shear rates ( $25s^{-1}$ ,  $50s^{-1}$  and  $100s^{-1}$ ) are studied by NMR and rheometry. The case of xylene/dodecane in 15% water emulsion is presented in the figure 10 as an example.

### Methodology to determine induction and crystallization times

In rheology, for every water cuts and shear rates, the apparent viscosity shows the same trend: an increase, an overshoot and then a stabilization of the viscosity.

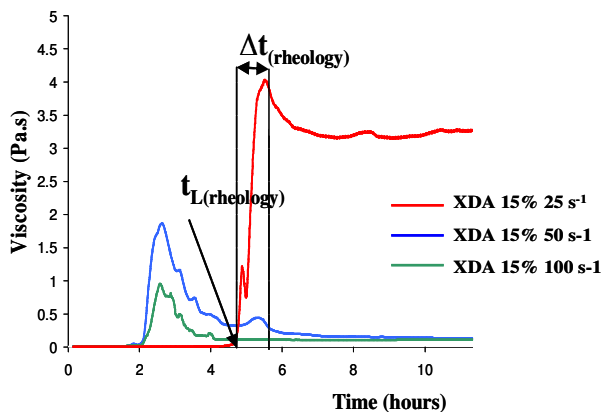


Figure 10: Example of viscosity curve for ice suspensions in emulsion 15% water cut and 25s<sup>-1</sup>

Agglomeration of particles leads to an increase in the effective volume fraction  $\Phi_{\text{eff}}$  of suspension which is translated by an increase viscosity (5). In rheology,  $t_L$  is determined at the onset of increasing viscosity and  $\Delta t$  is associated with the time of increasing viscosity (figure 10).

In NMR,  $t_L$  is determined when the first solid amplitude appears (3 min in figure 11) and  $\Delta t$  is determined when the whole water is transformed in ice (141 min in figure 11).

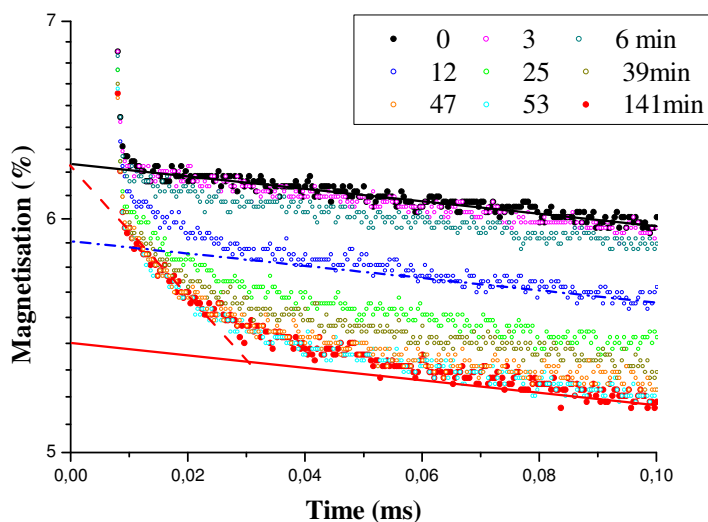


Figure 11: FID Echo solid measurements for water in ice conversion for XDA emulsion 15% water cut and 25s<sup>-1</sup>

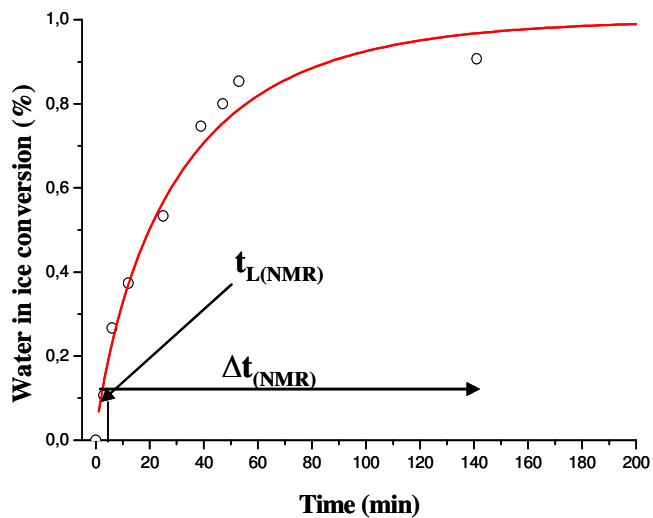


Figure 12: Water in ice conversion for XDA emulsion 15% water cut and 25s<sup>-1</sup>

In the figure 12, for this same sample, conversion water in ice is presented and obtained by NMR. The same shape of conversion curve is found for all water cut and shear rates, and we can later apply them a kinetic model and characteristic kinetics constants could be determined.

The same shear rate is imposed for the 2 techniques with a same geometry helix (Cf description in experimental methods). We compare, for the XA and XDA emulsions, induction time  $t_L$  (figures 13 and 14) and crystallization times  $\Delta t$  (figures 15 and 16)

### Induction times

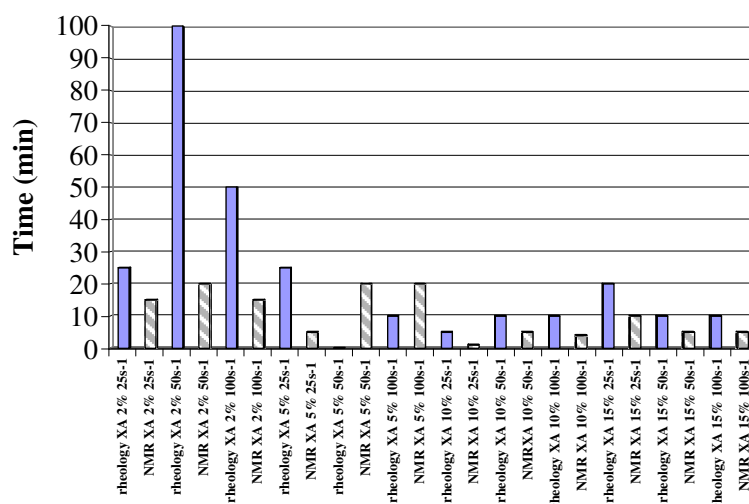


Figure 13: Induction time  $t_L$  for XA emulsion Comparison between rheology (blue) and NMR (hatched)

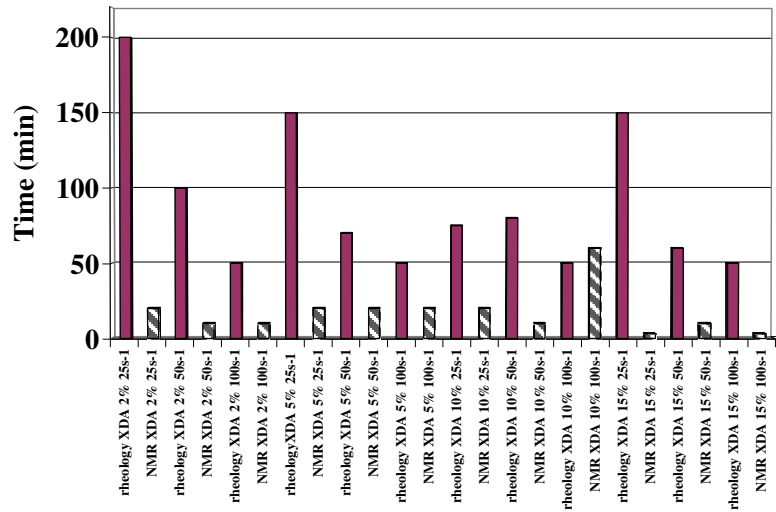


Figure 14: Induction time  $t_L$  for XDA emulsion  
Comparison between rheology (solid purple) and NMR (hatched)

For XA emulsions (figure 13),  $t_L \approx 20$  min in each case in NMR and rheology. So  $t_L$  is independent of water cut and shear rate. For XDA emulsions (figure 14),  $t_L$  is dependent of shear rate and water cut. The more important they are, the smaller  $t_L$  is. It is really visible with rheology results and less with NMR results.

In general,  $t_L$  is smaller in NMR than in rheology which is explained by the volume of sample. Indeed, in NMR sample is about 1mL and in NMR it is 50 mL. So in NMR entire sample is quicker at the good temperature than in rheology. So crystallization can occur faster in NMR.

#### Crystallization times

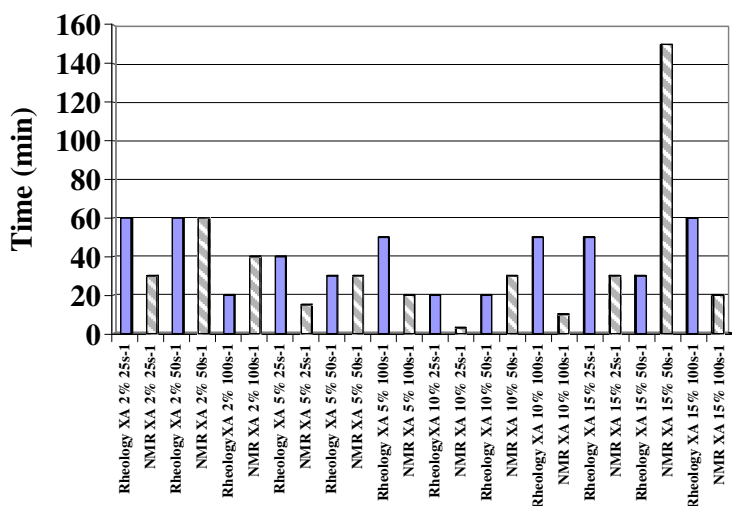


Figure 15: Crystallization time  $\Delta t$  for XA emulsion  
Comparison between rheology (solid blue) and NMR (hatched)

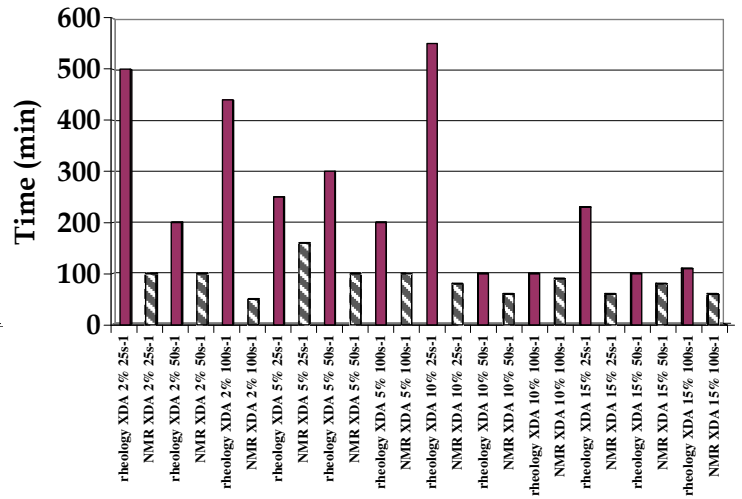


Figure 16: Crystallization time  $\Delta t$  for XDA emulsion  
Comparison between rheology (solid purple) and NMR (hatched)

For XA emulsions (figure 15), crystallization time  $\Delta t$  is about 50 min, and seems to be independent of water cut and shear rate. Contrary to this, for XDA emulsions (figure 16), the higher the water cut and the shear rate are, the smaller  $\Delta t$  is.

The difference in  $\Delta t$  (and in  $t_L$ ) for the two systems is explained by the different physico chemistry of the two emulsions. In the two systems, the same conditions on water cut and shear rate are imposed. There is only the physico chemistry which changes. Indeed, for XA emulsion, asphaltenes are soluble in xylene and so water droplet are not very stabilized and "protected" by asphaltenes. In opposition, for XDA emulsions, we are in the best conditions of stabilization [1] so water droplets are very isolated. Thus, steric barrier prevents contact between particles in XDA system in opposite to system XA. So crystallization spreads by contact between water droplet.

Moreover, NMR measurements enable us to determine water conversion in ice (figure 17).

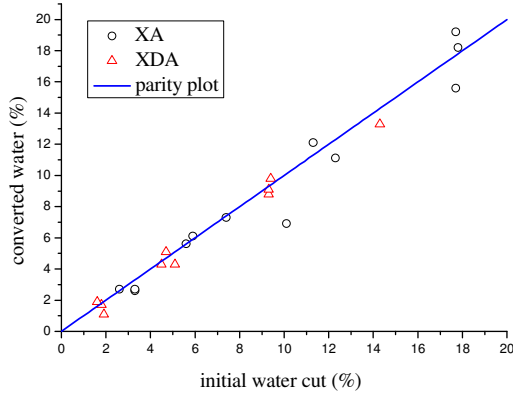


Figure 17: conversion water in ice in emulsion XA et XDA

In each cases, the whole water is converted in ice.

According to previously, effective volume fraction of suspension evolves with a power law:  $\Phi_{\text{eff}} \approx \tau^x$ . In ice case, for XA and XDA emulsions,  $\Phi_{\text{eff}}$  is very high, nearly 0.57 which is the maximum volume fraction. So ice particles agglomerate quickly and strongly and conditions blockage are encountered.

### Freon Hydrate suspensions

As dodecane, Freon is a flocculant of asphaltenes. So we are placed in the same physico chemical conditions than the case xylene/dodecane to compare the 2 systems.

Same parameters are studied: shear rate and water cut as for ice. Moreover, subcooling temperature is studied in the case of hydrates.

#### Water cut influence

water-cut	Induction time/min	$\Delta t/\text{min}$
0.05	960	150
0.07	150	90
0.1	30	60
0.3	30	30

Table 1: Induction times and  $\Delta t$  obtained with a 268 K temperature and a  $250 \text{ s}^{-1}$  shear rate

water-cut	Induction time/min	$\Delta t/\text{min}$
0.1	10	30
0.15	5	60
0.15	0	90
0.2	5	10
0.2	10	30
0.3	15	5

Table 2: Induction times and  $\Delta t$  obtained with a 268 K temperature and a  $100 \text{ s}^{-1}$  shear rate

The greater the water cut, the lower the induction time. So, it seems to correspond to nucleation by contact. The same influence is observed for  $\Delta t$  which show that agglomeration is by contact.

#### Shear rate influence

shear rate/ $\text{s}^{-1}$	Induction time/min	$\Delta t/\text{min}$
100	30	10
250	30	30
500	0	5

Table 3: Induction times and  $\Delta t$  obtained with a 268 K temperature and a 30% water cut

shear rate/ $\text{s}^{-1}$	Induction time/min	$\Delta t/\text{min}$
100	10	600
250	30	60
500	30	40

Table 4: Induction times and  $\Delta t$  obtained with a 268 K temperature and a 10% water cut

A little effect on induction time is observed with shear rate. Contrary to this, there is a strong relation between shear rate and  $\Delta t$ : the greater the shear rate, the lower is  $\Delta t$ .

Moreover, viscosity depends on imposed shear rate so aggregates size depends on shear rate.

#### Subcooling temperature influence

Temperature/K	Induction time/min	$\Delta t/\text{min}$
274	5520	10
271	3120	10
268	30	30

Table 5: Induction times and  $\Delta t$  obtained with  $250 \text{ s}^{-1}$  shear rate and a 10% water cut

For hydrate particle suspensions, aggregate size is controlled by shear rate (figure 18)

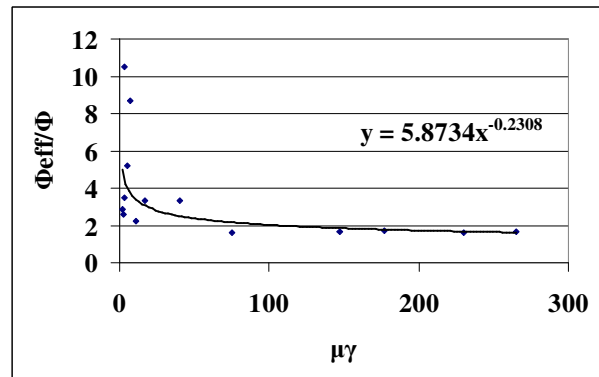


Figure 18: power law for hydrate particles suspensions

Thanks to equation (4), we can determine  $(3-D)m = 0.23$  and  $\tau_0^{(3-D)m} = 5.87 \text{ Pa}$  so  $\tau_0 \approx 2000 \text{ Pa}$ .

Thanks first results of modeling, fractal dimension  $D$  would be around 2.1 so, which  $m$  represents breakage mechanism of aggregate, will be around 0.25.

So, ice agglomeration is stronger than hydrate agglomeration. moreover, hydrate agglomeration seems to be reversible.

## CONCLUSIONS

Gas hydrates are crystalline compounds which may lead to pipelines blockage during oil production in offshore conditions. These particles, by an agglomeration mechanism, tend to progressively form a plug and so prevent production in pipelines. They can be modelled and compared with ice crystals.

So, this work deals with study of kinetics of formation and agglomeration and mechanisms agglomeration of hydrate and ice particles in emulsion in a hydrocarbon phase.

For this, two main characterisation techniques have in particular been implemented and been optimized for our system: NMR relaxometry and rheology. A calibrated shear rate from the shear rate imposed in rheology have been adapted in NMR in order to reproduce same experimental conditions and be able to compare the two measurement techniques. This is the originality of our works. Moreover, NMR gives information on the formation kinetics and the conversion rate water in ice crystals. The main perspective for the rest of our work is to study formation of Freon hydrate crystals formation too.

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