



Evaluation of water/mineral oil separation after methane hydrates dissociation using an AA formulation

Anne Siquin^{1*}, Brigitte Betro¹, Laurence Podesta-Foley¹, Emilie Abadie², Jean-Philippe Gingras².

¹IFPEnergies nouvelles, Rueil-Malmaison France, *anne.siquin@ifpen.fr

²Total Energies CSTJF, Pau, France

Abstract

The study aims at assessing the impact of gas hydrates formation and dissociation in presence of an anti-agglomerant (AA) on the water quality after oil/ water separation. To do so, experimental tests consisted in forming pure methane hydrates in a mixture of water + aromatic petroleum-cut solvent added with anti-agglomerant (AA) additive in a high pressure cell, evaluating the slurry obtained then dissociating the hydrates and evaluating the phase separation at 50°C. The separated phases are then characterized to determine the quality obtained after separation. After preliminary characterizations (compatibility tests, superficial and interfacial tensions). The hydrates formation is followed by the conversion rate and by a qualitative evaluation of the suspension obtained (visual and kinetics of particles settling). After the hydrates dissociation, the systems are brought at 50 °C and the phase separation was visually followed under pressure. After depressurization, the volume of each phase water/solvent and emulsion are quantified. The respective content of water in the solvent and of the solvent in the water are measured. The droplet size distributions in case emulsion are measured. An AA additive has been tested with two solvents, at different salinities of the water phase as well as three water cuts (30, 50 and 80 %).

Keywords

Water/oil separation; Anti-Agglomerant Additive; methane hydrates

Introduction

To avoid hydrates blockage in gas dominant pipeline [1, 2], the use of anti-agglomerant additives (AA) can be envisaged. AA additives allow the formation of fine hydrates particles slurries transportable in the liquid hydrocarbon along the production line [3]. In the specific cases of “dry gas fields”, no or very small quantity of liquid hydrocarbon are produced and the only liquid flowing in the line is water. In these specific cases, the use of an AA for hydrates management can be considered only if a non-aqueous liquid phase can be also injected in the production pipeline as a continuous phase for the hydrates slurry.

This study aims at exploring the feasibility of this solution, assessing first AA efficiency at forming fine dispersed and transportable hydrates particles slurries in the water/non aqueous solvent depending on water cut (WC) and water salinity. In a second step, the evaluation of the impact of the AA and of the hydrates' dissociation step on the water/non-aqueous phase separation and on the two liquids phase's quality was performed. These two points are of importance for water discharge and for non-aqueous phase reinjection in the pipeline.

Methodology

A dedicated workflow has been applied for this study; it is presented below.

Systems and samples Characterization

One commercial AA additive was tested and diluted into two aromatic solvents pre-selected as non-aqueous phase for this study: Solvesso® (ExxonMobil) and Solvarex® (TotalEnergies). Two water salinities (1g/L and 30g/L) were explored. Interfacial and superficial tension measurements at atmospheric pressure were performed to characterize these systems.

Gas hydrates formation under agitation

The T-314 experimental rig was used to form, characterize, and dissociate gas hydrates. The experimental rig comprises 4 high pressure cells “Fig. (1)”. The cells can work independently the one from the others. They are equipped with sapphire windows allowing visualization under pressure. Macroscopic parameters such as pressure and temperature (P, T) were monitored. Using these data, the water into hydrates conversion rate and the hydrates quantity in the liquid phase (HiL) were determined.

After the formation, a visual qualification of the slurries formed was done by stopping the agitation and qualifying the particles settling. In case of sedimentation, the ability of particles to re-disperse

was assessed by progressively increasing the stirring rate. The slurries behaviors results were captured by photos and videos.

Gas hydrates dissociation under agitation and impact on separation

The hydrates dissociation step was performed by heating the cell, maintaining a constant pressure. The visual evolutions of the hydrates disappearance and of the liquid phase's separation versus time were captured using a camera.

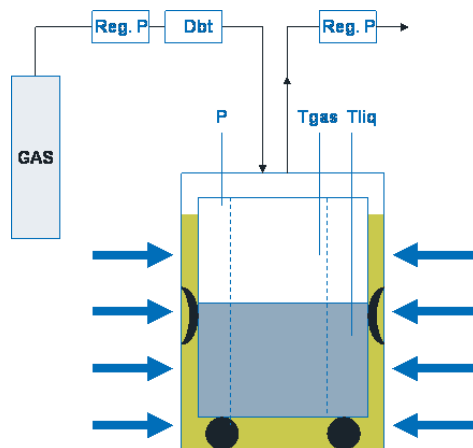


Figure 1. Schematic of the cell

Liquid characterization

After hydrates' dissociation and depressurization, the cells were opened. The final state of the system was evaluated in terms of volume of each phase. The quantity of residual water in the solvent was done using the Karl Fischer dosage and the Total Organic Carbon (TOC) was measured in the water phase.

Experimental Procedure

The tests were run in semi-batch configuration (constant pressure controlled by gas feeding during temperature decrease and hydrates formation). Two identical tests were performed for each condition explored. The procedure comprises "Fig. (2)" the following steps:

- cooling of the cell, two methane flushes and cell pressurization,
- hydrates formation,
- particles settling (followed by a stirring restart in case of sedimentation),
- dissociation,
- depressurization and cell opening.

Hydrates to be formed are pure methane hydrates. The working pressure is 80 bar. The hydrates equilibrium temperature predicted by Multiflash 6.1 for pure water and pure methane at 80 bar is 11 °C.

Particles settling phase.

At the end of the formation, the stirring was stopped, and the settling of the particles recorded by a camera. This phase could be prolonged up to one night depending on the moment when the formation ends. After the settling, and if particles were concentrated at the bottom of the cell, the restart at slow stirring rate was performed to characterize the slurry quality and the particles

ability to be moved from a dense layer to a homogeneous particles suspension. The phenomenon was filmed.

Hydrates dissociation

Hydrates dissociation was induced by heating the cell at constant pressure (80 bar). The targeted high temperature was 50 °C. The agitation is fixed at 300 rpm. When the target high temperature was reached the stirring was stopped and the gravity separation was filmed. After this period, the cell was depressurized, and the proportions of each phase were measured, the liquid phases characterized (oil content in water, water content in oil, emulsion continuous phase...).

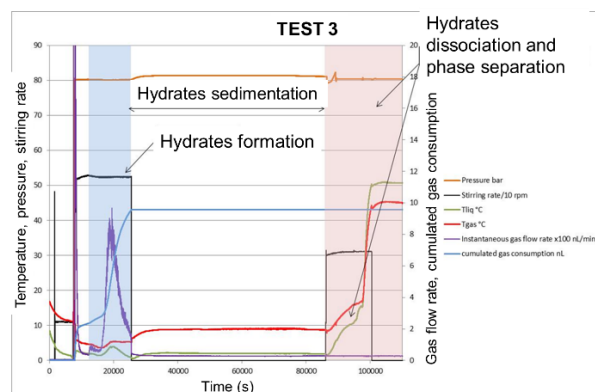


Figure 2. Overview of the different phases of a hydrates test

Results and Discussion

Table 1 details the test matrix. Among the conditions explored, comparisons of the results of cases 3 and 8 will be discussed (effect of the solvent) as well as cases 6 and 7 for the WC effect and finally 7 and 9 for the effect of the AA concentration.

Table 1. Test matrix.

Case	Solvent	WC (% vol.)	[NaCl] (g/L)	[AA] (% wt vs Water)
3	Solvesso®	50	30	3
4/5	Solvesso®	50	1	3
6	Solvarex®	30	1	3
7	Solvarex®	80	1	3
8	Solvarex®	50	30	3
9	Solvarex®	80	1	1.87

Effect of the solvent

For the cases 3 and 8, the interfacial and superficial tensions in the two systems were similar ("Tab. 2").

Table 2. Interfacial and superficial tension measurements

	Solvesso® /AA	Solvarex® /AA
Interfacial tension (mN/m)	30.5	26.3
Superficial tension (mN/m)	<1	<1

The hydrates formations were also quite similar. The main results are gathered in Table 3.

Table 3. Summary of the hydrates' formation

Case	Formation	Conv. Rate* (%)	HiL** (%)
3	1/2	78.4	39.2
8	1/2	84.3	42.1

* conversion rate calculated from gas consumption (1 CH₄ for 6 H₂O)

** HiL = (conv. rate) X Water-cut

For both systems, hydrates formation was observed only in one of the two cells. The conversion rates were around 80 % and the hydrates in liquid (HiL) were around 40 %. The hydrates particles slurries did not present inhomogeneities and when the agitations were stopped the particles settling were very slow (see illustrations after one-night on “Fig. (3)”).



Figure 3. Hydrates slurries after sedimentation time

The macroscopical separation took place rapidly when the systems reached 50 °C (respectively in 1 and 2 minutes). In both systems the behaviors were similar for cells that had formed hydrates and the ones that had not. For case 3 conditions after the macroscopic separation, the two phases were turbid, the solvent became clear again after 3 to 4 hours (see “Fig. (4)”). For the case 8 conditions, the solvent was clear more rapidly (1 hour).

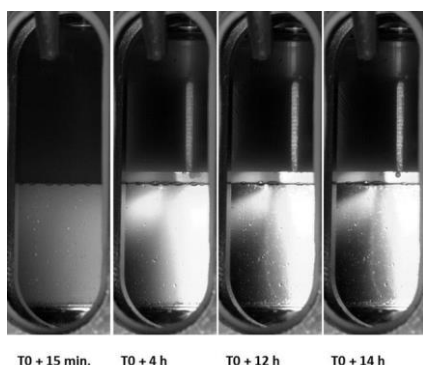


Figure 4. Water and solvent phases evolution for 14 hours (at 50°C and 80 bar methane) in case 3 conditions

Finally, water contents in solvents and TOC in water were measured. Both solvents contained less than 1% of water. On the other hands, the water phases contained important amount of carbon in case 3 (see “Tab. 4”). These quantities were much larger than the ones measured in case

8 even if the laps time after the end of dissociation were much longer (24 h at 50°C for case 3 conditions) than for case 8 (2 h @ 50°C and 2h @ ambient). In both conditions, the results obtained in the cells that formed hydrates were similar to those obtained in the cells where no hydrates formed.

Table 4. TOC contents in water for cases 3 and 8

TOC (g/L)	Cell with hydrates	Cell without hydrate
Case 3	27	24
Case 8	~7	6.3

The comparison between case 3 and 8 results shows that the nature of the solvent did not impact the kinetic of hydrates formation, nor the quantity of hydrates formed neither the efficiency of the AA at dispersing the hydrates particles. The main difference is found in the residual organic material found in the water phase after the hydrates dissociation. Residual solvent content is far less important when Solvarex® is used than when Solvesso® is used.

Effect of water cut

The case 6 and the case 7 present conditions where the system comprises Solvarex® and water at low salinity 1 g/L NaCl and two different WC: 30% for case 6 and 80 % for case 7. For these two systems the interfacial tensions were very similar (26.5 and 26.7 mN/m respectively). The superficial tensions were lower than 1 mN/m for the two systems.

The hydrates formations results are summarized in Table 5.

Table 5. Summary of the hydrates' formation

Case	Formation	Conv. rate (%)	HiL (%)
6	2/2	94.5 /36.0*	28.3 /12.1*
7	1/2	86	68.8

*pressure regulation failed loss of pressure in the cell

For WC 30 % (case 6), hydrates formation was observed in the two cells. The water into hydrates conversion rates were very contrasted. The two tests led to low/medium hydrates contents in the liquid (HiL). The slurries obtained were visually homogeneous. For WC 80 %, hydrates formation was observed in only one of the two cells, with a high conversion rate was measured leading to a high HiL. Visually it was difficult to conclude on the occurrence of hydrates deposit however the system seemed to be static (no movement observed at the sapphire window with stirring) and as hydrates formation presents “pulses” of hydrates formation a non-homogeneous slurry was anticipated.

Hydrates sedimentation in the 30% WC is rapid: 20 to 25% of clear solvent appeared at the top of the liquid after 1h to 1h30. In the 80 % WC no sedimentation was observed, even after 72 h (“Fig. (5)”).

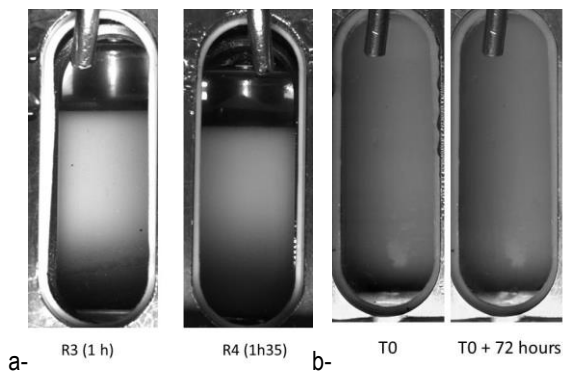


Figure 5. Hydrates slurries after sedimentation (Case 6 WC 30% left; Case 7 WC 80% right)

For case 6, after the dissociation the agitation was stopped, and the macroscopic phases separation was achieved after less than 2 minutes. The system was kept at 50°C during 1h after the depressurization the two phases were clear and the TOC in water was measured around 6.5 g/L. This value was measured immediately after the cell opening for one cell and 48h later for the other. This indicates that there was no time evolution of the carbon content in the water. For the case 7 (“Fig. (6)”) the system evolves only during the first minutes after the agitation stop.

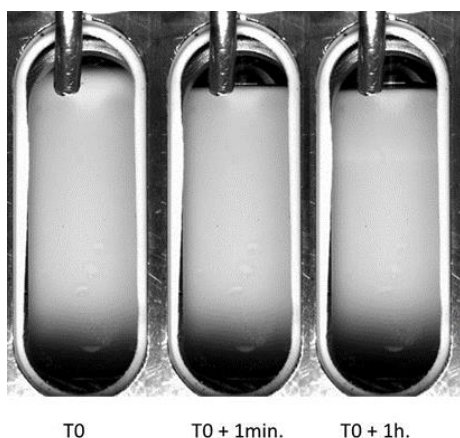


Figure 6. Macroscopic separation case 7

At the cells opening, the two systems (with and without hydrates formation) present stable emulsions (“Tab. 6”). The emulsion volume was slightly less important in the cell that has formed hydrates. Destabilization of the emulsion due to hydrates dissociation must be confirmed.

Table 6. Phase volumes at the cells opening for case 7

	A-Cell with Hydrates	B-Cell without hydrates
Solvent (mL)	15	5
Emulsion (mL)	65	75
Water (mL)	None	None

The emulsions were solvent-in-water type with bigger droplet for the A-cell emulsion $D_{V50} \sim 3 \mu\text{m}$ and $D_{V50} \sim 1.3 \mu\text{m}$ for the other. The A-cell emulsion

evolved to a clearer emulsion after 7 days, whereas the B-cell emulsion was perfectly stable during the same duration – no evolution was detected. The comparison between cases 6, 7 and 8 shows that the WC has a great importance on the AA performances. Indeed Cases 6 and 8 can be compared if we assume that the impact of salinity on the AA performances can be neglected – as it has been demonstrated for Solvesso® solvent. At low or medium WC (namely 30 and 50% see Case 8) the slurries formed were transportable, the macroscopic water solvent separation was rapid. When the WC is increased up to 80 % (to minimize the solvent volume in a potential solvent loop). The quantities of hydrates formed may be huge leading to a HiL that may reduce the hydrates slurry transportability. Moreover, such a system forms very stable solvent-in-water emulsions with very small droplets that can be crippling for the use of a solvent loop. The influence of the AA concentration was explored for this very high WC (case 9 results not shown). The decrease of the AA concentration led to non-homogeneous hydrates slurries and hydrate deposits. At the dissociation, stable emulsions were still formed indicating that this WC cannot be used for such solution.

Conclusions

An anti-agglomerant additive was tested with two solvents, at two salinities of the water phase and three water cuts (30, 50 and 80 %). The AA presented good performances in term of hydrate slurries quality and water/organic solvent phase separation. For all the tests performed, the solvent phase presented very low water content after the tests (less than 1 %). The Total Organic Content (TOC) in the water phase depended on the time spent before the quantification (longer time, lower TOC values). The solvent used had also a great influence on the TOC: in similar conditions the system with Solvarex® presented much higher water quality (lower TOC) than the one with Solvesso®. The study showed that the AA presented good performances at water cut of 30% and 50 % and at 1 or 30 g/L of NaCl in the water phase. The hydrates slurries were composed of small transportable hydrates particles, the macroscopic separation was rapid, and no emulsion was formed after hydrates dissociation. For the highest WC (80 %) with AA at 3 % wt. vs water concentration, the slurries were not homogeneous, and emulsions were systematically stabilized even if no hydrates have been formed. An attempt to lower the AA concentration led to formation of non-transportable slurry and to hydrates deposition at the cell wall. Moreover, stable emulsions were still formed. In conclusion, the concept of adding a non-aqueous solvent as an AA solvent and hydrates phase transportation medium in a production loop is feasible. Whatever the systems, very high WC must be avoided. For the AA studied, the best solvent is Solvarex® both

on hydrates slurries quality, on water/solvent separation and on water quality.

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Responsibility Notice

The authors are the only responsible for the paper content.

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