# Gas Hydrate Formation and Transport in an Acidic Crude Oil: Influence of Salt and pH†

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# Gas Hydrate Formation and Transport in an Acidic Crude Oil: Influence of Salt and pH[†]

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The anti-agglomerant (AA) performances of an acidic crude oil are evaluated in flow conditions using a high-pressure (HP) hydrate laboratory loop at a water cut of 10 wt %. The test procedure includes a 24 h fluid circulation in the hydrate stability zone, followed by a 3 h shut-in, and finally the restart of the flow. The influence of salts (NaCl, CaCl$_2$, and mixture) and pH of the water on the AA property has been investigated. The results obtained in flow conditions are consistent with previous tests in HP kinetic reactors and a HP rheological cell. The acidic crude oil with pure water exhibits moderate AA property. The AA property decreases in the presence of salt water and is lost with alkaline pH. This work confirms that, although naphthenic acids and mainly naphthenates (formed at alkaline pH) are surface-active compounds, they do not act as efficient natural AAs.

## Introduction

The thermodynamic conditions prevailing in production pipelines may be favorable to the formation of crystalline inclusion compounds, the so-called gas hydrates. These compounds arise from the ability of water molecules to form lattice structures through hydrogen bonding, which are stabilized by guest molecules (e.g., CH$_4$ and C$_3$H$_8$) under high pressure and low temperature.[1] Gas hydrates are a particular concern to the oil and gas industry, because the conditions for hydrate formation are often encountered in oil/gas pipelines, which can potentially result in a shutdown of production. In deep offshore operations, gas hydrates are prevented by the insulation of pipelines and/or the addition of chemical inhibitors. This can result in significantly increasing both capital and operating expenditure. Consequently, other methods are being considered. Among them, the intrinsic capability of some crude oils to transport hydrate particles without plugging is seen as an interesting potential option, and research[2–5] is being conducted to predict the natural anti-agglomeration properties of various types of crude oils.

Numerous factors, such as hydrodynamics, rheology, hydrates kinetics, mass transfer, etc., can play an important role in the transportability of hydrates by a crude oil.[2–5] However, a crude oil must first form stable water-in-oil (w/o) emulsions to exhibit anti-agglomerant (AA) property.[2,6] This first property is necessary but not sufficient. Indeed, when hydrates form, the crude oil must also confine the crystallization inside each isolated water droplet without interaction with the neighboring water droplets.

Some oilfields have already been successfully operated inside the hydrate stability zone[2,6] without any method for hydrate plug prevention. These fields produce crude oils that contain a significant amount of asphaltenes. Asphaltenes are heavy polar surfactants that are present in some crude oils[7,8] and are known to stabilize w/o emulsions. Skin formation around water droplets and particular rheological properties of the w/o interface in their presence have been reported.[9–11] Because of the surfactant nature exhibited by asphaltenes, it is believed that they play a leading role in the natural AA properties of some crudes.

Recently, many acidic crude oil fields have been discovered (Africa, Venezuela, or the North Sea). The biodegradation of

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crude oil[12] results in the formation of carboxylic acid compounds or naphthenic acids (in this paper, all of these acids, RCOOH, will be named naphthenic acids). These acidic crude oils can form w/o emulsions with long-term stability (months to years).[13,14] The nature of the water (alkaline pH or presence of salts) can increase the stability of emulsions because of the naphthenate salts, $(RCOO^-)_n M^{n+}$.[15–17] A previous work[14] performed on three distillation fractions of a West African crude oil has shown that naphthenic acids and naphthenates of low molecular weights (<500 g/mol) lower the interfacial tension but do not stabilize w/o emulsions, confirming the trends highlighted by Hemmingsen et al.[18] with a North Sea crude oil. However, the West African oil also contains other amphiphilic components, such as heavy resins and more specifically asphaltenes. These compounds allow for the formation of w/o emulsions, exhibiting a stability of several weeks for a wide range of conditions (pure water, brine, or alkaline waters).[14]

In previous work,[5] the AA properties of the same acidic crude oil were evaluated through experiments carried out with kinetic reactors and a rheological cell at high pressure. It has been demonstrated that the presence of salt waters and more specifically alkaline waters decreased the induction time for hydrate formation, increased the hydrate growth rate, and decreased the AA performance of the crude oil in comparison to the tendencies observed in the presence of pure water. These results suggested that naphthenic acids and especially naphthenates present in this acidic crude oil are not efficient species for the prevention of hydrate agglomeration.

The intrinsic capability of crude oils to transport hydrate particles is clearly linked to both the physicochemical properties of the system (crude plus water plus gas) and the hydrodynamic conditions applied to it (flow regime for the emulsion and hydrate formation, shut-in/restart for the hydrate particles, or emulsion sedimentation). The aim of the present work was to answer the following questions: "is the AA performance of the acidic crude oil the same in all flow conditions" and "is the order of the performance of the above AAs (i.e., pure water > salt waters ≫ alkaline waters) the same in different flow conditions"?

Answering these two questions with this particular acidic crude oil will give more information for the next step, which is the evaluation of the AA property in a semi-industrial loop (Lyre loop) in multiphase conditions. The ultimate aim is to use laboratory experiments to have reliable information for the Lyre loop and to use all of the available hydrate tests (rheological, kinetic tests, loops, etc.) to help field production, taking into account the natural AA property of some crude oils.

The AA performance of the acidic crude oil has thus been evaluated in a high-pressure laboratory flow loop with pure,

**Table 1. Crude Oil Analysis**

| system | content (wt %) | TAN (mg of KOH/g) | saturates (wt %) | aromatics (wt %) | resins (wt %) | asphaltenes (wt %)[a] |
|---|---|---|---|---|---|---|
| crude oil | 100 | 1.2–1.3 | 49.8[a] | 25.6[a] | 13.7[a] | 1[a] |
| <C$_{20}$ | 35.5 | ND[b] | 66.8 | 7.2 | 0 | 0 |
| >C$_{20}$ | 64.5 | ND[b] | 40.4 | 35.7 | 21.3 | 1.6 |

[a] Calculated from the fraction data. [b] ND = not determined.

salt, and alkaline waters and compared to that determined in kinetic reactors.

## Experimental Section

**Materials.** The acidic crude oil used in this study came from a West Africa deep-water field operated by TOTAL. Its characterization consisted of (i) measuring the total acid number (TAN), which corresponds to the mass of KOH in milligrams necessary to neutralize the acid contained in 1 g of oil [American Society for Testing and Materials (ASTM) D664], and (ii) separating the crude into two fractions (ASTM D2892). The light fraction (<C$_{20}$) was analyzed using gas chromatography (Carburane), whereas a saturates, aromatics, resins, and asphaltenes (SARA) characterization was conducted on the heavy fraction (>C$_{20}$). In this work, asphaltenes are defined as the *n*-heptane-insoluble fraction of the >C$_{20}$ fraction. All of the results are given in Table 1. This crude oil has a moderate acidity and contains significant amounts of resins (13.7 wt %) and asphaltenes (1 wt %).

All of the aqueous phases were prepared from deionized water. The deionized water was produced by the Millipore Milli-Q 185 E system (conductivity < $10^{-1}$ μS/cm). Sodium chloride (NaCl purchased from Fisher, purity of 99.5%), calcium chloride (CaCl$_2$, 2H$_2$O purchased from Merck, purity of 99.5%), and sodium hydroxide (NaOH purchased from Prolabo, purity of 97%) were used to prepare salt and alkaline waters.

Methane gas (G20 supplied by Air Liquide, specification NF-EN 437) was used as the hydrate-forming gas.

**Hydrate Laboratory Flow Loop and Procedure.** A schematic view of the laboratory flow loop is presented in Figure 1. The flow loop is made of the following components: (i) an AISI-316 stainless tube of 9.52 mm in external diameter, 7.8 mm internal diameter (i.d.), and 10 m in length, with a total inner volume of 0.803 L [It is coiled in a thermostatic bath, whose temperature is controlled with a cryostat; the rest of the line (between the inlet and outlet of the loop) is insulated by Armaflex], (ii) a stirring reactor with an internal capacity of 1.5 L and a maximum service pressure of 150 bar, (iii) a positive displacement screw pump for circulating the fluid, (iv) a transparent sapphire cell to visualize the formation and agglomeration of hydrates, and (v) a differential pressure gauge (Rosemount, 0–20.7 bar ± 0.075%) to measure the pressure drop between the inlet and outlet of the loop and a mass flow meter (Micro-Motion S40-S with a precision of ±0.2% on the flow) to record the liquid flow rate.

This laboratory flow loop is a liquid/liquid loop (aqueous and organic phases); i.e., gas hydrates are formed using the gas dissolved in the organic phase. When hydrates form, the gas inlet line, located between the loop outlet and the sapphire cell, supplies gas to maintain a constant pressure in the loop. The volume of gas supplied to the loop is given in L$_N$, i.e., at "normal conditions" (0 °C and 1 bar).

The hydrodynamic of the laboratory loop was studied some years ago (unpublished work). The loop calibration by Newtonian fluids of known viscosities has shown that the achievable flow pattern is mainly laminar. Although a deviation from a pure laminar flow pattern is induced by the coiled loop, this deviation is correctly described by the empirical correlation developed by Mishra et al.[19] In this work, given the system viscosities, the flow pattern was laminar in each case and the shear rate at the pipe wall was approximately 950 s$^{-1}$.

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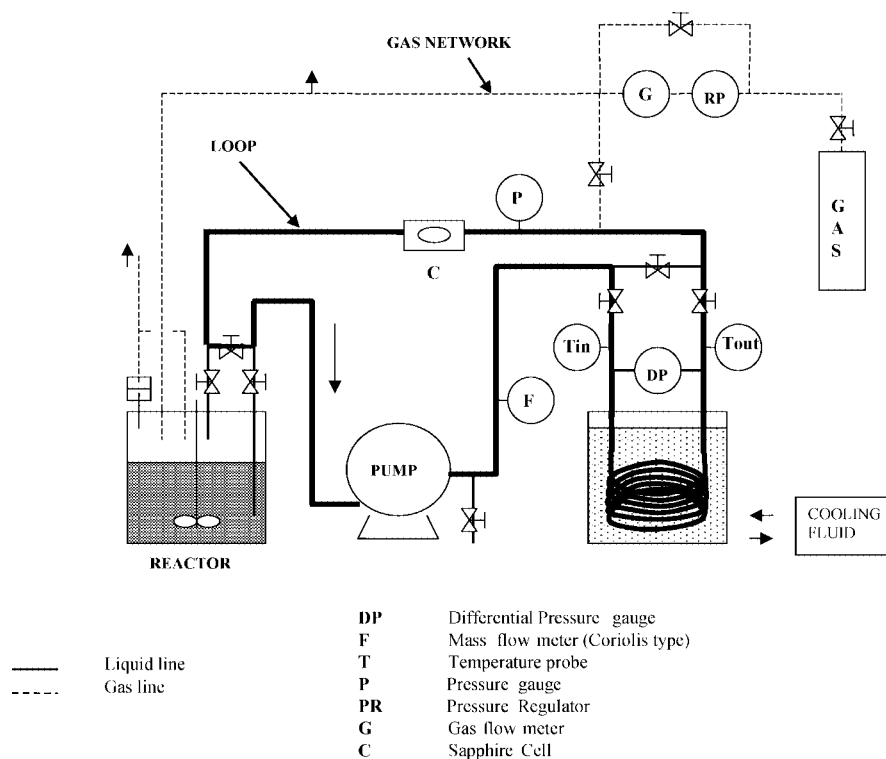
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**Figure 1.** Synoptic view of the IFP hydrate flow loop.

The data acquisition system records the variations of the following parameters: (i) the gas flow rate, GFR ($L_N$/min), (ii) the cumulated gas consumption, CC ($L_N$), (iii) the inlet and outlet loop temperatures, $T_{in}$ and $T_{out}$ (°C), (iv) the liquid flow rate circulating across the loop, LFR (kg/h), (v) the pressure in the loop, $P$ (bar), (vi) the pressure drop through the loop, DP (bar).

Hydrate formation is detected by (i) an increase in $T_{in}$ because of the exothermic character of hydrate formation, (ii) an increase in GFR, (iii) in some cases, a change of LFR and DP.

Extensive use of the loop has led to some conclusions regarding its limitations: (i) the dynamic viscosity of the transported fluid must be lower than about 80 mPa s and (ii) the maximum allowable water cut, leading to a transportable hydrate suspension, is about 15 vol %.

Because of the viscosity limitation of the loop, the acidic crude oil has been diluted with a naphtha solvent [acidic crude oil/naphtha ratio of 80:20 (vol/vol)]. Preliminary tests have shown that this solvent does not exhibit any AA property; as soon as hydrates started to form in the system, the hydrate particles agglomerate and plug the line.

The effect of dilution on both the droplet size distribution and stability of emulsions prepared using the protocol described by Arla et al.[14] has been evaluated by visual observations with an Olympus CH40 microscope and by bottle tests. For each type of water used, the droplet size distribution was similar to the ones measured for the emulsions formed with the nondiluted crude oil and the emulsions exhibited the same long period stability (several weeks).

The fluids tested in this work, i.e., the acidic crude oil and the aqueous phase, were introduced separately into the reactor. The water cut was fixed at 10 vol %. The reactor was then pressurized with methane at 70 bar and maintained at 17 °C. At this pressure, the three phase ($L_w$–H–G) equilibrium temperature is about 10 °C (CSMHyd software). The experiments were performed under isobaric conditions. The fluids were stirred at 500 rpm during 15 min to form an emulsion; afterward, the agitation rate was reduced to 150 rpm, and the emulsion pumped from the reactor and circulated in the loop at the LFR of 110 kg/h (0.9 m s$^{-1}$) for 1 h to extract possible gas bubbles trapped in the loop. Moreover, checking LFR during this last step allowed us to determine that the water cut of the tested fluid remained constant under the flow conditions. After 1 h, the reactor was bypassed, so that the fluid

circulated *only* in the loop. The data recording was then started. The hydrate stability zone was reached by decreasing the bath temperature from 17 to 0 °C. If no hydrate plug formation was detected, the flow conditions were maintained for 24 h. At the end of this period, the pump was stopped for 3 h and then restarted.

The crude oil is considered as a good AA system, if the four conditions listed below are encountered: (1) The hydrate formation does not induce any blockage (LFR = 0) or any large variation of LFR and DP. The GFR curve during hydrate formation exhibits a Gaussian shape, indicating that hydrate formation occurs in isolated water droplets and that no rapid propagation of crystallization is induced as shown by Palermo et al.[20] on the exothermic peak. (2) The hydrate slurry formed circulates in the loop during 24 h, and LFR and DP remain constant during the 24 h test. (3) The restart after the shut-in of 3 h is possible. (4) LFR and DP after the restart are roughly similar to those measured just before the shut-in period.

For each system and/or conditions to be tested, experiments were reproduced 3 times to check repeatability.

Using the procedure described above, the influence of the quality of the aqueous phase on the AA properties of the acidic crude oil has been evaluated. Three different types of aqueous phases have been tested: (1) A "pure water", which is the deionized water. This system is not realistic from an industrial point of view because production waters always contain salts. Nevertheless, it will be useful as a reference system. (2) A brine containing 35 g/L of NaCl and 7 g/L of CaCl$_2$ to mimic the formation waters encountered in oilfield operation. Waters containing only NaCl and only CaCl$_2$ have also been studied to discriminate the effect of each type of electrolyte. (3) An alkaline water with an initial pH of 12 before contacting the acidic crude. After the contact, the pH of the water decreases because of the reaction between the naphthenic acids RCOOH and OH$^-$, leading to the formation of naphthenates RCOO$^-$. The final pH has been found to be 8.3.[14] This system

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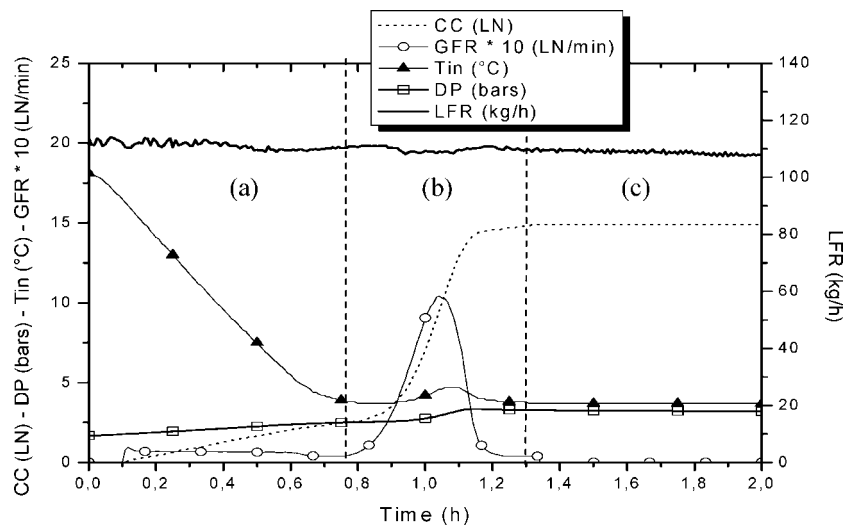
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Figure 1 legend:

| | |
|---|---|
| DP | Differential Pressure gauge |
| F | Mass flow meter (Coriolis type) |
| T | Temperature probe |
| P | Pressure gauge |
| PR | Pressure Regulator |
| G | Gas flow meter |
| C | Sapphire Cell |

Liquid line
Gas line

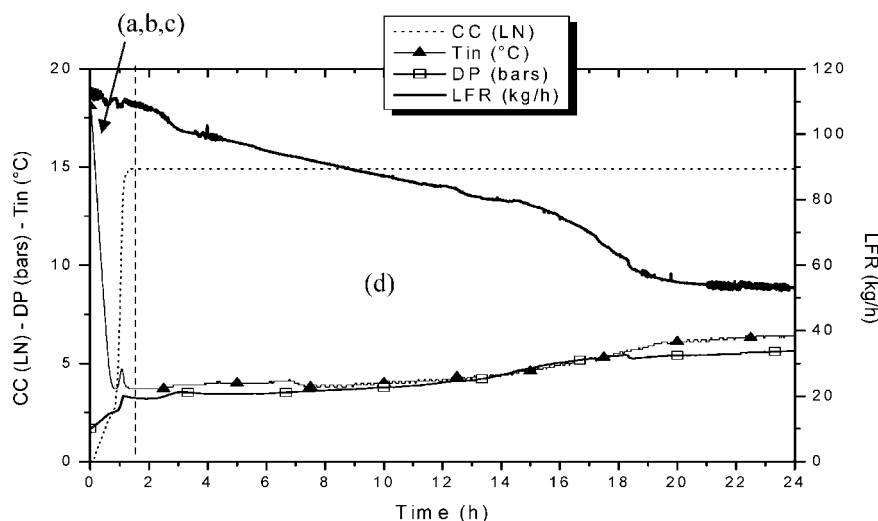**Figure 2.** Flow loop test for the pure water/oil system (hydrate formation).



**Figure 3.** Flow loop test for the pure water/oil system (24 h circulation).

simulates the practical case of oil production under alkaline conditions encountered after degassing of $CO_2$.

## Results and Discussion

Figure 2 illustrates the variations of GFR, LFR, CC, DP, and $T_{in}$ measured for the pure water/oil system during the first 2 h of the test. While the fluid is circulating in the loop at 110 kg/h (0.9 m s$^{-1}$) and constant pressure, the temperature is decreased to bring the system into the hydrate stability zone (zone a in Figure 2). A slight increase in DP because of the increase in liquid viscosity is measured. At the same time, because of the increase of the methane solubility in the crude oil with the temperature decrease, some amount of gas is supplied to maintain a constant pressure in the system. After a few minutes at about 4 °C, hydrate formation is detected by both an exothermic peak and a sharp increase in GFR (zone b). The GFR peak has a Gaussian shape. Hydrate formation does not induce any perturbation of the LFR, which stays almost constant at 110 kg/h. On the other hand, DP increases slightly from 2.5 to 3.2 bar, indicating some agglomeration between particles. Using the model developed by Camargo et al.,[21,22] the value of

DP measured after the hydrate formation corresponds to an apparent volume fraction of 23.4%, instead of 10%. Agglomeration occurs during the formation but is not detrimental (no important increase of the DP) because of the low water cut tested. However, we know that, if the diameter of aggregated particles is too large, the ratio diameter of aggregate/internal diameter of the loop ($D_{agg}$/i.d.) becomes a very important factor that can lead to a blockage along the line.

If the methane hydrate composition is assumed to be $CH_4 \cdot 6H_2O$, then the water to hydrate conversion rate, $\tau$, can be calculated by

$$\tau\ (\%) = [CC/V_{FL} WC/V_W/6 \cdot 22.4] \times 100 \qquad (1)$$

where $V_{FL}$, WC, $V_W$, and CC are the inner volume of the flow loop, the water cut, the molar volume of water, and the volume of gas consumed during the hydrate formation, respectively.

From Figure 2, CC in zone b increases from 2.5 to 14.9 $L_N$, which corresponds to a $\tau$ value of 74%.

At the end of the hydrate formation (zone c), GFR drops to zero, CC levels off, $T_{in}$ decreases to its value before hydrate formation, DP stabilizes to 3.2 bar, and LFR is similar to that measured before formation.

Figure 3 shows the evolution of the parameters for the pure water/oil system during the 24 h of the circulation test. Zone d in Figure 3 illustrates the moderate AA property of the acidic

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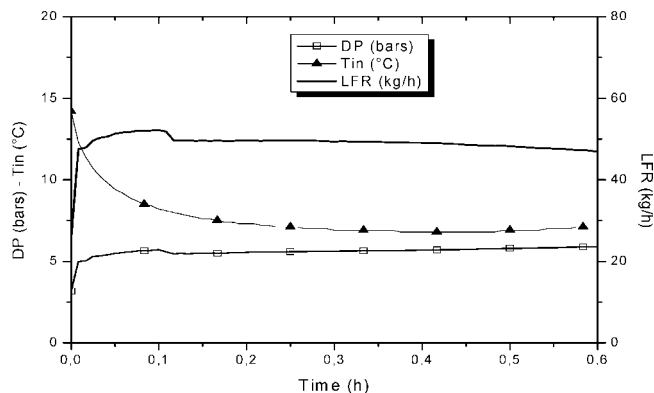(22) Sinquin, A.; Palermo, T.; Peysson, Y. *Oil Gas Sci. Technol.* **2004**, *59*, 41–57.

**Figure 4.** Flow loop test for the pure water/oil system (restart).



**Figure 5.** Flow loop test for the brine/oil system (hydrate formation).



**Figure 6.** Flow loop test for the brine/oil system (24 h circulation).



**Figure 7.** Flow loop test for the NaCl water/oil system.

crude. Although the hydrate formation did not induce drastic perturbations of the flow, both a gradual loss of LFR and an increase in DP are measured during this longer period of circulation. After 24 h, LFR falls to about half its original value, whereas DP has almost doubled. The increase observed for $T_{in}$ is a direct consequence of the flow loop configuration (see Figure 1), which imposes that the hydrate slurry circulates in the part of the flow loop located outside the thermostatic bath for longer periods as LFR decreases.

Although no hydrate deposits or hydrate particles could be directly observed through the sapphire window (because of opacity of the crude oil), the smooth decrease of LFR and smooth increases for DP and $T_{in}$ can be assigned to a progressive blockage by the largest aggregates in a singular point of the line. This progressive deposit of large aggregated particles will lead to the complete plugging of the line over a longer period.

Because the slurry is still transportable after the 24 h test, the test procedure was continued by a 3 h shut-in inside the hydrate stability zone, followed by restarting the pump. Before the shut-in period, the LFR was 53 kg/h and DP and $T_{in}$ were 5.6 bar and 6.4 °C, respectively. Figure 4 shows the evolution of these parameters after the restart of the flow. When the pump is restarted, the slurry is still transportable. After a few minutes, the slurry flows almost in the same conditions as before the shut-in period, with a LFR around 50 kg/h, DP of 5.7 bar, and $T_{in}$ around 6.9 °C. During the shut-in, the hydrate particles present in the liquid phase settle because of the effect of gravity and come into contact with each other. At the restart, the flow parameters are restored, leading to the conclusion that the amphiphilic species present at the interface of the hydrate particles facilitate the dispersion of the particles in the flow.

As a conclusion, the pure water/oil system exhibits some AA properties, especially during the hydrate formation phase, because all of the recorded data suggest that the hydrate crystallization occurs with low agglomeration, which led to the loop operating without any major problems. Nevertheless, when the hydrate suspension is circulated in the loop over several hours, a plug-like behavior is observed. In fact, although the aggregates formed at the hydrate crystallization are relatively small (16 elementary particles per aggregate; $D_{agg} \sim 5 \mu m$), they are large enough to create a deposit in the numerous singularities of the line with a small internal diameter (7.8 mm). Consequently, the four conditions defined for a good AA system are not fulfilled, and this system in this particular loop is classified as a moderate AA crude oil. Previous work[14] has shown that the pure water/acidic crude oil system formed w/o emulsions with long-term stability, mainly because of the asphaltenes present in the crude. These amphiphilic compounds
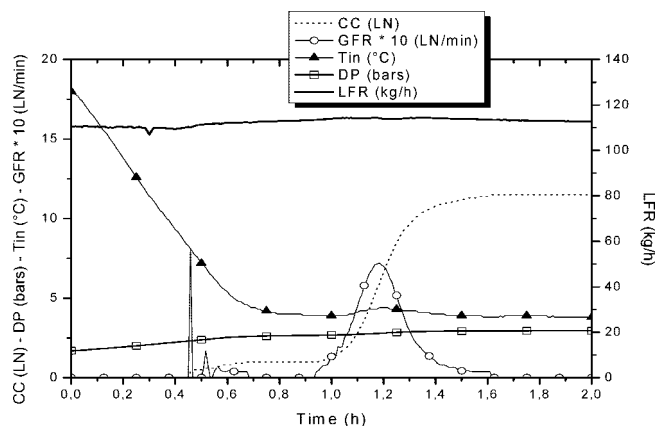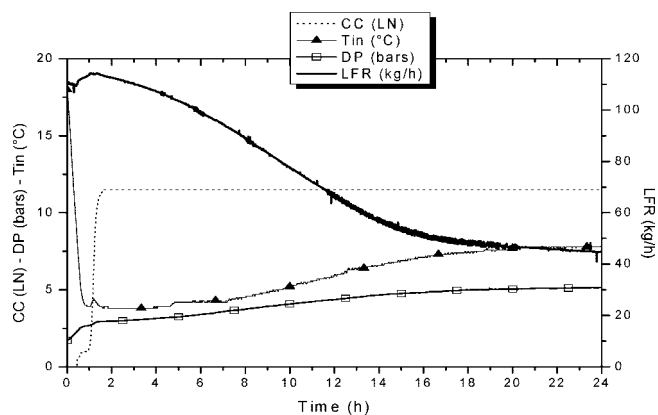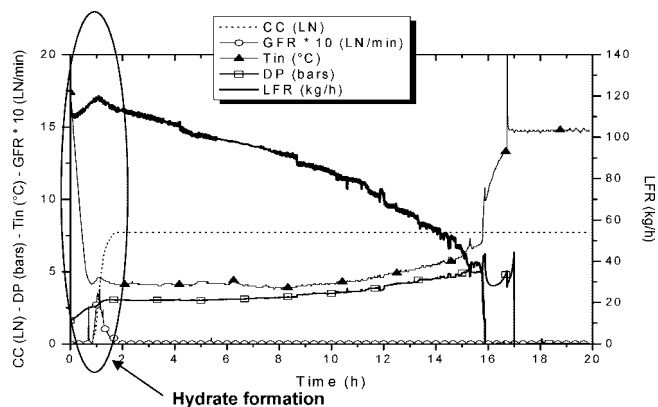
are believed to be the most likely agents responsible for the prevention of hydrate agglomeration.

Figures 5−8 show the influence of the brine, NaCl, and $CaCl_2$ on the AA property of the acidic crude oil. The results are summarized in Table 2 along with those obtained for the pure water/oil system.

During hydrate formation, the behavior observed for the salt water/oil systems presents similarities with that of the pure water/oil system (Figures 2 and 5). The GFR peak shape is Gaussian, and DP and LFR do not vary significantly. However, hydrate formation is slower, and only 62% of water has been converted to hydrates. This lower value for $\tau$ results from the high salt concentration. In hydrate formation, the crystallization and growth take place at the w/o interface because of the low solubility of gas in the water phase. As the hydrate forms and grows from the w/o interface, the salting out effect leads to an
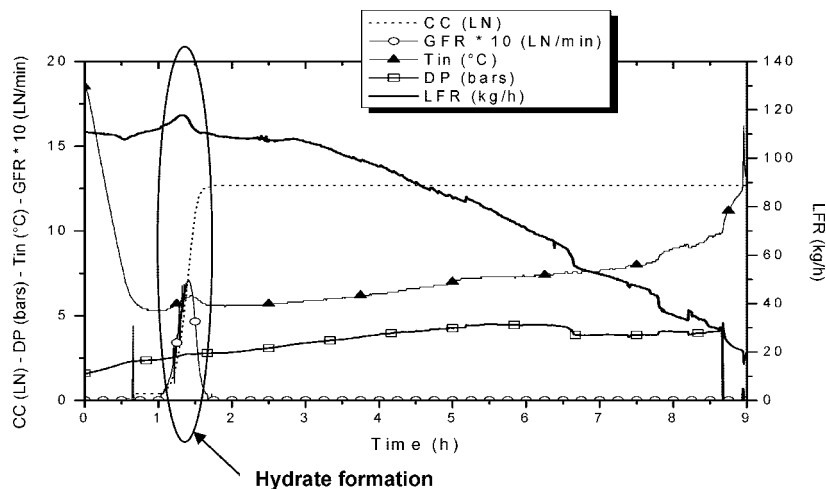
**Figure 8.** Flow loop test for the CaCl$_2$ water/oil system.

**Table 2. Flow Loop Test Results[a]**

| | | salt water | | | |
|---|---|---|---|---|---|
| | | brine NaCl plus CaCl$_2$ (35 plus 7 g/L) | NaCl (35 g/L) | CaCl$_2$ (7 g/L) | alkaline water (pH 12) |
| | pure water | | | | |
| | | | Hydrate Formation | | |
| $T_{in}$ (°C) | 3.8 (3.0/3.8) | 4.0 (3.9/4.0) | 4.2 (4.2/4.9) | 4.1 (4.1/4.7) | 4.8 (4.0/4.8) |
| maximum GFR (L$_N$/min) | 1.03 (1.03/1.40) | 0.75 (0.63/0.75) | 0.41 (0.30/0.41) | 0.71 (0.71/1.4) | 2.04 (2.04/2.3) |
| DP (bar) | 3.2 (2.9/3.2) | 3.0 (2.9/3.0) | 3.0 (2.7/3.8) | 2.8 (2.8/2.9 and unstable) | unstable |
| $\tau$ (%) | 74 (74/78) | 62 (62/62.1) | 45 (38/45) | 74 (74/78) | 82 (82/84) |
| | | | After 24 h | | |
| blockage, time | no | no | yes, after 16 h (11 h/16 h) | yes, after 8 h and 40 min (8 h and 40 min/ 10 h and 20 min) | yes, after 2 h and 6 min (2 h and 6 min/ 2 h and 20 min) |
| LFR (kg/h) | 53 | 44 | | | |
| DP (bar) | 5.6 (5.6/2.9) | 5.1 | | | |
| | | | After Shut-in | | |
| restart | yes | no | | | |
| LFR (kg/h) | 49 (40/49) | | | | |
| DP (bar) | 5.7 (5.7/1.7) | | | | |

[a] Values in parentheses are the minimum and maximum values measured for the three tests performed.

increase of NaCl and CaCl$_2$ concentrations in the core of the water droplets. As a consequence, the system moves outside the hydrate stability domain and then hydrate formation is stopped.

Figure 6 shows the 24 h circulation test for the brine/oil system. As for the pure water/oil system, the variations of LFR, DP, and $T_{in}$ are attributed to the slow buildup of a hydrate deposit in the loop. After 24 h, LFR falls to 44 kg/h (against 53 kg/h for the pure water/oil system). After the shut-in period, the restart was not possible; hydrate sedimentation has occurred, and the resulting pack of particles blocked the circulation of fluids in the loop. Therefore, the brine/oil system presents poorer AA properties than the pure water/oil system.

The variations of GFR, LFR, CGC, DP, and $T_{in}$ for the NaCl water/oil system as a function of time are shown in Figure 7. The hydrate formation is delayed, and because of the thermodynamic effect (salt concentration in the liquid water) only 45% of water has been converted to hydrates. Surprisingly, the NaCl alone has a much more important effect than the brine on these

parameters. The hydrate formation is more rapid, and the variation of GFR is not Gaussian, suggesting that the hydrate-forming water droplets are not totally isolated from each other. The crystallization propagates rapidly throughout the system, and agglomeration occurs. This agglomeration probably leads to rapid and complex changes in the particle size distribution; water droplets are crystallized; some aggregates are formed; and others are broken. These complex phenomena occur simultaneously and induce the increase of both LFR and DP. After the hydrate formation, LFR decreases constantly until the complete blockage of the line that occurs 16 h after the beginning of the test.

In Figure 8, the results obtained for the CaCl$_2$ water/oil system are shown. In this case, more hydrates are formed than for the NaCl water/oil system; $\tau$ is the same as that measured for the pure water/oil system (Table 2). As for the NaCl water/oil system, a peak for LFR is observed during hydrate formation, suggesting some crystallization and agglomeration of the hydrate particles. The effect is greater than with NaCl. After the hydrate formation, the deposit and/or agglomeration form quite rapidly

(DP increase and LFR decrease), and the line plugs about 9 h after the beginning of the test.

In the three tests described previously, the influence of salts on both $\tau$ and AA property of the systems is clearly highlighted. According to the predictions of the CMSHyd program, 7 g/L of $CaCl_2$ decreases the three-phase equilibrium temperature by about 0.1 °C compared to the pure water system at the same pressure. On the other hand, 35 g/L of NaCl decreases this temperature by about 1.4 °C. Consequently, the $\tau$ values obtained for NaCl (45%) and $CaCl_2$ (74%) to that obtained for pure water (74%) are logical. Surprisingly, the brine presents an intermediate value (62%), although the salt content (NaCl plus $CaCl_2$) is higher. This suggests that thermodynamic conditions may not be the only factor in governing $\tau$ values for these systems.

In Table 2, the maximum value of GFR ($GFR_{max}$) for the $CaCl_2$ water/oil system is noticeably lower than that measured for the pure water/oil system, although the two systems have the same $\tau$ value. In other words, the same quantity of hydrates is formed, but it takes a longer period for the $CaCl_2$ system to reach equilibrium. This slower kinetics of hydrate formation may be assigned to specific species present at the w/o interface: the calcium naphthenates. These species may hinder the oil/ water gas transfer.

The test with NaCl also presents a lower $GFR_{max}$ compared to the pure water/oil system, but because $\tau$ is also much lower, no conclusion can be drawn as to the predominance of the thermodynamic effect or of a possible kinetic effect of sodium naphthenates adsorbed at the w/o interface. Finally, because of the presence of the two salts at the same concentrations, the brine system should present a thermodynamic effect similar to that of NaCl alone. However, the values of $GFR_{max}$ and $\tau$ are noticeably higher than for the NaCl water/oil system, but they are similar to those of the $CaCl_2$ water/oil system. This may suggest that for the brine/oil system, the dominant species at the w/o interface are calcium naphthenates. Because these molecules limit the gas transfer at the interface, the kinetic effect dominates the thermodynamic one.

The AA property for the salted systems decreases in the order brine > NaCl > $CaCl_2$. The effect of $CaCl_2$ is complex: the kinetics of formation is slowed down with this system, but on the other hand, the agglomeration is more important. To establish a link between these two phenomena, we propose the following interpretation: if the kinetics of hydrate formation is slower, hydrate particles and water droplets coexist over a longer period. Consequently, the probability for hydrate particles to bind via capillary forces will be favored.[23] Because the brine gives much better results, the sodium and calcium salts create opposing effects: less hydrate is formed with a slightly higher kinetics than with the $CaCl_2$ system, and although the $CaCl_2$ effect has a greater impact, the NaCl salts indirectly induce less agglomeration. This conclusion can be drawn only if the following hypotheses are true: all of the water droplets are converted into hydrate, and the differences observed for $\tau$ are only due to the thickness of the hydrate layer around free water. In other words, although the amount of hydrates may be different between two experiments, the quantities of particles for each test are roughly similar.

Even if it is difficult to reach clear conclusions on the reasons for the differences seen between the salted systems, our tests clearly indicate that the species present at the w/o interface have a
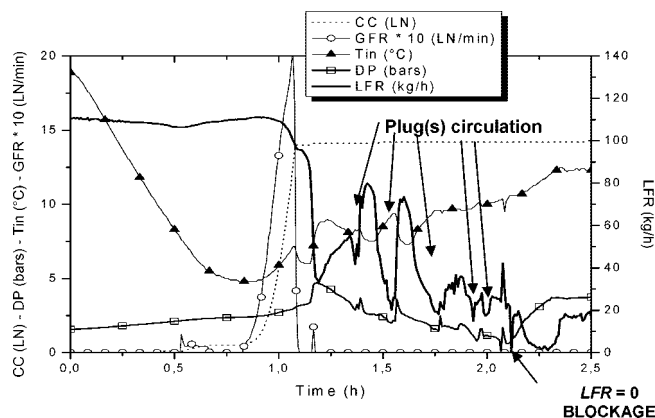


**Figure 9.** Flow loop test for the alkaline water/oil system.

preponderant effect on the quantities and the kinetics of hydrate formation and on the agglomeration degree of hydrate particles.

Figure 9 shows the hydrate formation with the alkaline water/ oil system. Hydrate formation is rapid with a maximum $GFR_{max}$ of 2.04 $L_N$/min, instead of 1.03 $L_N$/min for the pure water/oil system. The variation of GFR as a function of time during crystallization is not Gaussian; i.e., the agglomeration of hydrate particles takes place along with hydrate formation. The rate $\tau$ is much higher than for the other systems, and the hydrate formation induces instantaneously a steep decrease in LFR. LFR and DP strongly fluctuate, and the line is totally plugged in less than 1 h after hydrate formation. This system presents a very high degree of agglomeration; the moderate AA effect measured with pure water is totally lost in the presence of alkaline water.

Under this alkaline pH, significant amounts of sodium naphthenates $RCOO^-$ are generated from the complex blend of naphtenic acids, and they are undoubtedly responsible for this catastrophic behavior. Indeed, although naphthenates are highly interfacially active ($\Gamma \sim 0.1$ mN/m), leading to a decrease of the water droplet size distribution, they significantly reduce the stability of w/o emulsions.[14,24] Moreover, as demonstrated by Arla,[24] the lightest sodium naphthenates (<270 g/mol), which are hydrosoluble, may act as hydrate promoters; i.e., hydrate crystallization is not limited to the water droplet interface but can also extend within the bulk. For this reason, the highest conversion of water to hydrate has been encountered with this system. In conclusion, the high water/oil specific area (smaller droplet size distribution) induces rapid kinetics of hydrate formation (Figure 9) and high water to hydrate conversion (Table 2), and the lower stability of the emulsion induces high agglomeration, plug formation, and then line blockage.

In a previous study,[5] we found that the ability of the aqueous phase to increase the stability of water/acidic crude oil emulsions in order of decreasing rank was pure water > brine ≫ alkaline water. Measurements in high-pressure kinetic reactors and a high-pressure rheological cell gave the same order for the AA performance of the acidic crude oil. This confirmed the idea that good AA crude required, first of all, the formation of a stable w/o emulsion. The present work not only confirms this link but also shows that the AA performances are not apparatus-dependent.

## Conclusions

The capacities of a diluted acidic crude oil for the transportation of gas hydrates were studied in a laboratory flow loop as

(23) Taylor, C. J.; Dieker, L. E.; Miller, K. T.; Koh, C. A.; Sloan, E. D. *J. Colloid Interface Sci.* **2007**, *306*, 255–261.

(24) Arla, D. Acides naphténiques—Hydrates de gaz: Influence de l'interface eau/huile sur les propriétés dispersantes d'un brut acide. Ph.D. Thesis, Université de Pau et des Pays de l'Adour, France, 2006.

a function of different types of aqueous phase: pure water, three salt waters (35 g/L NaCl, 7 g/L CaCl$_2$, and brine), and an alkaline water (initial pH of 12). A hydrate experiment lasted typically 24 h, comprising the crystallization stage (first 2 h) and the circulation of the slurry. Then, restart of the slurry after a 3 h shut-in was undertaken.

The studied crude oil exhibited moderate AA properties with pure water mainly because of heavy resins and asphaltenes. The slurry was transportable during 24 h. Restart was possible, but a progressive increase in the pressure drop and a constant decrease of the liquid flow rate were also observed with this system. The moderate AA properties of the crude oil were partially lost with the salt waters because restart was not possible with the brine and a blockage occurred with the two salts alone before the end of the circulation stage. Finally, the crude oil did not show any AA properties when it was put in contact with the alkaline water. In that case, blockage occurred very rapidly, during the crystallization stage, so that it was not even possible to circulate the slurry. This catastrophic behavior was assigned to naphthenates RCOO$^-$.

The trends in terms of AA properties of the acidic crude oil observed with the laboratory flow loop were similar to the ones found in the kinetic reactor and in the rheological cell: pure water > brine ≫ pH 12. This result is really encouraging because it shows that the impact of the physical chemistry of the crude oil on its AA properties especially during the crystallization stage does not seem to depend upon the experimental setup. However, these experiments performed on a conservative flow loop (quite small diameter with numerous singularities) have also shown the influence of the hydrodynamics of the system on the transportability of the slurry, especially during the circulation stage and/or the shut-in. An evaluation of the AA performances of the pure water/oil system and brine/oil system in more realistic multiphase flow (gas plus liquid and larger loop diameter, for example) would be of great interest to define more precisely whether or when acidic field development will require a special hydrate treatment.