MEASUREMENTS OF RELEVANT PARAMETERS IN THE FORMATION OF CLATHRATE HYDRATES BY A NOVEL EXPERIMENTAL APPARATUS

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ABSTRACT

Studying clathrate hydrates is, ideally, a simple task: one just have to keep water under a gas pressure. However, when trying to collect measurements in an accurate and repeatable way, things mess up. When, in particular, kinetic characterizations are required, not only pressure and temperature have to be measured: also particular parameters such as gas evolved/trapped during time, heat released/adsorbed during time, critical phenomena related to additive addition, etc, should be collected in a finer way.

In the last years a growing interest has been devoted to investigations on the effects of a wide range of compounds capable to affect the thermodynamics and, in particular, kinetics of clathrate hydrate formation. The study of the effects of these compounds, called *conditioners*, requires an improvement of the performances of usual lab facilities by introducing a new strategy for the measurement of further characterizing parameters. Presently no standardization of the apparatus designed for clathrate hydrate studies exists, nor any commercial instrumentations are available. Generally, apparatus used are custom-made by the same research team according with the peculiar research requirements.

To do this we have designed, built, calibrated and tested a novel apparatus that, in addition to the ability of measuring usually unexplored parameters, is based on the idea of obtaining as many parameters as possible in a single formation batch. This in order to solve the problem of collecting a dataset that can be processed homogeneously, thus minimizing errors due stochastic behaviours.

Using such an apparatus, several kinds of measurement are presented here, which are related directly to the clathrate hydrate investigation fields, but also more generally related to the study of equilibrium phases involving gaseous components.

*Keywords*: PID, PWM, CMC, process control, gas solubility, hydrate formation, hydrate thermodynamics, hydrate kinetics, induction time.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>Mv/Mv1/Mv2</td>
<td>Metering Valves</td>
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<td>Nml</td>
<td>Normal ML</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<td>PAL</td>
<td>Phase Alternating Line</td>
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<td>Pc</td>
<td>Pressure Gauge</td>
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<td>PIC/TIC/LIC</td>
<td>Pressure/Temperature/Liquid-Flow Indicator Controller</td>
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<tr>
<td>PID</td>
<td>Proportional Integrative Derivative Algorithm</td>
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<td>Pr</td>
<td>Pressure Reducer</td>
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<tr>
<td>Pt1/Pt2</td>
<td>Temperature Probes</td>
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<td>Pt100</td>
<td>Platinum 100 Ohm Temperature Probe</td>
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<td>PWM</td>
<td>Pulse-Width Modulation</td>
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<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
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<tr>
<th>Td</th>
<th>Dissociation Temperature</th>
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<td>Tf</td>
<td>Formation Temperature</td>
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<td>THF</td>
<td>Tetrahydrofurane</td>
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INTRODUCTION

Typically an apparatus designed for hydrate studying is composed by a reaction chamber capable to withstand the pressure required by the hydrate former gas. Generally, this reaction chamber is made from a cylinder with flanged cover in order to allow for the operator, where required, to recover the solid hydrate produced. Cooling is generally obtained by means of a cooling bath, or in some cases by implementing in the chamber an internal cooling coil. A fine control of the temperature is generally important where the aim of the research is not the mere synthesis of the hydrate, but a finer investigation of clathrate properties. Thus generally one or more internal temperature probes are installed.

As relates to the pressure, generally this is provided by means of the connection of the chamber with a pressurized tank, when the experiments require a pressure not greater than the cylinder pressure. Otherwise a pressure booster is used. The pressure can be regulated by means of a classical mechanical pressure regulator and measured with a pressure gauge. Generally, piezo gauges are used that allow for digital measurement and control. One of the critical issues for the hydrate apparatus is the mixing device. The simplest approach is to use a classical external magnetic stirrer with internal stirring bar, but being the hydrate usually solid, it will eventually block the stirring system, and this situation may affect the measurement due to changes in mass transfer. Classical stirring for viscous systems achieved by electric motor-driven blades cannot be applicable to a pressurized chamber due to the need of a rotating seal that generally is complex and capable to withstand only a low pressure. A possible solution to the stirring problem is a different design for the system, in which the apparatus is based on a “rocking cell”. In this approach, the chamber is loaded with steel balls, and mounted onto an apparatus capable to oscillate or "rock", thus the balls moving inside the chamber provide for the mixing. Another approach can be the use of a magnetically coupled system that works exactly as the motor-driven blades, but overcomes the sealing problem with a magnetic coupling system.

Recently a novel approach for the stirring was proposed, i.e. the use of ultrasonic waves. In this case an ultrasonic probe transfers mechanical energy to the water, thus offering a sort of agitation. The effect is remarkable in terms of efficiency but it is not so clear if in this case we are dealing with a "normal" agitation. In fact, ultrasonic waves induce several kinds of reactions in water which is the topic of the branch of chemistry called sonochemistry. Moreover, physical phenomena such as cavitation are involved. Thus ultrasonic agitation should be considered more than a simple mechanical agitation.

For what concerns the experimental procedure, different apparatus allow for different investigation strategies, and one of the main differences is about the pressure dropping or constant pressure approach. In the first, the chamber is loaded with gas up to a certain pressure, and when the hydrate forms a lot of gas is trapped and pressure drops, thus the amount of gas trapped is obtained by measuring that drop of pressure. Obviously in such a case, the result strongly depends on the apparatus design and in particular on the ratio between water and gas within the chamber. In the constant pressure approach, on the other hand, a system capable to supply the gas absorbed during formation is employed in order to keep the pressure constant during formation. In this case, collected data are less affected by the design of apparatus, and the problem is to optimize a system that allows for a fine pressure control. Another problem is to add fluids during hydrate formation. In this case, an injection system capable to work against the pressure inside the chamber is required. Generally, piston pumps are used but the problem is that pumps that allow for a fine metering of the injected liquid are very expensive, and adding a liquid to a closed system will modify the liquid/gas ratio, resulting in pressure changes that may affect the measures. Thus the injection of liquid under pressure remains a critical issue.

A further problem is that of being able to have a visual access to the chamber inside. Indeed, such a visual monitoring of the reaction allows to collect much more information. This problem could be solved with an optical pressure cell, but this also needs an internal illumination. Being the chamber closed, capture images from the outside is much simpler than putting a lighting device within. Apparatus as those described are often applied for thermodynamic and certain kinetic characterizations, and there are other kinds of more complex apparatus designed for the study of...
hydrate formation inside pipelines. This kind of apparatus, generally called “flow loops” are designed to simulate pipeline conditions, and in particular the gas stream conditions. They are often dedicated to studies of hydrate prevention. Moreover there are several kinds of different devices designed for specific measurements, in particular for crystallographic characterization, rheology etc. They generally are devices made in order to allow for hydrate measurements coupled to existing instrumentation such as NMR, Raman Spectroscopy, X-Ray Spectroscopy, densimeters and viscosimeters etc. All those devices differ by themselves, and exploit different strategies to reproduce hydrate forming conditions in that facilities[1]

CONCEPTUAL DESIGN
In order to carry out the characterization of the effect of a conditioner on hydrate kinetics, several parameters have to be collected, and processed with a comparative analysis. It is also known that a different apparatus design may affect kinetic behaviours of hydrates, and moreover, the same hydrates are known to have an intrinsic stochastic behaviour. Therefore, once several data have been collected with different apparatus in different experimental trials and approaches, it is reasonably questionable if they can be analyzed as an homogeneous data set and if the results of such analysis can give reliable results. In order to rule out such doubts, it is desirable to collect as many characterizing parameters as possible for each experimental trial and thus with the same apparatus. Data collected in such a manner result self-consistent as well as homogeneous, and allow to obtain stable and accurate results. We have designed our apparatus in order to follow this concept, trying to refine as much as possible, measurements strategies, obtaining a lab apparatus that has shown interesting measuring ability.[2] Follow is reported a description of the several parts that constitute the apparatus.

CHAMBER
The reaction chamber, where the effective synthesis take place, was made of AISI 321 TP stainless steel and obtained from a unique piece of a steel cylinder, lathe-worked in order to avoid pieces welding and to achieve better structural strength. The cover of said chamber was realized with the same material and all the probes, inlet and outlet connections were fitted in it. Thus the chamber is left free from any fluid service connection in order to offer an easier sample recovery and allowing the change to a different chamber. The chamber and cover surface, both internal and external, were moreover teflonized in order to minimize hydrate adhesion on the surfaces and also allowing for a easier adhesion.

PRESSURE LINE
The pressure line is the hydraulic line that connects the pressurized tank to the reactor chamber. A first stage of pressure control is realized by means of a mechanical pressure reducer (Pr), with self-venting feature, provided by Tescom. Along the line follows an electropneumatic metering valve (Mv) provided by Kammer Ventile group FlowServe, then a mass gas flow meter (GFM) provided by Bronkhorst Hi Tec, and then the line ends into the chamber where a digital piezoelectric pressure gauge (Pc) provided by Foxboro group Invensys, is also connected. Finally, a digitally programmable process controller (PIC) provided by Eurotherm receives the process signals of pressure and gas flow from Pc and GFM and thus drives the Mv according with its program using a PID control strategy.
Pressure control occurs as follows: a first manual pressure setting, slight above the chosen experimental pressure is obtained by means of Pr, then the PIC preset program starts and acts its control, driving the Mv1, based on the chosen setpoint, program, and obviously signals coming from Pc and GFm. The pressure increase up to the set point and remains there until the start of gas absorption, due hydrate formation. Thus the Pc detects a slight pressure deviation from the setpoint that activate the control PID loop Pc-PIC-Mv1 opening valve in order to maintain the pressure set point. Thus a flow is generated along the line, which flow is detected and recorded by the GFm; such flow persists all over the hydrate formation phase and, at the end of that, the gas is trapped and the pressure set point is restored. The integration of such a flow will give the amount of gas uptake.

When a finer control of pressure is required, it is possible to activate the cascade control mode, Pc-GFm-PIC-Mv1, where the control PID loop involves also the GFm signal so that it can be possible to restore and control pressure, thus limiting the gas flow within a certain preset range. The cascade control may be also reversed, where the master control is not the pressure but the flow, GFm-Pc-PIC-Mv1. In this way, the flow is maintained at the set point by controlling that the pressure do not overcome another set point. This strategy is used when, besides the amount of gas uptake, a constant flow during time is also important.

Moreover, it is possible to set the control flow alone, GFm-PIC-Mv1, which is used when e.g. we require to simulate a continue gas stream in certain experiments. By switching the proper valves, it is also possible to revert the gas flow along the line; this is used to study hydrate dissociation where the Mv, in this case, vents the gas released during hydrate dissociation in order to keep the dissociating pressure constant. Also in this case vented flow is detected by GFm and integrated; this strategy is particularly useful for thermodynamic characterizations where it is possible to measure dissociation temperatures at certain preset and constant pressures.

Along the pressure line are also mounted a plenum chamber, before the GFm, and a gas cooling system that can be used or not as a function of the particular experimental setting. Thanks to the fine control strategy and the accuracy of the apparatus, it is possible to carry out experiments at a pressure within the range of 0-210 bar with a precision of pressure control of 0.05 bar, and measure within the range of 0-500 Nm3/min with a precision of 0.2% of FS. This strategy of pressure and flow control allows for a fine recording of thermodynamic data and further for an accurate monitoring of the kinetics of the process, where a fully programmed experiment guarantees maximum reproducibility of experimental conditions.

**TEMPERATURE CONTROL**

The temperature control is obtained by means of a custom-made Peltier cooling system. The reaction chamber is coated with a 10 mm thick copper jacket which is in contact with the Peltier cold place from the bottom, whose hot place is mounted onto an heat sink supplied with tap water. The Peltier module is a high power module of 200W at 18A 12V, powered by a high power H-bridge DC/DC converter (Tc) that works based on PWM strategy at 32Khz of switching frequency. The DC source is obtained from 2 lead battery serially connected and kept under charge by a classical battery charger. In the copper jacket is mounted a...
Pt100 temperature probe (Pt1) and another one is inserted inside the chamber (Pt2). The Pt1 is the control probe while the Pt2 is the measure probe. The signals from Pt1 and Pt2 are sent to a temperature process controller (TIC) also provided by Eurotherm, that receives those signals and drives the Tc activating the PID control loop Pt1-TIC-Tc. Thus during cooling, the TIC drives the Tc in order to power the Peltier module that cools the jacket according to the preset program and signals from Pt1. The chamber is consequently cooled. The Pt2 measures the internal temperature related to experimental events.

By proper driving signals from the TIC the Tc have also the feature to revert current flow, thus the Peltier module switches from cooling to heating mode, which is useful in the dissociation step. The TIC can be also provided by an amperometric probe (Ap) in order to measure the A that are powering the Peltier.

Figure 3: Conceptual scheme of the temperature control line realization.

This signals is also detected by TIC that can switch also in A control mode. Therefore a Ap-Pt1-TIC-Tc PID cascade control loop is activated and the Peltier is supplied with a constant A flux, that means constant heat flow until a certain preset T. In this modality it is possible to execute warming or cooling ramps in constant heat flow, in order to carry out also calorimetric measurements. Also a Pt1-Pt2-TIC-Tc PID cascade control loop is usable where certain critical experimental temperature events detected by Pt2 may function as threshold point to activate different steps of the experimental program. According to the described T control strategy, it is possible to carry out experiments in a temperature range of -30 / +70°C with a control accuracy of 0.02°C.

**LIQUID ADDITION LINE**

The liquid addition line is the section of the apparatus that allows for liquid injection inside the chamber under experimental conditions. As an alternative to the use of expensive and complex pressure metering pumps, our apparatus exploits the principle of the communicating vessels. A vessel is mounted in a higher position with respect to the reaction chamber, the top of that vessel is connected to the top of the reaction chamber while the bottom of the vessel is also connected to the top of the reaction chamber. So a closed hydraulic line is obtained that remains necessarily under the same pressure. Along the line that comes from the vessel bottom to the chamber top are mounted another electropneumatic metering valve (Mv2), that is normally closed, and a mass liquid flow meter (LFm) both provided by Bronkhorst Hi Tec. A further digital process controller (LIC) also provided by Eurotherm, is connected thereto. The vessel is preventively filled with the liquid to be injected by means of a side line, and then all the apparatus is pressure loaded, so both the reaction chamber and the vessel achieve the same pressure. In this way the liquid contained into the higher positioned vessel is free to drop into the reaction chamber only driven by the height difference. Moreover this injection strategy is particularly efficient in maintaining the pressure: in fact for each ml of liquid that drops from the vessel to the chamber, an equivalent ml of compressed gas is free to rise from the chamber toward the vessel top. In that way the pressure is kept constant by default because during injecting no fluids are added to the system, but only moved from a vessel to the other.

This strategy allows for a fine investigation on gas absorption phenomena, in fact the fluids both in the reaction chamber and the vessel are saturated by the reaction gas, thus any possible gas absorption or release, detectable by pressure change, must be only due to the onset of critical phenomena due e.g. to the addition of some conditioner. As for the other control loops, for the liquid injection is also possible to work in an automatic fashion. By means of the LFm-LIC-Mv2 PID control loop, it is possible to add exacts
amount of liquid or inject liquid in constant flow mode. Moreover by means of a custom made pressure conductometric probe (Cp), it is possible to set a LFm-Cp-LIC-Mv2 PID control loop, that can start or stop the injection according to certain threshold signals received from Cp measurement.

CONDUCTOMETRIC PROBE
One of the most practical methods for solute concentration measurement is the conductometric way. Conductometric determinations are one of most used techniques of measurement due to its intrinsic sensibility, that allow for high electric response also for little variation of analyte concentration for all charged analytes. The problem of applying conductometric determinations to clathrate hydrate investigations is the lack of availability of specific probes capable to withstand the high pressures required for hydrate forming conditions. Thus in order to solve this problem a custom-made conductometric probe was designed, manufactured and calibrated. The probe was realized with a piece of a 6mm stainless steel tubing that housed two faced plates of gold fitted to the steel body by means of a particular epoxy resin synthesized within our laboratory. The epoxy resin must feature a proper mechanical resistance and also a sealing ability, in order to avoid gas leakage, and solvent resistance in order to avoid resin swelling once immersed into the reaction mixture. The commercially available resins do not offer all those features in one product, so the synthesis of a novel resin was required. Thus, instead of the classic bidentate DGEBA resin, we used a tetradentate resin, the 4,4’-Methylenebis(N,N’diglycidylaniline), which was cured with a bidentate amine such as the α,α’-Diamino-α-xilene. The use of these two particular types of molecules allows to obtain a 3D network polymerization instead the classical 2D that shows an higher mechanical resistance and excellent chemical resistance also for chlorinated solvents. A problem with that resin was its quasi-crystalline behavior that reduced the effect of surface adhesion. Thus the resin was additioned with organo-silanes known as adhesion promoters and the steel surfaces treated with a particular etching process in order to create surface coarseness and silicate coating, for compatibility with the silanes used into the resin. Thus by the use of said resin, we were able to manufacture a conductometric probe capable to withstand 200 bar of hydrogen, in a temperature range of -40 to +100°C and capable to resist almost all solvents including chlorinated solvents. The gold electrodes are further platinum plated with the classical electrodeposition method and then the cell constant was measured at 0.933. Further variable frequencies calibration have shown as that the probe shows an high linearity at the common conductometric frequency measurement giving a signal relative to the only capacitive contribute thus not affected by inductive components.

Figure 4: Conceptual scheme of the liquid injection system and additives concentration control.
STIRRING
Being the stirring a critical issue, as above mentioned, it was tried to improve the performance of classical magnetic stirrer by replacing the commercial magnets with the high power Neodymium Iron Boron magnets. The result was a remarkable improvement in stirring strength with sensible benefit in the experimental procedure.

INTERNAL ILLUMINATION AND VIDEO MONITORING
As introduced above, one of the critical issues is the internal illumination in order to allow for the video camera to capture visible images. Generally the illumination is provided by external sources through an optic cell or fiber optics. In the present device, we used internal Light Emitting Diodes (LED) to illuminate the chamber, i.e. a cluster of 15 LEDs, with different wavelengths has been mounted, internally to the chamber, around the aisle of a Plexiglas viewing cell housed on the center of the cover. 5 LEDs are in the IR wavelength, 5 are white, and 5 are in the UV wavelengths. Being the LED a solid system without any enclosed cavity, its collapse is avoided under pressurization, thus it can be used directly inside the chamber. The electric supply is provided by a custom-made, 4-pole electric bulkhead realized with the same resin used for the conductometric probe.

In the external side of the viewing cell is housed a PAL analog video camera connected to a PC by means of a video acquisition card. Proper software is used for video acquisition and recording.

DATA ACQUISITION
All the process signals are based on the analogical transmission standard of 4-20 mA. This standard was chosen because, unlike V or mV transmission standards, avoid signals losses along wire lengths or in multiple connections. All the process signals are acquired by a 16bit A/D converter that then retransmits such digitalized signals on RS232 standard. A custom developed software is used to record data in a comma-separated file format, that can be further analyzed with others commercial software. Our software allows for time acquisition setting, thus data can be sampled with a frequency in the tenth of a second up to hours of frequency in order to follow both very fast and long time experimental settings.

MEASUREMENT EXAMPLES
Following are reported several examples regarding measurements capability of our apparatus. In Figure 6 is reported typical recorded data for a methane hydrate formation experiments. By our apparatus, it is well clear how the gas absorption peak (Gu) is well structured and easily integrable, and the important kinetic parameters such as Induction Time (It) and Formation Time (Ft) are well detectable. With the internal temperature profile (pink line), it is possible to observe how the formation temperature peak (Tf) can be detected, while the area subtended to that peak, with a proper preliminary calibration, can be related to the heat of formation. Along the same curve, during a subcooling stage, a further peak is detectable (If), which is related to the unreacted-water freezing; the magnitude of this peak gives an
idea of the amount of water that has not reacted with gas to form the clathrate. Corresponding to this latter peak, in the gas flow line (cyan) a flow spike is detectable, which is due to the back flow resulting from ice expansion during freezing.

Figure 6: Example of typical gas hydrate synthesis, where typical profiles of temperature, pressure, gas flow and flow integration are reported.

Comparing Figure 6 with Figure 7, it is readily apparent how the parameters are subjected to a remarkable oscillation. Formation temperature peak is no longer detectable and information related to heat of formation cannot be extracted. In this example, it is important to note how the pressure (red line) is not constant during formation, with an evident drop, and the presence of the typical double (or in certain cases triple or more) sorption peak (light blue line), due to the mechanical hysteresis of the pressure regulator, that causes multiple loading actions.

Figure 7: kinetics of methane hydrate formation with PID control disabled.

Figure 8 reports an example of formation end dissociation experiment for methane hydrate carried out by means of our patented procedure based on nano-emulsions[3]. According to this novel approach, the measurements of certain parameters are easier and refined. It is also important to note how the flux and temperature peaks are more structured and can be easily integrated. Moreover, carrying out hydrate dissociation in a constant pressure fashion, bleeding continuously the released gas, a thermodynamic characterization of the investigated system can be easily carried out. Then, the dissociation temperature under a given pressure (Td) can be obtained in a faster and easier way. One of the most important feature of this particular procedure, is its ability to separate hydrate from unreacted water that is retained into the emulsified system. For that reason, the subcooling ramp, following the formation stage, does not show any further peaks related to ice formation.

Figure 8: methane hydrate formation and dissociation loop carried out by means of the procedure described in EP07010346 [3]

Figure 9 reports an experiment carried out with our apparatus by using our nano-emulsion procedure. In particular, the feature of liquid addition under constant pressure was exploited in order to simulate a semi-batch industrial application for continuous hydrate production. Once hydrate formation starts, as shown by the cyan line, the addition of water is started, in order to restore the water/oil ratio of the emulsion. It is apparent from the reported profiles how the hydrate formation, during water addition, proceeds in a continuous way.
Continuous Methane Hydrate Synthesis

Figure 9: example of methane hydrate formation by continuous addition of water.

The designed apparatus also allows for thermodynamic characterizations: with a proper experimental design, it is possible to measure dissociation and formation temperatures in a finer way. Figure 10 reports an example of thermodynamic characterization of THF hydrate. Blue line reports temperature profile of the cooling bath, according to the controller program, while the pink line reports temperature inside the chamber. In the latter, breaks due to hydrate formation and dissociation can be observed. Note how the temperature plateaus at 4.2°C, achieved during formation and dissociation, are in excellent agreement with the literature value.

Figure 10: thermodynamic characterization of THF hydrate.

Another important feature of our apparatus is its ability to determine Critical Micellar Concentrations (CMC) under hydrate forming conditions. Once pure water is charged and pressurized into the reaction chamber, a concentrated surfactant solution is injected inside, by means of the injection system described above. The increase of conductivity is then measured by means of a custom-made pressure-resistant conductivity probe. Comparing Figure 11 with Figure 12, it is apparent how the constant-pressure injection system allows for a fine measurement of conductivity values. Where a classical injection system is used instead, namely a liquid pushed inside by means of a greater pressure, the system is not capable to compensate the volume of the injected liquid, thus resulting in a pressure drift (red line) and consequent hindering of liquid addition, as observable by the opposite drift of the liquid flow profile (violet line). Data recorded according to Figure 11, are then analyzed by integrating liquid flow values over time, and obtaining instantaneous added volume values. Such values are then converted into concentrations and plotted vs conductivity, in order to obtain the classical CMC curve reported in Figure 13. Thus, it was possible to determine whether SDS and other surfactants were capable to form micelles under clathrate-forming condition.[5]

Figure 11: recorded data from conductivity measurements under clathrate forming conditions, with constant-pressure injection system allowed.

Figure 12: recorded data from conductivity measurements under clathrate forming conditions according to prior art methodology.
According to the described procedure[3], it is important to choose a proper bulk phase capable to dissolve as much former gas as possible, in order to create an environment rich in the investigated gas. To do that, it is important to determine the solubility of certain gases into a liquid under a certain pressure. A particular experimental procedure is set in order to carry out measurements of gas solubility. A stainless steel cylinder of an exact (100 cc) volume has been manufactured, and placed into the empty reactor. Then a pressure loading ramp, up to 100 bar, is programmed and executed under constant temperature using hydrogen, as reported in Figure 14. By means of a fine pressure flow PID control strategy, the hydrogen flow can be easily integrated, and the integration gives the amount of gas needed to fill the reactor free volume, at 100 bar under a constant temperature. Subsequently the stainless steel cylinder is replaced with the same exact volume of solvent and the same programmed ramp executed again. The integration of the gas loading flow, in this case, gives the amount of gas needed to fill, at 100 bar and constant temperature, the same reactor free volume plus an additional amount due to gas solubilization into the solvent, Figure 15. Subtracting to this latter value the flow integration obtained from the use of the 100cc cylinder, we obtained the net value of the hydrogen gas dissolved into the investigated solvent, as reported in Figure 16.
CONCLUSIONS

Our research group started to study hydrates in 2003, and the first feat was that of designing and manufacturing an apparatus able to make refined measurements [6]. We have carried out, by means of that apparatus, the first CMC characterization under hydrate forming conditions, thus obtaining interesting results [5]. According to our experience, we believe that refining measurements, in particular for what concerns kinetic characterizations, is important in order to clarify several uncertain kinetic behaviors of clathrate hydrates. Moreover we believe that our proposed idea to collect as many data as possible for a single experiment is the right way to enhance characterization accuracy, making experimental data homogeneously comparable. With the object discussed above, we planned further implementations to our apparatus. One of the most important problems is to get a structural characterization in addition to the kinetic and thermodynamic ones. Unfortunately, in order to do that, the collection of an experimental sample is required, to be successively submitted to a structural characterization facility. For example, fiber optic probes for Raman spectroscopy and Dynamic Light Scattering are commercially available, which could be very useful in structural characterizations. Therefore, an objective of further implementation will be the application of such probes to our apparatus.

As discussed above, kinetics of hydrate formation is still unclear, and probably one of the critical steps is the early crystal nucleation. Hence having an investigation ability casting light on that early stage could be very important. One of the best methodologies to study similar phenomena is the Dynamic Light Scattering (DLS) generally used to study self-aggregation phenomena. Our objective is to realize a DLS high pressure probe that allows us to make DLS measurements directly during the early events of hydrate formation. With the same object, we are also planning to implement IR and UV-Vis high pressure fiber optic probes, for a better study of self aggregation phenomena during hydrate formation. Finally, we are also making implementations in terms of rheological measurements, by means of magnetically-coupled stirring systems.

REFERENCES