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CHARACTERISATION OF GAS HYDRATES FORMATION USING A NEW HIGH PRESSURE MICRO-DSC

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Abstract

Gas hydrates are solid structures formed from water and gas under low temperature and high pressure conditions. Differential scanning calorimeter, operating under high pressure, is a very useful technique for the determination of the thermodynamic properties and the kinetics of gas hydrate formation. Specific gas tight controlled pressure vessels have to be used to obtain the hydrate formation in complex fluids.

Based on the MicroDSC technology, a new High Pressure MicroDSC with a vessel (0.7 cm^3) operating up to 400 bars between –45 and 120°C is introduced for this type of research.

An example of the use of the HP MicroDSC is given with the formation of gas hydrates in drilling muds. With the increasing number of deep offshore drilling operations, operators and service companies have to solve more and more complex technical challenges. Extreme conditions encountered at these depths require an adaptation of the drilling muds. The range of temperature (down to –1°C) and pressure (up to 400 bars) are favorable conditions to the formation of hydrates. HP MicroDSC is used to determine the thermodynamic properties and kinetics of hydrate formation in mud formulations, particularly in the presence of large amounts of minerals.

The technique allows the detection of phase transitions *vs*. time, temperature and pressure. Using such a technique, dangerous areas of hydrate formation in drilling muds formulations (water-base and oil-base) can be predicted.

Keywords: calorimetry, DSC, gas hydrates

Introduction

Gas hydrates are solid structures formed from water and gas under low temperature and high pressure conditions. Gas hydrate is a crystalline solid consisting of gas molecules, each surrounded by a cage of water molecules. Sir Humphey Davy discovered in the early nineteenth century the hydrate of chlorine and more studies have been performed

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by his very famous student, Michael Faraday. In the twentieth century, the industrial importance of gas hydrates was established. Today the investigations on gas hydrates are becoming more and more important in different fields of applications.

The problem of the formation of gas hydrates (especially methane) is very well known by the oil industry and has been studied in the field of oil and gas transportation [1, 2]. In the twentieth century, with the expansion of the natural gas industry, the production, processing and distribution of gas became high pressure operations. Under pressure, pipelines were becoming plugged with 'ice', except that 'ice' was a gas hydrate ! Today every oil and gas company has a flow insurance department to detect and predict the formation of gas hydrates in the pipelines and the processing equipment.

The plugging of annulars (offshore extraction) by hydrate formation in drilling muds is another important field of research [3]. With the increasing number of deep offshore drilling operations, operators and service companies have to solve more and more complex technical challenges. Extreme conditions encountered at these depths require an adaptation of the drilling muds. The range of temperature (down to –1°C) and pressure (up to 400 bars) are favorable conditions to the formation of gas hydrates.

More and more countries are interested in the investigation of gas hydrates trapped in marine sediments and in permafrost. Gas hydrates occur abundantly in nature, both in artic regions and in marine sediments. Methane trapped in marine sediments as a hydrate represents a huge carbon reservoir [4]. The worldwide amounts of carbon bound in gas hydrates is conservatively estimated to total twice the amount of carbon to be found in all known fossil fuels on earth. Methane hydrate is stable in ocean floor sediments at water depths greater than 300 m.

The storage and transportation of natural gas using gas hydrate is another growing field of research. For methane hydrate, the melting of 1 cm^3 of ice produces the escape of 164 cm^3 of methane.This specification makes the storage of natural gas using gas hydrates very promising.

The concern is also about the stability of gas hydrates and the effect on the global warming. According to the stability of the gas hydrates, an increase of temperature of the ocean temperature by 1 or 2°C may produce a possible release of methane into the atmosphere with all the impacts on climate changes [5].

The usual way to determine the thermodynamic conditions of the formation of hydrates in drilling mud formulations is to use a PVT cell with visual observation and simultaneous temperature and pressure measurements. This technique requires heavy instrumentation and often cannot be used if solid particles are present in the formulation. Moreover the PVT cell does not give a quantitative evaluation of the kinetic properties of hydrate formation.

Handa [6, 7] has used calorimetry to determine compositions, dissociation enthalpies and heat capacities of hydrates. Koh *et al.* [8] has recently used DSC to test hydrates inhibitors at atmospheric pressure. Fauconnier *et al*. [9] has also used DSC at atmospheric pressure for studying formation of hydrates in water-in-oil emulsions.

More recently, an innovative and easy technique based on DSC has been introduced by the French Institute of Petroleum (IFP) to characterize hydrate formation in drilling fluids up to 100 bar [10–12]

In order to work under higher pressure (up to 400 bar), an innovative methodology (patent of the French Institute of Petroleum, IFP) has been developed, in collaboration with Thermal Consulting and Setaram Companies, using a new High Pressure MicroDSC to determine the thermodynamic properties and kinetics of hydrate formation in mud formulations, particularly in the presence of large amounts of minerals. This technique allows the detection of phase transitions *vs*. time, temperature and pressure. Using High Pressure MicroDSC, dangerous areas of hydrate formation in drilling mud formulations (water-base and oil-base) can be predicted.

Experimental

The first studies on hydrate formation performed in the laboratory of IFP were carried out on a Setaram DSC111 (Calvet based principle) [10–13]. The first experimental results have shown that the DSC technique is very convenient for the investigation of gas hydrates under high pressure and provide data at the same level of precision than the classical PVT technique while much less time consuming. However it is difficult to exceed a working pressure of 100 bar with the DSC111, and the volume of the experimental vessel is limited for the investigation of mud solutions containing mineral particles.

Considering that the DSC is very appropriated for this type of research, a new high pressure calorimeter has been designed, based on the MicroDSC technology developed and manufactured by Setaram. The MicroDSC technology is based on a symmetrical heat-flux design, according to the Calvet principle. The transducers made of semiconductors are located inside a thermostated bulky calorimetric block, fully surrounding the experimental vessels (Fig. 1).

This design ensures a high sensitivity and an excellent level of precision to the MicroDSC instrument.

The HP microDSC uses Peltier cooling and heating principle. The main advantage is that no refrigerating fluid, such as liquid nitrogen is needed for cooling the instrument. The minimum temperature that can be reached is –45°C, and the maximum temperature is 120°C. This way of working is especially very important for the development of on-site calorimeters.

The gas tight high pressure vessels (Fig. 1) are designed to work up to 400 bar and to contain 0.5 mL of sample. They are made of Hastelloy C276, which allows the analysis of corrosive fluids such as drilling fluids. The screwed top is equipped with a doughnut ring coupled to an antiextrusion ring. It is welded to a thermal line.

The vessels are placed inside the calorimetric block and are connected to a gas high_pressure panel (Fig. 1) including a one-stage compressor. The gas panel is designed to purge the vessels under inert gas, measure the pressure of reacting gas, apply, control and monitor the pressure inside the experimental vessels. The gas can be pressurized with a gas compressor (pneumatic pump) and stored in two accumulators. Two pressure regulators control the pressure in the vessels. Measurements up to 400 bar are easily performed.

The sample solution is introduced in the hastelloy vessel. A static methane pressure is applied on the sample. On the reference, a silicone solution (presenting no thermal transition in the investigated temperature range) is used.

Gas (for example methane) pressure is applied to both the sample and reference vessels, via the pressure control panel. The pressure is measured using a precision manometer and controlled during the test with a resolution of 1 bar.

With such a pressurization, only the vessels are under pressure. The DSC detector remains at atmospheric pressure.

The high pressure vessels can be re-used after a suitable cleaning.

Results

Methane hydrate dissociation in water

In a last work [12, 13], the thermal cycle for measuring the methane hydrate dissociation in water has been described. A water solution under a defined methane pressure is cooled down to –30°C to allow water crystallization and the hydrate formation, then is heated up to 20°C at a slow scanning rate. After the ice melting, an endothermic peak linked with the hydrate dissociation is detected. With the new HP MicroDSC, investigations at high pressure have been performed. A Millipore milli-Q gradient A10 deionised water is used for the test. A methane pressure varying from 50 bar to 350 bar is applied on the sample.

As seen in the previous work, the temperature of methane hydrate dissociation (onset temperature of the dissociation peak) increases with the methane pressure (Fig. 2). It is seen by the area under the peak that the amount of methane hydrate is proportional to the methane pressure. It is also noticed that for methane pressure above 100 bar, a small exothermic peak is detected before the endothermic dissociation effect. At this point, it is suggested that this exothermic effect is related to a recrystallization of the hydrate prior to its dissociation.

The results obtained for the dissociation temperature *vs.* methane pressure (Fig. 3) have been compared with data published by Sloan [1].

A very good correlation is observed between the data obtained with different experimental techniques for establishing the methane hydrate stability curve.

Hydrate dissociation in water and NaCl solution

The same experimental procedure is used to investigate salt solutions under methane pressure. 14% NaCl solutions are cooled at –30°C under variable methane pressure, then heated up at 1°C min^{-1}. The methane pressure varies from 75 to 390 bar .The aqueous phase melting appears in two peaks: the eutectic melting at –21°C and the progressive melting of ice in equilibrium with the saline solution around –10°C. Hydrate dissociation appears at higher temperature and the dissociation temperature increases with methane pressure (Fig. 4).

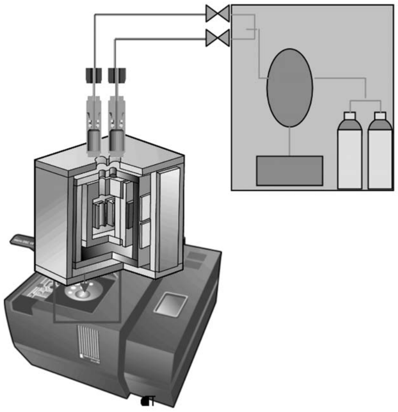

Fig. 1 The HP MicroDSC with the HP vessels and the HP gas panel

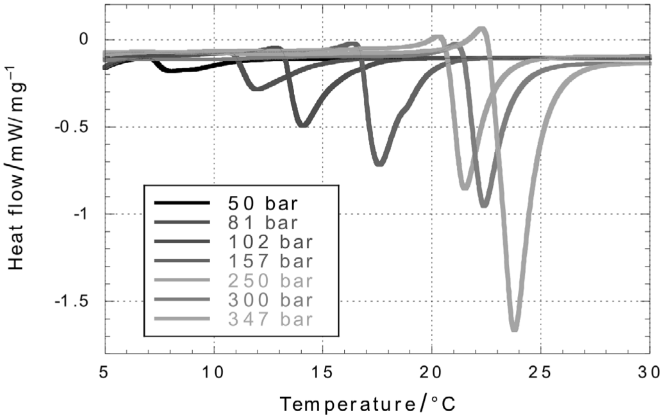

Fig. 2 DSC curves of pure water under variable methane pressure

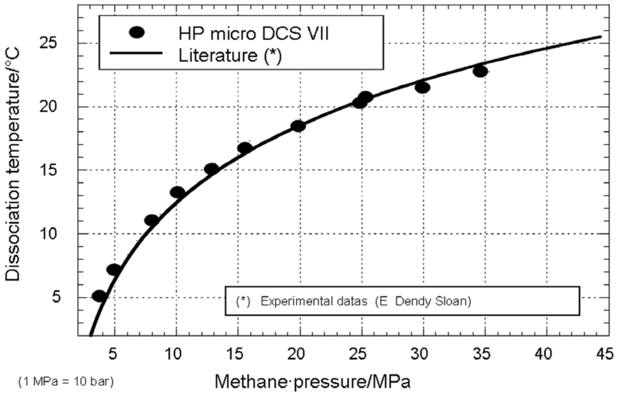

Fig. 3 Methane hydrate stability curve in deionised water

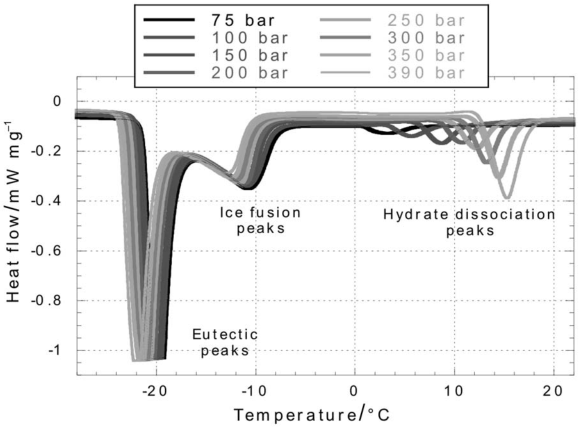

Fig. 4 DSC curves of 14% NaCl solution under variable methane pressure

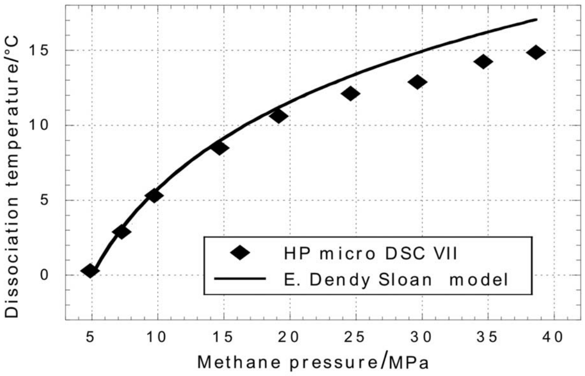

Fig. 5 Methane hydrate stability curve in NaCl solution

The obtained data (dissociation temperature *vs*. methane pressure) are compared with the model established by Sloan [1].

There is a good fitting for methane pressure up to 200 bar. For higher pressure, the model predicts dissociation temperature that are higher than the experimental values. At 400 bar, the difference is quite significative (about 2°C). This discrepancy shows that an experimental test remains very important especially for on-site purposes.

Hydrate dissociation in NaCl and ethyleneglycol solution

Ethyleneglycol is one of the most used additive to inhibit the formation of hydrates, especially during the drilling operations. In order to know what are the effects of such an additive, differents tests are run on a NaCl solution (100 g L^{-1}) containing an ethyleneglycol solution (5.1wt%) under different methane pressures, varying from 50 to 390 bar.

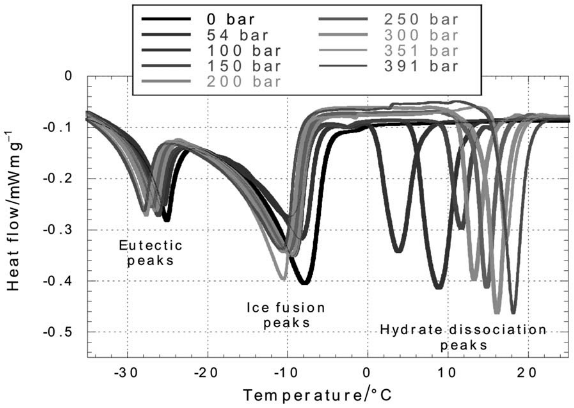

Fig. 6 DSC curves of NaCl solution with ethyleneglycol under variable methane pressure

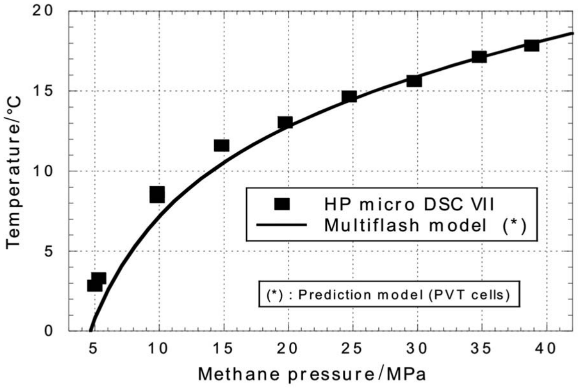

Fig. 7 Methane hydrate stability for a NaCl solution with ethyleneglycol

After detecting the eutectic melting and the ice melting, the dissociation of methane hydrate is again clearly detected and the temperature of dissociation again increases with the methane pressure (Fig. 6).

The obtained data (dissociation temperature *vs.* methane pressure) are compared with the Multiflash model [1], a prediction model obtained from measurements with a PVT cell. A very good fitting is observed for the full range of pressure.

In fact there are no experimental values in the litterature on the thermodynamic inhibition of methane hydrates in the presence of both NaCl and ethylene glycol.

By comparing the data obtained on Figs 5 and 7, it is noticed that the introduction of ethyleneglycol in the salt solution allows to shift the dissociation temperature at a higher value, for a significative pressure.

A systematic determination of equilibrium data of methane hydrates in such types of ternary solutions (water, NaCl, ethyleneglycol) can help to build an abascus in order to optimize the composition of the aqueous phase of drilling fluids as a function of drilling conditions. As the best efficiency has to be reached at the lowest cost, this type of experimental approach is a very useful tool for the optimization of thermodynamic inhibitors mixtures.

Conclusions

The first experimental data obtained with the new High Pressure MicroDSC are very promising and show that this technique is very accurate for the prediction of the formation of gas hydrates under very high pressure conditions. A very good correlation is obtained with data obtained with different experimental techniques (especially the PVT cell).

Compared with classical PVT techniques, the MicroDSC technique is easy to use and less time consuming. It requires smaller sample volumes and can be applied to all types of fluids, whatever their density and viscosity. More tests are now to be performed on more complex solutions (especially emulsions used for the drilling operations) in order to establish an instrument that will be ready to be used for on-site measurements, especially in the case of deep offshore operations.

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