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An Innovative High Pressure Mixing Cell for Microcalorimetry: Application to Gas Hydrates

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Abstract: High pressure differential scanning calorimetry (HP-DSC) is of importance in several fields involving gas hydrates, such as oil and gas production, flow assurance, carbon dioxide capture and storage, and refrigeration. Gas hydrates are ice-like crystals that contain gas molecules in molecular cavities. To improve classical calorimetric cells used for gas hydrates characterization, we present here our last prototype: a calorimetric cell equipped with an in-situ mechanical agitation system, which allow performing experiments both under pressure and agitated conditions. The μ -cell, called MICROMIXCELL®, was developed for micro-calorimetry analysis (experiments carried out using a μ DSC7 evo from SETARAM Instrumentation). In this work, thermophysical properties of the cyclopentane hydrate a model clathrate hydrate which forms at atmospheric pressure were measured. Technical details of the system and results are given and commented. The use of such novel calorimetric mixing cells opens a wide range of possibilities for the analysis of complex fluids, which must be analyzed in both pressurized and agitated conditions.

Keywords: microcalorimetry, DSC, mixing cells, gas hydrates, thermophysical properties.

Introduction

Clathrate hydrates are molecular crystals, composed of a network of water molecules forming cavities where other type of molecules of suitable size and shape can be engaged in specific thermodynamic conditions [1]. Clathrates formed by combination of water and gas, are called gas hydrates (and sometimes simply hydrates). They crystallize generally at low temperature (typically a few degrees above 0°C) and high pressure (typically a few MPa). Although gas hydrates have fascinated the scientific community since their discovery at the end of the 19th century, these compounds are not fully understood to date. They are known since the 30s in the Oil and Gas industries as the massive crystallization of hydrates in off-shore and deep off-shore pipelines can cause serious production losses and safety problems (this particular domain of interest is named flow assurance). However, due to their interesting intrinsic properties, hydrates are nowadays involved in many other domains than flow assurance, to develop for example novel gas separation processes, gas storage materials, refrigeration systems, and desalination units [2]. Therefore, their characterization deserve an increasing attention, to obtain stringent key properties useful both on a fundamental and practical level.

Calorimetry techniques are commonly used to detect phase transitions, measure the kinetics of thermal events, and determine thermophysical properties of materials such as phase change enthalpy or specific heat. However, in some cases, the technique faces limitations linked to the fact that the gas hydrate formation in the calorimetric cell occurs at the gas-liquids interface. It leads to problems such as inefficient gas dissolution, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, and difficulties to crystallize these compounds even at low temperature.

This study presents our last prototype of calorimetric cell equipped with an in-situ mechanical agitation system, which allow performing experiments both under pressure (max 15 MPa) and agitated conditions (until 1000 RPM). This cell, named MICROMIXCELL®, was developed in the University

of Pau and Pays de l'Adour (UPPA) for micro-calorimetry analysis. This invention was recently patented [3].

In this paper, results obtained with and without agitation are presented, and compared to previous one obtained at macro-scale with another calorimeter. To illustrate the potentialities of such an invention, the crystallization of cyclopentane hydrate a model clathrate hydrate, which forms with water (H₂O) and cyclopentane (CP) at atmospheric pressure and moderately cold temperature according to the reaction shown in Figure 1 was considered in this work. Note that, in the conditions of this work, CP and H₂O are immiscible (i.e. the CP/H₂O mixture forms two liquid phases).

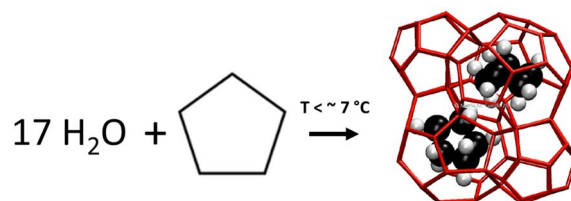


Figure 1: reaction to form the cyclopentane hydrate

Materials and methods

Cyclopentane (reagent grade, 98%) was supplied by Acros Organics and have been used without supplementary purification. The water used (ultra pure water, resistivity of 18.2 MΩ.cm) was produced by a laboratory water-purification system from Purelab.

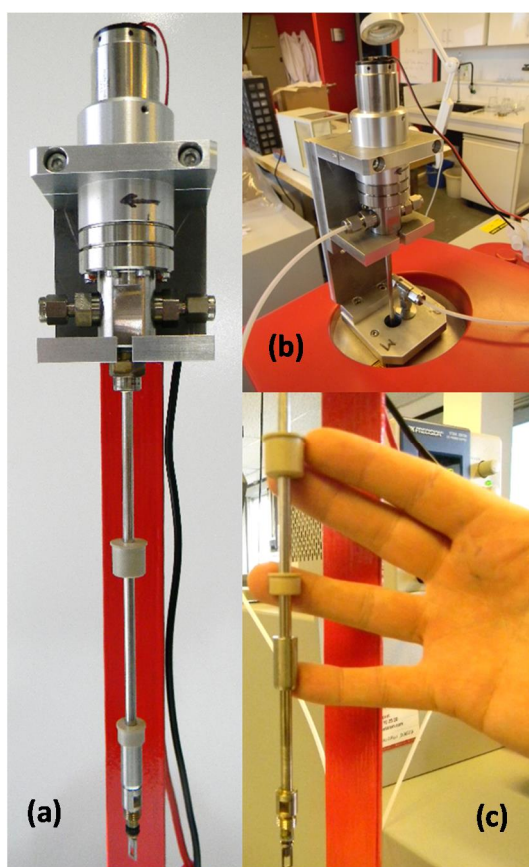


Figure 2: Different views of the Micromixcell. (a) General view; (b) the cell is installed on the μ DSC7 evo from SETARAM; (c) picture giving an idea of the dimensions of the main elements.

The experiments have been performed using a μ DSC7 evo from SETARAM Instrumentation. This calorimeter operates between 228 K and 393 K thanks to Peltier elements. For experiments under pressure, the two cells (measurement and reference) can be connected to a high pressure gas panel (details on apparatuses and supplementary information can be found elsewhere [4]).

The heat-flow signals of the calorimeter were calibrated and its temperature measurement was corrected using the method of standard materials melting (ISO standard ISO11357-1).

The measurement cell was the novel cell prototype (volume of $\sim 300 \mu\text{L}$) shown in Figure 2. The reference cell is a standard stainless steel cell model filled with 0.2 MPa of Nitrogen (purity 99,9999, provided by Linde Gas). For all the experiments, the quantities of water and CP used were calculated taking in account the stoichiometry of the CP-hydrate (CP-17H₂O), with a CP excess of 30 wt.% to compensate CP evaporation.

Results and Discussion

Multi-cycle protocol with no agitation (N = 0)

The classical method to analyse hydrates using μ -DSC and non-agitated calorimetric cells systems consists in a succession of temperatures cycles (a cycle is a cooling ramp followed by a heating ramp). This method has proved to perform well with various hydrates systems different from CP hydrate (e.g. with CO₂, CH₄, THF): the crystals are nucleated at low temperature (during the cooling ramp), and the water to hydrate conversion [4] is progressively increased from cycle to cycle by melting (during the heating ramp) the ice formed at low temperature. Due to the fact that CP and water are two immiscible liquids at ambient conditions, the formation of CP-hydrate is very difficult, even with this protocol. Although CP hydrate is known to form at temperatures below $\sim 7^\circ\text{C}$ [5], Figure 3 shows that a succession of 20 temperature cycles from -20 to 1°C (during ~ 60 h) is still not sufficient to convert all the water in hydrates. As shown in Figure 3(b), two peaks are visible in the last heating ramp (from -20 to 25°C): the first one (the highest) corresponds to the melting of ice formed by crystallisation of the water fraction that was not converted into hydrate, and the second one to the CP-hydrate dissociation. As a mixture of solids (ice + CP-hydrate) is not suitable to properly calculate the thermophysical properties (e.g. the phase change enthalpy or the specific heat), this configuration was not retained.

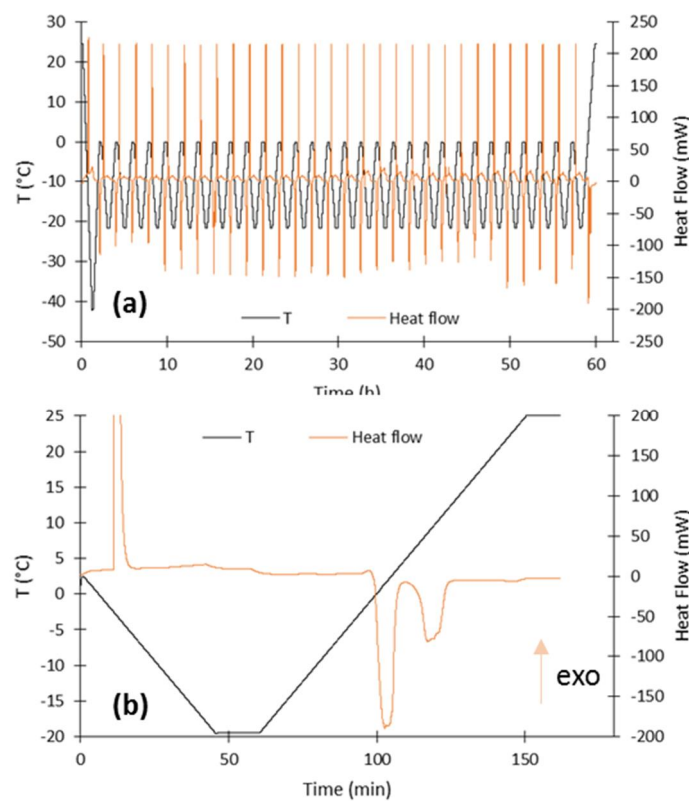


Figure 3: Thermograms obtained without agitation in the measurement cell. (a): Succession of 20 temperature cycles from -20 to 1°C ; (b): last temperature cycle.

One cycle method: effect of the agitation (N = 485 RPM)

The influence of the agitation can be deduced from the thermograms shown in Figure 4. The experiment consists in just one cycle (one cooling ramp from 25 to -40°C , and one heating ramp from -40 to 1°C), followed by a plateau at 1°C (to form the CP-hydrate). At the end of the plateau, the temperature is decreased rapidly to -10°C to freeze the residual free water (if any residual water is present at this stage), and a final heating ramp is done (from -10 to 25°C) to determine the thermophysical properties of interest. For the case $\tilde{\text{without agitation}}$ (see Figure 4(a)), the agitation is off during all the duration of the experiment. In the case $\tilde{\text{with agitation}}$ (see Figure 4(b)), the agitation is started (N = 485 RPM) only during a short period (~ 100 min) on the temperature plateau, and then maintained off till the end of the experiment. Three experiments have been performed for each case with a good reproducibility.

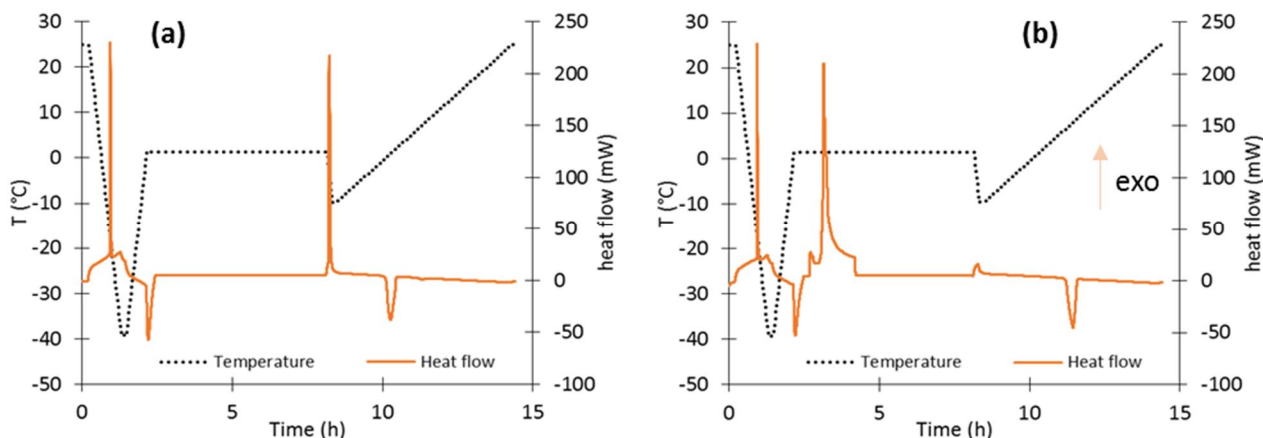


Figure 4: Comparison of thermograms obtained without agitation (a), and with agitation (b), in the measurement cell.

With no agitation and one temperature cycle, only one peak is obtained during the final heating ramp. The onset temperature of this peak is very close to 0°C confirming that only ice has crystallized. In contrary, in the case with agitation, the large exothermic peak on the plateau is the signature of the CP-hydrate crystallization (added to the heat generated by the friction of the agitator). Interestingly, only one peak located is visible during the final ramp. The onset temperature of this peak (6.8 ± 0.3 °C) confirms that this is unambiguously CP hydrate: the conversion is total (no ice present as no peak at 0°C). The dissociation enthalpy of the CP hydrate can thus be estimated at $\Delta H_{\text{diss}} = 362 \pm 3 \text{ J.g}^{-1}$ of water. These results are in very good agreement with recent results obtained with a macro mixing cell ($\sim 8 \text{ cm}^3$) mounted on a Tian-Calvet calorimeter (model BT 2.15, SETARAM) where the dissociation temperature and enthalpy of the CP hydrate were found at 7.0 ± 0.5 °C and $377 \pm 27 \text{ J.g}^{-1}$ of water, respectively [5].

Conclusions

A novel prototype of mixing cell has been tested for microcalorimetry measurements on cyclopentane hydrates. The results have shown that if no agitation is present in the measuring cell, the thermophysical properties of such complex mixtures are very hard to measure properly as ice always coexists with the hydrate, even by using the classical multi-cycling protocol. However, we have demonstrated that the MICROMIXCELL® allow achieving easily a full water hydrate conversion, in a few hours. The use of such novel calorimetric mixing cells opens thus a wide range of possibilities for the analysis of complex fluids, which must be analyzed rapidly in both pressurized and agitated conditions.

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