



## Determination of thermophysical properties of cyclopentane hydrate using a stirred calorimetric cell



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### ARTICLE INFO

#### Article history:

Received 26 June 2017

Received in revised form 16 April 2018

Accepted 19 May 2018

Available online 21 May 2018

#### Keywords:

Calorimetry

Cyclopentane hydrate

Clathrate

Equilibrium data

Dissociation enthalpy

### ABSTRACT

The cyclopentane hydrate, formed by combination of cyclopentane (CP) and water, is frequently used as a model system for clathrate hydrate compounds as it can form at atmospheric pressure and at temperatures below about 280 K. However, due to the immiscibility of CP and water, the dissociation enthalpy is challenging to obtain experimentally because total conversion of water to hydrate is difficult to achieve in quiescent conditions. Only two dissociation enthalpy values are available in literature, and a difference of 25 kJ.mol<sup>-1</sup> between them clearly indicates a discrepancy. In this study, a stirring calorimetric cell was used with a Tian-Calvet heat-flow calorimeter, to measure phase change properties. The technical system made it possible to form pure CP-hydrate with complete conversion of water to hydrate. The dissociation temperature and dissociation enthalpy of the CP-hydrate (with max 5 wt% of residual liquid CP) were measured at 280.2 ± 0.5 K and 115,400 ± 7600 J.mol<sup>-1</sup> of CP (377 ± 27 J.g<sup>-1</sup> of water; 307 ± 21 J.g<sup>-1</sup> of hydrate), respectively. This high enthalpy value opens new ways for using CP-hydrates in cold storage and refrigeration applications.

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### 1. Introduction

Clathrates are crystalline compounds composed of molecules (named “hosts”) whose crystal lattices develop cavities that encage other molecules (named “guests”), thereby stabilizing the structure. Clathrate hydrates are formed by water molecules and C1–C4 hydrocarbon gases up to methylcyclopentane or benzene [1]. Gas hydrates form at low temperature (typically a few degrees above 273 K) and high pressure (typically a few MPa). They are often encountered in oil and gas production where, in certain conditions, they can block flow lines, valves and wellheads, causing serious production losses and safety problems [2]. In studies on hydrate properties, e.g. to understand complex interactions between hydrates and surfactants [3–5], the cyclopentane (CP) hydrate is often used as a model system because it can form at atmospheric pressure and moderately cold temperatures (lower

than 280.1 to 280.8 K [1,6]). Interestingly, the CP-hydrate is believed to be a good analog of the natural gas hydrates that form under pressure [7] owing to the low solubility of CP in water. The CP-hydrate has a crystallographic structure termed “structure two” (sII): each unit cell is composed of 16 small cavities forming pentagonal dodecahedrons and 8 large cavities forming hexakaidecahedrons. The unit cell is formed of a network of 136 hydrogen-bonded water molecules, and the CP molecules are enclosed in the large cavities (Fig. 1) of this structure with a stoichiometric water/CP molar ratio of 17:1 [8]. The molar weight of the CP-hydrate (with a stoichiometric water/CP molar ratio of 17:1) is 376.39 g.mol<sup>-1</sup>.

Calorimetry techniques are commonly used to detect phase transitions, measure the kinetics of thermal events, and determine the heat capacity of materials [9]. Many calorimetric studies have been performed on gas hydrates since the 1980's, starting with those of Handa, Dalmazzone and co-workers who studied the thermal properties of a variety of clathrate hydrates [10–13]. Later on, it was shown that reliable hydrate dissociation temperature data, and consequently practically applicable hydrate stability curves,

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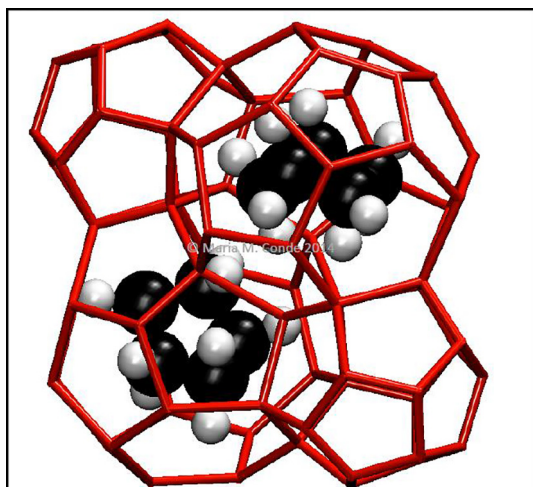


Fig. 1. Structure of the cyclopentane hydrate.

could be obtained using calorimetric measurements [14,15]. For the gas hydrate analyses, the Differential Scanning Calorimetry (DSC) or microcalorimeters used were able to perform measurements in controlled pressure conditions. This technique, applied with classical high-pressure calorimetric cells (i.e. where the fluids are not stirred) still has some limitations due to the fact that the gas hydrate generally forms at the interface (water/gas or water/oil) [16]. The low interfacial surface area between CP and water, in addition to the lack of in-situ stirring, leads to: (i) long induction times (i.e. a long period before the start of crystallization), and (ii) the formation of a hydrate crust covering the CP/liquid interface which prevents complete water-to-hydrate conversion within a reasonable time. Accordingly, and despite the common uses of CP-hydrate, the determination of the phase change enthalpy (also called formation or dissociation enthalpy,  $\Delta H_d$ ) is rather difficult and challenging using DSC.

Karanjkar et al. (2012) [17] used a  $\mu$ DSC to study a pure system with excess CP, applying a cooling ramp from 293 to 228 K. They demonstrated that only ice formed and that the use of an emulsion stabilized with surfactant instead of a pure system resulted in the formation of an ice/hydrate mixture. To overcome these limitations and obtain phase transition properties – such as the CP-hydrate dissociation enthalpy – studies were conducted on CP/water emulsions stabilized by the addition of surfactants. Nakajima et al. (2008) [18] emulsified water and CP with surfactants to form the CP-hydrate in a stirring reactor, removed some hydrate particles and analyzed them by DSC. They reported a value of  $\Delta H_d = 106,900 \text{ J}\cdot\text{mol}^{-1}$  of CP. Zhang et al. (2008) [8] proceeded quite similarly: in a DSC they applied a heating ramp to a previously formed CP-in-water or water-in-CP emulsion, and from the dissociation peak determined a value of  $\Delta H_d = 82,300 \pm 4000 \text{ J}\cdot\text{mol}^{-1}$  for the CP-hydrate. Although other studies involving both calorimetry and cyclopentane-based hydrate systems can be found [19,20], these two  $\Delta H_d$  values are the only ones we have found in literature. The discrepancy between them (about  $25 \text{ kJ}\cdot\text{mol}^{-1}$  of CP) requires new experiments to more accurately determine the true value.

In this work, the enthalpy of dissociation of pure CP-hydrate was determined using a customized stirred high-pressure calorimetric cell mounted on a heat-flow calorimeter. This cell overcomes some of the existing limitations encountered with conventional high pressure calorimetric cells in which the fluids are left in static conditions. Therefore, this stirring cell, developed initially for experimentation with gas hydrates under pressure, was used here to accurately determine the thermophysical properties of the CP-hydrate.

## 2. Materials and methods

### 2.1. Calorimeter and stirred calorimetric cell

The development was based on a Tian-Calvet heat-flow calorimeter (model BT 2.15) manufactured by SETARAM Instrumentation, France. The main feature of Calvet-type calorimeters is their network of thermocouples surrounding the calorimetric cell in which the samples are placed, making it possible to measure the heat-flow in all directions and thereby reliably determine the enthalpies of transition. The sensor is differential, meaning that the heat-flow data of the sample are constantly compared against the heat-flow data of a reference cell. The aim here is to deduct heat effects linked with the heat capacity of the cell, potential pressure variations, or other interfering thermal phenomena.

For subambient operations, the calorimeter is cooled using a cryothermostat with ethanol as the coolant fluid, making it possible to perform experiments under temperatures as low as 243 K. For more details on the calorimeter and a view of the complete apparatus refer to Plantier et al. (2013) [21].

A schematic view of the prototype of the stirred calorimetric cell is shown in Fig. 2. This mixing cell was developed and patented in 2012 by the CNRS and the Laboratory for Complex Fluids and their Reservoirs of the University of Pau and Pays de l'Adour. A detailed description of the invention is given by Torr e et al. (2012) [22]. In short, the cell body which contains the samples is a 17 mm outer diameter stainless-steel cylinder. Due to high-pressure resistance requirements, it is designed with thick walls

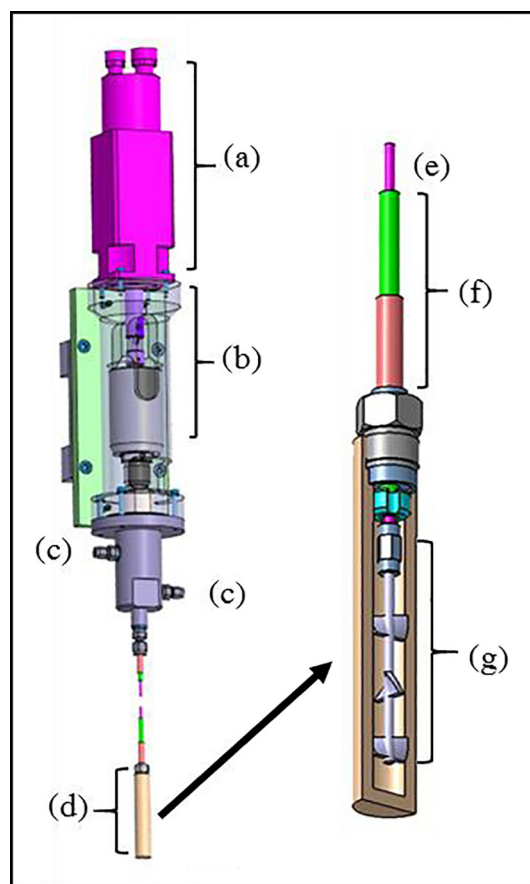


Fig. 2. Schematic view of the high-pressure stirred calorimetric cell with a magnetic agitator coupling: (a) agitating motor; (b) magnetic coupling; (c) gas inlet/outlet; (d) measurement cell; (e) agitator shaft; (f) high pressure tubes; (g) agitator.

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