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Henry Delroisse, Frédéric Plantier, Laurent Marlin, Christophe Dicharry, Laura Frouté, et al.. Determination of thermophysical properties of cyclopentane hydrate using a stirred calorimetric cell. Journal of Chemical Thermodynamics, 2018, 125, pp.136-141. 10.1016/j.jct.2018.05.023 . hal-02000404

HAL Id: hal-02000404

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Delroisse, Henry and Plantier, Frédéric and Marlin, Laurent and Dicharry, Christophe and Frouté, Laura and André, Rémi and Torré, Jean-Philippe *Determination of thermophysical properties of cyclopentane hydrate using a stirred calorimetric cell.* (2018) The Journal of Chemical Thermodynamics, 125. 136-141. ISSN 0021-9614

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

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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^{-1} 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^{-1} of CP (377 ± 27 J.g^{-1} of water; 307 ± 21 J.g^{-1} of hydrate), respectively. This high enthalpy value opens new ways for using CP hydrates in cold storage and refrigeration applications.

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^{-1}.

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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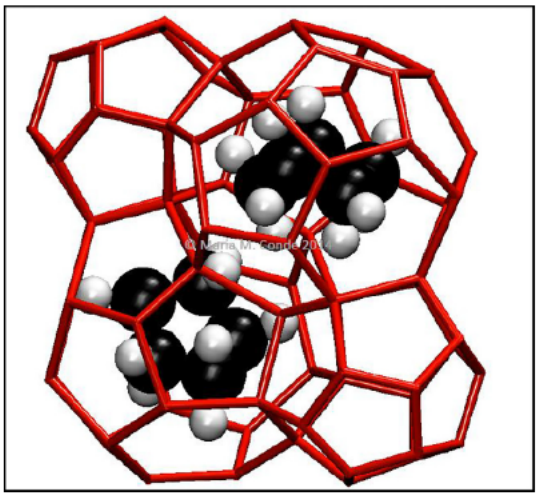

Fig. 1. Structure of the cyclopentane hydrate.

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, ΔH_d) is rather difficult and challenging using DSC.

Karanjkar et al. (2012) [17] used a μDSC 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 $\Delta H_d = 106{,}900\ J.mol^{-1}$ 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 $\Delta H_d = 82{,}300 \pm 4000\ J.mol^{-1}$ for the CP hydrate. Although other studies involving both calorimetry and cyclopentane based hydrate systems can be found [19,20], these two ΔH_d values are the only ones we have found in literature. The discrepancy between them (about 25 $kJ.mol^{-1}$ 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 subambiant 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 Torré 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

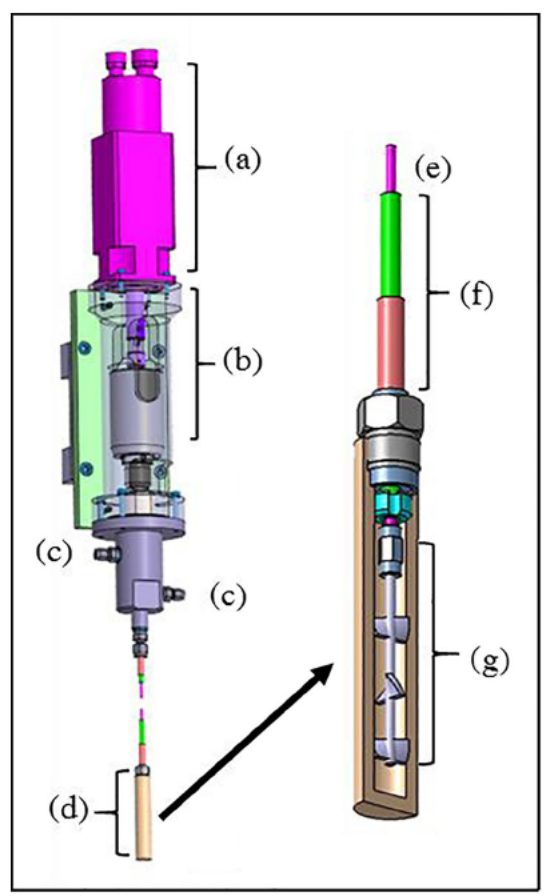

Fig. 2. Schematic view of the high-pressure stirred calorimetric cell with a magnetic agitator coupling: (a) agitating motor; (b) magnetic coupling; (c) gas inlet/outlet; (d) measurement cell; (e) agitator shaft; (f) high pressure tubes; (g) agitator.

which can nevertheless accommodate a sample volume of approx. 7 cm^3. The cell body connection is rendered leak tight through the use of a 316L stainless steel part which is compressed by a stainless steel 303 nut closed by the operator. Although in this study the system was used at atmospheric pressure, the whole setup is cap able of working under pressures as high as 20 MPa. The mechanical agitation in the measuring cell is ensured by a stirrer that is screwed onto the agitator shaft. The agitator used was a triple impeller made of stainless steel, composed of three stages of curved blades positioned at different heights (Fig. 2). Each agitator is 9 mm in diameter and 5 mm high, with 15 mm between adja cent impellers (center to center distance). The link between the wellhead and the measuring cell is provided by two concentric tubes which allow the agitator shaft to rotate freely in the tubes. Agitator rotation is propelled by an ATEX brushless motor powered by a Kollmorgen frequency drive, all provided by Rosier Mecatron ique. The agitating motor is connected using a magnetic coupling (from PARR). On the upper part of the system, a clamping system is used to connect the shaft from the cell to the stirring motor axis from the magnetic stirrer. The stirring rate is limited to 500 rota tions per minute (RPM).

2.2. Materials

Cyclopentane (98% reagent grade) was supplied by Acros Organics. The pure water used (resistivity of 18.2 MΩ.cm) was pro duced by a laboratory water purification system from Purelab. The calibration standards are of analytical grade. The gas used in the reference cell is nitrogen with a purity of 99.999%, supplied by Linde. Extra pure Gallium (purity of 99.99999%), used to check the calibrations, was provided by Sigma Aldrich. Information on the sources and purities of all the materials is resumed in the sam ple table (Table S1) of Supporting Information. Note that chemicals were used without supplementary purification.

2.3. Calibration methods

The calibration of a calorimeter aims to establish an analytical relationship linking the electrical signal delivered by the apparatus and the quantity of energy released or absorbed by the system. This step is of paramount importance for every thermophysical analysis. The experimental conditions for analysis and calibration should correspond as closely as possible, particularly regarding the quantity of energy to be measured [23].

The calibrations of the system (i.e. the calorimeter equipped with the stirring cell) in temperature and enthalpy were done using 6 components (see Tables S1 and S2 of Supporting Informa tion). This selection of compounds has been done to cover a large range of temperature (from about 263 to 310 K) and enthalpy (from 21 to 334 $J.g^{-1}$). The experimental protocol used by Plantier et al. [21] was followed for the calibration experiments. An exam ple of a typical thermogram (fusion of ice) is presented in Fig. 3. The experimental melting points obtained with the calibration standards, graphically compared to the standard references in Fig. 4, agree with the data from the literature (numerical data given in the Table S2 of Supporting Information). The enthalpy calibra tion curve i.e. the reference value of the fusion enthalpy (in $J.g^{-1}$) obtained from literature vs. the electrical calorimeter signal (in $\mu V\ s.g^{-1}$) measured experimentally is shown in Fig. 5 (see Table S2 of Supporting Information for numerical data).

It shows a linear variation in the surface area of the fusion peak of each compound (in $\mu V\ s.g^{-1}$) versus the enthalpy of fusion (from literature). The slope of this line gives the enthalpy calibration con stant (denoted S, as it is also called sensitivity of the calorimeter), which is used to directly convert the electrical signal of the sensors (expressed in μV) into power (expressed in mW). Furthermore, we

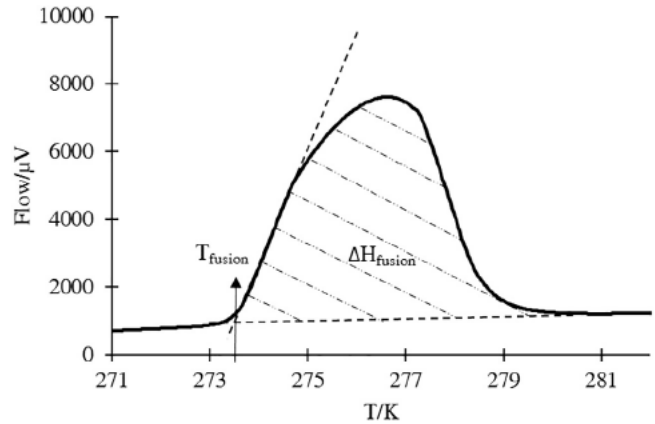

Fig. 3. Typical thermogram showing the fusion of ice.

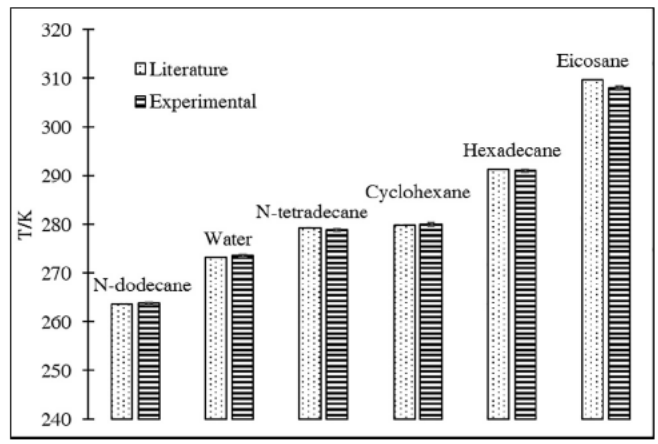

Fig. 4. Comparison of experimental and literature melting points for the reference samples.

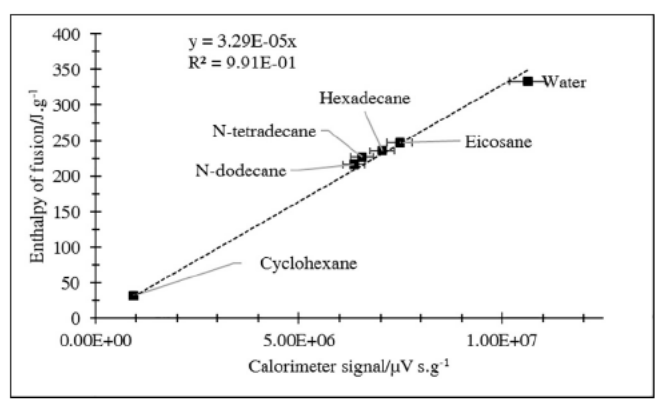

Fig. 5. Enthalpy calibration curve.

demonstrated that the calibration constant exhibits negligible vari ation in the temperature range of this work (i.e. 263 K < T < 310 K). Therefore, for this calorimeter mixing cell system the enthalpy cal ibration constant is $S = 3.29 \times 10^{-5}\ J.\mu V^{-1}.s^{-1}$ in the temperature range [263 K 310 K]. The standard uncertainties of the method was calculated taking the deviations of the all the experimental measurements from the standard values; the results give 4.2% of the enthalpy value and ± 0.5 K for the fusion temperature.

The temperature and enthalpy calibrations have been validated by using extra pure Gallium (Ga): three reproducible experiments

were performed with Ga and the average values with standard uncertainties were: $T_{fus}^{exp}(Ga) = 303.4 \pm 0.5$ K and $\Delta H_{fus}^{exp}(Ga) = 83.3 \pm 3.4$ J.g^{-1} Our experimental values were in good agreement with the reference values ($T_{fus}^{ref}(Ga) = 302.9146$ K and $\Delta H_{fus}^{ref}(Ga) = 80.097 \pm 0.032$ J.g^{-1}) taken from Archer (2002) [24].

2.4. Experimental protocol for CP hydrate analysis

The measuring cell was filled to a total volume of 4.7 cm^3. CP and water were introduced in the cell with a molar CP excess of 30% relative to stoichiometric proportions (17 mol of water for 1 mol of CP in the CP hydrate) and the measuring cell was placed in one of the two calorimeter wells. The reference cell was filled with nitrogen at 0.2 MPa, and placed in the second well. The experiments were done under variable agitation speeds ranging from 50 to 200 RPM. Several temperature cycles were necessary to obtain a full water to hydrate conversion. With only one cycle, conversion was never complete. Three experiments involved two cycles: 2 of the 3 experiments gave incomplete water to hydrate conversion and only one resulted in a conversion of about 97% of water in hydrates. With three temperature cycles (N = 100 RPM), the experiments were reproducible and a full water to hydrate conversion was always obtained in these conditions. Consequently, a protocol with three temperature cycles was chosen in order to systematically achieve a full water to hydrate conversion. A schematic representation of the temperature cycles in a typical experiment (with three cycles) is presented Fig. 6.

The temperature of the cells is first stabilized at 298 K (point A) and the agitation is started at a constant rotation speed. From point A to B, the temperature is decreased at a cooling rate of 0.1 K.min^{-1} and let to stand at 274.1 K for 19 h (from B to C) to form the CP hydrate. The temperature was then increased to 281.1 K at a rate of 0.1 K.min^{-1} (from C to D) and let to stand 2 h at 281.1 K to dissociate the hydrates formed (from D to E). Two new cycles (formation at 274.1 K and dissociation at 281.1 K) were run (from points E to F). A last formation was performed at 274.1 K for 19 h (from G to H). Note that stirring is stopped 2 h before the end (i.e. after 17 h) to prevent any heat from being released (by friction between the stirrer and the hydrate formed) in the last heating step of the protocol, where the thermophysical parameters are measured. Before this, a low temperature step is run to crystalize any residual water present in the cell, which allowed us to verify whether the water to hydrate conversion is total or partial. The temperature was then decreased, at a rate of 0.1 K/min (from H to I), from 274.1 K to 263.0 K. This low temperature was kept constant for 2 h. Finally, the temperature was increased at a rate of 0.1 K.min^{-1} up to 298 K (point J) to measure the thermophysical hydrate properties and dissociate/melt all the hydrates formed.

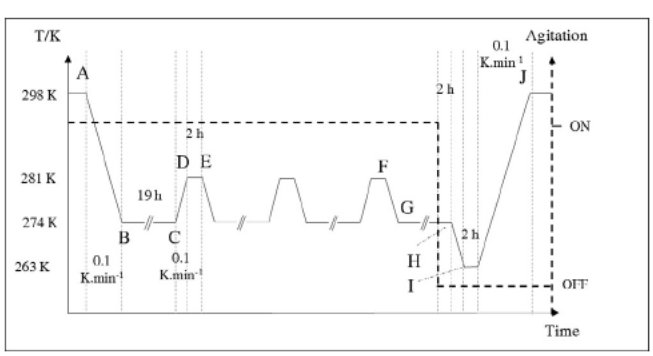

Fig. 6. Schematic representation of the experimental protocol.

3. Results

To illustrate the effect of the agitation on water to hydrate conversion, Fig. 7 shows a series of thermograms obtained for experiments performed at various stirrer speeds varying from 0 to 200 RPM. The thermograms show the endothermic peak that corresponds to CP hydrate dissociation. For these experiments, only one formation cycle was performed at 274.1 K before the dissociation step from 274 to 298 K at 0.1 K.min^{-1} (no decrease to 263 K at the end of the formation). As no peak was observed on the thermogram, we conclude that without agitation, hydrates did not formed in these conditions. This result confirms that the formation of hydrates is very difficult in a static system [13]. Fig. 7 shows that in stirred systems, the area of the peak increases until it reaches a maximum value at 100 RPM. As the quantity of heat absorbed during hydrates dissociation is directly proportional to the water to hydrate conversion, we can conclude that the quantity of hydrates formed is lower at 50 RPM compared to 100 RPM (estimated to be about 5 times as high at 100 RPM). In addition, as the area of the dissociation peak is about the same at 100 and at 200 RPM, it can be concluded that it is unnecessary to speed up the agitator above 100 RPM. Consequently, in all the experiments presented in the following, the agitation rotation speed was set to 100 RPM. These experiments demonstrate that in situ agitation plays a preponderant role by (i) breaking the crystallization metastability (i.e. reducing the induction time), and (ii) increasing the water to hydrate conversion. The benefits of in situ agitation are related to the development of multiple liquid/liquid interfaces (drops of CP dispersed in water), to the increase of the heat and mass transfer coefficients by forced convection into the cell, and to the limitation of unconverted water trapped inside the solid hydrate particles [17] and isolated water pockets. Therefore, with in situ agitation hydrates formed more rapidly and in larger quantities.

Nevertheless, the very simple experiments that produced the results shown in Fig. 7 do not establish whether or not free water is present in the cell following hydrates formation. To demonstrate this, the temperature was decreased to 263 K (after the initial formation at 274.1 K) to freeze any remaining free water into hydrates. The results corresponding to the formation at 100 RPM with a stoichiometric CP/water solution (i.e. a molar ratio for CP to water equal to 17/1) and one cycle of formation are presented in Fig. 8(A), which clearly shows two endothermic peaks. The first starts at 273.0 ± 0.5 K and corresponds unambiguously to the melting of ice. We noted that if an initial stoichiometric composition of water and CP is used, there was always unconverted water at the end of the experiment whatever the number of formation dissociation cycles. Partial evaporation of the CP during the experiment could be responsible for the remaining water not being con

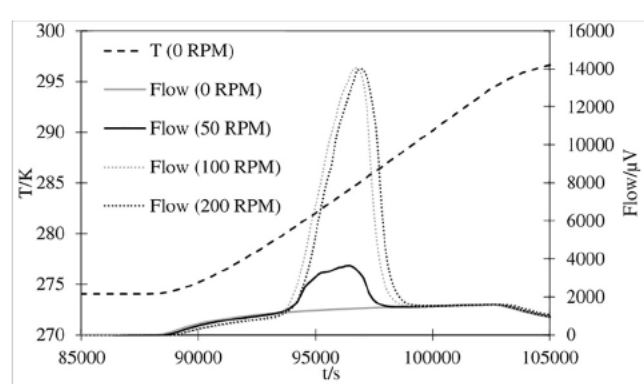

Fig. 7. Dissociation peak of the CP-hydrate versus agitation rotation speed.

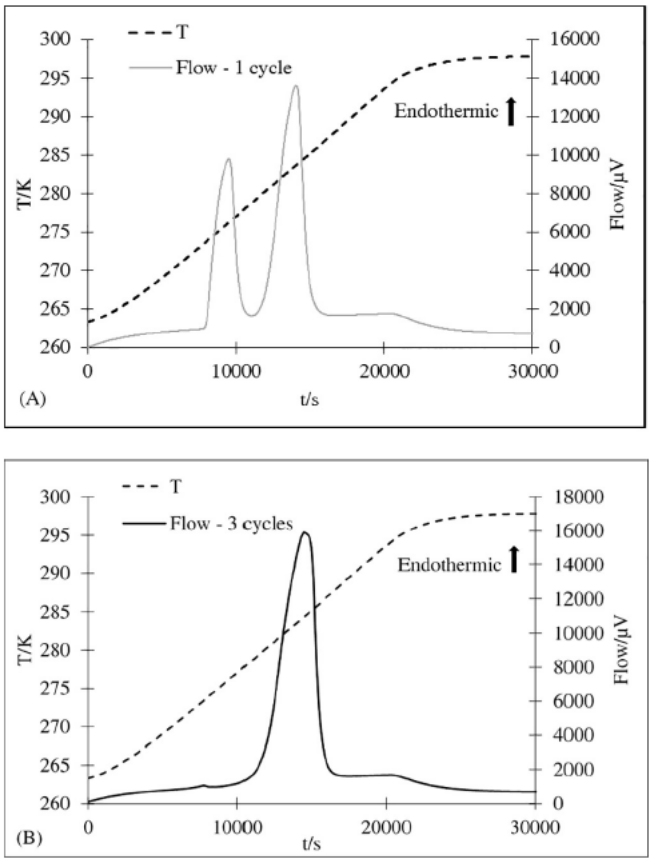

Fig. 8. Calorimetric trace of CP-hydrate system with an initial stoichiometric water/CP system after one cycle of formation (A) and a typical CP-hydrate peak of dissociation after 3 cycles of formation-dissociation with 30% CP in excess (B).

verted into hydrate. To improve the protocol and reach a complete water to hydrate conversion, an excess of CP was initially added, and 3 formation dissociation cycles were successively performed. The excess of CP corresponded to a mole fraction excess of 0.3 (i.e. an excess of 0.35 g of CP) relative to the exact stoichiometric quantities of water and CP required for the CP hydrate to form (0.74 g of CP + 3.24 g of water). As shown in Fig. 8(B), no more ice was present (as no peak is present at 273 K) which means that all the water present is converted to CP hydrate. The stirring com bined with three formation/dissociation cycles thus resulted in only pure CP hydrate with no remaining free water. Note that a small amount of free CP remains in the cell at the end of the exper iments. A mass balance on the analyzed sample showed that only 0.2 g of free CP remains at the end of the experiment, representing <5% of the total mass initially introduced in the calorimetric cell. Therefore, the presence of residual liquid CP was neglected in the calculations.

To determine the dissociation enthalpy and temperature of the CP hydrate, the same method as in Plantier et al. [21] was used. The typical thermogram obtained during hydrate dissociation is shown in Fig. 8(A) (case with 3 cycles). Four independent experi ments were conducted and the results are summarized in Table 1. The reproducibility of the dissociation enthalpy is good (<4%). The dissociation temperature of 280.2 ± 0.5 K is in very good agree ment with literature data [1,6]. The average enthalpy of dissocia tion obtained (CP hydrate with max 5 wt% of residual liquid CP) is 115,400 ± 7600 J.mol^{-1} of CP (377 ± 27 J.g^{-1} of water; 307 ± 21 J.g^{-1} of hydrate). It is worth noting that this value of enthalpy is relatively high (for example in comparison to the one for ice with 333 J.g^{-1} of water), opening interesting avenues for use as novel

Table 1
Experimental values of dissociation temperature and dissociation enthalpy for CP-hydrate measured at atmospheric pressure (P = 1020 hPa[a]) with max 5 wt% of residual liquid CP. The molar mass of CP is 70.1 g.mol^{-1}.

v	Dissociation temperature/K [b]	Dissociation enthalpy/J.mol^{-1} of CP[c]
1	280.2	115,900
2	280.1	115,800
3	280.2	115,700
4	280.2	114,000
Average	280.2	115,400

[a] the standard uncertainty for the pressure is u(P) = 10 hPa.
[b] the standard uncertainty for the dissociation temperature is u(T) = 0.5 K.
[c] the standard uncertainties for the dissociation enthalpies (ΔH_d /J.mol^{-1} of CP) are $u_1(\Delta H_d)$ = 7500; $u_2(\Delta H_d)$ = 8000; $u_3(\Delta H_d)$ = 7400; $u_4(\Delta H_d)$ = 74 00; $u_{avg}(\Delta H_d)$ = 7600.

phase change materials (PCMs) in refrigeration and cold storage applications [25]. The standard uncertainty takes account of the reproducibility error and the precision of the calibration constant. Our value of the dissociation enthalpy is close to the result obtained by Nakajima et al. [14], suggesting that the value pro posed by Zhang et al. [8] was underestimated.

4. Conclusion

The use of a mechanically stirred calorimetric cell resulted in the unprecedented formation of pure CP hydrate in a calorimetric cell, with 100% water to hydrate conversion without having to resort to either a previous step of ice formation or emulsification of CP in water using surfactant(s). In situ agitation contributes to reducing the induction time before hydrate crystallization, increas ing the contact surface between water and CP liquid phases, break ing the hydrate crust that generally forms in static conditions at the CP/liquid interface, and reducing unconverted water trapped inside the hydrate particles. As the measurement of enthalpy involves the determination of a calibration constant, a calibration was performed in temperature and enthalpy using standards with well known properties. The dissociation temperature of the CP hydrate was measured at 280.2 ± 0.5 K. The total water to hydrate conversion reached during the experiments made it possi ble to determine the dissociation enthalpy of the CP hydrate (with max 5 wt% of residual liquid CP) at 115,400 ± 7600 J.mol^{-1} of CP (377 ± 27 J.g^{-1} of water or 307 ± 21 J.g^{-1} of hydrate). Such a high dissociation enthalpy value, combined with the properties of this hydrate to form at atmospheric pressure and around 280 K, make the CP hydrate a very attractive candidate for phase change mate rials (PCMs) in cold storage and refrigeration applications.

Acknowledgments

The authors wish to acknowledge the "Atelier de Physique" of the University of Pau for their help in developing and manufactur ing the elements of the calorimetric cell prototypes. We extend our thanks to J. Diaz for technical help, to E. Normandin, F. Guerton for technical assistance in instrumentation and to M. Conde for the illustration of CP hydrate. The authors are also grateful to Aqui taine Science Transfert, to Carnot institute ISIFoR (Institute for the Sustainable engIneering of Fossil Resources), and to Arkema Ceca for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jct.2018.05.023.

References

[1] E.D. Sloan, C.A. Koh, Clathrate Hydrates of Natural Gases, Third ed., CRC Press, Taylor & Francis Group, Boca Raton, Fl, 2008.

[2] E.F. Hammerschmidt, Formation of gas hydrates in natural gas transmission lines, Ind. Eng. Chem. Res. 26 (1934) 851–855.

[3] C. Lo, S. Zhang, A. Couzis, P. Somasundaran, J.W. Lee, Adsorption of cationic and anionic surfactants on cyclopentane hydrates, J. Phys. Chem. C. 114 (2010) 13385–13389.

[4] Z.A. Aman, K. Olctt, K. Pfeiffer, E.D. Sloan, A.K. Sum, C.A. Koh, Surfactant adsorption and interfacial tension investigations on cyclopentane hydrate, Langmuir 29 (2013) 2676–2682.

[5] N. Abojaladi, M.A. Kelland, Can cyclopentane hydrate formation be used to screen the performance of surfactants as LDHI anti-agglomerants at atmospheric pressure?, Chem Eng. Sci. 152 (2016) 746–753.

[6] R. Sakemoto, H. Sakamoto, K. Shiraiwa, R. Ohmura, T. Uchida, Clathrate hydrate crystal growth at the seawater/hydrophobic–guest–liquid interface, Cryst. Growth Des. 10 (2010) 1296–1300.

[7] L.C. Price, Aqueous solubility as petroleum as applied to its origin and primary migration, Am. Assoc. Petrol. Geol. Bull. 60 (1976) 213–244.

[8] Y. Zhang, P.G. Debenedetti, R.K. Prud'homme, B.A. Pethica, Differential scanning calorimetry studies of clathrate hydrate formation, J. Phys. Chem. B 108 (2004) 16717–16722.

[9] T. Hatakeyama, Z. Liu, Handbook of Thermal Analysis, John Wiley and Sons Ltd, 1998.

[10] Y.P. Handa, R.E. Hawkins, J.J. Murray, Calibration and testing of a Tian-Calvet heat-flow calorimeter Enthalpies of fusion and heat capacities for ice and tetrahydrofuran hydrate in the range 85 to 270 K, J. Chem. Thermodyn. 16 (1984) 623–632.

[11] Y.P. Handa, Heat capacities in the range 95 to 260 K and enthalpies of fusion for structure-II clathrate hydrates of some cyclic ethers, J. Chem. Thermodyn. 17 (1985) 201–208.

[12] M. Kharrat, D. Dalmazzone, Experimental determination of stability conditions of methane hydrate in aqueous calcium chloride solutions using high pressure differential scanning calorimetry, J. Chem. Thermodyn. 17 (2003) 1489–1505.

[13] D. Dalmazzone, M. Kharrat, V. Lachet, B. Fouconnier, D. Clausse, DSC and PVT measurements: methane and trichlorofluoromethane hydrate dissociation equilibria, J. Therm. Anal. Calorim. 70 (2002) 493–505.

[14] W. Lin, D. Dalmazzone, W. Fürst, A. Delahaye, L. Fournaison, P. Clain, Accurate DSC measurement of the phase transition temperature in the TBPB-water system, J. Chem. Thermodyn. 61 (2013) 132–137.

[15] J.-P. Torré, D. Haillot, S. Rigal, Roger de Souza Lia, C. Dicharry, J.-P. Bedecarrats, 1,3 dioxolane versus tetrahydrofuran as promoters for CO_2-hydrate formation: thermodynamics properties, and kinetics in presence of sodium dodecyl sulfate, Chem. Eng. Sci. 26 (2015) 688–697.

[16] S.R. Davies, K.C. Hester, J.W. Lachance, C.A. Koh, E.D. Sloan, Studies of hydrate nucleation with high pressure differential scanning calorimetry, Chem. Eng. Sci. 64 (2009) 370–375.

[17] P.U. Karanjkar, J.W. Lee, J.F. Morris, Calorimetric investigation of cyclopentane hydrate formation in an emulsion, Chem. Eng. Sci. 69 (2012) 481–491.

[18] M. Nakajima, R. Ohmura, Y.H. Mori, Clathrate hydrate formation form cyclopentane-in-water emulsion, Ind. Eng. Chem. Res. 47 (2008) 8933–8939.

[19] C.A. Whitman, R. Mysyk, M.A. White, Investigation of factors affecting crystallization of cyclopentane clathrate hydrate, J. Chem. Phys. 129 (2008) 174502-1–174502-6.

[20] A. Ahuja, G. Zylyftari, J.F. Morris, Calorimetric and rheological studies on cyclopentane hydrate-forming water-in-kerosene emulsions, J. Chem. Eng. Data 60 (2014) 362–368.

[21] F. Plantier, L. Marlin, D. Missima, J.-P. Torré, Development of a new type of high pressure calorimetric cell, mechanically agitated and equipped with a dynamic pressure control system – Application to the characterization of gas hydrates, Rev. Sci. Instrum. 84 (2013) 125107-1–125107-7.

[22] J.-P. Torré, F. Plantier, L. Marlin, Cellule de mesure calorimétrique et dispositif de support pour cette cellule, Patent # PCT/EP2013/065820, 26 July 2013.

[23] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitão, M.V. Roux, L.A. Torres, Reference materials for calorimetry and differential thermal analysis, Thermochim. Acta 331 (1999) 93–204.

[24] D.G. Archer, The enthalpy of fusion of gallium, J. Chem. Eng. Data 47 (2002) 304–309.

[25] B. Castellani, E. Morini, M. Filipponi, A. Nicolini, M. Palombo, F. Cotana, F. Rossi, Clathrate hydrates for thermal energy storage in buildings: overview of proper hydrate- forming compounds, Sustainability 6 (2012) 6815–6829.

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

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SUPPORTING INFORMATION

Table S1. Sample table.

Chemical name	Source	Mole fraction purity [a, b]
Cyclopentane	Acros Organics	0.98
Cyclohexane	Sigma-Aldrich	0.995
Eicosane	Sigma-Aldrich	0.99
Gallium	Sigma-Aldrich	0.9999999
Hexadecane	Acros Organics	0.99
N-dodecane	MP Biomedicals	0.995
N-tetradecane	Acros Organics	0.99
Nitrogen	Linde gas	0.99999
Water	Produced by a laboratory water-purification system	Ultra pure (resistivity of 18.2 MΩ.cm)

[a] purities provided by the suppliers.
[b] all the materials have been used without supplementary purification.

Table S2. Experimental data measured at atmospheric pressure (P = 1020 hPa [1]) and reference values used for the calibrations of the calorimeter.

	Experimental values		**Reference values (litt.)**	
Chemical name	**Melting point /K**	**Calorimeter signal / µV s.g^{-1}**	**Melting point /K**	**Fusion enthalpy /J.g^{-1}**
N-dodecane	263.7 [a]	6.35 ×10^{6} [a']	263.59 [1]	216 [1]
Water	273.5 [a]	1.06 ×10^{7} [b']	273.15 [2]	333.6 [3]
N-tetradecane	278.9 [a]	6.56 ×10^{6} [c']	279.03 [1]	227 [1]
Cyclohexane	280.0 [a]	9.34 ×10^{5} [d']	279.82 [4]	31.8 [4]
Hexadecane	291.0 [a]	7.05 ×10^{6} [e']	291.34 [1]	236[1]
Eicosane	308.1 [a]	7.48 ×10^{6} [f']	309.65 [5]	247 [5]

[1] the standard uncertainty for the pressure is u(P) = 10 hPa.
[a] Standard uncertainty (/K) for experimental melting points (T_f^{exp}) values used for the calibration temperature: u(T_f^{exp}): 0.5.

[a'-f'] Standard uncertainties (/µV s.g^{-1}) for values of the electrical calorimeter signal (ECS) used for the enthalpy calibration: u(ECS): [a'] 2.5 ×10^{5} ; [b'] 4.2 ×10^{5} ; [c'] 2.6 ×10^{5} ; [d'] 3.7 ×10^{5} ; [e'] 2.8 ×10^{5} ; [f'] 3.0 ×10^{5}.

REFERENCES

[1] H.L. Finke, M.E. Gross, G. Waddington, H.M. Huffman, Low-temperature thermal data for the nine normal paraffin hydrocarbons from octane to hexadecane, J. Am. Chem. Soc 76 (1954) 333–341.

[2] W.M. Haynes Eds. CRC Handbook of chemistry and physics, 94th ed. 2013-2014, CRC Press, Taylor & Francis Group, Boca Raton Fl.

[3] R. Feistel, W. Wagner, A new equation of state for H_2O Ice Ih, J. Phys. Chem. Ref. Data 35 (2006) 1021–1047.

[4] R.A. Ruehrwein, H.M. Huffman, Thermal data. XVII The heat capacity, entropy and free energy of formation of cyclohexane. A new method of heat transfer in low temperature calorimetry, J. Am. Chem. Soc, 65 (1943) 1620–1625.

[5] J.C. van Miltenburg, H.A.J. Oonk, V. Metivaud, Heat Capacities and Derived Thermodynamic Functions of n-Nonadecane and n-Eicosane Between 10 K and 390 K. J. Chem. Eng. Data, 44 (1999) 715–720.