

## **DSC AND PVT MEASUREMENTS**

### **Methane and trichlorofluoromethane hydrate dissociation equilibria**

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#### **Abstract**

The dissociation of gas and model hydrates was studied using a classical thermodynamic method and a calorimetric method, in various aqueous media including pure water, high concentration calcium chloride solutions and water-in-oil emulsions. Methane hydrate dissociation temperatures *vs.* pressure curves were determined using pressure *vs.* temperature measurements in a constant volume cell (PVT), and high pressure differential scanning calorimetry (DSC), at 5 to 10 MPa gas pressure and at temperatures ranging from  $-10$  to  $+12^{\circ}\text{C}$ . PVT and DSC results are in good agreement, and concordant with data available in literature. From a thermodynamic point of view, there are no measurable differences between bulk solutions and emulsions. From a kinetic point of view, due to the considerable surface of interface between the two phases, emulsions allow the formation of much greater amounts of hydrate than solutions, without any agitation. Model hydrate of trichlorofluoromethane was studied in 9 to 27 mass% calcium chloride solutions in emulsion in oil, using DSC under atmospheric pressure, at temperatures ranging from  $-20$  to  $+5^{\circ}\text{C}$ . A diagram of dissociation temperature *vs.* salt concentration is proposed.

**Keywords:** dissociation equilibria, DSC, methane hydrate, PVT, thermodynamics, trichlorofluoromethane hydrate

#### **Introduction**

The problem of the formation of insertion compounds named gas hydrates between light hydrocarbons and water is well known in the field of oil and gas transportation and has been studied for long [1]. With the development of deep off shore oil recovery, the problem of hydrate formation in drilling fluids is becoming increasingly serious, too.

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Drilling fluids, also called drilling muds, are complex mixtures used for lubricating the drilling tools, composed of a liquid phase in which various solid particles are dispersed. The liquid phase may be either a water-in-oil emulsion or an aqueous solution of polymers. In both cases, the water phase also contains diverse hydrate inhibitors, such as calcium or sodium chloride, or glycol. The pressures and temperatures encountered at the bottom of seas are favourable to hydrate formation between hydrocarbons and the mud water phase, even in very high inhibitor concentrations. Hydrates can modify the physical properties of the mud and may be responsible for subsea equipment plugging causing both safety and economic problems.

The usual techniques used for studying hydrates in water or aqueous solutions are not always easily applicable to muds, which are complex, multiple phase mixtures. Also, classical thermodynamic techniques require a considerable time of experiment for accurate results. Differential scanning calorimetry (DSC) is a rapid and sensitive technique, broadly used for the characterization of any kind of phase change [2]. It seemed interesting to test the application of DSC to the determination of dissociation equilibrium curves of hydrates in various aqueous media, including highly concentrated salt solutions and water-in-oil emulsions. In order to demonstrate the validity of this application, it was necessary to compare DSC results with equilibrium points obtained using a more classical technique, such as measurements of pressure variation *vs.* temperature at constant volume (PVT).

Very few papers about the study of hydrates by calorimetry can be found in the literature. Handa [3–5] has determined the compositions, dissociation enthalpies and heat capacities of hydrates of xenon, krypton, methane, propane, ethane, isobutane and natural gas hydrates using a Calvet calorimeter from SETARAM.

Koh *et al.* [6] from the King's College of London have recently used DSC in order to test hydrates inhibitors. The study was performed at atmospheric pressure on hydrates of tetrahydrofuran. They measured supercooling degrees for different types of inhibitors and performed isothermal studies in order to observe crystallisation of THF hydrates as a function of time. Some TTT curves (time-temperature-transformation) were therefore plotted that allow the comparison of inhibitors properties on the kinetics of hydrate formation.

Fouconnier *et al.* [7] used DSC at atmospheric pressure for studying the formation of hydrate of trichlorofluoromethane in water-in-oil emulsions stabilised by a non-ionic surfactant (Berol 26). It was done in collaboration with Pr. Sjöblom's team from the University of Bergen, who studied kinetics of hydrates formation in the same system by dielectric spectroscopy [8]. Hydrates formation was actually observed by DSC analysis. It was shown that the amount of hydrates formed depends on the sample volume, the temperature reached during the cooling step, and time.

No example of gas hydrate study under pressure by DSC was reported. More generally, very few data concerning hydrate stability in very concentrated salt solutions, especially calcium chloride solutions, are available. We report here the results obtained on two types of hydrates, one model hydrate of trichlorofluoromethane, which forms at atmospheric pressure, and methane hydrate at pressures from 5 to

10 MPa, in calcium chloride solutions in concentrations up to 27 percent in mass, in bulk phase or water-in-oil emulsion.

## Experimental

### *Sample preparation*

For methane hydrate determinations, calcium chloride solutions were prepared by careful weighing, using freshly distilled water and 99.5%  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  purchased from Fisher Scientific. Solution concentrations were verified by density measurement, using a Paar DMA 55 vibrating tube densimeter. This procedure was intended to avoid errors possibly due to an absorption of water by the very hygroscopic salt during storage or weighing. The relative densities of the solutions at 20°C were compared with reference data [9], and the concentration was found to be accurate within 0.2 mass per cent, with an uncertainty of no more than 0.01%. Emulsions were prepared using 30% in volume of  $\text{CaCl}_2$  solution and 70% of oil and an appropriate emulsifier. The mixture was mechanically dispersed using an Ultra Turrax T8 at 25000 rpm during 10 min. A cylinder of methane, 99.5% of purity under 21 MPa, from Messer, was used as gas supply.

For model hydrate determinations, emulsions were prepared using Exxol D 80 as the oil phase (aliphatic and cyclic hydrocarbons from C10 to C13), and Berol 26 (ethoxylated nonyl phenol) as the emulsifier. The proportions were 60% mass/mass of aqueous solution and 40% of oil. A Polytron PT 3000 was used for dispersion, at 10000 rpm during 10 min.  $\text{CCl}_3\text{F}$  was then incorporated to the emulsion and the mixture kept at 1°C until utilisation.

### *PVT measurement device and procedure*

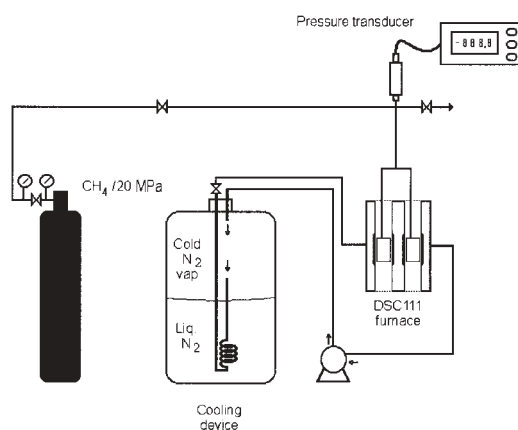
Hydrate dissociation point measurement using a pressure-temperature plot recorded in a constant volume cell is commonly used for high pressure hydrate. Such isochoric procedure has been described in details [1]. It provides an alternative to visual observation, and may thus be applied to opaque media, such as emulsions.

The points reported in this paper were obtained using a 100 cm<sup>3</sup> jacketed glass cell, temperature regulated by mean of glycol circulation. The cell was fitted with pressure and temperature sensors, and agitated using a jerking system and a mercury wave. It was designed to be operated at a maximum pressure of 10 MPa, and at temperatures as low as -20° C in order to accelerate the hydrate formation, which can take several days. The estimated uncertainty of the dissociation temperatures obtained using this method is  $\pm 0.5^\circ\text{C}$ .

### *DSC device and procedure*

A DSC111 from SETARAM was used for DSC determinations. Standard vessels were used for  $\text{CCl}_3\text{F}$  hydrate study.

For methane hydrate, the DSC111 was equipped with controlled pressure vessels. The vessels are fitted with a single gas inlet tube, allowing to apply a static gas pressure onto the sample. They are designed to be operated under a maximum pressure of 10 MPa. Both the reference and sample vessels were fed with methane under constant pressure through a gas control panel, as shown in Fig. 1. Inlet pressure was adjusted through a single stage pressure regulator, and was measured and recorded by mean of a 0–16 MPa pressure sensor, with a resolution of 0.01 MPa.



**Fig. 1** High pressure DSC measurement device

The sample temperature cannot be measured directly by DSC, but it can be obtained with good accuracy from the furnace temperature, provided that cautious calibration is performed. The temperature and heat flow sensitivities were precisely recalibrated within the temperature range of interest for this study, using the melting peaks of 99.99999% mercury (melting point:  $-38.8^{\circ}\text{C}$ ) and 99.9999% gallium (melting point:  $29.8^{\circ}\text{C}$ ) samples. As a test, the pure water melting curve under various methane pressures were recorded. Temperature uncertainty was found to be lower than  $0.1^{\circ}\text{C}$ , between 0.1 and 9.3 MPa, at any heating rate from 0.25 to  $4^{\circ}\text{C min}^{-1}$ . Heat measurement accuracy was better than 1% in the same conditions.

## Results and discussion

### *Methane hydrate: PVT and DSC results*

Figure 2 reports a typical T/P diagram recorded during a PVT test. From initial pressure and temperature conditions (point  $P_0$ ), the mixture was cooled down until hydrate formation was observed (point  $P_1$ ). This formation was accompanied by a strong pressure drop due to the gas consumption, and sometimes by a slight temperature rise due to the reaction heat. The mixture was then heated at  $0.2^{\circ}\text{C per hour}$ . The gas released by the hydrate dissociation, beginning at point  $P_2$ , caused an important

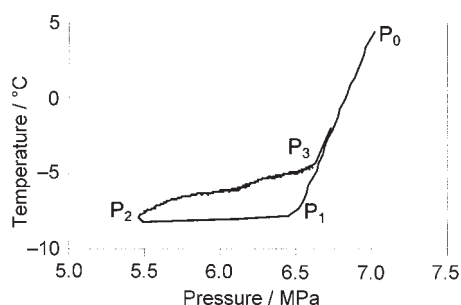


Fig. 2 Temperature vs. pressure during a PVT measurement cycle

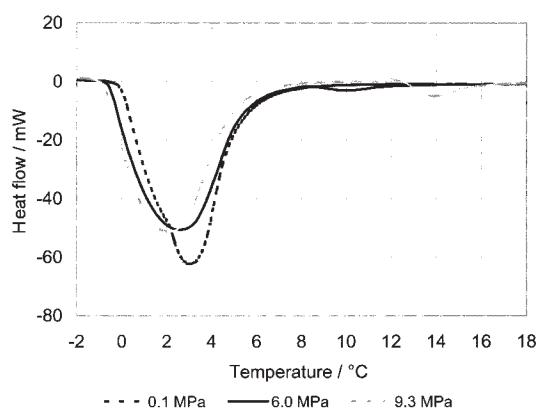
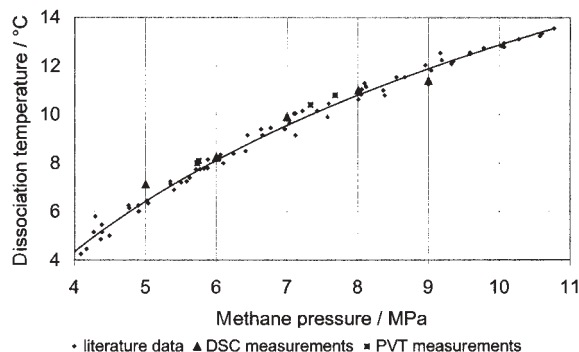


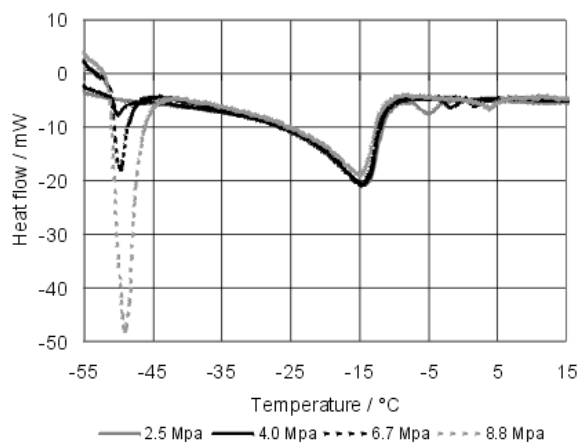
Fig. 3 DSC curves of pure water at various methane pressures

pressure rise until point  $P_3$ , where the dissociation trace interrupts the initial cooling trace; the change in slope of the curve  $T(P)$  indicates that no more hydrate dissociates after point  $P_3$ , and thus, that the dissociation was complete at this point. Assuming that the heating rate was slow enough to ensure thermodynamical equilibrium,  $P_3$  was taken as the dissociation equilibrium point. A second cycle was performed systematically in order to test the repeatability of the results.

Figure 3 reports the DSC curves obtained when heating a pure water sample after complete crystallisation at various methane pressures. The ice melting occurs first, at a temperature that is slightly decreasing upon pressure raise, following the usual water melting point vs. pressure law. Under sufficient methane pressure, a second peak occurs then, at a temperature that is strongly pressure dependent. We attributed this peak to hydrate dissociation and took the onset temperature as the dissociation equilibrium temperature at the given pressure. Several equilibrium points were also measured by PVT technique. Figure 4 shows the results obtained using both PVT and DSC, compared with many literature data, as compiled by Sloan [1]. It can be asserted that DSC measurements show very good agreement with PVT results, as well as other hundreds of methane hydrate dissociation points in pure water reported in literature.



**Fig. 4** Dissociation temperature of methane hydrate in water vs. pressure - PVT and DSC results compared to literature data



**Fig. 5** DSC curves of a 20% mass/mass  $\text{CaCl}_2$  solution at various methane pressures

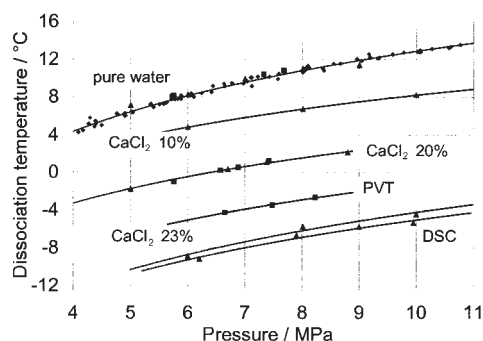
In Fig. 5 are reported several examples of curves recorded on heating a 20% in mass  $\text{CaCl}_2$  solution under various methane pressures, featuring successively the melting of the  $\text{H}_2\text{O}-\text{CaCl}_2$  eutectic, at about  $-51.5^\circ\text{C}$ , the melting of ice in equilibrium with a  $\text{CaCl}_2$  solution which concentration progressively decreases, and a strongly pressure dependent peak attributed to hydrate dissociation. Table 1 reports the points obtained in three calcium chloride solutions, containing 10, 20 and 23 mass percent of salt. DSC series 1 and 2 were measured using two different solutions, prepared by different operators. In addition, PVT measurements with 23%  $\text{CaCl}_2$  solution were repeated using first the solution alone, and then the solution plus the oil used for preparing emulsions, in the same proportions that in emulsions but without the emulsifier so that the emulsion could not form. This was made to test whether the oil would exhibit any inhibition effect on hydrate formation. As it can be seen in Table 2, the presence of an oil phase in the PVT cell does not affect the results measurably.

**Table 1** Temperatures of methane hydrate dissociation in calcium chloride solutions, DSC and PVT results at various pressures

DSC		PVT	
Methane pressure / MPa	Dissociation temperature / °C	Methane pressure / MPa	Dissociation temperature / °C
10 w/w %CaCl <sub>2</sub> sol.			
5.99	-1.8	-	-
8.01	6.7	-	-
10.01	8.2	-	-
20 w/w % CaCl <sub>2</sub> sol.			
4.99	-1.8	5.76	-1.0
6.71	0.3	6.57	0.2
7.38	1.1	6.88	0.5
8.80	2.1	7.42	1.2
23 w/w % CaCl <sub>2</sub> sol.			
Series 1		Aqueous phase only	
5.98	-8.9	6.65	-4.3
8.01	-5.8	7.48	-3.5
10.01	-4.5	8.23	-2.7
Series 2		Aqueous phase + oil	
6.20	-9.2	6.82	-4.1
7.91	-6.7	7.30	-3.5
8.99	-5.8	7.85	-3.0
9.95	-5.4	8.18	-2.2

These results are plotted in  $T(P)$  diagram reported in Fig. 6. No experimental data were found in literature for concentrated calcium chloride solutions. PVT and DSC points are perfectly concordant for the 20% solution.

For 23% solutions, PVT and DSC results show important discrepancies, DSC points being 4 to 5°C lower than PVT points. Since the two techniques gave very concordant results with pure water and 20% CaCl<sub>2</sub> solution, the difference observed with the 23% CaCl<sub>2</sub> solutions is surprising. As the two sets of experiments were conducted in different laboratories and by different operators, we assume that it should be attributed to a difference in salt concentration. Considering the very strong salt effect at these concentrations, a difference of no more than 1 to 2 percent in mass would be sufficient to explain the shift in dissociation temperatures. The two series of DSC points also exhibit some differences, of nearly 0.5°C over the whole pressure range. Two different solutions, prepared in the same conditions, and which concentrations were verified by density measurement and found to be 23.0±0.2 mass%, were used



**Fig. 6** Dissociation temperature of methane hydrate vs. pressure in various calcium chloride solutions - PVT (square marks) and DSC (triangle marks) results

for these determinations. The composition of solutions used in the PVT measurements were not verified, and we thus suggest that DSC points are more accurate for the 23 mass%  $\text{CaCl}_2$  solution.

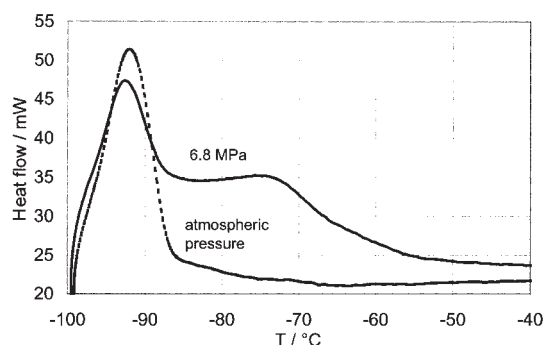
#### Methane hydrate in water-in-oil emulsions

Heat flow signals during the cooling period were recorded as a test of stability and droplet size homogeneity of the emulsion. Because the temperature at which crystallisation occurs is a function of sample size, the crystallisation of the aqueous phase in a mono-disperse water-in-oil emulsion should result in a perfectly regular gaussian peak. The temperature of the peak maximum, which corresponds to the most probable temperature of crystallisation, is an indication of the droplet size [10]: the lower the crystallisation temperature, the thinner the droplets are. Any modification in shape or position of this peak indicates an alteration of the emulsion properties. Figure 7 reports two examples of curves recorded during the cooling sequence with an emulsion, at atmospheric pressure and under 6.8 MPa of methane. The two ice crystallization peaks are perfectly gaussian shaped, indicating that pressure does not affect the emulsion stability. The eutectic crystallization could not be observed in emulsion because the supercooling degree reached during cooling was not sufficient.

Under methane pressure, an additional peak is observed prior to ice crystallization, which we attributed to hydrate formation, occurring at a very low temperature after rupture of metastability. The peak shape clearly indicates that hydrate formation proceeds until ice crystallization occurs.

Figure 8 reports the curves recorded during the heating sequence of an emulsion composed of a 20% mass/mass  $\text{CaCl}_2$  solution in oil, under 8.0 MPa of methane. Upon heating, curves of water-in-oil emulsions under methane pressure are generally composed of two peaks, often appearing partially merged and difficult to distinguish: the first one caused by the ice progressive melting, and the second one attributed to hydrate dissociation. As eutectic does not crystallize, its peak of melting is normally not present on curves, and when it is, this is an indication that the emulsion was not stable.

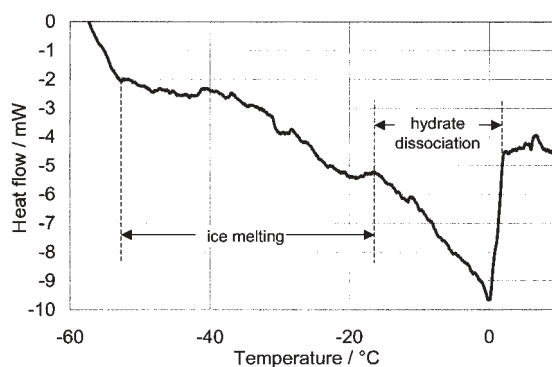




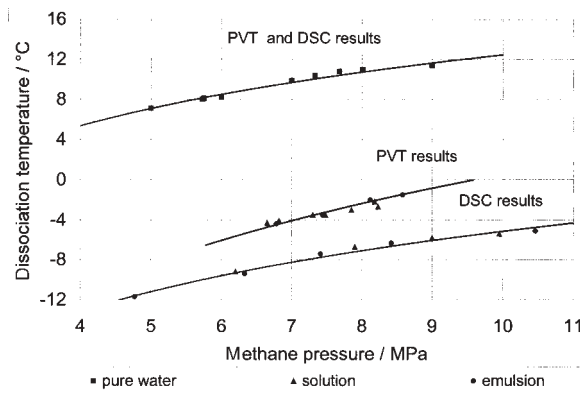
**Fig. 7** DSC curves recorded during cooling of an emulsion at atmospheric pressure and under methane pressure

The dissociation peak exhibits a progressive shape that can be interpreted as follows: in bulk solutions, if no efficient agitation is provided, the hydrate formation occurs at the liquid-gas interface and stops when methane diffusion toward the water phase is impeded by the hydrate film, leaving the salt concentration nearly unchanged. Hydrate dissociation in this case is a mono-thermal transformation occurring at the equilibrium temperature corresponding to the pressure fixed.

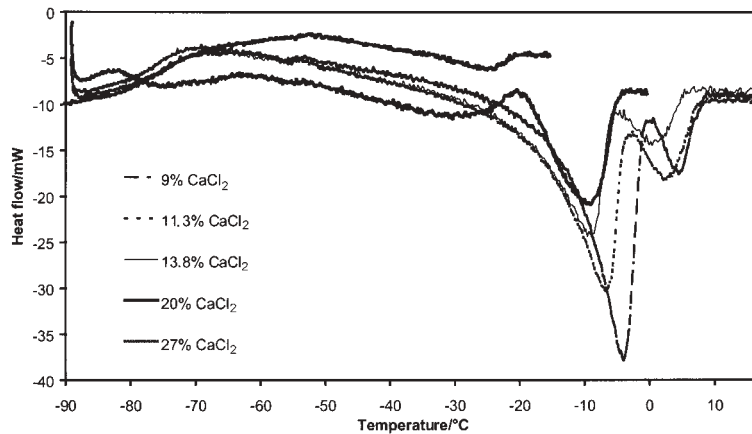
Emulsions offer a much greater interface between the aqueous phase and the methane rich phase, allowing the formation of considerably greater amounts of hydrate. The lack of agitation is not limiting in this case since methane dissolution in oil and diffusion to the oil/water interface is much faster than in a bulk aqueous phase. Hydrate formation causes the salt to concentrate in the remaining water. Thus, when equilibrium is reached, the hydrate is in presence of a very concentrated salt solution. According to the shell model proposed by Hanai *et al.* [11], each droplet in the emulsion may be represented as a hydrate shell surrounding a salt solution core which concentration depends on the shell thickness. During the heating phase, hydrate dissociation proceeds as a succession of equilibrium states between methane hydrate and a calcium chloride solution which concentration progressively decreases. Initial salt



**Fig. 8** Example of a water-in-oil emulsion (20% mass/mass  $\text{CaCl}_2$ ) heating curve at a methane pressure of 8.0 MPa



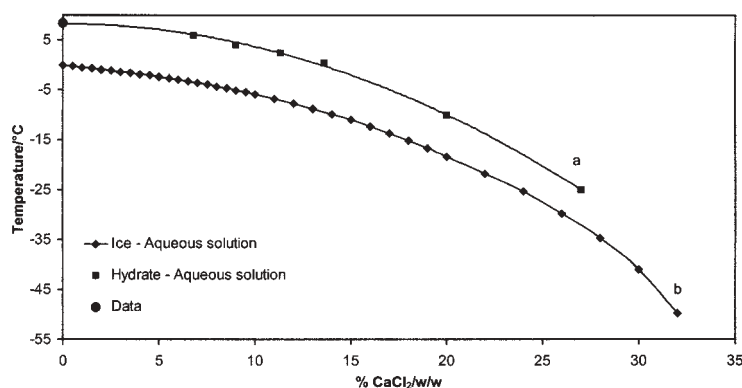
**Fig. 9** Hydrate dissociation temperature vs. methane pressure in bulk calcium chloride solutions and water-in-oil emulsion measured by PVT and DSC



**Fig. 10** DSC curves showing the dissociation of trichlorofluorocarbon hydrate in water-in-oil emulsions of varying calcium chloride concentration

concentration is reached back when the last hydrate crystal disappears; at this point, the heat flow is maximum. The equilibrium temperature must be obtained in such case by projecting the peak top on the temperature axis, in a direction parallel to the raising front of a mono-thermal transformation, such as the eutectic melting, in order to account for the thermal resistance of the heat flow sensor.

Table 2 reports the methane hydrate dissociation points obtained using an emulsion containing 70% of oil and 30% of a 23 mass%  $\text{CaCl}_2$  solution. As for solutions, the discrepancies between the two sets of results should be attributed to a slight difference in salt concentration. Notice that the emulsions used for these measurements were prepared using the same solutions as in the bulk dissociation points measurements. Thus, the difference in concentration between DSC and PVT measurements was rigorously the same in emulsion experiments than in bulk experiments.



**Fig. 11** Dissociation temperature of  $\text{CCl}_3\text{F}$  hydrate in water-in-oil emulsion vs.  $\text{CaCl}_2$  concentration measured by DSC, compared with the water- $\text{CaCl}_2$  phase diagram

**Table 2** Temperatures of methane hydrate dissociation in water-in-oil emulsion, DSC and PVT results at various pressures

DSC		PVT	
Methane pressure/MPa	Dissociation temperature/°C	Methane pressure/MPa	Dissociation temperature/°C
4.77	-11.7	6.78	-4.4
6.33	-9.4	7.44	-3.5
7.41	-7.4	8.12	-2.0
8.42	-6.3	8.58	-1.5
10.46	-5.1		

These results are presented in a  $T(P)$  diagram in Fig. 9, in which PVT and DSC points concerning pure water are repeated as reference points. Equilibrium points measured in bulk solution are also reported in the same diagram, so it can be seen that bulk and emulsion points are not significantly different, provided that the salt concentration in the aqueous phase is the same. This is an important point, that confirms that neither the oil nor the emulsifier have any effect on the hydrate stability, and that thermodynamic conditions of stability established in the bulk phase are still valid in emulsion. In particular, thermodynamic models used to predict hydrate stability could be applied to emulsions with no further modification.

#### *Model hydrate of trichlorofluoromethane in water-in-oil emulsion*

Examples of curves obtained on heating water-in-oil emulsions of varying calcium chloride concentration in the presence of trichlorofluoromethane are reported in Fig. 10. Emulsion stability depends greatly on the salt concentration. With the lower concentrated solutions, emulsion instability is attested by the presence of a small peak at  $-52^\circ\text{C}$ , featuring the melting of small amounts of the water- $\text{CaCl}_2$  eutectic, which is

never observed with a stable emulsion. The further peak is attributed to ice progressive melting, and the last one to hydrate dissociation. As for methane hydrate in emulsions, equilibrium temperatures were obtained by projecting the peak top on the baseline, in a direction parallel with the raising front of a mono-thermal transformation, such as the eutectic peak of a bulk solution.

The results can be represented in a diagram of equilibrium of  $\text{CCl}_3\text{F}$  hydrate as a function of  $\text{CaCl}_2$  concentration, reported in Fig. 11 together with the binary phase diagram of the  $\text{H}_2\text{O}-\text{CaCl}_2$  system. The point marked 'Data' corresponding to pure water comes from Wittstruck *et al.* [12]. Obviously, the salt concentration has very similar effects on the  $\text{CCl}_3\text{F}+\text{H}_2\text{O}$  hydrate-liquid equilibrium and on the water solid-liquid equilibrium. The same type of diagram on methane hydrate at varying pressure is under study.

## Conclusions

This work demonstrates the feasibility of thermodynamics study by differential scanning calorimetry, not only on model hydrates that form at atmospheric pressure, but also on high pressure gas hydrates. Results are in good agreement with literature data, as well as PVT points presented in this paper for pure water. In high concentration calcium chloride solutions, PVT and DSC are in good agreement too, despite the discrepancies observed in some cases, caused by slight differences of concentration.

One important conclusion of the study is that the thermodynamic conditions of stability of methane hydrates do not seem to be modified from bulk solutions to water-in-oil emulsions, as shown by PVT as well as DSC results. However, DSC measurements show that kinetics of hydrate formation, independently of any agitation, is much faster in emulsion than in solution, due to the much greater specific area of the interface between water and the methane-rich phase.

DSC is especially appropriate for studies in complex systems such as emulsions, where the lack of agitation is not limiting, and it would be interesting to apply the method to a complete drilling mud in order to test the kinetic and thermodynamic effects of solid particles on hydrate formation and stability. Further work is also needed to determine the hydrate enthalpy of dissociation in a broad range of temperatures. This would be useful for curves integration, leading to the possibility of quantitatively studying hydrate formation kinetics.

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