Characterization of CO_2 clathrate formation and dissociation using High Pressure DSC

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BACKGROUND

Carbon capture and sequestration (CCS) technologies play a critical part in the attempts to reduce the atmospheric carbon dioxide content. Common CO_2 sequestration techniques involve direct injection into geologic formations such as depleted oil or gas reservoirs, or deep unminable coal seams.

An alternative approach is the injection of CO_2 into natural methane hydrate deposits in ocean sediments. In this case, formation of carbon dioxide hydrates is expected, together with a dissociation of methane hydrates. Examples include:

- SECOHYA (SEparation of CO_2 by HYdrate Absorption, France)
- SUGAR (Submarine GAs hydrate Reservoirs, Germany)

EXPERIMENTAL CALORIMETRY SET-UP

Calorimetry has proved to be a valuable technique in the investigation of gas hydrate formation and dissociation [1,2]. It allows determining compositions, dissociation enthalpies and heat capacities. As high pressure is needed for gas hydrate investigations, calorimeters have been designed with vessels operating up to 1 000 bars and temperatures between –120℃ and 600℃. A dedicated high pressure panel is attached to the HP calorimeters to cover the pressure range. Tests can be conducted under isothermal, isobaric, temperature scanning or pressure scanning conditions.

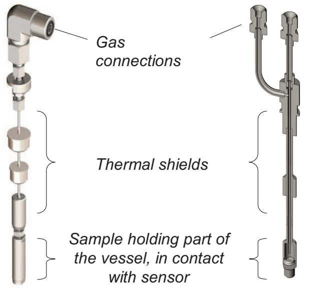

Figure 1 – Schematics of the high pressure vessel used with µDSC7 (left, -45℃ to 120℃, up to 400 or 1000bar) and SENSYS (ri ght, -120℃ to 600℃, 400bar)

This approach, together with the Joule effect technology used to calibrate these Calvet calorimeters, allow the sensitivity of the instrument (i.e. the electrical signal / evolved sample heat effect ratio) to be pressure independent. It avoids repetitive and long standard melting calibration procedures at each tested pressures.

CO_2 HYDRATE MELTING

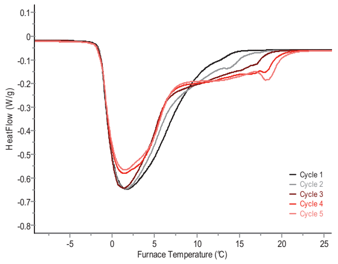

Figure 2 – DSC thermograms recorded during successive heating cycles of a same sample of 10% THF aqueous solution

A sample of 269.51mg of 10wt% THF solution in water was tested under 20 bar of CO_2. It was heated up to 80℃ to erase any thermal history, and then cooled down to -20℃. Then it was thermally cycled between -20℃ and 70℃ at 1℃.min^{-1}.

Figure 2 shows the decrease of the free water melting peak (0 to 10℃) with cycles and the appearance of a CO_2/THF co-hydrate melting peak (10℃ to 17.5℃) and of the hydrate melting peak (17.5℃ to 20℃).

EFFECT OF CYCLING

Figure 3 shows the mathematical separation (Marquard routine fitting assymetric Gaussian peaks) of the three underlying peaks of heating cycle 5.

The heat of melting of the CO_2 hydrate is equal to 12.18 J.g^{-1} of solution, i.e. 13.56 J.g^{-1} of water. The comparison with litterature value of the heat of dissociation of CO_2 hydrate (ΔH_{diss}= 500,11 J.g^{-1} H2O [3]) allows determining a ratio of hydrate formation of 2.7%.

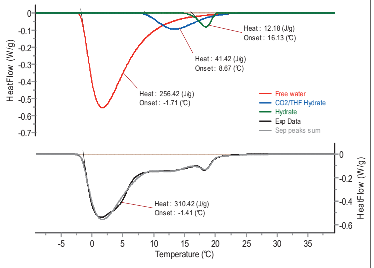

Figure 3 – Separation of the thermal contributions of the melting of free water, CO_2/THF co-hydrate, and CO_2 hydrate for heating cycle 5

Figure 4 shows the effect of 28 heating and cooling cycles between -15℃ and 5℃ at 1℃.min^{-1} on a 37.55mg sample of the same THF solution. A constant CO_2 pressure of 20 bar was applied. Free water melting peak disappreared in favor of the co-clathrate and the hydrate.

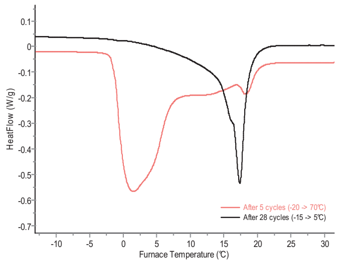

Figure 4 – Comparison of the number of heating / cooling cycles

EFFECT OF THF

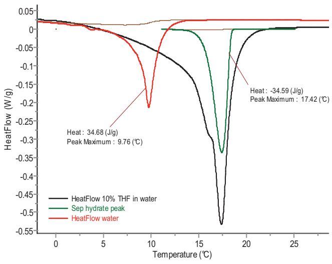

Figure 5 – Comparison of DSC thermograms recorded after cycling a water sample (red) and a 10% THF aqueous solution (black) 28 times between -15℃ and 5℃. The green curve corresponds to the separation of the CO_2 hydrate form of the water / THF test.

A 29.48 mg sample of deionized water was tested under 20 bar of CO_2. It was cycled between -15℃ and 5℃ at 1℃.min^{-1} 28 times and then heated up to 70℃ at 1℃.min^{-1}. Figure 5 clearly shows the stabilizing effect due the presence of THF in the hydrate structure (peak temperature shift of 7.7℃).

Despite the absence of water melting peak, hydrates of pure water and THF melting peaks respectively correspond to 6.93% and 6.92% only. Free water probably did not crystallize or slowly melted during the cycles

CONCLUSION

High Pressure DSC is a fast, repeatable and accurate method for the studies of formation and dissociation of carbon dioxide hydrates. It provides the thermodynamic data necessary to understand their structures.

For instance, it was shown that a few test allowed checking the enhancing or inhibiting effects of additives on CO_2 hydrate formation for sequestration. The measurement of heat of formation/dissociation is also a key point in the promising development of CO_2 hydrates as a crystalline suspension in secondary refrigeration fluids.

[1] Prediction of Gas Hydrates Formation With DSC Technique, C. Dalmazzone, B. Herzhaft, L. Rousseau, P. Le Parlouer, D. Dalmazzone, Society of Petroleum Engineers 84315 (2003)

[2] Modelling of the available latent heat of a CO2 hydrate slurry in an experimental loop applied to secondary refrigeration, S. Marinhas, A. Delahaye, L. Fournaison, D. Dalmazzone, W. Fürst, J-P. Petitet, Chemical Engineering and Processing 45 (2006) 184–192

[3] Kanget al. JCT 2001, 33(5), 513 –522

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