

Morphology and distribution structure characterization of methane hydrate formed in the presence of amphiphilic anti-agglomerant additive.

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I. Micro differential scanning calorimeter

I.1. Apparatus

The impact of AA additive on the natural gas dissociation has been investigated by using a micro differential scanning calorimeter from Kep Technologies (Figure S1). Two cells have been prepared: the first cell contain the sample, and the second cell contain natural gas as reference cell.

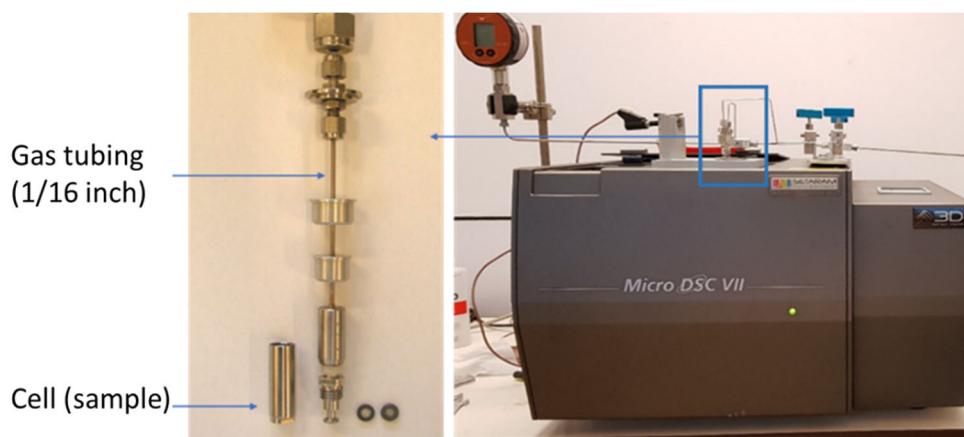


Figure S1 : Differential scanning calorimeter apparatus and cells.

The apparatus measures the temperatures of the sample (T_s) and the reference (T_r). The experimental measurement is based on the heat flow difference between the sample and the reference as a function of temperature and is defined by Equation S1.

$$\frac{dh}{dt} = (C_e - C_r) \frac{dT_p}{dt} + R \cdot C_e \cdot \frac{dq^2}{dt^2} + \frac{dq}{dt}$$

Equation S1

Where dh/dt represent the heat exchange by the sample (W). dq/dt is the power recorded by the apparatus (W). C_e , C_r are the heat capacities of the sample and the reference (J/K). T_p is the temperature of the thermostat block (K). R is the thermal resistance between the sample and the furnace (K/W). t is the time (s).

I.2. Procedure

The experimental procedure consists of 3 stages:

- In the first stage, a cooling cycle is performed from 20 to -40 °C at a cooling rate of 10 °C/min, where the aqueous phase transform into ice (Figure S2).
- In the second step, 20 cycles of cooling/heating are carried out between -40 °C and 5 °C at a constant rate of 3 °C/min (Figure S2). In this stage, during the cooling cycle from 5 to -40 °C, the water transforms into ice, and during the heating cycle from -40 to 5 °C (above the melting temperature of ice), the ice transforms into liquid water, which instantly converts into natural gas hydrate. Repeating the cycles 20 times allow to maximize the conversion rate of water into natural gas hydrate.

- Finally, in the third step, a heating cycle is applied from $-40\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ at a very slow heating rate of $0.1\text{ }^{\circ}\text{C}/\text{min}$ (Figure S2). This step is of interest, because during this stage, hydrates dissociate, and dissociation peaks are obtained on the thermogram.

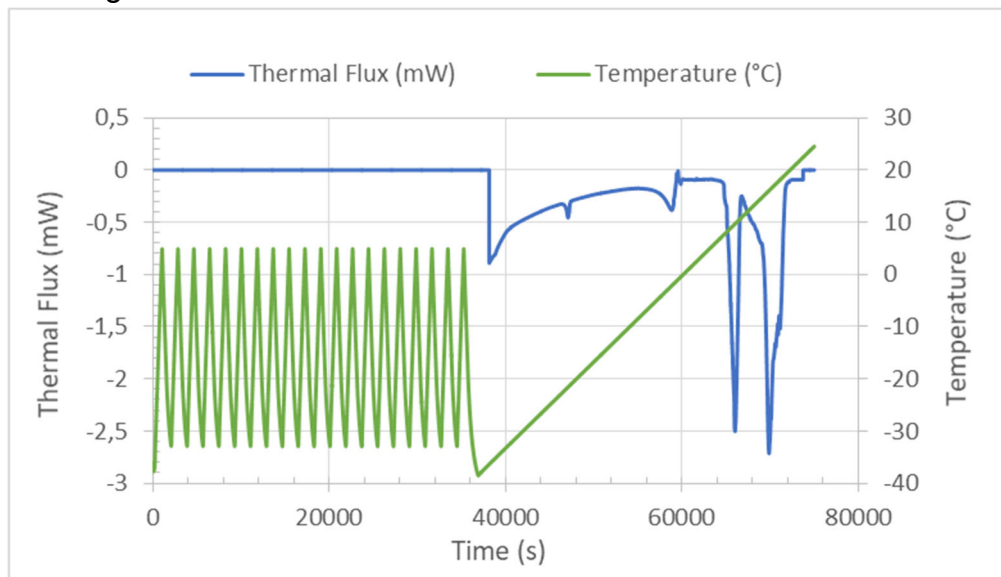


Figure S2: Calorimeter experimental Procedure

I.3. System Studied

The experiments were conducted for water/natural gas systems in the presence of amphiphilic anti-agglomerant additive (AA), at a constant pressure of 70 bar, and without agitation. The salinity of the aqueous phase is 5 g/L NaCl.

I.4. Thermograms and dissociation points

Without additive AA, various endothermic peaks were detected during the dissociation of natural gas hydrates at 70 bar (Figure S3). These peaks correspond to the dissociation of hydrates of structures SI and SII. The dissociation temperature of hydrate structure I is $7.9\text{ }^{\circ}\text{C}$. The dissociation temperature for hydrate structure II is $14.8\text{ }^{\circ}\text{C}$. Other bands appear between 18 and $20\text{ }^{\circ}\text{C}$. In the presence of AA additive, no dissociation peak detected for hydrate structure I in the temperature range of 8 to $11\text{ }^{\circ}\text{C}$ (Figure S3), unlike the dissociation of hydrates without the AA additive. The dissociation peaks of hydrate structure SII are detected in the same temperature range as well as the reference system without additive (Figure S3). With AA additive the hydrates dissociating is close to $15\text{ }^{\circ}\text{C}$ and a main peak at close to $18\text{ }^{\circ}\text{C}$.

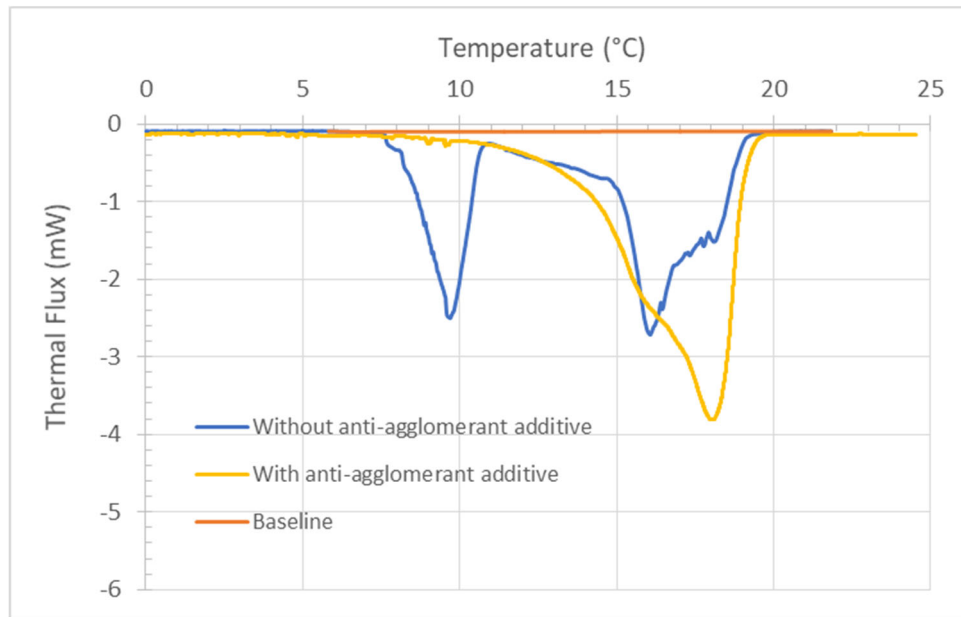


Figure S3 : Thermogram of natural gas hydrate dissociation at 70 bar with AA additive at 1% wt. (yellow curve) and without AA additive (blue curve), at a dissociation rate of 0.1 °C/min.

II. Raman Spectroscopy and estimation of phases distribution

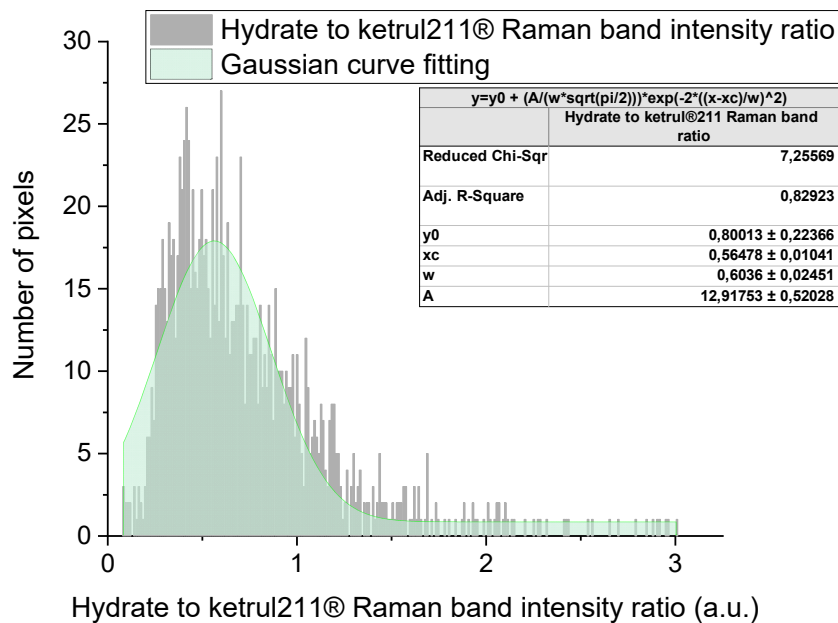


Figure S4 : Raman data for 1200 pixels over Intensity's values.

The relative concentration value has been estimated by analysing the Raman intensities. In this calculation, the Raman polarizability variations have been neglected. The following method has been used:

- The 2D mapping data (Figure 9) have been extracted and plotted by the number of 1200 pixels over the intensity's value (Figure S4).

- The curve has been fitted then by the Gaussian function. The top threshold of the curve represents the Gaussian function's center coordination (x_c, y_c). Here, x_c represent the maximum intensity value have been achieved by the most pixels. By this, all pixels up to x_c represent the hydrate-rich-zone, and all pixels below the x_c represents the ketrul211®-rich-zone.
- The integral of the whole curve has been applied (I_0). Then, the area of the curves from the threshold x_c was integrated (I_c). The ratio of integral (I_0/I_c) give the methane hydrate-rich-zone inside the 2D area.