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MODULATED DSC FOR GAS HYDRATES ANALYSIS

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Modulated DSC has been applied to the study of methane, ethane and propane hydrates at different hydrate and ice concentrations. The reversing component of the TMDSC curves, makes it possible to characterize such hydrates.

Methane and ethane hydrates show the melting-decomposition peak at a temperatures higher than the ice contained in the sample, while propane hydrate melts and decomposes at lower temperature than the ice present in the sample. The hydrate peaks tend to disappear if the hydrate is stored at atmospheric pressure. Guest size and cavity occupation fix the heat of dissociation and stability of the hydrates, as confirmed by parallel tests on tetrahydrofurane hydrates.

***Keywords:** DSC modulated, ethane, gas hydrates, methane, propane hydrates*

Introduction

Gas hydrates (or clathrates) are ice like structures composed by a host lattice consisting of hydrogen-bonded water molecules that host small gaseous molecules (CH_4, C_2H_6, C_3H_8, CO_2, H_2S, etc.). In nature they are ubiquitous and can occur if T and P conditions are satisfied [1–5].

Three clathrate hydrate structures are currently known, identified by the symbols sI, sII and sH [1, 2, 6]; the existence of the sH structure was confirmed more recently and extended the size of the largest possible guests. Structure I can host small molecules such as methane and ethane, while structure II can also host larger molecules such as propane and isobutane [6–8]. The cubic sI cell contains $46H_2O$ molecules, two 12-hedra (5^{12}) and six 14-hedra ($5^{12}6^2$); where 5^{12} is used to indicate that the polyhedron contains 12 five-member ring faces. The cubic sII cell contains 136 water molecules, eight large voids ($5^{12}6^4$) and sixteen 12-hedra [8]. Structure H hydrates will not be considered here.

Methane molecules preferably occupy and stabilize the 5^{12} cavities; when 'alone', they are contained also in $5^{12}6^2$ cavities of sI. Ethane occupies the $5^{12}6^2$ cavities of sI.

Propane molecules stabilize the $5^{12}6^4$ cavities of sII, while the smaller cavities are left empty and, therefore, not stabilized by the gas; as a consequence the maximum gas content of propane hydrate is inferior respect to methane and ethane hydrates: in fact, the hydration number is 5, 9–7.6 and 17.0 respectively for CH_4, C_2H_6 and C_3H_8 hydrates [2, 6].

Natural gas mixtures containing propane usually form sII hydrates [6, 8]; in the same way, if a substance with a suitable molecular diameter, such as tetrahydrofurane, THF, is added to the water/methane system, a sII hydrate may form [2, 9].

A number of techniques have been employed to study gas hydrates [1, 6]; however, the successful application of these techniques is sometimes hampered by their inability to distinguish between ice and hydrate or by the necessity to have especially modified apparatus to produce the hydrate inside the analytical instrument.

NMR and Raman spectroscopy are normally used for hydrate characterization [10–12]. Differential scanning calorimetry (DSC) is a rapid and sensitive technique: it has been used by a number of authors to study gas hydrates [7, 13–19].

Because the gas hydrates are generally stable under pressure of the hydrate forming gas, the calorimeters should generally be equipped for studying of samples under pressure, or the technique should be limited to the study of model hydrates [1, 14].

Modulated DSC (TMDSC) is a technique that overcomes a number of limitations of conventional analytical calorimetry; up to now it has been mostly used to study polymer transitions. A recent application to propane hydrate is known [19].

The TMDSC concept involves the imposition of a sinusoidal wave on a thermally linear heating ramp so that portions of each cycle are at different heating and cooling rates, although the general overall trend is a linear change in average temperature.

The mode of modulation affords the thermal analyst an opportunity to study a physical or chemical change in greater detail.

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One of the major contributions of this technique and analysis is that total heat flow rate can be separated into two additional signals following the general differential function proposed by some authors [20].

$$\delta Q/\delta T=C_p dT/dt+f(T,t)$$

The first term of the equation is directly correlated to the heat capacity of the material, while the second is a function of temperature and time characteristic of tests. These terms can be plotted separately in two curves. One of these curves represents the component which is heating rate-dependent (i.e. which in phase with the modulated heating); it is frequently defined as 'thermodynamic' component and associated to a 'reversing heat flow'. The second curve corresponds to the rate of heat flow which depends only on the absolute temperature (i.e. which is out of phase with the modulated heating): it is usually defined a 'kinetic' component and associated to a non-reversing heat flow.

Events associated with polymers which are non-reversing on the period of the oscillation are: molecular relaxations, cold crystallization, evaporation, thermoset cure, and decomposition.

The changes in C_p at the glass transition and the endothermic effect due to melting are, on the contrary, normally reversible.

The purpose of the present paper was to study the possibility of applying the TMDSC technique, at normal pressure, to the characterization of hydrocarbon gas hydrates such as methane, ethane and propane hydrates. In particular, the possibility to distinguish the sI and sII crystal structures and to detect the presence of ice was investigated.

Experimental

Materials

Hydrocarbon hydrates were prepared in a stirred vessel similar to that used by Stern *et al.* 1996 by combining pressurized gas with granular ice seeds at low temperature. The experimental procedure has been described in a previous paper [19]. The composition of the gases is reported in Table 1; the hydrate content in the obtained icy solid is given in Table 2. The amount of hydrate formed during the process was evaluated from the pressure drop in the reactor and by measuring the mass losses of the overcooled hydrates, on an analytical balance [19]. This was possible at room pressure also for methane hydrate which is preserved in bulk for a short time as much as 80 K above its nominal equilibrium temperature, at one bar pressure [21, 22].

The purpose of the work was to prepare hydrates containing a certain amount of ice, to be analyzed by TMDSC; these types of hydrates are found in the natural state and are normally produced in laboratory unless special procedures are applied [22, 23]. In our case the hydrate concentrations were 42–34, 36–14 and 20–8%, respectively for CH_4, C_2H_6, C_3H_8 (Table 2).

Samples overcooled to –20°C were used for the TMDSC tests. Due to the hydrate poor stability at room conditions, the exact mass determination of the CH_4 hydrate samples used for DSC test was not possible; in fact, both weighing and transferring them to TMDSC instrument took a time longer than the preservation time of methane hydrate.

Tetrahydrofurane (THF) hydrates were prepared as reference purposes by mixing THF and water in the ratio 1/17, at 2°C.

Methods

All TMDSC tests were carried out on a Thermal Analyst model 2920 (TA Instruments). A refrigerating cooling system was used with a flow rate of 50 mL min^{-1} of nitrogen. The instrument was calibrated for the temperature using indium at heating and cooling scanning rates of 2°C min^{-1}. The heat flow was calibrated with heat of fusion of indium, the heat capacity constant was calibrated with the heat capacity of sapphire using modulation amplitude of ±0.5°C every 60 s. Samples (10–15 mg) were heated at 5°C min^{-1} heating rate, with a modulation amplitude ±0.5°C every 60 s in temperature range between –20 and 20°C.

Results and discussion

The TMDSC curves of pure ice are given in Fig. 1, as a reference; the ice fusion peak is at 0.9°C in the reversing heat flow curve, which is better defined in respect to the similar total (or DSC traditional) curve.

The non-reversing curve also shows an exothermic effect, probably due to molecular relaxation phe-

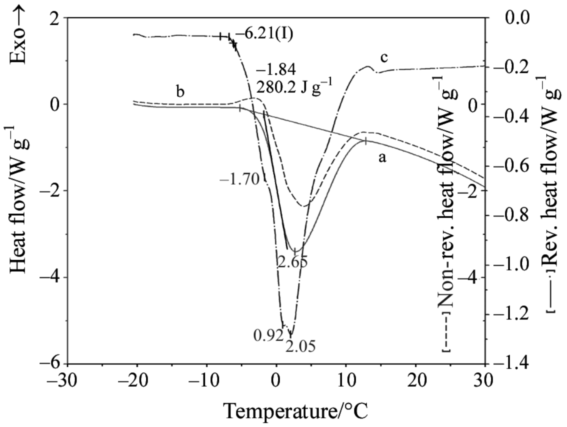

Fig. 1 TMDSC curves of pure ice. a – total heat flow; b – kinetic component; c – reversing component

Table 1 Gas composition (vol %)

	C_3H_8	C_2H_6	CH_4	H_2O	H_2	N_2	Ethylene	Propylene	Other hydrocarb	i-C_4H_{10}	n-C_4H_{10}	CO_2	CO	S^-
Propane	99.9	0.04		0.0003	0.013			0.001	0.005	0.03	0.01	0.0005	0.0001	0.0001
Ethane	0.005	99.6	0.09		0.25		0.05	0.005						
Methane			99.7	0.002		0.25			0.048					

Table 2 Hydrate content in the sample

	Hydrate mass/%	
Sample	A	B
Propane	20	8
Ethane	36	14
Methane	42	34

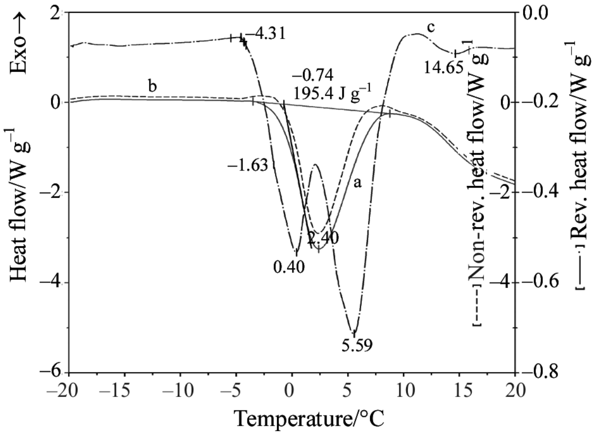

Fig. 3 TMDSC curves of ethane hydrate (35%); a – total heat flow, b – kinetic component, c – reversing component

nomena [24]. The TMDSC curves at room pressure of CH_4, C_2H_6 and C_3H_8 hydrates produced as previously described, are shown in Figs 2–4, respectively. In each figure the continuous line represents the traditional DSC curve, while the dash-dotted and dashed lines are referred to the reversing component and to the non-reversing component, respectively.

Methane hydrates have recently been studied by Dalmazzone *et al.* using a pressure DSC system and a $CaCl_2$ solution [16, 17]; the hydrate dissociation peak is visible under high CH_4 pressures, after the progressive melting of ice. No DSC data are available for ethane hydrates.

In the TMDSC curves of CH_4 hydrate (Fig. 2) the total and non-reversing curves show a unique endothermic effect, while the reversing curve is split into two peaks with the apex at 0.25 and 4.47°C, respectively. The first peak is due to the melting of the ice and the second is due to melting and decomposition of the CH_4 hydrate.

The ethane hydrate TMDSC curves (Fig. 3) are similar due to the fact that the same sI structure is common to both CH_4 and C_2H_6 clathrates. Both for CH_4 and C_2H_6 hydrate samples, the second peak is reduced when the hydrate content in the sample is less, and tends to disappear if the TMDSC tests are performed long after hydrate formation (Fig. 4).

Due to slightly different hydrate compositions and to a number of unavoidable experimental factors, the repeatability of the tests was defined by ten analysis for each hydrate.

A quantitative TMDSC evaluation of the hydrate CH_4 and C_2H_6 content in the sample seems not possible, also due to the partial superimposition of the ice and hydrate peaks.

In respect to pure ice curves, in the hydrate tests there is a shifting of the fusion peak to lower temperatures; the simultaneous presence of both ice and hydrate structures seems to weaken the ice lattice.

In the case of propane hydrate (Fig. 5), the total heat flow is similar to the corresponding ice curves, but the reversing curves are completely different. A new endothermic effect appears with the onset at –4.34°C and a peak temperature at –1.47°C; the ice fusion is superimposed at 3.05°C. The area of the hydrate peak is proportional to the content in the sample [19], as shown in Fig. 6 and tends to disappear if the hydrate is stored at low pressure.

Apparently the differences between CH_4 and C_2H_6 curves on one side, and C_3H_8 curves on the other side, could be attributed to the existence of different

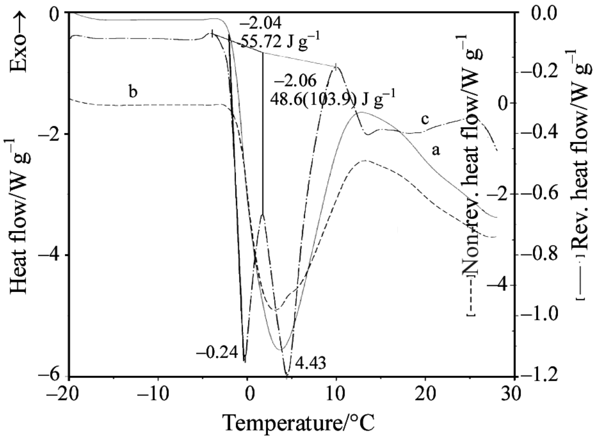

Fig. 2 TMDSC curves of methane hydrate (44%); a – total heat flow, b – kinetic component, c – reversing component

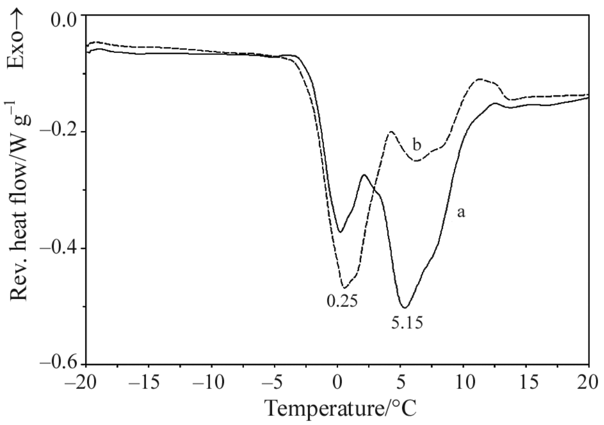

Fig. 4 Reversing TMDSC curves of methane hydrates with different ice content; a – 20% hydrate, b – 8% hydrate

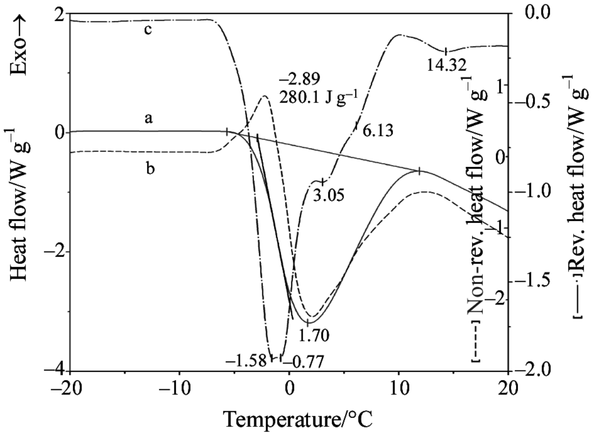

Fig. 5 TMDSC curves of propane hydrate (20%); a – total heat flow, b – kinetic component, c – reversing component

structures: sI for both methane and ethane hydrates, and sII for propane hydrate. In fact, propane sII hydrate is less stable in respect to sI hydrates due to a minor cavity occupation [2, 6, 8] and forms sII hydrates with 17.0 maximum hydration number, while methane and ethane forms sI hydrates with 5.9 and 7.6 hydration number, respectively [6].

However, this hypothesis was not confirmed by some TMDSC tests carried out on THF which forms sII hydrates like propane [2, 9]. Figure 7 shows the TMDSC curves of THF hydrates, where the THF hydrate peak (at about 8°C) comes after the ice peak, according to previous studies [25].

Therefore, the switch between the peak sides for ice and hydrate in CH_4 (or C_2H_6) hydrates and C_3H_8 can be better explained in terms of heat of dissociation of the hydrate structure, which is not only function of the hydrogen bonds in the crystal, but it is also determined by cavity occupation; guest size and occupation fix the heat of dissociation [2] and stability; as a consequence, the decomposition of propane hydrates is shown by the TMDSC curves at lower temperature, in respect to methane and ethane hydrates.

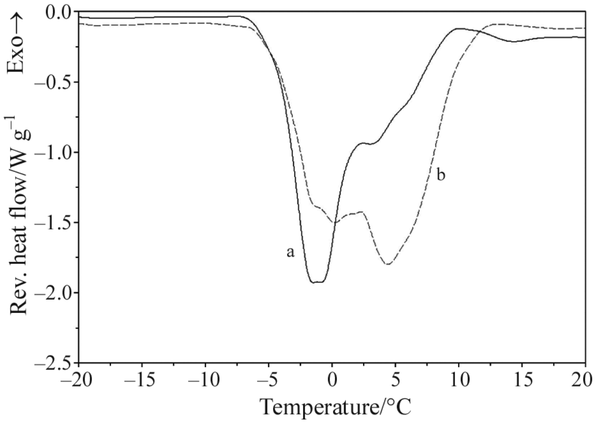

Fig. 6 Reversing TMDSC curves of propane hydrates with different ice content; a – 20% hydrate, b – 8% hydrate

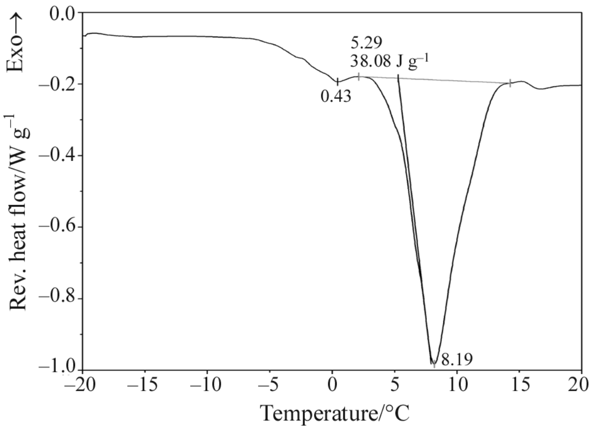

Fig. 7 TMDSC reversing curve of THF hydrate

The THF hydrates, forming the same sII structure of propane, are more stable than propane hydrates because of the higher cavity occupation: in fact in this case a stoichiometric hydrate is formed [25].

Conclusions

The thermal modulated DSC can be used to study hydrate structures. Differently from the normal DSC, the reversing component of TMDSC can highlight differences between different hydrates. Methane and ethane hydrates (sI) decompose after the melting of the ice present in the sample; on the contrary, propane hydrates melt and decompose at temperatures slightly lower than the ice; however, THF hydrates, which have the same sII structure of propane hydrates do not show the switch between the ice and hydrate peaks. This behavior seems to confirm that the results of the dissociation and stability tests depends both on hydrogen bonds and cavity occupation.

The hydrate melting peak area is roughly proportional to the hydrate content in the sample; for propane hydrates it can give an indication of hydrate content.

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