Formation of trichlorofluoromethane hydrate in w/o emulsions studied by differential scanning calorimetry

Abstract The presence of trichlorofluoromethane hydrate in bulk water and in water-in-oil emulsions has been detected by differential scanning calorimetry. Hydrates have been observed during the heating of samples introduced into the head of a calorimeter. The amount of hydrate crystals was found to be dependent on the sample volume, the temperature reached during the cooling performed prior to the heating, and the time spent at the subambient temperature. These results confirm the kinetic aspects of hydrate formation and show that ice crystals may act as hydrate nucleating agents. Furthermore, two polymorphic forms are suspected to exist, but this must be confirmed by another technique.

Key words Clathrate hydrate – CCl$_3$F – Water in oil emulsion – Calorimetry

Introduction

At low temperature and under high pressure conditions, present in off-shore oil and gas exploitation and processing, water molecules may incorporate some natural gases and form crystalline ice-like compounds, called clathrate hydrates. During the multiphase transport of crude oil, water and natural gases, these conditions may occur, leading to the formation of clathrate hydrates, which in turn can lead to serious problems such as plugs in pipelines. The interest of the oil industry in these hydrates has, consequently, given rise to some extensive studies [1]. In order to avoid hydrate formation, thermodynamic approaches have been used to a great extent but without success. It was then proposed that surfactants be added in order to form emulsified clathrate hydrates. In this way, transportation is made easier, agglomeration is reduced and it is possible to recover components by breaking the emulsions formed [2, 3]. In order to obtain information about the formation of emulsified hydrates, different studies dealing withhydrate formation in a model water-in-oil emulsion have been undertaken, using time-domain dielectric spectroscopy [4, 5]. In this paper, it is shown that by means of differential scanning calorimetry (DSC) on the emulsions, it is possible to detect hydrate formation through the energy involved in the melting of the hydrates formed during cooling of the emulsions. This work has been carried out in collaboration with Professor Sjöblom’s team. In order to obtain more information on the hydrates themselves, their formation in bulk water has been studied by DSC.

Material and methods

Bulk hydrate crystal formation was studied using a DSC 111 Setaram calorimeter. The volume of the calorimeter cell is approximately 250 $\mu$l. Due to the insolubility of CCl$_3$F in water, and the small size of the cell, the hydrate crystals had to be prepared outside the cell. Hydrates were obtained in a beaker by adding CCl$_3$F to bulk water in stoichiometric proportions at 1 $^\circ$C, under constant vigorous stirring for at least 1 h. The prepared crystals were introduced into an aluminium cell and put in the calorimeter head at 1 $^\circ$C. The conversion of water into hydrate...
crystals is never complete; therefore some of the bulk water always remains within the crystals. It was necessary to determine the mass of the crystals in order to calculate the enthalpy of hydrate dissociation. For that purpose, the cell was cooled from 1 °C to −34 °C to freeze the enclosed water, followed by heating to 14 °C to observe ice melting and hydrate dissociation.

Hydrate formation in dispersed systems was studied using a DSC 2 Perkin Elmer calorimeter. For that purpose a sample was introduced into an aluminium cell, the volume of which was around 20 ml, placed in the calorimeter head and submitted to various cooling-heating cycles (rates: 2.5–5 °C/min).

The materials used for making the emulsions are described in detail in Ref. [3]. Using a mixer (Polytron PT 3000 at 7200 rpm for 10 min), deionized water containing 1 wt% NaCl was dispersed in an oil phase consisting of a mixture of aliphatic and cycloaliphatic hydrocarbons (Exxol D-80). The commercial surfactant used was the non-ionic, tetraoxyethylene nonyl-phenyl ether (Berol 26). After mixing, the emulsion was cooled to 3 °C, the temperature at which hydrate formation is expected to take place. According to Ref. [3], as soon as this temperature is reached CCl₃F should be added and is believed to dissolve in the oil phase. The amount of CCl₃F added was 1.0 mol ratio relative to water.

Results and discussion

Bulk samples

The melting thermogram of the bulk hydrate crystals obtained by subsequent heating is shown in Fig. 1. The range of temperatures between −34 °C and −12 °C is not presented because no signals were observed.

Two separate signals (I and II) are observed, one starting at about 0 °C (I) and the second at about 10 °C (II). The first signal has been attributed to melting of the ice formed during cooling, and the second signal at 10 °C has been attributed exclusively to the dissociation of hydrate crystals. CCl₃F forms a hydrate which is stable up to 8.5 °C and has the composition CCl₃F·16.6 H₂O [6]. The energy of hydrate dissociation is given by the following expression:

\[
L_{\text{hydrate}} = \frac{\Delta H_{\text{hydrate}}}{m_{\text{hydrate}}}
\]

The mass of the hydrate crystals \(m_{\text{hydrate}}\) is calculated by taking the difference between the total sample mass and the water mass. The mass of water is deduced from the area of the ice melting peak (I), which gives the energy involved during the transition and permits us to determine the quantity of water, knowing its latent heat of fusion. \(\Delta H_{\text{hydrate}}\) is deduced from the area of signal II. Using this method, the enthalpy of hydrate dissociation is estimated to be 234 J g⁻¹.

Dispersed systems

No hydrate crystals were observed when the emulsion was maintained at 3 °C for 2 h without stirring. This result is in agreement with the statement that kinetic effects have to be taken into account during hydrate formation [7, 8]. Therefore, nucleation phenomena and the probability of hydrate formation, involving parameters such as time, temperature and volume of sample, have to be considered. Another factor which has to be taken into account is the influence of nucleating agents promoting nucleation. The results obtained from working with bulk systems have shown that ice crystals could be hydrate nucleating agents, insofar as the hydrate crystal formation in bulk iced water is immediate. This point was proved by the following experiment. The emulsion was regularly cooled from

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Fig. 1 First cycle thermogram showing the melting of ice and dissociation of hydrate crystals formed in bulk water