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Effect of hydrate formation/dissociation on emulsion stability using DSC and visual techniques

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ABSTRACT

A key factor in hydrate risk management for an oil-dominated system is the stability of the emulsified water with gas hydrate formation. We show via differential scanning calorimetry (DSC) that gas hydrate formation and dissociation has a destabilizing effect on water-in-oil (W/O) emulsions, and can lead to a free water phase through agglomeration and coalescence of dissociated hydrate particles. High asphaltene content crude oils are shown to resist hydrate destabilization of the emulsion. Span80 was successfully used as an analog to asphaltene surface activity. Based on our experimental results, a new conceptual hydrate-induced destabilization model is proposed.

1. Introduction

Gas hydrates are crystalline clathrate compounds comprised of hydrogen bonded water cavities which encapsulate suitably sized gas molecules at high pressures and low temperatures. Gas hydrate formation in subsea gas and oil transmission lines can block flowlines, resulting in catastrophic safety and economic problems. As gas and oil exploration and production move to ultradeep water (>8000 ft of sea water), the risk of hydrate formation increases significantly (Sloan and Koh, 2008). Under these conditions, traditional methods of hydrate avoidance become increasingly uneconomic and ecologically unsound. Emulsion stability has been suggested to be a determining factor for hydrate agglomeration during shut-in conditions in a pipeline and also one key factor under flowing conditions (Fadnes, 1996; Hemmingsen et al., 2007). One conceptual picture for hydrate formation in water-in-oil (W/O) emulsions is shown in Fig. 1.

The ability for the emulsified droplets to remain segregated under shut-in conditions as well as flowing conditions with hydrate formation/ dissociation is crucial to preventing hydrate plug formation. This paper focuses on the effect of hydrates on emulsion stability, and the ability of the emulsified droplets to stay segregated with hydrate formation. The stability of W/O emulsions with hydrate formation was investigated with differential scanning calorimetry (DSC), using different crude oils with varying emulsion stability.

2. Experimental method

2.1. Apparatus

A high pressure micro-differential scanning calorimeter (μ-DSC VIIa, Setaram Inc.) was used to measure the thermal properties of ice and hydrate in W/O emulsified systems. The μ-DSC can be used to measure properties at both atmospheric and pressurized conditions (Setaram, 2003). The pressure is controlled by a gas pressure panel in which a piston can be used to charge the sample with gas at pressures ranging from 1 to 400 bar.

The thermocouples in the calorimetric furnace measure the temperature difference between the reference and sample cells, and the heat necessary to achieve a zero temperature difference between the cells is recorded (Sorai, 1998).

The W/O emulsified samples were prepared using a Cyclone IQ^2 Microprocessor Controlled Homogenizer (VirTis Co.). The homogenizer shaft used was a 10 mm rotor/stator shaft assembly. The homogenizer emulsified the mixture at 8000 rpm for 150 s. The emulsion characteristics depend on the preparation procedure (Salager, 2007) (i.e. homogenization speed, time, addition of water). For these experiments, the water was added to the oil drop-wise during the homogenization.

2.2. Modes of operation

A 10–30 mg sample was placed into the sample cell. Methane, at 150 bar, was introduced into the sample cell at 30 °C. Two different modes were used in the DSC: ramped and isothermal.

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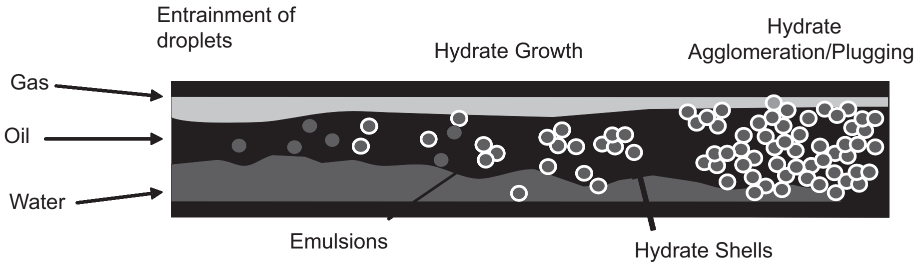

Fig. 1. Conceptual picture of hydrate agglomeration and plug formation in water-in-oil emulsions in a flowing condition.

Table 1
Crude oil properties

Crude oil	Viscosity (cP) 20 °C	Asph. (wt%)	Resin (wt%)	TAN
Crude A[a]	247	7.12	9.36	N/A
Crude B[b]	262	6.2	20.5	0.7
Crude C[b]	147	4.6	9.9	0.3
Crude D[b]	22	3.3	11.2	2.5

[a] Measurements by Baseline DGSI Analytical Laboratories (SARA).

[b] Measurements by Norwegian University of Science and Technology (SARA).

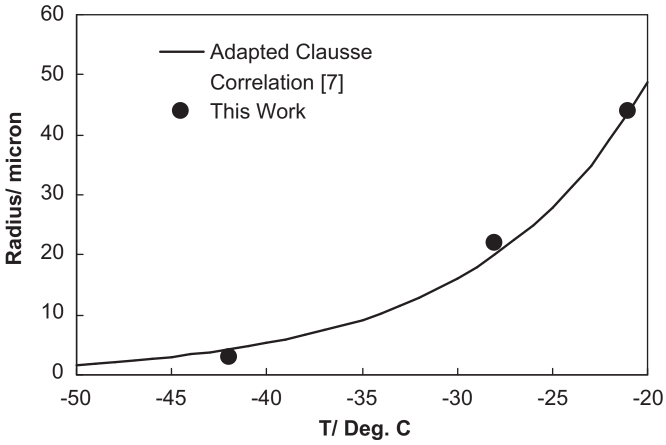

Fig. 2. Radius of water droplets versus ice nucleation temperature (Clausse et al., 2005). Dots are measurements performed in this laboratory (Lachance, 2008).

The temperature-ramp mode was used to cool the sample from 30 to −45 °C at 0.5 °C/min. The sample temperature was then increased to 30 °C. This cooling–heating cycle was repeated three times to observe the effects of ice/hydrate on the emulsions.

The isothermal mode was used after the sample was cooled from 30 to −10 °C at 0.5 °C/min. The sample was held at this temperature for approximately 6 h. Upon hydrate formation, the sample was heated to dissociate the hydrate. The runs were repeated two times to observe the effect of hydrate on the emulsions (no ice formation was observed in these isothermal runs).

2.3. Materials

Crude oils were used as the continuous phase of the W/O emulsions. The oils that were used in this study are listed in Table 1.

The emulsion stability was measured using the DSC over a one month time period using the procedure outlined by Clausse et al. (2005), who showed that larger droplets nucleated at higher temperatures compared to smaller droplets. Fig. 2 shows the Clausse correlation along with measurements from this laboratory (Clausse et al., 2005; Lachance, 2008). These trends provided the basis for determining emulsion destabilization in our crude oils. As the emulsion was destabilized, the droplets coalesced to form larger droplets compared to the droplets in the original, stable emulsion. Fig. 3 shows an example emulsion stability test with the Crude A.

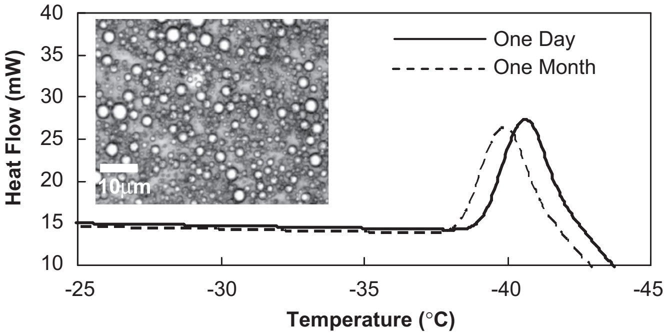

Fig. 3. Emulsion stability test of Crude A. Thermograms for emulsions after 1 day and after one month time. Inset: microscope image of the water-in-oil emulsion aged for 1 day.

Table 2
Emulsion stability of crude oils using DSC

Crude	ΔT °C	Stability	Drop size (µm)
Crude A	0.6	High	< 10
Crude B	0.9	High	< 10
Crude C	1.2	High	< 10
Crude D	7.2	Moderate	5–25

$\Delta T = |T(1\,\text{day}) - T(1\,\text{month})|$ High $= \Delta T < 2\,^\circ$C, moderate $= 2\,^\circ\text{C} < \Delta T < 8\,^\circ$C, low $= 8\,^\circ\text{C} < \Delta T < 15\,^\circ$C.

After ageing the emulsion for one month, the ice nucleation peak shifted to a higher temperature compared to the one day-old emulsion, indicating coalescence/emulsion destabilization. The shift in the ice nucleation peak by less than 1 °C in Crude A indicates that this crude is very stable. Additionally, using the Clausse correlation, the droplet size in Crude A was determined to be less than 10 µm. This was in agreement with the microscopic image (inset Fig. 3). Table 2 shows the results of the emulsion stability tests for all the crude oils in this study.

Crudes A–C formed stable emulsions, while Crude D showed moderate destabilization in the 1 month time period. No free water phase was observed with these crude oils. HPLC water (Aldrich Inc.) was used in these studies at a concentration of 30 wt% in oil. Hydrates were formed using methane (99.99% purity, AirGas) at 150 bar ($T_{\text{diss.}} = 16.3\,^\circ$C, Ballard, 2001).