

Evaluation of anti-agglomerate hydrate inhibitor in water-in-crude oil emulsions of different water cut

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A commercially available anti-agglomerant was evaluated in water-in-crude oil emulsions at different water cut. The injection of an anti-agglomerant to an emulsion affects the induction time and rate of hydrate formation. When the anti-agglomerant was injected before emulsification, the anti-agglomerant performed better due to the higher number of anti-agglomerant molecules at the hydrate surface has been increased. The transition from stable a water-in-crude oil emulsion to a stable hydrate-in-crude oil suspension takes place without hydrate agglomeration in the presence of the anti-agglomerant, so the results obtained can be applied for developing deep-water transport technologies of crude oil under pipeline conditions.

Keywords: crude oil, water-in-crude oil emulsions, gas hydrates, hydrates inhibitors, anti-agglomerant

1. Introduction

Gas hydrates are crystalline solids that form at high pressure and contain molecules of water and gases such as methane, ethane, propane, and carbon dioxide (Sloan 2000). Through its structure, hydrate particles have the capacity to agglomerate, which poses serious risks to pipeline in multiphase transport of crude oil water and gas. Particularly, it can lead to blockage of long-distance transport pipelines (Gayet et al. 2005). The risk of hydrate agglomeration increases substantially under the low-temperature conditions at North regions. This especially applies to the Arctic sea shelf, with crude oil produced under severe climatic conditions.

Risks of gas hydrate formation can be reduced by injecting of different chemicals. For example, thermodynamic inhibitors (THIs) such as methanol are often added to subsea petroleum transport streams to prevent hydrate formation (Anderson, Prausnitz 1986). However, THIs are economically inefficient and can be a risk for the

environment due to the large volumetric requirements and high toxicity. Low dosage hydrate inhibitors (LDHIs) can be the solution since they require a significantly lower dosage (from 0.5 to 3.0 wt %) compared to THIs (Kelland 2006). Two types of LDHIs exist namely kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). KHIs delay nucleation and decrease hydrate growth rate. AAs prevent agglomeration of hydrate particles, but not their formation, and enable the transport of gas hydrate as a slurry. The main economic advantage of LDHIs is a significant reduction in capital costs by reducing the chemical consumption and operating expenses (Heidaryan et al. 2010), regardless the unit costs of LDHIs are higher than THIs. Despite a number of advantages, AAs have still not widely studied as, for example, THIs. Only a limited number of works related to evaluating AAs in emulsions can be found in the literature (Zheng et al. 2017, Sun et al. 2015, Zhao, Sun, and Firoozabadi 2016, Gao 2009, Huo et al. 2001, [Chen et al. 2013](#), [Song et al. 2020](#)). Most of these publications have been performed using model systems. Meanwhile, behaviour of real crude oil systems has been poorly described. Therefore, this work is aimed at the evaluation of the commercial AA in relation to the formation of methane hydrate in water-in-crude oil emulsions at various water cuts in order to create stable hydrate-in-crude oil dispersions, suitable for transportation. The influence of AA and method of its introduction on the kinetic of hydrate formation has been determined.

2. Materials and methods

2.2. Materials

A dewatered North Sea crude oil (19° API) was used as an oil phase to prepare water-in-crude oil emulsions. The amount of emulsified water in the crude oil sample is 0.06 %. The content of saturates, aromatics, resins, and asphaltenes (SARA) is equal to 37.4,

44.1, 16.1, and 2.54, respectively. The aqueous solution of sodium chloride with a concentration of 3.5 wt. % (Sigma Aldrich, USA) was used as an aqueous phase. A commercially available anti-agglomerant (AA) provided by Nalco Champion was used as a low dosage hydrate inhibitor for hydrate blockage prevention. The AA contains a quaternary surfactant as an active component. The concentration of AA used was 2.0 vol. % based on the aqueous phase volume fraction in the emulsion sample. Methane (99.5 % purity) was used as hydrate-forming gas.

2.2. Water-in-crude oil emulsions and their characterization

Water-in-crude oil emulsions (W/CO) were prepared by mixing with Ultra-Turrax T25 Digital homogenizer (IKA, Germany) at 8000 rpm for 5 min at the ambient temperature (23 ± 1 °C). Aqueous phase volume fraction in emulsions or water cut (ϕ) was 10, 20, 30 and 40 vol. %. The following types of W/CO emulsions were prepared: emulsions, which does not contain AA, and emulsions containing AA where: (a) – AA was added into the experimental cell filled with freshly prepared emulsion sample, i.e. after emulsification; (b) – AA was dropwise added into the mixture of crude oil and aqueous phase during emulsification immediately after adding an aqueous phase. The average diameter of aqueous droplets in emulsions obtained is equal to 3 μm and practically independent on the aqueous phase volume fraction in emulsions.

The stability of W/CO emulsions was studied by using LUMiSizer Dispersion Analyzer 613.2-122 (LUM, Germany). The intensity of transmitted light was measured as a function of time and position over the entire sample length in a cuvette during centrifugation. Emulsion samples were centrifuged at a speed of 2,493 rpm at 20 °C to capture 255 transmission profiles at an interval of 68 s using a wavelength of 865 nm. Figure 1a shows that the transmission along the cell remained constant and close to 0 % during centrifugation, which means that aqueous droplets remained well-dispersed in

the crude oil under centrifugal forces, and therefore no light was transmitted. The overlay of the profiles obtained immediately after the start of the centrifugation (68 s) and after the centrifugation (17340 s) confirms the high separation stability of the emulsions.

The viscosity of the emulsions was measured using a Physica MCR 302 stress-controlled rheometer (Anton Paar, Austria) with a cone-plate measuring unit at ambient pressure. The viscosity of emulsions is growing by several orders of magnitude with the decrease of temperature from 30 to 4 °C (Figure 1b). The higher the concentration of the emulsion, the more sharply the viscosity increases. As the dispersed phase volume fraction increases, the inter-drop interactions lead to increase friction, thereby causing the viscosity growth.

2.3. Hydrate formation test

The hydrate formation experiments were performed with Sapphire Rocking Cells RCS20 apparatus (PSL Systemtechnik, Germany). RCS20 contains 20 pressure cells made of sapphire tubes. Each tube has a volume of 20 mL and equipped with a stainless-steel ball and pressure transducer. The cells were rocking which causes a ball to roll back and forth the entire length of the test cell, mixing the enclosed fluid-gas mixture. In each hydrate test, the cells were filled with 10 mL of analysed fluid. System, contained 20 sapphire cells and filled with analysed fluids, was immersed into a glycol/water tank and held at 24 °C for 1 hour. Then, the analysed fluids were saturated with methane at 24 °C for 6 hours at the constant rocking rate of 2 rocking/min at angle of 45° until no further gas consumption was observed. The gas working pressure was set at 200 bars. After that, the system was cooled from 24 °C to 6 °C at the constant cooling rate of 3 °C/hour into the hydrate region to make sure that hydrates will be formed. Then, the system was held at 6°C for 13-18 hours at the constant rocking to

evaluate the effectiveness of the AA. The amount of methane consumed during the hydrate formation was calculated as the difference between the number of moles of the gas present in the cell at time t_0 (beginning of the experiment) and the number of moles of the gas at time t :

$$\Delta n = \left(\frac{PV}{ZRT} \right)_0 - \left(\frac{PV}{ZRT} \right)_t \quad (1)$$

where P, V and T refer to the pressure, volume and temperature respectively; Z is the compressibility factor (Gayet et al. 2005, Peng, Robinson 1976) and R is the universal gas constant.

3. Results and discussion

3.1. Hydrate formation in emulsions without anti-agglomerant

The samples of model brine and crude oil were first evaluated to determine the hydrate formation potential. The typical profiles of the cell pressure and ball running time for synthetic brine are shown in Figure 2a. The sharp pressure drop indicates the beginning of the hydrate formation as the gas molecules are incorporated into the denser gas hydrate structure. The time required from the start of the experiment to the first sign of hydrate formation is also known as induction time (t_{ind}). Figure 2a demonstrates that induction time of hydrate formation in model brine is equal to approximately 5 hours. At the same time, the ball is completely immobilized by hydrates and cannot move between sensors (the ball running time is 0).

Hydrate formation is not observed in the dry crude oil sample since it does not contain any water (Figure 2b). The pressure steadily decreases with time before reaching a plateau due to the solubility of methane in the undersaturated crude oil. This decrease is also related to the change in pressure with temperature. The steel ball moves

freely between two proximity sensors in the crude oil sample during the experiment duration.

The sample of W/CO emulsion at water cut of 30 %, which did not contain the AA, was evaluated by recording the pressure and the ball running time (Figure 2c). The initial sharp pressure drop corresponds to the absorption of the gas in the system (Section 1, Figure 2c). As the equilibrium is reached, the pressure linearly decreases due to the change in temperature inside the cell during the cooling step (Section 2, Figure 2c). The second sharp drop is attributed to the gas hydrate formation, where the induction time of hydrate formation is equal to ca.7 hours (Section 3, Figure 2c). After 7 hours the pressure slowly decreases, i.e. gas hydrates continue to form but at a much slower rate (Section 4, Figure 2c). Fig. 6c also shows that steel ball does not move between the sensors inside the cell filled with an emulsion sample of 30 % water cut after the pressure drop was observed. Thus, once the hydrate plugs are formed, the ball is trapped, so it cannot pass the sensors anymore.

Similar experiments were performed for emulsion samples with the water cuts of 10, 20 and 40 vol. % (Table 1a). As the volume fraction growth, the induction time slightly decreases, whereas the pressure, at which a sharp drop observed, becomes higher (Table 1a). The probability of hydrate nucleation in emulsions increases with an increase in the water content due to the raising of the gas-water interfacial area.

3.2. Effectiveness of anti-agglomerant

The commercial anti-agglomerant (AA) was introduced into W/CO emulsion at water cut of 30 % before and after the emulsification to evaluate the effectiveness of the AA. The AA prevents hydrate agglomeration and consequently eliminate the following cell blockage by hydrates; the ball freely moves along the cell between two sensors (Figures 3a, 3b). Once the hydrates formed, the ball motion becomes slower, apparently,

reflecting the increasing the viscosity of hydrate-in-crude oil suspension. The AA increases the induction time of hydrate formation up to 12 hours when it is introduced after the emulsification. The addition of the AA before emulsification leads to an even greater increase in the induction time of hydrate formation and moves this parameter up to 12-14 hours (Figure 3b). The analogical experiments were performed at the water cut of 10, 20 and 40 % (Table 1b).

The amount of methane consumed during the hydrate formation was calculated using the Equation 1 and presented in Figure 4. First, a slight decrease in the methane content was observed in the range of 0.5 to 10 or 14 hours, which is attributed to the gas dissolution and following hydrate nucleation. Thus, the induction time of hydrate formation can be defined as a width of this interval. Then, the amount of methane consumed sharply increased, with an accompanying rapid growth of hydrates due to the incorporation of gas molecules into the dense hydrate structure. With the increase in the number of gas molecules consumed, the hydrate formation rate gradually declines until the process of hydrate formation is complete. The instantaneous rate of hydrate formation was calculated as a slope of the linear portion of the kinetic curves of methane consumption which corresponds to the stage of the hydrate growth. As shown in Figure 5, the rate of hydrate formation is slightly lower for the systems where the AA was introduced before emulsification. It should also be noted that the amount of methane consumed, and the rate of hydrate formation regularly increase with an increase of aqueous phase volume fraction. Thereby, if the AA is injected before emulsification, the induction time of hydrate formation increases, whereas the amount of methane consumed slightly decreases because the AA can adsorb onto the water-oil interface together with natural surfactants of crude oil (asphaltenes, naphthenic acids, etc.) during the emulsification. As a result, a greater number of the AA molecules

located on the droplet surface. As the AA interact with the hydrate surface, the number of the AA molecules on the hydrate surface increases further during the hydrate growth, thereby reducing the number of zones where hydrates can aggregate. In consequence, the transition from the water-in-crude oil emulsion to hydrate-in-crude oil suspension takes place without hydrate agglomeration.

4. Conclusions

The commercially available anti-agglomerant (AA) was evaluated in water-in crude oil emulsions at different water cut (10-40 vol. %) by using a rocking cell apparatus. It was shown that the AA proved to be more effective in water-in crude-oil emulsions, with the AA addition before emulsification. In this case, the induction time of hydrate formation increases by approximately 2-4 hours, while the instantaneous rate of hydrate formation decreases, in comparison with emulsions where AA was injected after emulsification. The results obtained are expected to provide a scientific basis for the development of new technology of subsea transportation of liquid hydrocarbons even at low temperatures specific to the far North region.

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