Study of self-preservation of gas hydrates in suspensions in oils

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Abstract. Impact of different parameters on the decomposition rates of hydrate at negative temperatures with depressurisation method has been studied. In previous work it was demonstrated that decomposition rates of hydrates suspensions in oil at static conditions can be limited by the self-preservation phenomenon. Our experimental research shows that appearance of self-preservation depends on many parameters such as components composition of oil, presence of shear in the system while decomposing hydrates and probably on the history of the sample.

1. Introduction

Gas hydrates are crystalline inclusion compounds which framework is built of water molecules and gas molecules are located in the cages of the framework. Typically the interaction between the guest gas molecules and the host water framework is van-der-Waals type [1]. Gas hydrates are formed at high pressures and/or low temperature conditions and their exact P-T stability boundary depends on compositions of gas mixture and brine [1]. In the last years gas hydrates are attracting more and more attention primarily due to the fact that tremendous amount of energy is stored in the sea bottom and in permafrost regions in the form of gas hydrates [1,2].

Another reason of growing interest to gas hydrates both from researchers and from industry is their ability to plug oil and gas pipelines causing flow assurance problems [2,3]. The most traditional way to prevent the issues related to hydrates formation in the equipment is usage of hydrate thermodynamic inhibitors (THI) which shift hydrates stability boundary to higher pressure and lower temperatures [3,4]. In the last time two classes of low dosage hydrates inhibitors (LDHI) are becoming more and more widely used in industry: kinetic inhibitors (KHI) and anti-agglomerates (AA) [3,5]. The KHI impede hydrates nucleation or growth and their performance usually is limited by sub-coolings [5]. AA prevent hydrates particles from agglomeration so hydrates can flow downstream with oil as slurry [5].

Despite all efforts and money that companies put for prevention of hydrate plugs formation in the pipelines, the plugs still form and remediation measures are required to get rid of them [4,6,7,8]. In order to dissociate the hydrate plugs commonly people depressurize the pipelines [4]. After the pressure is bled off, the P-T conditions in the pipelines become outside of the hydrate stability boundary so the plug is supposed to dissociate. The dissociation rate of hydrate in the pipelines can be limited by kinetic effects. Hydrate self-preservation phenomenon is the kinetic effect of retardation of decomposition rate due to formation of ice shell around the hydrate particles [9]. This ice shell limits diffusion rate of the gas molecules outside of the hydrate which limits dissociation rates of hydrates [9,10]. Despite the fact
that with increase of hydrate particle size this effect becomes more pronounced [11] the experimental results show that self-preservation may take place with fine particles (size around few tens of microns) of hydrate if they are dispersed in crude oils [12,13].

In this work we tried to investigate if different parameters have impact on self-preservation while decomposing suspension of hydrates at negative temperatures. Experiments with different oils, different mixing speeds and with different histories of samples have been performed.

2. Experimental

2.1. Materials

Methane 99.99 % of purity was used as the hydrate forming gas. All emulsions were prepared with distilled water. Samples of oils were supplied by Tomsk Institute of Petroleum Chemistry. Two crude oils (A and B) and one oil after 30 days of biodegradation (A-30) were used for the studies. The basic properties of the used oils along with their SARA component composition are presented in Table 1.

Table 1. Basic physical properties and SARA component composition of oils used for studies.

| Oil  | Basic physical properties | Component composition % |
|------|---------------------------|--------------------------|
|      | Viscosity mPa s | Density g/cm³ | Saturates | Aromatic | Resins | Asphaltenes |
| A    | 3.47             | 0.845            | 83.3      | 3.0      | 10.2   | 3.5        |
| A-30 | 43.38            | 0.866            | 75.1      | 8.3      | 5.4    | 4.2        |
| B    | 37.14            | 0.876            | 82.3      |          | 12.1   | 5.7        |

2.2. Experimental apparatus

Autoclave stirred cells were used to perform the experiments. The schematic of the setup is given in Figure 1. The setup consists of the reactor cell (V=250 cm³) where the oil and water (or emulsion) were loaded. The reactor cell has impeller inside of it for agitation of emulsion/suspension during the experiment with controlled rotation speed. This configuration of setup was used for isochoric experiments (Figure 1 left).

For the experiments at isobaric conditions gas reservoir cell (V=250 cm³) and the pressure reducer controlling the pressure inside reactor (Figure 1 right) were additionally hooked up to the reactor cell. Pressure probes were connected both to the reservoir and to the reactor. The reactor had a temperature probe as well. This thermocouple was inserted to the cell in a way to measure temperature of the emulsion or suspension. Both gas reservoir and reactor were placed into the thermostats. Pressures inside the both chambers and temperature inside the reactor were recorded throughout the all experiments.

2.3. Experimental procedure

For all tests emulsions with mass ratio oil/water = 50/50 were used. Oil and water were loaded to the cell of reactor. The cell was purged at least 2 times with 10 bars of methane and pressurized with this
gas up to required pressure. The reactor has been left at 20°C while the impeller was spinning with rotation speed 650 RPM for 24 hours to saturate emulsion with gas. After emulsion saturation the temperature of thermostat with the reactor cell was set at -5°C so the P-T conditions inside the cell are within the hydrate stability boundary. Formation of hydrates was confirmed both with spike on the temperature curve and with increase of slope on the pressure decline curve. Hydrate formation stage was finished after pressure both in the reactor and in the reservoir becomes stable.

After that the cell was cooled down to -10°C and the pressure in the reactor was decreases down to 1bar. Increase of pressure in the reactor was observed due to decomposition of hydrates. In the end of each decomposition stage the temperature of the reactor cell was raised back up to 20°C to see if there was undecomposed hydrate. Typical pressure and temperature profiles for the gas formation and gas dissociation stages of experiments are shown in Figure 2.

![Figure 2. Typical pressure and temperature profiles for the hydrate formation stage (left) and hydrate decomposition stage (right).](image)

Peng-Robinson equation of state was used to calculate amount of gas consumed during hydrate formation process or quantity of gas released during the hydrate decomposition. Mass of formed or decomposed hydrates was calculated considering the composition of gas hydrate CH₄*6H₂O [14].

3. Results and discussion

3.1. Impact of presence of shear in the system and impact of chemical composition of oil

In previous work it was shown that at static conditions if hydrate suspension decomposes at negative temperatures the self-preservation effect always takes place regardless of oil in which hydrate was dispersed. Low decomposition rates of hydrate were observed for all studied suspensions with different oils. So first of all for us it was interesting to see if decomposition rate of suspended hydrate depends on the presence of shear. In Figure 3 the kinetic curves of hydrate decomposition process for cases when dispersion was agitated with mixing speed 100 RPM are presented. In the first series we performed experiments with A crude oil and A-30 biodegraded oil.
Figure 3. The kinetic curves of hydrate decomposition processes obtained with A crude oil and with A-30 biodegraded oil. Hydrate formation was performed at $T=-5^\circ C$, $P_{\text{const}}=125$ bar and at 100 RPM. Decomposition was performed at $T=-10^\circ C$ while mixing at 100 RPM.

Very high decomposition rates of hydrate were observed with A crude oil, all hydrates were decomposed after 3 hours. However decomposition rate of hydrate dispersed in biodegraded oil A-30 was dramatically lower compared to one obtained with crude oil (Figure 3). We believe that this dramatic difference can be explained by the change of component composition of oil due to biodegradation process (Table 1) and by adsorption of biodegradation products on the surface of the hydrate particles [15]. So far we can't propose the exact mechanism how products of biodegradation limit hydrate decomposition rate but we believe that adsorbing on the surface of hydrate they create more favorable conditions for formation of the ice shell around hydrate particles. This creates impedance for diffusion of methane molecules outside of hydrate particles limiting their decomposition rate.

Another conclusion from this series of experiments is probable dependence of hydrate decomposition rate on the presence of shear. Previous results obtained with A crude oil at the same temperature but at static conditions showed that self-preservation always took place (unpublished data), but in our experiments obtained when decomposition of hydrate was performed while mixing the suspension there was no self-preservation.

3.2. Impact of presence of mixing and of history of the sample of decomposition rate of hydrates suspension

The second series of experiments was performed to see impact of shear on the decomposition rate of hydrate as well. The tests were done with emulsion obtained with B crude oil. The hydrate formation stage for all experiments within this series was performed at isochoric conditions with initial pressure of methane 155bar. The mixing rate of impeller during the hydrate formation stage was adjusted at 200 RPM to speed up the hydrate formation process. The decomposition of hydrate was performed at different mixing velocities. The feature of this series of experiments is that all experiments were conducted with the same oil/water sample without reloading. After each test the oil/water mixture was heated up to 60°C and the temperature was kept at this value for 1 hour. This was done to make sure that all oil components that might precipitate during the experiments would be dissolved back in the oil. After that the temperature was decreased down to 20°C and the sample was pressurized with methane for experiment. Six cycles of experiment have been performed during this series. The kinetic curves for hydrate decomposition process obtained with this series of experiments for the first (at 0RPM) second (at 100 RPM) and sixth (0RPM) cycles are presented in Figure 4.
Dramatically different hydrate decomposition rates have been obtained in the first cycle and in the sixth cycle of experiments despite of in both cases the decomposition was conducted at static conditions. The same time there was no difference in decomposition rates of hydrate in the first cycle at 0 RPM and in the second cycle at 100 RPM. From these series of experiments one may conclude that history of the sample may have an impact on the presence of self-preservation phenomena while decomposing hydrate.

3.3. Impact of history of the sample on decomposition rate of hydrates suspension without mixing

The third series of experiments has been performed to separate impact of history of the sample from the impact of mixing on the decomposition rates of hydrate. For this series we loaded new oil/water sample. Several experiments of hydrate formation/decomposition have been conducted with that same sample without reloading. All experiments in this series were conducted with the same procedure. Hydrate formation was done at the same conditions as in the previous series, and all decomposition tests were done at static conditions without mixing. Kinetic curves for the hydrate decomposition process for the first and for the fourth cycles of series are presented in Figure 5.

Figure 4. Kinetic curves of hydrate decomposition processes obtained with B crude oil. Hydrate formation was performed at $T=-5^\circ C$, $P_{\text{init}}=155$ bar and at 200 RPM. Decomposition was performed at $T=-10^\circ C$ while mixing at 0, 100 and 0 RPM.

Figure 5. Kinetic curves of hydrate decomposition processes obtained with B crude oil. Hydrate formation was performed at $T=-5^\circ C$, $P_{\text{init}}=155$ bar and at 200 RPM. Decomposition was performed at $T=-10^\circ C$ without stirring.

The decomposition rates of hydrate on the first cycle and on the fourth cycle of hydrate formation / decomposition cycle were not significantly different from each other. From these results one can
understand that if hydrates are decomposed at static conditions it does not affect decomposition rates of hydrates in the next cycle.

Conclusions
Impact of different parameters on decomposition rates of hydrate was studied. It was shown that the presence of shear in the system may help to get rid of self-preservation effect and consequently to speed up hydrate decomposition rates dramatically.

Presence of shear does not lead to disappearance of self-preservation always and apparently this effect depends on composition of oil in which hydrates are dispersed.

Multiple hydrate formation/hydrate decomposition cycles may have an impact on the presence of self-preservation phenomenon. It was shown that after 6 cycles when hydrate was decomposed while mixing the suspension with different mixing speeds on the sixth cycle of decomposition there was no self-preservation even when hydrate was decomposed at static conditions.

No impact of the history of the sample on the decomposition rates of hydrate was observed if decomposition process was performed at static conditions.

More studies on this are needed to verify the exact reasons which lead to presence or non-preservation of self-preservation during the hydrate decomposition.

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