

Influence of surfactants on gas-hydrate formation' kinetics in water-oil emulsion

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Abstract. The kinetics of gas hydrate formation of propane in a water-oil emulsion is experimentally studied when three types of surfactants (SAA (surface acting agent)) - anionic type emulsifiers - are added to the aqueous phase. It is shown that all three types of surfactants decelerate the growth of the gas-hydrate in the emulsion and can be considered as anti-agglutinating and kinetic low-dose inhibitors. The most effective inhibitor of hydrate formation in water-oil emulsion of SV-102 surfactant was revealed. For comparison, experimental studies of gas-hydrate formation under the same conditions for bulk water have been carried out. It is shown that in bulk water, all the surfactants investigated act as promoters (accelerators) of hydrate formation. A qualitative explanation of the action mechanisms of emulsifiers in the process of gas-hydrate formation in water-oil emulsion is given.

1. Introduction

The current problem of the oil and gas industry in the northern conditions is the formation of gas-hydrate plugs in oil production and transportation systems [1, 2]. To prevent gas-hydrate formation, various classical thermodynamic inhibitors (for example, methanol, glycol or their combinations) are usually introduced into the system, shifting the phase equilibrium curve to higher pressures and lower temperatures [3]. The mechanism of hydrating inhibitors of thermodynamic action consists in reducing the activity of water in an aqueous solution and, as a consequence, in changing the equilibrium conditions for the formation of hydrates. To achieve the required effect, conventional thermodynamic inhibitors are used in large quantities. This requires a large operating cost to prevent hydrate formation in field conditions.

At the moment, alternative, so-called anti-agglutinating and kinetic low-dose inhibitors are being developed and tested in the oil and gas industry [4]. In view of their low concentration, they do not shift the phase equilibrium curves, but slow the formation of nuclei, the growth and adhesion of hydrate crystals, resulting in an easily transportable hydraulic fluid. In this case, there is no hydration on the walls of pipes and field communications. A great advantage of inhibitors of the kinetic type is the dosage, which is much lower than dosages of thermodynamic inhibitors. This makes it possible to reduce significantly operating costs. Kinetic inhibitors of hydrating also belong to the category of "environmentally friendly", which reduces the risks during transportation, storage and use. As a rule, a solution of organic polymers is used as kinetic inhibitors. It is assumed that the action principle of kinetic inhibitors is based on the prevention of the crystal hydrate nucleus formation by blocking the inhibitor of the crystallization center by a polymer molecule [5]. It is also known that one and the



same chemical, depending on its concentration and depending on the combination with other substances, can act as an inhibitor and as a promoter [6], but the mechanism of such action has not been sufficiently studied.

The objective of this research is an experimental study of the kinetics of propane gas-hydrates growth in water-oil emulsion in the presence of surface-active substances - emulsifiers of anionic type.

2. Experimental part

In the experiments, a water-oil emulsion based on the oil of the Urnensky field of Tyumen region was used. With the help of a mixer, the following samples of emulsions with 50% volume content of distilled water were prepared: 1) without surfactant (control emulsion, sample No. 1); 2) adding sodium sulfanol (sample No. 2); 3) adding neonol AF 9-12 (sample No. 3); 4) adding CB-102 (sample No. 4). The volumetric dosage of the surfactant was 2% of the aqueous phase volume of the emulsion for all samples. The choice of surfactants was determined by the fact that they are all highly effective anionic emulsifiers, thermobaric stable in the investigated temperature and pressure range, are highly soluble in water, economically available and environmentally safe.

A mixer with a blade speed of 1300 rpm was used to stir the mixture of oil, water and surfactants. The resulting emulsion had a homogeneous, more viscous than oil, consistency and a lighter color. Fig. 1 shows a photomicrograph of an emulsion obtained by means of an optical microscope. As can be seen from the figure, the droplet size did not exceed 10 μm .

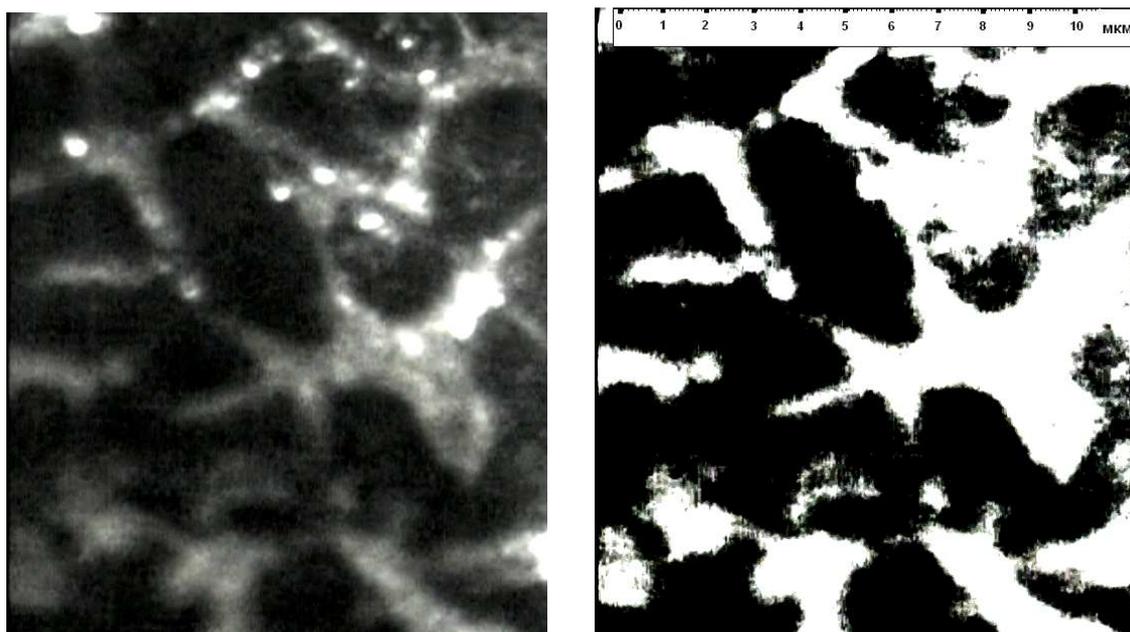


Figure 1. Microphotograph of water-oil emulsion 50/50%:
on the left - the original image; on the right - processed by the program PAINT.NET

The investigations were carried out at the automated installation "Gas hydrates" of Tyumen State University in accordance with the previously developed methods [7, 8, 9]. The results of the experiments were cyclic isothermal curves of gas pressure changes with time with the growth of gas hydrate from water-oil emulsion. One gas injection cycle lasted about 48 hours. For each sample of emulsions, 4 gas injection cycles were carried out under the same thermobaric conditions. It has previously been shown [2] that stable nucleation and growth of crystalline mass is observed by the beginning of the second cycle. That is why the comparison of the obtained experimental data of different emulsion samples started on the second cycle.

Approximating the $P(t)$ dependence of the exponential, one can find relaxation time τ , which characterizes the rate of growth of the gas hydrate. The reciprocal of the relaxation time is kinetic growth coefficient β [2]. Fig. 2 shows the dependence of coefficient β on the cycle number. As can be seen from the figure, all three inhibitors slow down the growth rate of the gas hydrate in the emulsion, but they act differently at different stages of gas hydrate growth. Dependences of the gas hydrate growth coefficient on the cycle number for samples of emulsions No. 2 and No. 3 are similar - the maximum difference is observed in the 1st cycle and is no more than 8%. For the sample of emulsion No. 4 (with SA-102 surfactant), a significant growth retardation was observed in the 4th cycle (almost twice as compared to the control sample).

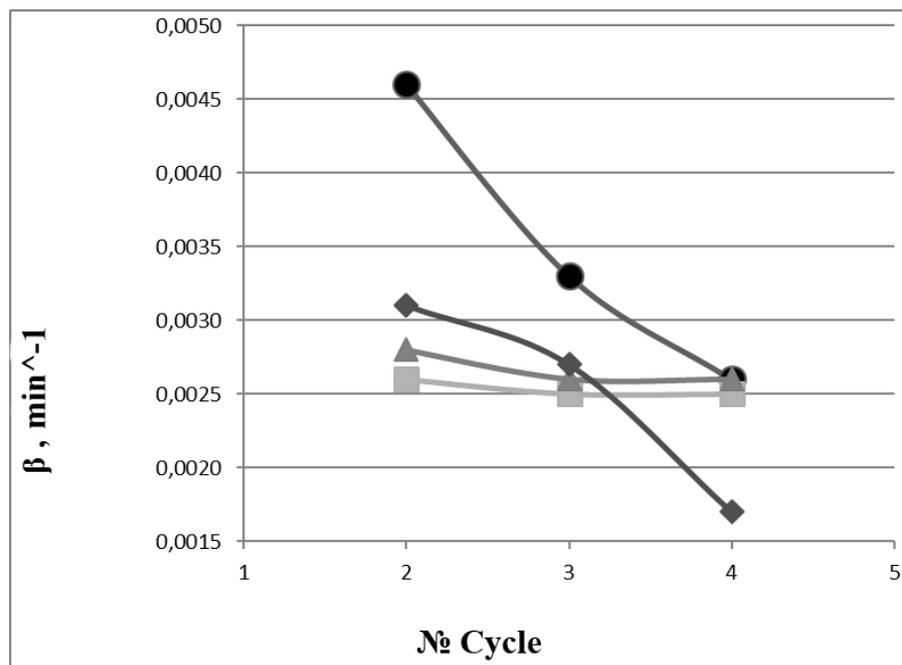


Figure 2. Dependence of the gas hydrate growth rate on the cycle number.

(● sample No. 1; ■ sample No. 2; ▲ sample No. 3; ◆ sample No. 4)

One of the important parameters characterizing the hydrate-containing environment is the coefficient of hydration, which determines the total fraction of moisture that has passed into the hydrate at a given moment in time.

Using the obtained experimental data of P-T parameters, it is possible to calculate the gas absorption by the equation of state of a real gas, taking into account the gas compressibility and solubility:

$$m_G = \frac{P_i \cdot V \cdot M}{R \cdot T_i \cdot z}, \quad (1)$$

where P_i — pressure at time t_i ; V — reduced volume of low-pressure chamber; M — molar mass of propane; R — universal gas constant; T_i — temperature at the moment of time t_i ; z — gas compressibility under given conditions.

From equation (1), it is possible to determine the mass of an ideal gas, converted into a hydrate per cycle:

$$\Delta m_{G-H} = \frac{\Delta P V M}{R T z}, \quad (2)$$

where ΔP — pressure change per cycle.

The gas mass difference at the beginning and at the end of the cycle when hydrate Δm_{G-H} forms allows one to calculate the mass of hydrate m_H and the mass of water m_{W-H} converted to the gas hydrate:

$$m_{W-H} = \Delta m_{G-H} \cdot 2,32, \quad (3)$$

where the coefficient of 2.32 is calculated based on the chemical formula of propane hydrate.

According to the data obtained, hydration factor K_H was calculated - the fraction of water converted into hydrate from the total amount of water in the sample.

$$K_H = \frac{m_{W-H}}{m_W} \cdot 100\%, \quad (4)$$

where m_W – initial mass of water in the sample.

The dependence of the hydration coefficient on the cycle number allows one to monitor the relative total mass increment of the gas hydrate by the end of each cycle and, thus, to compare the kinetics of different emulsion samples' growth. Figure 3a shows the results of calculations. As can be seen from the figure, all three surfactants under study reduce the interaction of gas and emulsion in comparison with the control sample, i.e. they are inhibitors of gas hydrate formation in water-oil emulsions. The greatest effectiveness of inhibition was found on the sample of emulsion № 4 (with the addition of surfactants CB-102).

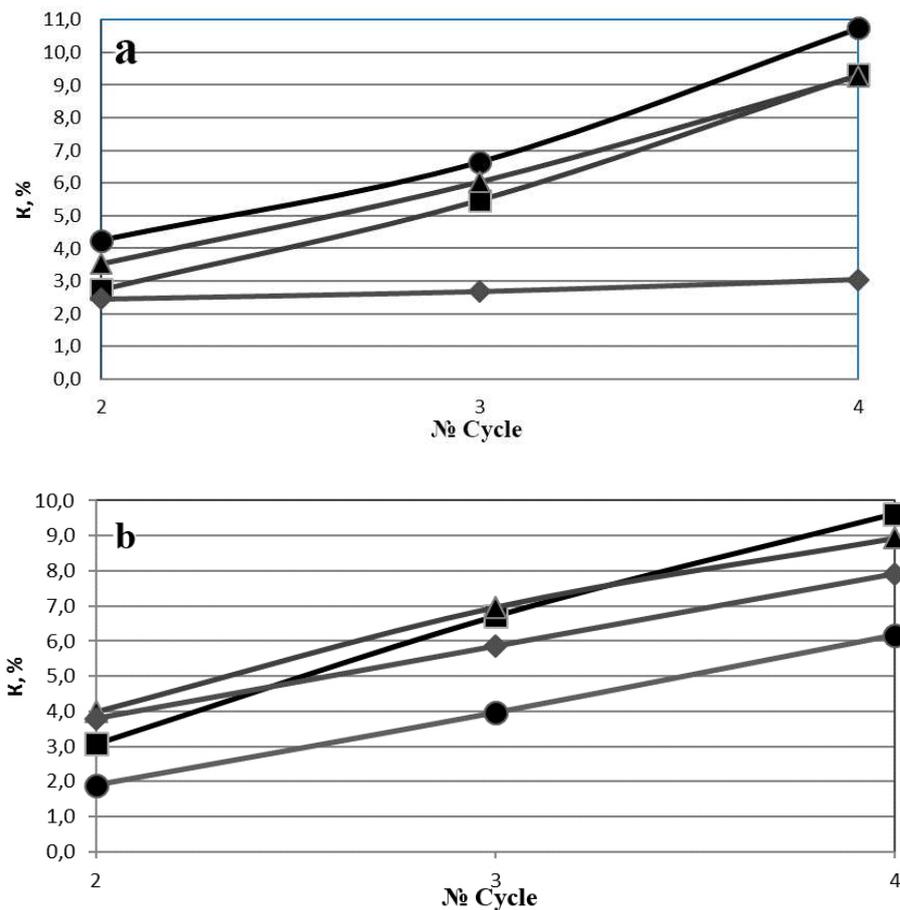


Figure 3. Dependence of the gas hydrate ratio on the cycle number: a - for water-oil emulsion, b - for water and aqueous solutions of surfactants

(● sample No. 1; ■ sample No. 2; ▲ sample No. 3; ◆ sample No. 4)

For comparison, similar experiments were carried out for bulk water (sample № 1) and for three corresponding surfactant solutions in distilled water at the same concentration. Fig. 3b presents the results of these studies. As can be seen from the figure, for bulk water, as expected, all three surfactants increase the rate of growth of the gas hydrate, i.e. they are promoters of gas hydrate formation. The offered mechanism for accelerating the growth rate of gas hydrate formation in an aqueous solution of a low-concentration surfactant was studied in detail earlier in research [10, 11]. The opposite effect discovered - the inhibitory effect of the surfactants studied in a dispersed medium - the water-oil emulsion - can be easily explained by the properties of emulsifiers. When the emulsifier is added to the water-oil emulsion at the water-oil interface, a shell is formed from the emulsifying substance, which prevents the gas from penetrating into the aqueous phase of the emulsion, and prevents the water droplets from converging (sticking together). Consequently, the emulsifiers in the initial stage of gas hydrate formation prevent the formation of nucleus of the gas hydrate in the emulsion and then inhibit the formation and growth of agglomerates from the nucleation centers of crystal hydrates. The higher efficiency of inhibition of CB-102 surfactants in comparison with other surfactants under study can be explained by the higher interfacial tension of its aqueous solution and oil [12, 13]. Thus, according to modern classification, the surfactants under study can be considered as anti-agglomerating and kinetic low-dose inhibitors of gas hydrate formation in water-oil emulsion.

To explain the high efficiency of inhibition of CB-102 surfactants in comparison with other surfactants, additional measurements of the surface and interfacial tension between aqueous solutions of surfactants and oil were carried out using a drop-test method. The results of these studies are presented in Table 1. As can be seen from the table, the interfacial tension between an aqueous solution of a surfactant based on CB-102 and oil is several times higher than that of other surfactant solutions.

Table 1. Results of surface and interfacial tension measurements

	NAME	σ , mN/m
Surface tension	Distilled water	(71±2)
	oil of Urnenskoye field	(34±2)
	Distilled water + surfactant (neonol AF 9-12)	(33±5)
	Distilled water + surfactant (sodium sulfanol)	(31±2)
	Distilled water + surfactant (CB-102)	(26±2)
Interfacial tension between 2% aqueous surfactant solution and oil	Water-Oil	(8.2±0,2)
	A solution of surfactants (neonol AF 9-12) in distilled water - oil	(3,2±0,1)
	A solution of surfactant (sodium sulfanol) in distilled water - oil	(2,1±0,3)
	A solution of surfactant (CB-102) in distilled water - oil	(16±1)

3. Conclusions

An experimental study of the kinetics of gas hydrate formation in water-oil emulsion in the presence of three highly effective emulsifiers of anionic type: sodium sulfanol, neonol AF 9-12, and CB-102, has been carried out.

When processing the obtained experimental data by the method of relaxation curves, it was found that all inhibitors reduce the kinetic coefficient of growth of the gas hydrate in the emulsion, but act differently at different stages of gas hydrate growth.

The calculation of the gas hydrate ratio confirms the inhibitory effect of all three surfactant types, which can be considered as anti-agglomerating and kinetic low-dose inhibitors. The most effective inhibitor of hydrate formation in the water-oil emulsion is CB-102.

To explain the high efficiency of inhibition of CB-102 surfactants in comparison with other surfactants, surface and interfacial tension measurements between aqueous solutions of surfactants and oil were carried out. It was found that the interfacial tension between an aqueous solution of a surfactant based on CB-102 and oil is several times higher than that of other surfactant solutions.

It is shown that in bulk water, unlike the emulsion, all three surfactants investigated act as promoters of hydrate formation, which is coherent with the already known studies.

A qualitative explanation of the surfactants action mechanisms in the process of gas hydrate formation in water-oil emulsion is given.

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