

# SAFRANINE O, AN ACID-RESISTANT AND ENVIRONMENTALLY FRIENDLY KINETIC HYDRATE INHIBITOR

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## ABSTRACT

Hydrate formation and blockage are commonly encountered in gas and oil transportation pipelines, causing significant equipment damages and financial loss. The development and utilization of environmentally friendly and low dosage kinetic hydrate inhibitors (KHIs) could help remit hydrate formation and protect the pipelines. Safranin O is considered a promising candidate with huge potential. Safranin O is soluble in water and self-assembles into macromolecules with antifreeze protein properties. In this work, it was found that 0.1 wt% safranin O could completely inhibit the formation of methane hydrate at a subcooling of 7.7 °C. Upon a higher dosage of 1 wt%, the inhibition subcooling could be further extended to 8.59 °C. In the both CIR and SGR, the inhibitory effect of 0.5% mass fraction safranin O was better than 0.5% mass fraction PVCap. This will effectively limit the formation of hydrate at a wide temperature and pressure range. The results could provide a brand new KHI with promising applications in the prevention of hydrate blockage in gas pipelines.

**Keywords:** kinetic hydrate inhibitors, safranin O, antifreeze protein, acid-resistant.

## NONMENCLATURE

### *Abbreviations*

KHIs	kinetic hydrate inhibitors
CGI	crystal growth inhibition

## 1. INTRODUCTION

Gas hydrates are nonstoichiometric compounds with one or more other molecules species in the lattice of water molecules, which divided into three structural families cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH).[1] Natural gas hydrates, an important source of methane gas in marine sediments and permafrost regions, have recently received widespread attention as important future energy sources.[2,3] In the oil and gas transportation industry, especially in the offshore flowline, the conditions in the pipeline are conducive to the formation of gas hydrate resulting in the blockage in the transportation pipeline.[4]

In order to avoid hydrate formation, two kinds of additives, thermodynamic inhibitors, such as methanol, diethylene glycol, ethylene glycol, glycerol ethylene glycol and low dosage hydrate inhibitors are widely used in the oil and gas industry.[5] The former achieves the aim of inhibition by shifting the equilibrium to a lower temperature or a higher pressure zone. Usually, in order to achieve the desired effect, a larger amount of inhibitor (up to 50 wt % of the water present in the systems) is added in the actual application process, but such inhibitor is toxic to marine and harmful to the pipeline, and thus leads to restriction for practical application. The low dosage hydrate inhibitors include anti-agglomeration and kinetic hydrate inhibitors (KHIs). anti-agglomerations are surfactants which could prevent hydrate particles agglomeration and postpone crystal growth process, but the effects fails when water cut exceeds 50 %.

KHIs are water soluble polymer that are able to delay retard the formation of hydrate crystals. The doses of the

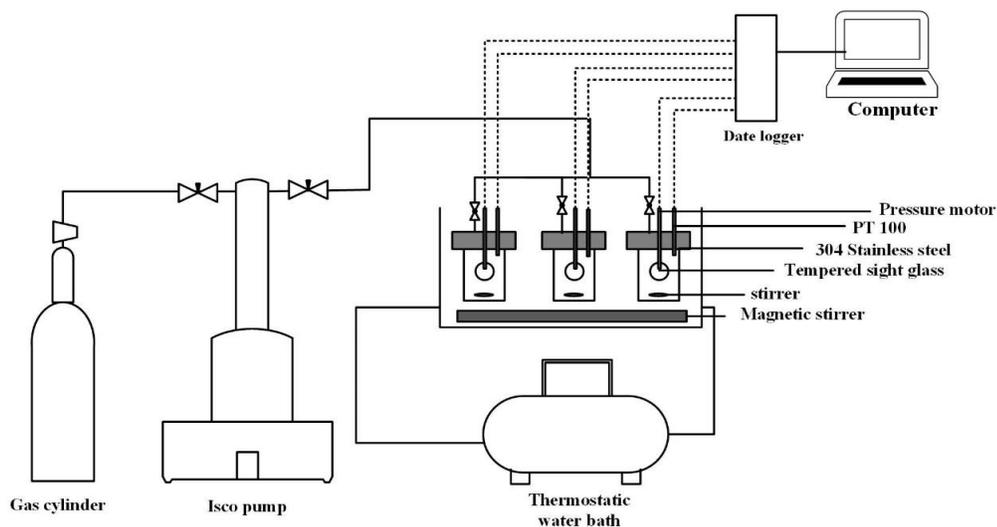


Figure 1. Schematic diagram of experimental setup

KHIs, such as polymers of N vinylcaprolactam (PVCap), N-methyl-N-vinylacetamide and 2-alkly-2-oxazoline, are significantly lower than THIs. Up to now, much research has been undertaken on inhibition mechanism, but the exact mechanism of inhibition mechanism is not yet well known so far. It is generally believed that the inhibition mechanism is that the hydrophobic group water substructure and hydrophilic group form hydrogen bonds water molecules could lower water activity. However, KHIs are low biodegradable in the seawater condition, thus it is urgent to find and develop environmental-friendly KHIs.

Safranin O, a kind of biological dye, has so far been found to be no environmental hazard. We used crystal growth inhibition (CGI) to evaluate its effect as hydrate inhibitor. The results shown that safranin O could delay methane hydrate formation and noticeably inhibit hydrate growth in the present of hydrate particle. Besides, the inhibitory effect was still good under acidic conditions.

## 2. PAPER STRUCTURE

### 2.1 Materials

Safranin O was purchased from Shanghai Macklin Biochemical Co., Ltd. Ethylene glycol were obtained from Kermel Chemical Co., Ltd. Methane with 99.995 % mass fraction was supplied by Dalian Special Gases Co., Ltd. The conductivity of the deionized water used in the experiment was 18.5  $\Omega$ .

### 2.2 Apparatus

The custom built 316 stainless steel were designed to evaluate safranin O in the range of 288.15 - 273.15 K and 0-7.5Mpa. These setups are illustrated in Figure 1. The cells made of 304 stainless steel and the volume is 245mL. There are tempered glass windows on both sides of the cells for observing hydrate. Throughout the experiment, autoclave cells temperature was controlled by a refrigerated liquid circulator (Polyscience, USA), and the refrigerant is ethylene and deionized water. The magnetic stirrer turns polytetrafluoroethylene (PTFE)-coated magnetic bar to completely mixing solution. The temperature and pressure in the pressurized vessel are monitored by platinum resistance thermometers (PT100) with an accuracy of  $\pm 0.01$   $^{\circ}\text{C}$  pressure transducer with an accuracy of  $\pm 0.01$  MPa. The results were recorded by date logger connecting with a computer.

### 2.3 Methods

The crystal growth inhibition (CGI) evaluation technique was used to determine the subcooling performance area of KHI under certain pressure and dose. This method was developed by Anderson and his collaborator of Herriot Watt University and testified to be reliably in practice. The system with small amount of hydrate crystals (typically, 0.5% of aqueous phase as hydrate) is cooling to the hydrate stability region. According to the hydrate growth rates, CGI can be divided into several parts provided in Table 1.

Table 1. KHI induced CGI region and typical hydrate growth rates.

Region	Full region name	Typical hydrate growth rates $v_g(\%/h)$
CIR	Complete inhibition Region	0
SGR (VS)	Slow growth region (very slow)	0.01 ( $V_g < 0.05$ )
SGR (S)	Slow growth region (slow)	0.1 ( $0.05 \leq V_g < 0.5$ )
SGR (M)	Slow growth region (moderate)	1 ( $0.5 \leq V_g < 5$ )
RGR	Rapid growth region	10 ( $5 \leq V_g$ )
SDR	Slow dissociation Region	Dissociation rate 1 order of magnitude less than for no KHI

## 2.4 Results

CGI can eliminate the test error caused by random nucleation when evaluating inhibitors, and the growth rate of crystals can represent the inhibition effect of inhibitors. When the system cooled to a high subcooling, the gas hydrate begin to generate with the decrease of temperature. And the system will starts to heat up once it reached the certain temperature, in that case, most of the hydrate dissociate, and thus leaving a very small amount fraction of hydrate. Then the system was gradually cooled again, and the cycle was repeated for 2 times.

Figure 2 shows the process of CGI of cooling and heating curves for the blank (no safranin O) methane-water system. During the first cooling operation, there is no ‘hydrate history’ in the solution, and nucleation occurs during the subcooling. Once the gas hydrate started nucleating, it began to grow rapidly. When the temperature decreased from 276.23 K to 275.22 K, the growth rate grown up quickly from 0.0 % to 5.02 %. When the crystal growth rate reaches its maximum velocity, the system temperature suddenly moves towards higher temperature, because that the heat released by the formation of a large amount of hydrate in a short period of time could not be absorbed by the environment in time. In the process of heating

decomposition, the decomposition curve of hydrate basically coincides with the phase equilibrium curve. When the liquid heated to 284.5 K, the system gradually cooled down again, and the system contained 0.35 % hydrate. In the presence of hydrate particle, the growth rate of hydrate crystal reached 5.02% at 286.08k, and the growth rate at the same temperature was higher than that in the system with no history. The growth rate reached 18.5 %/hr at 279.89 K, and it is far faster than the typical hydrate growth rates of RGR. When cooling stopped, 23 % of water converted to hydrate, which is almost twice the conversion rate of the previous cycle.

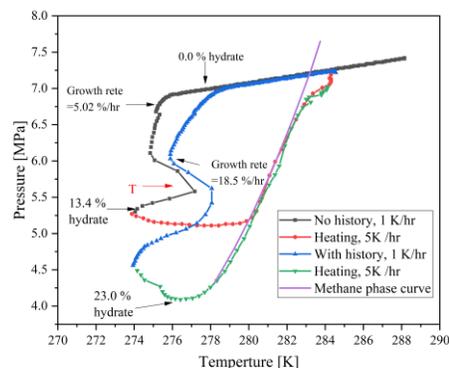


Fig. 2. PT plot showing typical hydrate formation and dissociation in pure methane-water system

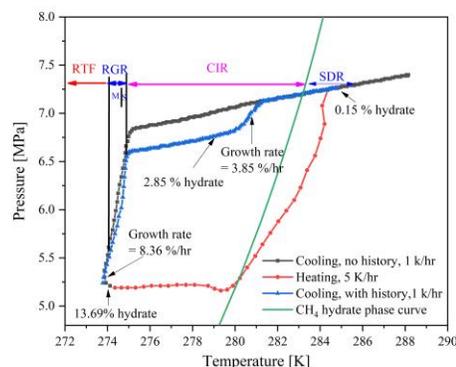


Fig. 3. PT plot showing typical hydrate formation and dissociation in methane-water system with 1 wt % safranin O.

Subsequently, the inhibitory effect of safranin O with a range of concentrations from 0.1 wt% to 0.5 wt % on methane hydrate was investigated. Figure 3 shows an example cooling and heating curve for methane-water - safranin O (1 wt% aqueous solution) as a plot of pressure versus temperature. On the first cooling run (1.0 °C / hr), hydrate nucleating occurs at 275.14 K. Compared with the blank group, the growth rate with 1.0 wt% safranin O is more slowly, and there was no

temperature surge in the autoclave. This pattern was rapidly heated to dissociate the hydrate when the temperature reached 274 K. The system was cooled back into the hydrate region with 0.15% hydrate present. Initiatory, no crystal growth was observed before 281 K, and after that point, the pressure began to decrease on account of hydrate formation, besides that, the maximum growth rate is 3.85 %/hr and soon slows down to zero. No subsequent decrease in pressure due to hydrate formation was observed in the 280-275K range. The growth of this fault type, that is the formation of a small amount of hydrate after that, did not affect the inhibition of hydrate by saffron, so it was still considered to be within the CIR. It was not until 274.9K that the rate began to increase slowly and continuously, but rapidly due to the presence of hydrate particles. The same was true in other groups. However, during the whole cooling process, the maximum rate is 8.36 %/hr, which was far less than the maximum rate in the blank group, and the final water conversion rate in the system was not increased by the presence of hydrate crystals, which is also far less than 23 % hydrate.

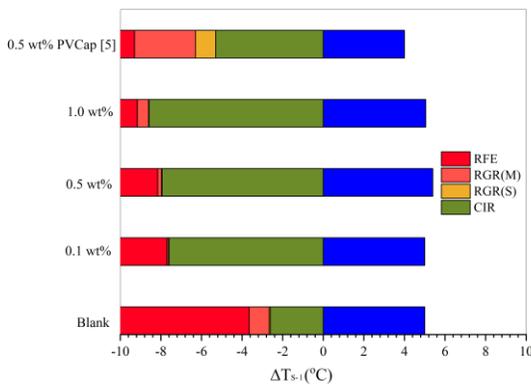


Fig. 4. Effect of Safranin O with different mass fractions on the subcooling

In Figure 4, we summarized the degree of subcooling of safranin O with a mass fraction of 0.1 %, 0.5 % and 1 % in the inhibitor-induced CGI region. The blank group results was in good agreement with the experiment and literature data, which indicated the credibility of our experiment results. Safranin O remarkably retards the hydrate particle growth and new crystal formation in the methane hydrate stability region. After adding 0.1% mass fraction safranin O, the degree of subcooling in the region of blank group lowered from -2.6 °C to -7.6 °C. As the mass fraction of safranin O increases, the subcooling of each inhibitory region moved to lower temperature. When the mass fraction of Safranin O increased from 0.1% to 1.0%, the CIR and RFR moved to

the low temperature zone 1.01 °C and 1.46 °C, respectively. In the both CIR and SGR, the inhibitory effect of 0.5% mass fraction safranin O was better than 0.5% mass fraction PVCap.[5,6] It was striking that no pollution of safranin O to the environment.

## 2.5 Conclusions

In conclusion, Safranin O is found to be a natural and abundant gas hydrate kinetics inhibitor. Even under acidic conditions, Safranin O can still effectively inhibit the growth of hydrate crystals. Compared to the pure water scenario, the rapid growth region of 1% wt Safranin O case was extended from 5.5 °C to low temperature zone. During the whole cooling process, the maximum growth rate of hydrate crystal was 8.9 %/hr, which was much lower than the pure water scenario (13.9 %/hr). Besides, no temperature rise was observed, indicating the absence of large amount of hydrate formation. Safranin O showed good inhibition performance, high biodegradability and high economic efficiency, and thus could be a promising substitute for KHIs in the natural gas and petroleum industries.

## ACKNOWLEDGEMENT

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