

# RHEOLOGICAL OF METHANE HYDRATE FORMED FROM EMULSION

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## ABSTRACT

Methane hydrate formation has been a crucial factor affecting the blockage of in subsea oil and gas transportation pipelines. To study the rheological properties of hydrate slurries, methane hydrate were formed in situ from water-oil emulsion with different water cut (20 vol%-70 vol%). Meanwhile, viscosity measurement and yield stress measurement were conducted with a high-pressure rheometer. Emulsion exhibit a shear-thinning behavior and increase in viscosity under hydrate formation. Hydrate slurry viscosity and yield stress had a significant increase with increasing water volume fraction. And hydrate formed in oil-in-water emulsions were more likely to aggregate and cause blockage than in water-in-oil emulsions.

**Keywords:** Flow assurance, Methane hydrate, Rheology, Emulsions, hydrate slurry viscosity.

## 1. INTRODUCTION

Gas hydrate formed at an environment of high pressure and low temperature [1] often occurs in subsea oil and gas transportation pipelines, and results in pipeline blockage [2]. It was estimated that the oil and gas industry spent over \$200 million on hydrate prevention every year [3]. Currently, hydrate blockage has recognized a primary flow assurance challenge in the deep water [2].

More than 60 percent of the world's crude oil was produced as emulsions [4]. Especially in the subsea oil and gas transportation pipeline, the water may be as little as below 1% or as much as over 70% of the total amount of liquid. When the liquid flow from the reservoir into the well bore or through turbulent flow on chokes and valves and on centrifugal pump impellers, the liquids are subject to vigorous agitation, resulting in emulsification [5]. So an understanding of the rheological

properties of hydrate-oil slurries is of great significance to hydrates management and prevent hydrate blockages [6].

Many researchers [7,8] investigated the viscosity of hydrates slurry formed by using TBAB, THF or cyclopentane as guest molecules for the application of hydrates technology in refrigeration field at a lower pressure condition. However, methane hydrate need a strict environment of low temperature and high pressure environment, which the guest molecules of hydrate first need to transport through the oil phase and then form hydrates at the water-oil interface.

The objective of this work is to study the rheological properties of methane hydrate slurries. Methane hydrate were formed in situ from water-oil emulsion with different water cut (20 vol%-70 vol%). Meanwhile, viscosity measurement and yield stress measurement were conducted with a high-pressure rheometer.

## 2. EXPERIMENTAL METHODS

### 2.1 Apparatus.

The experimental apparatus used in this work are shown in Fig. 1. The rheological properties were measured with a rotational rheometer (Haake Mars 60, Thermo Fisher Scientific, Germany). The cylinder pressure cell had been designed to work safely under the pressure of 40 MPa, with a steel outer cylinder and a titanium inner cylinder in a concentric cylinders (cup-and-bob). The diameter of outer cylinder internal is 39.00 mm, while the diameter of inner cylinder is 38.00 mm. The effective volume of the pressure cell is 52 ml (exclude the volume of the rotor).

### 2.2 Emulsion preparation

Emulsions with different water cut (ranged from 10vol% to 70vol%) are prepared with deionized water and n-decane (viscosity of 0.9 cp and density of 0.790 g/cm<sup>3</sup> at 2 °C).

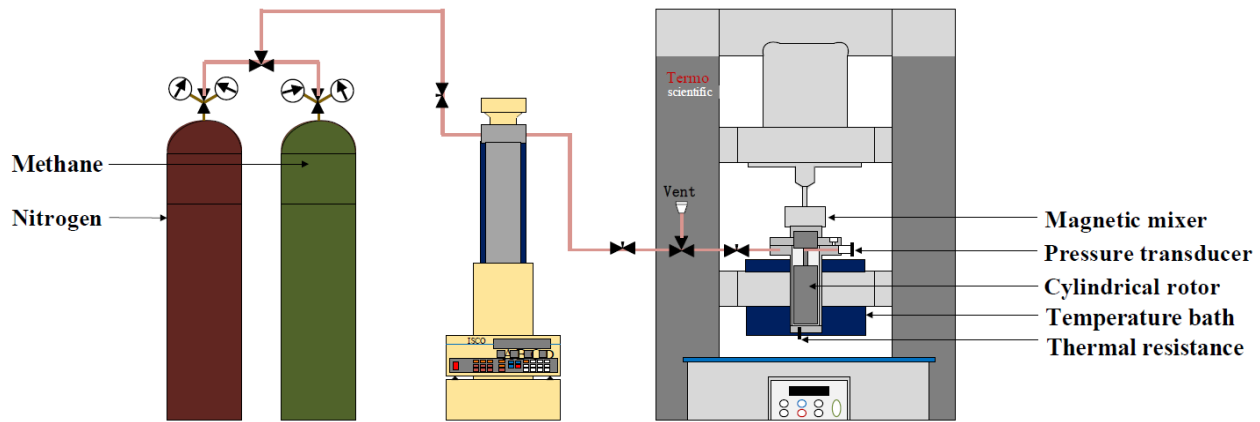


Fig 1. Schematic diagram of the experimental apparatus.

In all cases, the additive as emulsifier agents are composed of two non-ionic surfactants, Sorbitan monooleate (Span 80, MW428.61g/mol, Ahkuer), Polysorbate 80 (Tween 80, MW 1310 g/mol, Ahkuer) with a mass ratio of 1.28. The surfactant mixture with HLB value of 9 had a good synergistic effect on stabilizing a water-decane emulsion[9], and occupied 5 wt% of the total oil phase.

The emulsions were prepared using a high shear dispersion emulsification homogenizer (Shanghai, Shanghai Ouhor Machinery Equipment Co., Ltd., China) operating at 10,000 rpm. The rotor and stator diameter of the dispenser were 17 mm and 25 mm respectively. Initially, a certain quality of Span 80 and Tween 80 were mixed and added into mineral oil as the oil phase. The mixture was stirred with a high-speed homogenizer at 10000 rpm for 1min to ensure complete mixing of the mineral oil and surfactants. Keeping stirring, deionized water with 10 vol% of the total volume was injected slowly each time at an interval of 40 seconds, until the water cut reached the requirement, finally stirring at 10000 rpm for 5 min to ensure the sufficient emulsification[9]. Since mixing occurred at a high shear rate, the emulsion sample was sealed with a glass-sheet during this process to prevent evaporation of volatile components.

### 2.3 Experimental procedure

Before each experiment, the cell was cleaned with deionized water and dried. Then, 16 ml emulsion was added into the cell. If the emulsion was over cylindrical rotor too much, the hydrate formed would be mostly distributed on the top of the rotor, leading to the unreliability of the system, and too little sample would

result in a large error in the measurement. So the added emulsion was just over the cylindrical rotor.

The standard measurements involve a number of steps, which are outlined as follows:

(1) Viscosity measurement of water-decane emulsion: Incrementally step up from  $0.1 \text{ s}^{-1}$  to  $2500 \text{ s}^{-1}$  on a log scale at  $20^\circ\text{C}$ . During the shear ramps, each point is taken at steady-state, defined as three viscosity readings within 3% of each other.

(2) Cooling to set the system from  $20$  to  $2^\circ\text{C}$ ,  $212 \text{ s}^{-1}$  shear rate.

(3) Methane gas was injected into the cell until the system pressure reached 13 MPa.

(4) Hydrate formation conducted under  $212 \text{ s}^{-1}$  shear rate and  $2^\circ\text{C}$ , until system pressure and slurry viscosity were no longer reduced for 12h or rotate stopped for maximum torque reached.

(5) Yield stress measurement: Ramp shear stress from 1 to 1000 Pa on a linear scale at  $2^\circ\text{C}$  after an 1 h hardening step.

### 3. RESULTS AND DISCUSSION

Viscosity results for emulsion prepared with different water cut measured at ambient pressure and room temperature are presented in Figure 2. Since the viscosity of the emulsion is closely related to the choice of the oil phase, for a better comparison, viscosity in this paper refers to the relative viscosity which means the ratio of apparent viscosity to the actual viscosity of the oil phase. Because of the increase in packing of the water droplets, when the water cut was below 60 vol%, the relative viscosity of emulsions had a significant increase with the increase of water proportion. But when the water cut reached 70 vol%, the continuous phase of the

emulsion inverted from oil to water, and relative viscosity decreased obviously. Meanwhile, all emulsion exhibited the shear-thinning behavior. With the increasing of the shear rate, the relative viscosity curves dropped first and then gradually became smooth. It may be because the rupture of clusters or droplet aggregates followed by droplet alignment and deformation under a high shear[10].

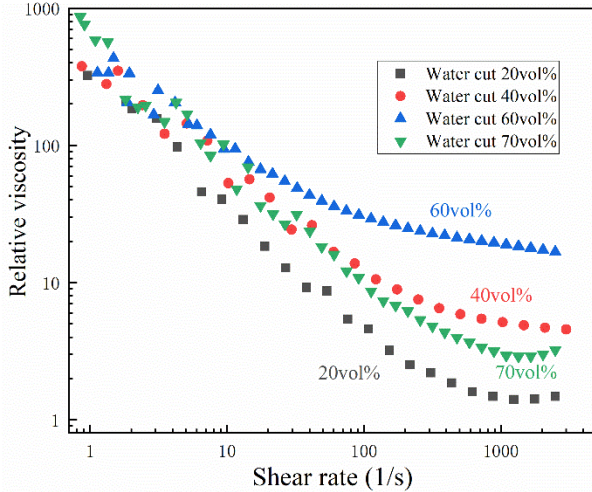


Fig 2. Viscosity results of emulsions with different water cut

Methane hydrate were formed in situ from emulsion with different water cut in the rheometer pressure cell. And all case has a the initial pressure of 13 MPa, while the stirring speed and temperature were kept at 50 rpm ( $212 \text{ s}^{-1}$  of shear rate) and  $2 \text{ }^\circ\text{C}$ . Because all experiments were carried out with the isochoric processes, the hydrate production, which equal to the amount of methane encapsulated in hydrate, could be calculated through the pressure and temperature, and the calculation process was similar with Li et al.[11].

The water conversion fraction and the related viscosity evolution of different water cut were shown in Fig.3. For the emulsion with 20 vol% water cut, as the hydrate began to form, the viscosity of the emulsion remained constant or slightly increased. It was because the solids were created from the emulsified liquid water droplets. When the hydrate content reached a certain value, the number of hydrate particles increased, they were free to move around and collide with other hydrate particles or water droplets, leading to the aggregation, and the slurry viscosity increased dramatically. At this time, the viscosity measured fluctuated greatly. It may be because that the hydrate aggregates have grown too large and their size approached the width of the gap between the concentric cylinders[12]. But after the huge increased, the viscosity decreased slowly as the hydrate formation stopped, and then reached a constant value.

It may be resulting from the fragmentation of hydrate aggregates under shear, and the interstitial liquid was released. It decreased the effective volume fraction of particles and, thus, decreased the viscosity.

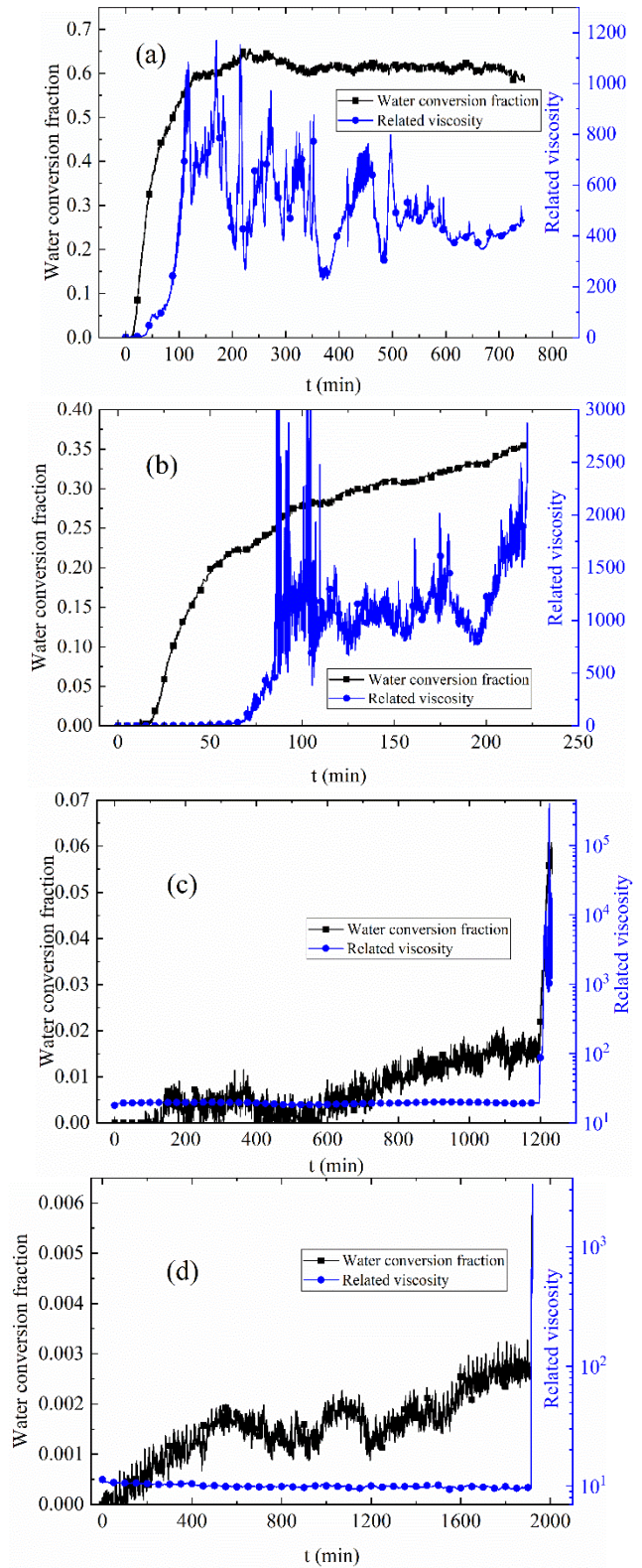


Fig 3. Water conversion fraction and the related viscosity evolution of hydrate formation in emulsion with different water cut. (a) 20 vol%; (b) 40 vol%; (c) 60 vol%; (d) 70 vol%.

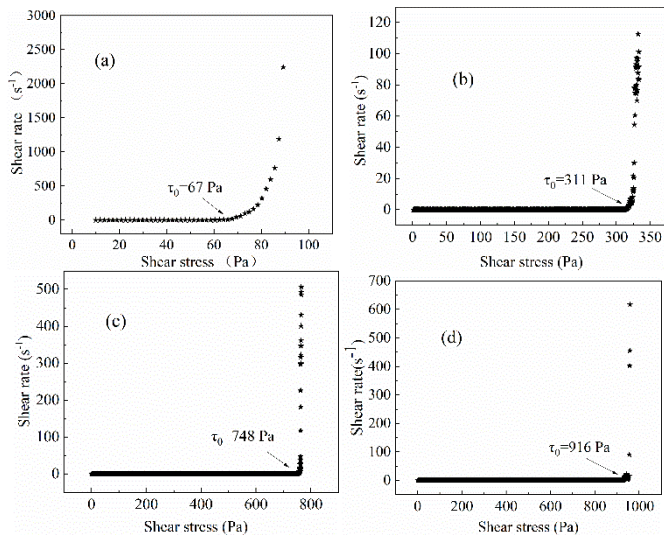


Fig 4. Yield stress of hydrate slurry formed by emulsion with different water cut. (a) 20 vol%; (b) 40 vol%; (c) 60 vol%; (d) 70 vol%.

Viscosity evolution of 40 vol% water cut was similar with emulsion with 20 vol% water cut. But because of the larger water proportion, the hydrate particles were more likely to collide with other hydrate particles or water droplets. Only a low water conversion rate was required to increase the viscosity of hydrate slurry significantly, and the viscosity was much higher than in the emulsion with 40 vol% water cut.

On the contrary, the viscosity evolution of emulsion with 60 vol% and 70 vol% water cut have a great difference. With hydrate formation, the viscosity remained constant first, and had a sudden increase. At this point, the required torque to maintain the rotation reached the upper limit of the instrument, and the formation experiment was terminated. As for the emulsion with 70 vol%, only needed 0.6% of the water convert to hydrate to produce blockages. It was because the continuous phase of the emulsion had changed to the aqueous phase.

After hydrate formation, yield stress had been measured at 2 °C after an 1 h hardening step. The yield stress results were presented at Fig. 4. The higher the moisture content of the emulsion, the larger the yield stress after it was converted into hydrate slurry and hardened for one hour.

#### 4. CONCLUSION

Methane hydrate was formed from water-oil emulsion with different water cut. Emulsion exhibited a

shear-thinning behavior and increased in viscosity under hydrate formation. Hydrate slurry viscosity and yield stress had a significant increase with increasing the water cut. And hydrate formed in oil-in-water emulsions were more likely to aggregate and cause blockage than in water-in-oil emulsions.

#### ACKNOWLEDGEMENT

This study was financially supported by the National Natural Science Foundation of China (Grant Nos.51676024 and 51890911), the National Key Research and Development Program of China (Grant Nos. 2017YFC0307305 and 2016YFC0304001), and the National Science and Technology Major Project (Grant No. 2016ZX05028-004-004).

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