Effects of dodecyl benzene sulfonic acid between hydrate particles and droplets

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Abstract. In order to understand the effect of Dodecyl benzene sulfonic acid (DBSA) on the aggregation mechanism of hydrate, the interaction between cyclopentane (CyC₅) hydrate particles and droplets under different concentrations of DBSA and different temperatures was measured by micro mechanical force device (MMF). The mass concentration range of DBSA used in the experiment is 0.0001% ~ 0.05%, and the experimental temperature is 1℃ and 5℃, respectively. The experimental results show that DBSA can effectively reduce the interfacial tension between oil and water, thus reducing the adhesion between hydrate particles and droplets and preventing hydrate aggregation. In the experimental concentration range, the higher the concentration of DBSA, the stronger the ability to reduce the adhesion. The adhesion can be reduced by 97.56% at 1℃ and 90.95% at 5℃. The change trend of the adhesion with the concentration is almost the same at the two temperatures.

1. Introduction

Natural gas hydrate is a kind of cage compound formed in low temperature and high pressure environment. Hydrate accumulation will lead to oil production pipelines blockage, bring safety and environmental problems, but also cause serious economic losses, which has become one of the main flow assurance issue in the process of oil and gas production and gathering[1].

There are four aspects in the process of hydrate blockage, and hydrate accumulation is considered to be the main factor of pipeline blockage[2]. In order to prevent hydrate aggregation, hydrate anti-agglomerants (AAS) has attracted great attention in recent years. At present, the research on the effect of AAS on hydrate aggregation mechanism was usually divided into macro and micro aspects, and it was easier to explain the anti aggregation mechanism from the micro perspective. Further insights into the hydrate agglomeration process were proposed by Fidel-Dufour[3]. At the early stage of the agglomeration, once some droplets converted into hydrate particles, there are two basic interactions between (i) hydrate particle and particle, (ii) hydrate particle and unconverted water droplet. With the unconverted water fully formed hydrate, the interactions between hydrate particles will dominate the agglomeration. However, many experimental and theoretical studies only focus on the interaction between hydrate particles. In contrast, the important interaction between hydrate particles and droplets...
is rarely reported. Dodecyl benzene sulfonyl acid (DBSA), as a kind of common AAS, has also been reported in the previous literature on the effects of DBSA on the adhesion between particles of hydrate\cite{4-5}. In this paper, micromechanical force device (MMF) was used to study the interaction between particles and droplets of cyclopentane (CyC5) hydrate under the action of DBSA, and the effect of DBSA on interfacial tension was tested to clarify the influence mechanism of DBSA on the micro force of hydrate particles and droplets.

2. Materials and methods

2.1. Chemicals

Cyclopentane and water can form type II hydrate under normal pressure, and the phase equilibrium temperature is 7.7°C. It is more suitable to be used as a substitute for indoor natural gas hydrate. The purity of CyC5 in this paper is 96%, which was purchased from Aladdin company\cite{6}.

Dodecyl benzene sulfonyl acid (C18H30O3S), also known as linear alkyl benzene and dodecyl benzene sulfonyl acid, is a kind of anionic surfactant. Studies have shown that alkyl aromatic sulfonates (dobanax Series) can be used as anti-agglomerants agents in hydrate control\cite{2}.

2.2. Water droplet and hydrate particle measurements

As shown in Figure 1, the hydrate micro force test device is used in this experiment, which consists of four parts: (i) Micro operating system, including optical microscope (DV-100, Magnification: 50-500x) and high-precision three-dimensional control platform (LY125, Stroke: 50mm, Accuracy: 10μm), the experiment is mainly carried out in a stainless steel tank on a micro platform. The platform is controlled by a metal rod to make the test sample move accurately; (ii) Microscopical system, the displacement of droplets and hydrate particles can be recorded in real time by micro digital camera. According to the elastic coefficient of glass fiber, the force can be measured and analyzed by Hooke's law; (iii) Temperature control system, constant temperature water bath (Scientz DC-2006, Operating temperature: -20°C -99.99°C, Temperature control accuracy: 0.01°C) is connected with a stainless steel hydrate generating tank, and the fluid temperature in the tank is measured by a temperature sensor; (iv) CyC5 real time replenishment system, due to the strong volatility of CyC5, in order to maintain the constant liquid volume in the operation unit, a micro supply unit is configured to make up.

The measurement of micro aggregation force between hydrate particles and droplets is very important to understand the aggregation mechanism of hydrate and the anti-aggregation mechanism of DBSA. However, due to the limitation of testing methods, the previous experimental test on the micro aggregation force of hydrate was only limited to the measurement of the interaction between dry hydrate particles. Based on the previous test and continuous exploration, this paper put forward the test steps as shown in Figure 2\cite{7}.
First, a very small droplet is made on the glass fiber, and then the droplet is immersed in liquid nitrogen for 20s to form ice particles. The ice particles are quickly transferred to the cooled CyC₅ vessel, and gradually increased the temperature, resulting in the ice particles melting and hydrate formation. When the set temperature is reached, the moving rod at the end is immersed in the cyclopentane vessel and kept for 30min to make it balance. Then, another droplet is made on the glass fiber, and the droplet is transferred from the glass fiber to the surface of the aluminum sheet in CyC₅. Finally, after the droplet is equilibrated for 30min, the measurement is started, and the measurement steps are shown in Figure 2. The initial positions of the droplets and hydrate particles are shown in Figure 2 (c). Moving the flat plate makes the droplets approach the hydrate particles to make them contact. At the moment of contact, the droplets quickly wet the hydrate particles, and the particles are "sucked" into the droplets to form a liquid bridge (Figure 2 (d)); Next, the droplet is moved in the opposite direction, gradually away from the hydrate particles (Figure 2 (e)), until it is completely separated (Figure 2 (f)). In order to reduce the effect of hydrodynamic force on the interaction between droplets and hydrate particles, the droplet moving speed is controlled at 7-9 μm/s. The whole process is recorded in real time, and the recording speed is 30 Frame/s. The real-time displacement of hydrate particles is analyzed by ImageJ software. Combined with the elastic constant of glass fiber, the real-time force between droplet and hydrate particles can be obtained by Hooke's law.

In order to study the effect of DBSA on the adhesion between hydrate particles and droplets, samples with concentrations of 0.05%, 0.01%, 0.005%, 0.001% and 0.0001% were prepared, and the interfacial tensions of the samples were tested, which were 5.1mN/m, 9.3mN/m, 16.1mN/m, 26.2mN/m, 32.3mN/m.

3. Results and discussion

3.1. Interaction behavior of hydrate particle-droplet in CyC₅ with DBSA

Figure 3 shows the interaction process between hydrate particles and droplets and the change curve of adhesion force with plate displacement after adding 0.05% DBSA. It can be seen from the observation curve that when the hydrate particles contact with the droplets, there is a "suction" moment to suck the particles into the droplets. The wettability of the droplet decreases due to the existence of DBSA, and the moving plate makes the liquid bridge force between the droplet and the particle in a tensile state. Compared with the tensile process of the droplet and the particle without DBSA, the liquid bridge strength decreases obviously, which is one of the reasons for the decrease of the adhesion force between the droplet and the particle. When the liquid bridge continues to stretch, the adhesive force will not drop immediately when it reaches the maximum value, but will remain at the maximum value with the liquid bridge stretching, but this value will not remain too long. The plate continues to move, the adhesive force will drop, and the liquid bridge will break at a certain moment, and the adhesive force will return to zero. After the fracture of the liquid bridge, the hydrate particles rebound back to the initial position. At this time, part of the water in the liquid bridge remains on the plate, and some of it adheres to the
surface of the particles and spreads rapidly. At the same time, it increases the surface roughness of the hydrate, which is one of the important reasons for the decrease of the adhesion.

Figure 3 Typical hydrate particle-droplet interaction force profile and corresponding microscope images of a measurement cycle in CyC₅ with 0.05% DBSA

3.2. Analysis of results
The change of the force with the displacement of the plate during the contact separation process between hydrate particles and droplets was measured at 1℃ and 5℃. Figure 4 shows the hydrate particle-droplet interaction at 1℃ and 5℃ with different concentrations of DBSA. As shown in the figure, at 1℃, with the concentration changing from low to high, the adhesion force values between hydrate particles and droplets are 0.0363mN, 0.0282mN, 0.0151mN, 0.0137mN, 0.0017mN, respectively. It can be seen that the force between hydrate particles and droplets decreases significantly after adding DBSA. The reason is that DBSA has a strong ability to reduce the interfacial tension between cyclopentane and aqueous solution, resulting in a significant decrease in its adhesion. When the temperature is 5℃, the change trend of the force between hydrate particles and droplets with the concentration is similar to that at 1℃. With the increase of concentration, the adhesion force values are 0.0348mN, 0.0265mN, 0.0176mN, 0.0154mN, 0.0048mN.

Figure 4 Adhesion force of hydrate particle with DBSA in different concentration under 5℃

According to the experiment of hydrate particle droplet interaction in 3.1, the liquid bridge plays a leading role in the whole process. The liquid bridge force can be divided into two parts: the interfacial tension and the capillary force caused by the curvature of the liquid bridge[8]. The details are as follows:

\[
F = \pi R_p^2 \sin^2 \phi_p \Delta P - 2\pi R_p \sin \phi_p \gamma_{ow} \sin \left( \phi_p + \theta_p \right)
\]

(1)

where \(\gamma_{ow}\) is the interfacial tension between hydrate and the bulk fluid, \(\theta_p\) the contact angle between the
hydrate particle and the liquid bridge, $\phi_p$ is the embracing angle, and $R_p$ is the harmonic mean radius of two gas hydrate particles, $\Delta P$ is the hydrostatic pressure inside and outside the liquid bridge surface.

It can be seen from equations (1) that the force between hydrate particles and droplets is directly proportional to the interfacial tension between water and liquid hydrocarbon. The addition of DBSA can significantly reduce the interfacial tension. According to the above formula, the predicted value of the force between particles and droplets at 5°C is calculated and compared with the measured adhesion value. It can be seen that the theoretical predicted value can well reflect the variation law of the measured value, and has high consistency, as shown in Figure 4. Therefore, the interfacial tension is the main factor affecting the anti polymerization performance of DBSA.

4. Conclusions

The effect of DBSA on the interaction between particles and droplets of CyC₅ hydrate was studied by using a micromechanical force device. The results showed that DBSA could reduce the adhesion between particles and droplets by reducing the interfacial tension between oil and water, so as to prevent hydrate aggregation. For different concentrations of DBSA aqueous solution, the higher the concentration, the stronger the ability to reduce the interfacial tension, and the lower the adhesion between hydrate particles and droplets. At different temperatures, the trend was almost the same. The results of this paper can provided a new understanding for the study of anti polymerization mechanism of DBSA, which is helpful to analyze the action mechanism of other anti polymerization agents with similar functional groups as DBSA.

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