Study on the Adhesion Force between Wax Crystal Particles and Hydrate Particles

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ABSTRACT: In this work, to solve the problem of pipeline blockage caused by the accumulation of hydrate particles and wax particles and to explore the interaction characteristics of adhesive force between gas hydrate particles and wax particles as well as droplets, a high-pressure triaxial mobile device was used to measure the adhesion strength between cyclopentane hydrate particles and different commonly seen phases in the pipeline, including cyclopentane hydrate particles themselves, liquid droplets, and wax crystal particles. These experiments were conducted at different temperatures. The results showed that the adhesion between hydrate and wax particles was decreased with the increase in temperature; this is because the wax is amorphous, the heat absorbed when the temperature rises only increases its average kinetic energy, and the stronger the kinetic energy, the lower its viscosity, resulting in reduced adhesion between particles. Meanwhile, this adhesion was also affected by the concentration of wax. As the wax concentration increased from 1 to 5.32 wt % and then to 8.14 wt %, the adhesion between hydrate and wax particles was first decreased and then increased. This was because when the wax crystal concentration was below 5 wt %, a higher wax molecule concentration meant a more hydrophobic surface, which restricted the formation of a capillary liquid bridge between particles and thus reduced the interforce between wax crystal particles and hydrate particles. When the wax crystal concentration was between 5 and 8 wt %, the change of hydrophobicity was no longer the dominating factor, the increase in wax concentration blocked the hydrate molecular diffusion path, which caused a higher hydrate viscosity, therefore leading to a decreased hydrate molecular diffusion rate and a reduced conversion rate of the liquid bridge in hydrates, the lower conversion rate could subsequently lead to the increasing size of micropores in the hydrate shell, and adhesion between particles was increased.

1. INTRODUCTION

Gas hydrates refer to the nonstoichiometric clathrate complexes formed by the main components of gas (such as methane, ethane, propane, and carbon dioxide) and water under high pressure and low temperature conditions.1,2 The low-temperature and high-pressure environment provides favorable conditions for the formation of gas hydrates,3 hydrate particles can be agglomerated together by the capillary force between the particles and then deposited or precipitated on the pipe wall by the adhesion eventually, and these precipitations will increase the pressure drop and cause blockage.4 Pipeline blockage can increase local pressure, decrease production efficiency, and cause potential safety issues. If left unhandled, this situation may lead to significant economic losses. In addition to the blockage of pipelines by hydrates, wax precipitation and deposition are also common problems posing a major threat to the guarantee of submarine flow.5 Many crude oils contain long-chain hydrocarbons dissolved in the bulk phase, and these hydrocarbons constitute a paraffin wax component within the oil. When the temperature and composition are favorable, these wax components will remain as part of the oil phase; however, when the temperature is below the wax appearance temperature (WAT) or the composition of the oil changes, the wax will precipitate and form a three-dimensional structure,6 making paraffin no longer completely soluble.7 These precipitations will reduce the flow cross-sectional area, increase the pressure drop, and eventually block the flow if severe enough.8 Therefore, to fundamentally understand and control the aggregation of hydrate/wax particles, the microscopic force characterization and microscopic interaction of the hydrate/wax particles in the flow system are targeted as the key factors to keep the hydrate slurry safe.

Because cyclopentane (CyC5) and tetrahydrofuran (THF) can form hydrates at normal pressure, which is easy to operate and observe, the interactions between the particles and the...
surface of these hydrates were first studied. Delroisse et al. studied the influence of temperature on the interactional force between ice particles and THF hydrate particles and found that between −10 and 2 °C, the interaction force of THF hydrate particles was decreased with the decrease in temperature, and the interaction force between ice particles and THF particles followed the same trend under the same conditions. Wang et al. measured the force between THF hydrate particles in n-decane on the basis of Delroisse et al. and found that the force between hydrate particles was not only related to temperature but also proportional to the contact force, contact time, and interface energy of the medium where the particles were located. Brown and Koh measured the interaction force between CyC₅ hydrate particles at 3.2 °C in the presence of crude oil and found that the interaction force between CyC₅ hydrate particles was lower than that in the pure water system. Brown et al. tested the effects of annealing time and surfactants on cohesion between cyclopentane (CyC₅) hydrate particles. They found that annealing time reduced the cohesion between particles at different temperatures and the strength of the hydrate shell of the surfactant was reduced compared with that of pure hydrate. Lee et al. studied the force between CyC₅ hydrate particles in the presence of thermodynamic inhibitors and found that the thermodynamic inhibitors could change the hydrate phase equilibrium condition, making the hydrate formation process require greater driving force, and the inhibitors also increased the force between the hydrate particles. In addition, the water layer and corrosion on the outlet pipe wall will affect the growth and deposition of the hydrate film, and the salinity might also affect the agglomeration of hydrate particles.

Although the research on the force between hydrate particles has been relatively complete, it is not directly helpful to the research on the adhesion between hydrate particles and wax particles. Brown et al. used a micromechanical force meter to study the interactions between waxes (both deposited and dissolved) and antiagglomerate-treated hydrates. Waxes had been found to significantly alter the cohesion and bonding forces caused by hydrate particles, but this effect in the presence of anticoagulants might vary depending on the composition of the anticoagulants. In addition, in the process of marine hydrate resource exploitation and submarine oil and gas transportation, the low temperature and high pressure outside the deep-water pipeline would affect the growth of the thin layer of hydrate on the pipe wall as well as the accumulation process of hydrate particles, and the presence of wax also had a great impact on the pipeline transportation. Therefore, the temperature and pipe wall conditions played important roles for the mechanism study of the adhesion forces between hydrate particles, between hydrate and wax particles, and between particles and the pipe surface, as well as for the accumulation and deposition mechanism of gas hydrate particles in the deep-water gas pipeline.

2. EXPERIMENTAL SECTION

2.1. Experimental System and Materials. The adhesion force between particles was measured by a high-pressure triaxial moving platform device (Figure 1). The device is composed of a main pressure reaction kettle, a temperature control system, and a data acquisition system. The function of the main pressure kettle is to provide a stable low-temperature and high-pressure environment for gas hydrate particles; the highest working pressure is 10 MPa, and the lowest working temperature is −10 °C. This experiment was mainly to explore the effects of temperature and wax concentration on adhesion between particles under atmospheric pressure.

The main reactor was installed with a micrometer-level moveable control console attached to a glass fiber needle, and another fixed glass fiber needle was glued to the side wall of the main reactor. When measuring the adhesion between hydrate particles, two hydrate clusters would be fixed on the ends of the two glass fiber needles. When measuring the adhesion between hydrate particles and the interface, the hydrate cluster on the movable needle would be replaced with the samples to be measured. During the experiment, an hG-928CSY series microscope and industrial CCD imaging system mounted on the microscope were used to observe and record the experimental process through the window of the upper cover of the pressure kettle, and it has its own light source. The outer wall of the main pressure kettle is a sandwich structure;
therefore, the coolant can flow in the interlayer space to ensure the temperature stability during the experiment. The main materials used in the experiment are shown in Table 1.

| name          | component | purity (%) | manufacturer               |
|---------------|-----------|------------|-----------------------------|
| cyclopentane  | C5H12     | 96         | Runzhi Chemical             |
| Kunlin Paraffin No. 60 | C22H46 | 99         | China National Petroleum Corporation |
| deionized water | H2O      |            | laboratory-made             |

2.2. Experimental Methods. 2.2.1. Formation Method of Hydrate Particles and Wax Crystal Particles. The formation method of gas hydrate particles was as follows: First, a drop of liquid was dripped on the glass fiber with a syringe and the glass fiber was placed in the main reactor. The temperature was adjusted to subzero to produce ice particles. Then, the ice particles were placed in cyclopentane for 30 min to generate hydrate particles. The produced hydrate particles were then rapidly placed in a reaction kettle. The temperature of the reactor was fixed in advance accordingly for different experiments. The formation process of cyclopentane hydrate particles at −2 °C is shown in Figure 2. When the cyclopentane hydrate particles were left standing for 200 s, a thin layer of hydrate was formed on the surface of the particles, and there was no obvious change inside. The surface and interior of the particle changed after 480 s, the surface became rough, and the hydrate was gradually generated from the outside to the inside. The hydrates inside the particle were basically formed after 800 s, and the particle was a translucent hydrate shell wrapped in free water.

The wax crystal particle generation method was as follows: paraffin was dissolved in industrial white oil with a certain proportion, and then the solution was dropped on glass fiber through a syringe and the temperature was adjusted to low for wax crystal particles to generate.

2.2.2. Measurement Method. The measurement procedure of intergranular adhesion is shown in Figure 3. The movement of particles was controlled by a moving micrometer-scale triaxial mobile platform. The hydrate cluster at the end of the glass fiber was placed under the light path of the inverted microscope (step 1), the other clusters of particles were placed at the end of the manual micromanipulator arm (fixed arm) and kept stationary, and the automatic micromanipulation arm was moved (moving arm) to make the two clusters contact with each other (step 2); this movement was continued until the glass fiber was deformed for a certain distance as shown in step 2 of Figure 3. This procedure allowed the particles to make full contact and then they were slowly pulled apart. Due to the existence of adhesion force between particles, the glass fiber at the end of the manipulator would bend, and the particles on it would move together under the action of adhesion force and adhesive offset (step 3). When the particle movement exceeded the critical value (δ), the elastic force of the glass fiber was greater than the adhesion force, the adhesion between the particles was destroyed, and the two particles would be separated rapidly under the action of the elastic force of the glass fiber (step 4).

The completion of the above steps 1 to 4 was recorded as one experiment, and the time interval between the two experiments was 15 s. The adhesion force F between particles was calculated according to Hooke’s law:

\[ F = k\delta \]

where \( F \) is the interparticle force, and \( K \) is the elastic coefficient of the glass fiber, which is obtained from the calibration experiment conducted in advance. \( \delta \) is the maximum displacement of the hydrate particle before separation from the measured particle/surface.

During the experiment, the annealing time was 30 min because the hydrate formation rate was different when the hydrate particles were in contact with other particles in different temperature ranges. The particle contact time was at least 10 s when investigating the influence of other factors on the adhesion force. For the full contact of particles, accuracy, and repeatability, the interparticle force of each pair was tested at least 30 times and then averaged, and the error bar corresponded to the 95% confidence interval of the geometric distribution.

Since the cluster diameters were different in the experiment, and the variation of diameters would affect the force, comparison of the adhesion forces between particles with different cluster sizes required the elimination of the influence of cluster size; the standardized adhesion force \( F_s \) was used as the final measurement result of the adhesion force between particles. The normalized force \( F_s \) between the two hydrate particles was equal to the measured actual force \( F \) divided by the effective radius \( R^* \):

\[ F_s = \frac{F}{R^*} = \frac{F(R_1 + R_2)}{2R_1R_2} \]

\[ R^* = \frac{2R_1R_2}{R_1 + R_2} \]

3. RESULTS AND DISCUSSION

In this paper, a high-pressure triaxial mobile platform was used to measure the adhesion between cyclopentane hydrate particles and wax particles at different temperatures and at different wax concentrations. In the process of the experiment, the temperature from low to high were set as −2, −1.5, −1, 0,
1, 2, and 3 °C. Considering the purpose of this experiment, the wax content is selected for testing according to the wax content recommended by industry. The concentrations of wax crystals were 1, 3.12, 5.32, 6.5, and 8.14 wt%.

3.1. Measurement of the Adhesion Force between Hydrate Particles and Droplets. First is the hydrate particle and liquid droplet adhesion force experiment. The adhesion force versus temperature result is shown in Figure 4 below, showing that the hydrate particle and droplet adhesion force was decreased with the rise of temperature. At −2 °C, the average adhesion force between particles was 0.0883 mN/m with a standard deviation of 0.0035 mN/m; when the temperature rose to 3 °C, the average adhesion force dropped to 0.00634 mN/m with a standard deviation of 0.00254 mN/m. To explain this phenomenon, the morphology changes of hydrate particles in the testing process at −2 °C (Figure 7) and 2 °C (Figure 8) were analyzed.

The reason for this trend and phenomenon was that the liquid bridge would be formed when the hydrate particle and liquid droplet contacted with each other, the solid hydrate would quickly spread to the central liquid bridge, and the existence of solid hydrate would lead to the increase in adhesion force between the hydrate particle and the liquid droplet, especially at −2 °C, as shown in Figure 6. In 2 °C, besides the small amount of hydrate formed at the boundary of the initial contact area, the whole test process had no apparent hydrate formation, as shown in Figure 7. This phenomenon was mainly because of the high temperature and low degree of supercooling. This variation rule is the same as the results measured in the literature, as shown in Figure 5 below.

According to Figures 4, 6, and 7, the following conclusions can be drawn: In the process of contact between hydrate particles and droplets, the resulting liquid bridges will be transformed into solid hydrates. The formation of solid hydrates will lead to an increase in the contact area and an increase in the force range, which will significantly increase the force between the hydrate particles and droplets and the adhesion between the drops, and the lower the temperature, the higher the amount of hydrate formed and the greater the adhesion between the hydrate particles.

3.2. Measurement of Adhesion between Hydrate Particles. The variation trend of the adhesion force between hydrate particles with temperature is shown in Figure 8. As shown from the figure, when the temperature was −2 °C, the average force between hydrate particles was 0.0144 mN/m with a standard variance of 6.92 × 10⁻⁶ mN/m; when the temperature was 3 °C, the average force rose to 0.0269 mN/m and the standard variance was 0.00129 mN/m. Results showed that the adhesion force between hydrate particles was increased with the increase in temperature, and this trend was the same as in the literature. As shown in Figure 9, when the temperature is −6.0 °C, the interparticle adhesion is 0.0022 N/m; when the temperature is −2.5 °C, the interparticle adhesion is 0.03 N/m. It can be seen that at the temperature in the range of −6.0 to −2.5 °C, the adhesion force between THF hydrate particles increases with the increase in temperature, and THF and cyclopentane are very similar in structure, so it can be used as a reference experimental group to compare this time. The experimental results are compared and analyzed.

The analysis showed that the change of liquid bridge volume due to the temperature change was the main reason for the variation of adhesion force with temperature. When the temperature gradually increased to the melting point, the surface of the hydrate particles would melt and form a microliquid layer. The thickness of the microliquid layer decreased with the increase in supercooling degree. When the surface of hydrate particles was covered with such a layer of liquid, a liquid bridge could be formed during particle contact. When the temperature rose, the surface of solid particles melted more, the thickness of the microliquid layer was increased, and the volume and area of the liquid bridge were also increased, leading to the increase in adhesion force between hydrate particles. This change can be seen in Figure 10.

3.3. Measurement of the Adhesion between Hydrate Particles and Wax Particles. In the development of deep-sea oil and gas fields, the coexistence of wax crystals and gas hydrates in one system occurs. When the pipeline is under more extreme conditions, hydrate formation and wax deposition are likely to occur simultaneously. The presence of wax will affect and change the interfacial tension of the
particles and the interaction between the particles, thereby affecting the adhesion between the particles. Therefore, understanding the force between wax crystal particles and hydrate particles at different temperatures and concentrations plays an important role in understanding the generation mechanism of blockages in the pipeline and in ensuring the normal operation of the pipeline.

3.3.1. Influence of Temperature on the Adhesion between Hydrate Particles and Wax Particles. The variation trend of the adhesive force between hydrate particles and wax particles with temperature is shown in Figure 11. According to the figure, the adhesive force between hydrate particles and wax particles was decreased with the increase in temperature. According to the experimental data of the group with the wax concentration of 5.32%, when the temperature was at $-2^\circ$C, the average adhesion force between particles was 0.0348 mN/m and the standard variance was 0.00139 mN/m. When the temperature rose to $3^\circ$C, the average adhesion force between
particles and droplets dropped to 0.0123 mN/m, and the standard variance was 6.06 × 10⁻⁴ mN/m. To explain this phenomenon, the morphology changes of hydrate particles in the testing process at −1.5 °C (Figure 12) and 1 °C (Figure 13) were analyzed.

At the temperature of −1.5 °C, a fine liquid bridge was formed when the wax crystal particles contacted with the hydrate particles, and a solid hydrate was formed on the liquid bridge by the hydrate particles below during the separation. This phenomenon was gradually obvious on the liquid bridge after separation. Under the condition of 1 °C, a large liquid bridge was generated when the wax crystal particles contacted with the hydrate particles, and the liquid bridge was gradually stretched during the separation. However, only a little solid hydrate was generated on the liquid bridge by the hydrate particles below, and no obvious hydrate formation was found during the separation.

On the other hand, due to the viscosity of paraffin, it reflects its flow characteristics. The higher the viscosity, the lower the flow characteristics. Because paraffin is amorphous, there is no fixed melting point, but the crystal has a fixed melting point. The crystal and amorphous structures are shown in Figure 14. When the temperature rises, the crystal absorbs heat, the average kinetic energy of the molecules and atoms inside it rises, and the temperature also rises, but it does not destroy its spatial lattice, there is still a regular arrangement, and the spatial lattice begins to disintegrate. In the process of the crystal absorbing heat, the absorbed heat is used to destroy the spatial lattice of the crystal part by part. Due to the irregular arrangement of molecules and atoms, the noncrystal does not need to destroy its spatial lattice after absorbing heat but is only used to increase the average kinetic energy. Therefore, the higher the temperature, the stronger the kinetic energy inside the paraffin and the higher its flow characteristics. The lower the viscosity, the lower the adhesion between the wax crystal particles and the hydrate particles.

In the previous experiment on the effect of temperature on the interforce of hydrate particles, a higher temperature led to a larger liquid bridge between hydrate particles and resulted in an increase in the interforce of hydrate particles. In this experiment, due to the strong hydrophobicity and lipophilicity on the surface of wax particles, even if the temperature was increased and the liquid bridge volume on the surface of hydrate particles increased, the interforce between wax particles and hydrate particles could not be increased.

Figures 12 and 13 show the schematic diagrams of the separation morphology change process of the cyclopentane hydrate particles and wax crystal particles under the temperature conditions of −1.5 and 1 °C, respectively, which can be clearly seen from the two figures. The liquid bridge to the particles changes with temperature.

Combined with the above reasons, a higher temperature led to the smaller interforce between wax and hydrate particles.
3.3.2. Influence of Wax Crystal Concentration on the Adhesion between Hydrate Particles and Wax Particles. To explore the influence of wax crystal concentration on the adhesion between hydrate particles and wax crystal particles, experimental data of five groups of wax crystal particles with different concentrations at different temperatures were grouped into the same scatter plot, as shown in Figure 11. The figure shows that the adhesion force between wax crystal particles and hydrate particles changed with the change of concentration under the same temperature condition. When the wax concentration was 1 wt %, the adhesion between particles was the largest, and when the wax concentration was 5.32 wt %, the adhesion between particles was the smallest, and the adhesion forces under the conditions of other concentrations of wax crystal particles followed the same trend and were distributed between them.

To understand the causes of the above phenomena, another experiment was conducted to measure the changes of the plane and the indirect antennae of water droplets with different wax contents, and the boundary line of contact between water droplets and the plane was taken as the reference line. In Figure 15a,b, the contact angle was increased from 65° to 78° for the concentration of 1 to 5 wt %. For the wax concentrations below 5 wt %, a greater concentration meant stronger surface hydrophobicity, which would affect the formation of the capillary liquid bridge between particles; therefore, the interforce between wax and hydrate particles was reduced.

In Figure 15b,c, the contact angle was increased from 78° to 86° for the concentration of 5 to 8 wt %. Although the contact angle was increased, the increased angle was only 8°, which was much smaller than 13° for the wax concentration of 1 to 5 wt %. Moreover, Figure 16 indicates that when the liquid droplets contacted with wax, the wax on the plane would transfer to the liquid droplets. When the hydrate particles contacted with wax crystal particles, the generated solid hydrate would contact with wax on the liquid bridge, thus increasing the adhesion force between hydrate particles and wax crystal particles. When the wax crystal concentration was increased from 5.32 to 8.14 wt %, the adhesion force tended to increase. The reason can be explained as follows: when wax particles contacted with hydrate particles, a thin layer was formed on...
the contact surface. When the temperature rose, the cyclopentane molecules diffused from the inside of the hydrate particles to the surface of the hydrate particles and moved along with the liquid bridge to the wax crystal particles, and the solute wax would also move toward the liquid bridge. When the wax concentration was increased, its lipophilicity and hydrophobicity were enhanced. The wax molecules blocked the diffusion path of cyclopentane hydrate molecules, which would increase the bulk viscosity and reduced the diffusion rate of hydrate molecules, thereby reducing the conversion rate of hydrate in the liquid bridge, which led to an increase in the size of the micropores in the hydrate shell, finally resulting in an increase in force.

On the other hand, when the wax crystal concentration was increased from 5.32 to 8.14 wt %, Figure 17 shows that some fine and dense indentation marks would be formed on the surface of the wax crystal particles. These indentation marks would not only increase the surface roughness of the wax crystal particles when in contact with the hydrate particles but also increase the contact area of the liquid bridge, thereby increasing the adhesion between the wax crystal particles and the hydrate particles.

4. CONCLUSIONS

In this paper, a high-pressure triaxial moving platform was used to measure the adhesion between cyclopentane hydrate particles, cyclopentane hydrate particles and wax particles, and hydrate particles and liquid droplets under different temperatures, and the following conclusions were drawn.

Interparticle forces between hydrate particles were found to be increased with the rise of temperature, while particle interatomic forces between hydrates and liquid droplets would be reduced with the increase in temperature. The analytical results showed that due to the increase in temperature, the volume and area of the liquid bridge between the hydrate particles gradually increased and the adhesive force was gradually increased. For the hydrate particle and droplet, the liquid bridge generated during the contact would be transformed into solid hydrate; when the temperature rose, less solid hydrate was generated, hence smaller force.

The force between the hydrate particles and the wax particles was studied with the temperature change because wax itself had certain properties. As an amorphous phase, its viscosity could be reduced with higher temperature, and as a hydrophobic particle, the liquid bridge generated on the hydrate particle surface at higher temperature had little effect on the adhesion force; therefore, the force was decreased.

Finally, the force between the hydrate particles and the wax crystal particles changed with the wax crystal concentration. A greater wax concentration led to a smaller adhesion between the particles in the range of 1 to 5 wt %; a greater wax concentration led to a greater adhesion between particles in the range of 5 to 8 wt %. Concentrations beyond 8 wt % have not been tested, and further research is needed in the future.

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Notes
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