Effect of CO₂ injection on interfacial tension of oil-formation water system under high temperature and pressure

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Abstract. The interfacial interaction between CO₂ and oil and water is one of the important factors affecting the effect of CO₂ enhanced oil recovery. Taking dead oil in Zhoucheng Oilfield as an example, the variation of interfacial tension between crude oil-carbonated water two-phase system and oil-formation water two-phase system was studied by pendant drop method. The influence of different CO₂ saturation on the equilibrium interfacial tension of oil-formation water system and changes of equilibrium interfacial tension between crude oil-carbonated water system and crude oil-formation water system were analyzed. Moreover, previous studies did not reflect the experimental phenomena of extracting light hydrocarbons from oil droplets by CO₂ through gas-water interface. This paper provides experimental research and analysis for this experimental phenomenon. The results show that the equilibrium interfacial tension of crude oil-carbonated water system decreases with the increase of pressure, and the dissolution and diffusion of the system becomes more and more obvious with the increase of pressure. The medium exchange occurs between oil and carbonated water, and the phenomenon of partial miscibility occurs. There is a threshold pressure value between crude oil and formation water with different CO₂ saturation. Each group of samples has its threshold pressure and optimum CO₂ injection rate. It's not that the more CO₂ injection, the better oil displacement effect. This research provides a reference for us to save the cost of CO₂ flooding.

1. Introduction
In recent years, with the rapid development of the global economy and population explosion, carbon dioxide (CO₂) emissions have increased year by year. CO₂ flooding can not only effectively improve oil recovery, but also reduce greenhouse gas emissions, which is of great significance to improve the environment [1-2]. For the reservoirs in the middle and later stages of development, there are still a large number of remaining oil remaining in the reservoirs after water flooding, and it is difficult to further improve oil recovery [3-5]. CO₂ flooding has been widely used because it can effectively improve recovery and carbon sequestration after water flooding. In the development of American oilfields, CO₂ flooding can increase oil recovery by 10%-20% [6-8]. China has already applied CO₂ flooding in North China, Jilin and Shengli oilfields, and achieved good development results [9-11].

In CO₂ enhanced recovery technologies such as CO₂ flooding and CO₂ huff and puff, the interfacial interaction of CO₂-oil-water is one of the important factors affecting the development effect of oil wells [12-15]. At present, the mechanism of CO₂ EOR technology is mainly focused on the interfacial tension characteristics of CO₂-crude oil system. The interfacial interaction characteristics and mechanism of CO₂-formation water-oil system are less studied. Previous studies did not show the

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experimental phenomena of extracting light hydrocarbons from oil droplets by CO₂ through gas-water interface [16-18], and this paper provides experimental research and analysis for this experimental phenomenon. Moreover, the variation of interfacial tension of crude oil-carbonated water system under different reservoir pressures and different CO₂ solubility was measured accurately [19-22]. The variation of equilibrium interfacial tension of crude oil-formation water system and crude oil-carbonated water system were compared. Each group of samples has its threshold pressure and optimum CO₂ injection rate, these two parameters are conducive to reducing the cost of CO₂ flooding.

2. Experiment

2.1. Experimental samples
The crude oil used in the experiment is degassed crude oil from Zhoucheng Oilfield. The density of crude oil is 0.9224 g/m³, and the viscosity is 156.55cp. The experimental temperature is 74 ℃. The purity of CO₂ and nitrogen used in the experiment are 99.995% and 99.9995% respectively. The composition of brine is shown in Table 1:

| Temperature (℃) | pH    | Na   | K⁺   | Mg²⁺ | Ca²⁺ | Sr²⁺ | Ba²⁺ | Cl⁻  | SO₄²⁻ | CO₃²⁻ | HCO₃⁻ | Total salinity mg/L | Water type     |
|-----------------|-------|------|------|------|------|------|------|------|-------|-------|-------|----------------------|---------------|
| 33.20           | 6.90  | 7451.00 | 45.48 | 54.73 | 66.38 | 15.66 | 0.89 | 12386.12 | 4091.12 | 0.00 | 1427.23 | 25522.06 | CaCl₂ Produced water |

2.2. Experimental equipment and mechanism
The high temperature and high-pressure interfacial tensiometer manufactured by Sanchez Technologies was used. The working temperature is 0-200 ℃ and the working pressure is 0-70 MPa. The diameter of the needle is 0.82 mm in the experiment. The densitometer produced by Anton Paar Company was used in the experiment. The maximum pressure is 70 MPa and the maximum temperature range is 200 ℃. The experimental installation is shown in Figure 1.

The mechanism of measuring the interfacial tension by pendant drop method is [23-25]:

\[
\gamma = \frac{\Delta \rho g d_e^2}{H}
\]

In the formula: \( \gamma \) is two phase interfacial tension, \( \Delta \rho \) is the difference of fluid density, kg/m³; \( d_e \) is the largest diameter of pendent droplets, m; \( 1/H \) is a function describing the shape factor of pendent droplets and related to the shape factor \( S \).
Shape factor $S$ is defined as $S = D_e/D_s$. $D_e$ is the diameter of droplets, and $D_s$ is the diameter of droplets plane that the distance from the plane to the bottom is equal to $D_e$.

The interfacial tension can be calculated by measuring the $D_e$, $D_s$ of the droplets in the experiment. The meaning of these specific parameters is shown in the figure 2.

![Figure 2. The mechanism for determination of inter-facial tension by pendent drop method.](image)

2.3. Experimental methods

2.3.1. Interfacial tension test procedures

a) The experimental system of petroleum ether cleaning was used. After cleaning, residual petroleum ether was purged with nitrogen.

b) Use alcohol and distilled water to wash needles, then dry them, and install the needles on the suspension device.

c) The air in the reactor is pumped out by a vacuum pump and maintained at -0.1 MPa for more than 30 minutes.

d) Transfer the oil sample into the crude oil injection pump.

e) Start heating the whole interface tensiometer by the heater system and use electric heater to heat oil injection pump, until the reactor and the oil injection pump both reach the experimental temperature (74°C).

f) Inject the formation water into the high temperature and high pressure reactor from the bottom valve until the reactor filled with formation water, then inject CO₂ at constant experimental pressure into the reactor from the top valve. Constant pressure pump, CO₂ container and reactor stay connected, and keep the pressure at experimental pressure for 24 hours to make sure the formation water saturated with CO₂.

g) Turn off the valves of the reactor.

h) Ensure that the needle immersed in the water phase to form an upper pendent oil drop. Every pressure point need to be stable for 24 hours to make sure the formation water saturated with CO₂. At least three droplets were photographed at each pressure point, each droplet should be stable for 30 minutes, and each droplet should take at least three photos.

i) Adjust the experimental pressure, repeat step f, g, h, until the end of the experiment.

2.3.2. Density measurement. In the process of calculating interfacial tension, it is necessary to determine the density of saturated carbonate water and crude oil under different pressures. Density is measured by high temperature and high-pressure densitometer.

The high temperature and high-pressure densitometer is connected with the drop chamber through a pipeline, and the temperature when measuring the density is 74 °C. Under each experimental
pressure condition, the saturated carbonate water in the suspension chamber was introduced into the densitometer through the pipeline, and the density of the saturated carbonate water in the suspension chamber was measured in real time. After the experiment complete, the crude oil in the crude oil injection pump was introduced into the high temperature and high-pressure densimeter to measure the density of crude oil at the experimental pressure point.

2.3.3. Flash evaporation experiment. The saturated carbonated water was transferred into the flash bottle and the volume and pressure of the sample were recorded. Connect the flash bottle with the gas meter, slowly release the gas into the gas meter, keep the pressure of the gas meter unchanged, record the volume change and temperature change of the gas meter. The mass changes before and after degassing in flash bottle were recorded, and the carbonate saturation was calculated by the measured data.

3. Results and discussion

3.1. Experiment phenomenon

3.1.1. Two-phase interface characteristics of crude oil-formation water system. Figure 3 (a), (b) and (c) are interface pictures of crude oil-formation water system under temperature of 74 ℃ and under pressure of 10MPa, 20MPa and 35MPa, respectively. It can be found that there is no dissolution and extraction phenomena between crude oil and formation water system under different pressure conditions with the increase of pressure. There are no obvious light hydrocarbon layers in the three groups of experiments, which indicates that there is no medium transfer between crude oil and formation water.

3.1.2. Three-phase interface characteristics of oil-co2-formation water system. Figure 4 shows a mass transfer between oil-carbonated water systems under temperature of 74 ℃. It can be seen in figure 4(a) that when the pressure is 5 MPa, there is no dissolution and extraction phenomena phenomenon between the oil droplets and the carbonate water system. When the pressure rises to 14 MPa, as can be seen in Figure 4 (b), a thin layer of light hydrocarbons can be found at the interface between oil droplets and carbonated water. In the oil-gas-water three-phase system, CO2 first contacts the gas-water interface, and then dissolves and extracts oil droplets through the interface. As the pressure rises, the extraction of light components in oil increases. As shown in Figure 4 (c), when the pressure rises to 30 MPa, the light component column mentioned by CO2 extraction is more obvious at the top of the oil drop, and the light hydrocarbon layer around the oil drop is thicker. It can be seen that increasing pressure is helpful to accelerate the passage of CO2 at the gas-water interface and to the extraction of
light components in the oil phase. Previous studies did not find the experimental phenomena of extracting light hydrocarbons from oil droplets by CO$_2$ through gas-water interface.

![Interface characteristics under 5MPa](image1)
![Interface characteristics under 14MPa](image2)
![Interface characteristics under 30MPa](image3)

**Figure 4.** Interaction between crude oil and formation water saturated with CO$_2$.

3.1.3. **Difference analysis of interface characteristics.** There is no mass transfer between crude oil and water system, and the change of pressure has no obvious effect on the interface characteristics between oil and water, so crude oil and formation water are completely immiscible in the reservoir. For the crude oil-carbonated water system, CO$_2$ will first diffuse into the crude oil through the gas-water interface, and then extract the light components from the crude oil in free gas form that previous studies did not show the experimental phenomena. Medium exchange occurs between crude oil and carbonated water, and there exists partial miscibility, which increases with the change of pressure.

3.2. **Analysis of experimental results**

3.2.1. **Effect of different saturation of CO$_2$ on interfacial tension of oil-water system.** The equilibrium interfacial tension between crude oil and carbonated water with different saturation is shown in the Figure 5. The equilibrium interfacial tension of the system decreases significantly with the increase of pressure. This shows that CO$_2$ can reduce oil-water interfacial tension, improve oil-water interfacial characteristics and enhance oil displacement efficiency. When P < 17.09MPa, the interfacial tension of water balance in crude oil-saturated CO$_2$ formation tends to decrease gradually. When P > 17.09MPa, the interfacial tension of water balance in crude oil-saturated CO$_2$ formation decreases slowly and basically remains unchanged.

![The equilibrium interfacial tension of oil-saturation carbonated water](image4)

**Figure 5.** The equilibrium interfacial tension of oil-saturation carbonated water.
Through a single degassing experiment of carbonated water under different pressure, the solubility chart of CO₂ in formation water was obtained. As shown in Figure 6, the solubility of CO₂ in water increases with the increase of system pressure. When P < 17.09 MPa, the solubility increased rapidly, and when P > 17.09 MPa, the solubility increased slowly and almost saturated. At the same time, compared with Figure 5 and Figure 6, it can be seen that with the increase of system pressure, the amount of dissolved CO₂ gas increases and the interfacial tension between oil and water decreases. When the system pressure reaches the threshold pressure of 17.09 MPa, the amount of dissolved CO₂ almost reaches the maximum. When the pressure reaches 17.09 MPa, the solubility of CO₂ increases slowly, and the interfacial tension of water balance between crude oil and saturated CO₂ formation decreases slowly and basically remains unchanged.

**Figure 6.** The solubility of CO₂ in the formation water under different pressure.

The experimental results show that when the pressure reaches 23 MPa, the interfacial tension between CO₂ and formation water can reach 12 mN/m, which indicates that the interaction between formation water and CO₂ system is difficult to achieve miscibility.

The threshold pressure exists in the system of crude oil and carbonated water with different saturation. When pressure is higher than the threshold pressure, the increase of dissolved CO₂ gas is slow, and the interfacial tension of the system will not decrease obviously with the increase of pressure. So it's not that the larger the CO₂ injection, the better the oil displacement effect. There is an optimum CO₂ injection in this system. For Zhoucheng crude oil and saturated carbonate water system, when the gas-liquid ratio is 23.69 and the solubility of CO₂ is 1.06 mol/kg, the interfacial tension is better and the cost is lower.

3.2.2. **Comparison of the changes of equilibrium interfacial tension of two systems.** As shown in Figure 7, the equilibrium interfacial tension of crude oil-formation water system remains basically unchanged with the increase of pressure. The equilibrium interfacial tension of crude oil-carbonated water system decreases obviously with the increase of pressure and the increase of CO₂ solubility. After dissolving CO₂ in formation water, the interfacial tension of crude oil-saturated CO₂ carbonate system is lower than that of non-carbonated system, and the difference between the two systems increases with the increase of pressure. The interfacial tension of oil-water balance decreased by 13.94% after CO₂ injection. It can be seen that CO₂ injection can effectively reduce the interfacial tension of oil-water balance.
4. Conclusions

(1) There is no obvious transfer between oil and formation water systems. In the oil-carbonated water system, the extraction of crude oil by CO₂ is gradually enhanced, when the pressure becomes higher, and the medium exchange between oil and carbonate water occurs, resulting in partial miscibility.

(2) There is a threshold pressure in the crude oil-carbonated water system with different saturation. When the pressure is lower than the threshold value, the amount of dissolved CO₂ gas increases and the interfacial tension between oil and water decreases with the increase of the system pressure. When the pressure is higher than the threshold value, the amount of dissolved CO₂ gas increases slowly, and the interfacial tension of the system will not decrease obviously with the increase of the pressure.

(3) The interfacial tension of oil and non-carbonated formation water is higher than that of oil-saturated CO₂ water system. With the increase of pressure, the interfacial tension of oil-saturated CO₂ water system increases gradually, and the interfacial tension of oil-formation water system basically maintain unchanged. Injecting CO₂ can effectively reduce the interfacial tension of oil-water system.

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