Determination of the Minimum Miscible Pressure of the Supercritical Carbon Dioxide and the Formation Oil System by the Pendant Drop Method

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ABSTRACT: *Carbon dioxide miscible displacement plays an important role in the field of miscible displacement for enhanced oil recovery. However, there is a very important relationship between the formation of miscible displacement and the minimum miscible pressure. The pendant drop method in the interfacial tension method was firstly used to predict the minimum miscible pressure of the supercritical carbon dioxide and the formation of oil in the test area oilfield. Under the condition of the simulated reservoir temperature 111.5 °C, the interfacial tension of the supercritical carbon dioxide and the formation oil system was tested experimentally by using formation oil samples of the test area oilfield. The range of test pressure was from 10.06 MPa to 28.57 MPa. Besides, the relation curve of the test pressure and the interfacial tension was drawn. The results show that under the reservoir temperature, the interfacial tension between the supercritical carbon dioxide and the formation oil shows an approximately linear downward trend with increasing the test pressure. The mathematical expression was obtained by the linear regression analysis. According to the extrapolation, the vanishing point of the interfacial tension was obtained. Then the minimum miscible pressure of the supercritical carbon dioxide and the formation oil system was determined. The actual test was carried out to verify the result by the pendant drop method. Finally, the minimum miscible pressure of the supercritical carbon dioxide and the formation oil system of the test area oilfield was determined to be 29.4 MPa.*

KEYWORDS: *Pendant drop method; Interfacial tension; Supercritical carbon dioxide; Minimum miscible pressure; Miscible displacement.*

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INTRODUCTION

Carbon dioxide miscible displacement plays an important role in the field of miscible displacement for enhanced oil recovery [1-4]. However, the formation of miscible displacement in a test area has a crucial relationship with the minimum miscible pressure [5, 6]. If the minimum miscible pressure is higher than the formation pressure, it is necessary to find some methods to reduce the minimum miscible pressure and make it lower than the formation pressure in order to realize miscible displacement [7, 8]; if the minimum miscible pressure is lower than the formation pressure, the miscible displacement can be achieved theoretically [9, 10]. The minimum miscible pressure is closely related to the oil-gas interfacial tension. The interfacial tension between carbon dioxide and formation oil decreases with the increase of system pressure. The lower the interfacial tension is, the higher the oil displacement efficiency is [11, 12]. When the system pressure is high enough, the oil-gas interface disappears, and the interfacial tension is zero. At this time, we can obtain the miscibility and the highest oil displacement efficiency [13]. By testing the interfacial tension between carbon dioxide and formation oil under different pressures at the formation temperature, the rule of oil-gas interfacial tension changing with injection pressure can be studied, and by testing the vanishing point of the oil-gas interface, the minimum miscible pressure between the carbon dioxide and the formation oil in one contact miscibility can be determined [14, 15].

The determination methods of minimum miscible pressure in domestic and foreign literature generally include laboratory experiments and theoretical calculations [16]. Laboratory experiments include a long slim tube displacement experiment, interfacial tension method, rising bubble meter method, vapor density method, and so on. Theoretical calculation methods include the empirical formula method, equation of state method, analog calculation method, and so on [17]. Compared with other methods, the interfacial tension method can not only be determined by direct observation of the contact miscibility state but also can be estimated by using the measured interfacial tension data, which is easy to operate and time-saving. There are also many methods to measure the gas-liquid interfacial tension. However, as the reservoir is usually in a state of high-temperature and high-pressure, the pendant drop method to measure the gas-liquid interfacial tension in the high-temperature and high-pressure system is widely employed [18]. The pendant drop method can be used to determine both the gas-liquid interfacial tension and the liquid-liquid interfacial tension, as long as there is a density difference between the two phases and one of the phases is transparent [19]. Therefore, in order to determine the minimum miscible pressure more quickly and accurately, the pendant drop method is used for the first time in this study to determine the minimum miscible pressure of the formation of oil in the test area and the supercritical carbon dioxide system.

EXPERIMENTAL SECTION

The experimental principle

The pendant drop method is an effective method for measuring the interfacial tension between gas and liquid and between liquid and liquid under high-temperature and high-pressure conditions [20]. The experimental principle of the method: when a larger density of liquid B forms a stable pendant drop in a smaller density of liquid A, the forces on pendant drop B are balanced, including buoyancy, interfacial tension, and gravity [21]. When the pendant drop is stable and the forces are balanced, the interfacial tension between the two phases can be calculated by the density difference between the two fluids, the profile size, and the shape of the pendant drop, and by applying the mathematical model [22]. If the density of fluid A is greater than that of fluid B, fluid B can form a stable static bubble in fluid A to measure the interfacial tension, that is, using bubbles formed by gas in the water for measurement [23]. This method can be called the static bubble method but is customarily often referred to as the pendant drop method [24].

In the pendant drop method, it firstly forms stable droplets on the tip of the capillary probe, then measures the configuration parameters of the pendant drop, including shape and size, and finally calculates the interfacial tension between gas and liquid using the Bashforth-Adams equation [25, 26]. There are many methods for calculating interfacial tension through mathematical models based on droplet configuration parameters, however, in view of the prediction results of various current mathematical models, the surface selection method by Andreas et al. is widely used and of practical value.

Andreas set:

$$S = d_s / d_e \tag{1}$$

$$H = \left(-\beta d_e / b\right)^2 \quad (2)$$

Where: d_e — the maximum diameter of the pendant drop, m; d_s — the diameter of the selected surface, m: defined as the length of the parallel line with the maximum diameter which intersects the contour curve of the droplet (the parallel line is made at the position with a vertical distance d_e from the vertex of the pendant drop). β and b are the shape factor and size factor respectively in the Bashforth-Adams equation.

The schematic diagram of the pendant drop surface selection method is shown in Fig. 1, d_e and d_s can be measured according to the droplet shape [27, 28].

The formula for calculating surface tension is shown as follows:

$$\gamma = \Delta\rho b^2 g / \beta \quad (3)$$

The following formulas can be derived from the Eqs. (1), (2) and (3).

$$\gamma = \Delta\rho d_e^2 g / H \quad (4)$$

$$1/H = f\left(d_s / d_e\right) \quad (5)$$

Where: γ— the interfacial tension between the two phases, mN/m ; g— gravity constant, m/s^2; $\Delta\rho$— density difference between the two phases, g/cm^3; $1/H$ is a function of d_s / d_e, and its value can be obtained by looking up the table of d_s / d_e values. Therefore, after d_s and d_e are measured by the projection method, H value can be obtained, that is, the interfacial tension can be calculated.

Experimental apparatus of pendant drop method

The experimental apparatus to test the interfacial tension between carbon dioxide and formation oil is the high-temperature and high-pressure pendant drop interfacial tension meter of Canadian PRI. The apparatus can test the interfacial tension between gas and liquid and between liquid and liquid. The test temperature can reach 180 °C, and the test pressure can reach 70 MPa, and the test range of interfacial tension is 80-0.008 mN/m. The schematic diagram of the experimental apparatus for testing the interfacial tension by the pendant drop method is shown in Fig. 2. The viscosity of crude oil under formation conditions is 1.89 mPa·s.

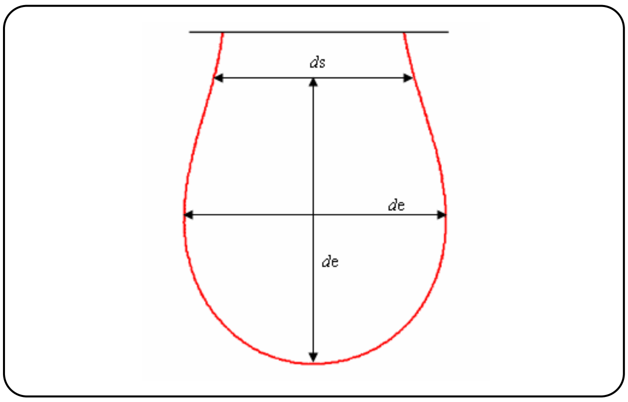

Fig. 1: The schematic diagram of the pendant drop method.

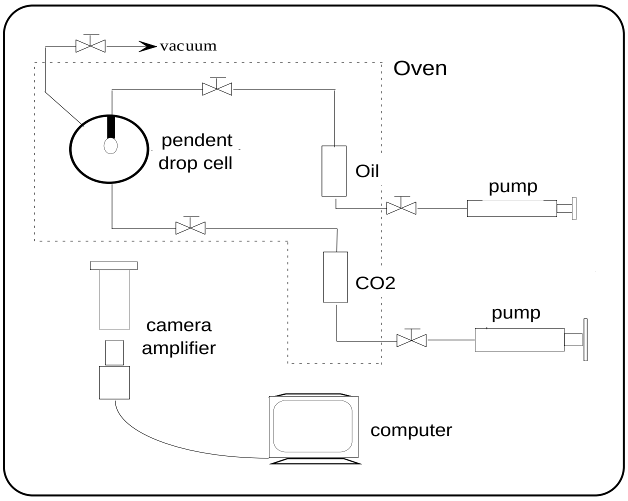

Fig. 2: The experimental apparatus schematic diagram for testing the interfacial tension by the pendant drop method.

Determination of interfacial tension

Firstly, the pendant drop chamber in the experimental apparatus should be cleaned with petroleum ether and toluene as the cleaning materials. After cleaning, it should be purged with hot nitrogen to remove the residual petroleum ether in the pendant drop chamber, and then the chamber should be vacuumed. The test system is heated to the required temperature (formation temperature) and then kept at a constant temperature, and then the system is pressurized to the required test pressure (formation pressure) while carbon dioxide gas is gradually injected into the pendant drop chamber.

After the test system, pressure and temperature tend to stabilize, the formation oil sample is slowly injected into the pendant drop chamber through the capillary probe at predetermined test pressure. At this time, the formation oil sample will form a suspended oil drop at the tip of the probe.

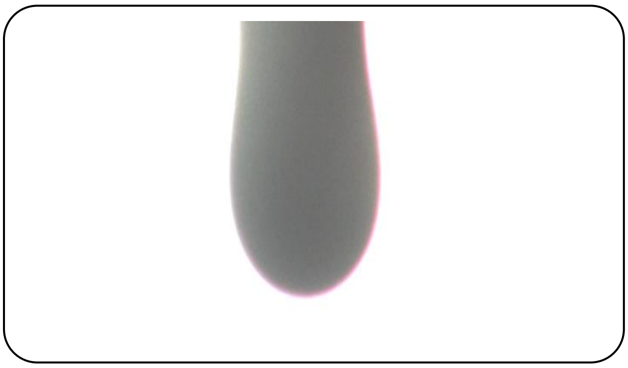

Fig. 3: The oil drop shape image at the pressure 12.17MPa (111.5 °C).

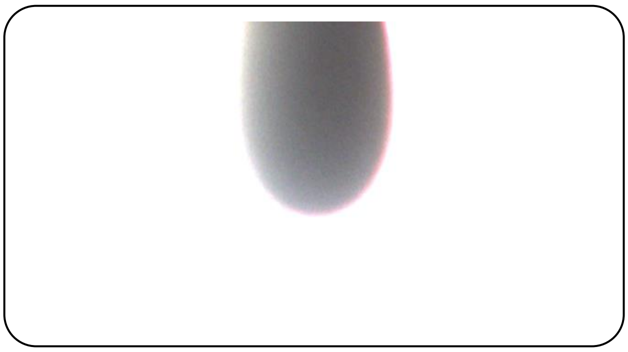

Fig. 4: The oil drop shape image at the pressure 19.81MPa (111.5 °C).

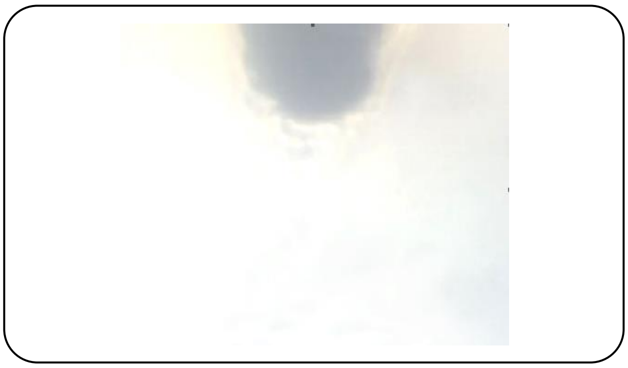

Fig. 5: The oil drop shape image at the pressure 25.22MPa (111.5 °C).

The oil drop will gradually become larger as the formation oil is injected. When a stable oil drop is formed on the tip of the probe, a picture of the oil drop's shape is shown in Fig. 3, Fig. 4, and Fig. 5 are taken with the camera system in the device. According to the shape of the oil drop, the interfacial tension between carbon dioxide and formation oil is calculated by Andreas's surface selection method. At this point, the interfacial tension test under a pressure is completed. After the pendant drop chamber is cleaned again, repeat the above steps to test the interfacial tension of the carbon dioxide-formation oil under other pressures until the formation oil cannot form a complete oil drop in carbon dioxide.

RESULTS AND DISCUSSION

In order to better show the changing rule of the interfacial tension under different test pressures, the initial pressure point of 10.06MPa is selected from a smaller pressure point of about 10MPa. Then increase the pressure value in turn to select different test pressure points, and measure the interfacial tension at each selected pressure point until the interfacial tension is close to zero. The final pressure point selected in this study is 28.57MPa. Moreover, enough pressure points should be selected to better reflect the trend of interfacial tension changing with pressure. The test data of interfacial tension, formation oil density, and carbon dioxide density under different test pressures during the experiment are shown in Table 1. According to the data in Table 1, the density of formation oil under different pressures can be determined by PVT experiments, as shown in Fig. 6. The carbon dioxide gas density can be calculated from the state equation, as shown in Fig. 7. The trend curve of interfacial tension with test pressure is plotted in Fig. 8.

The experimental results show that the interfacial tension between the formation of oil and carbon dioxide decreases with the increase of test pressure, and the decreasing trend is approximately linear. The mathematical relationship is obtained by linear regression analysis, with an intercept of 11.637, a slope of -0.3958, and a correlation coefficient of 0.9918.

$$IFT = -0.3958 \times P + 11.637 \quad (3)$$

Where: *IFT*—interfacial tension, mN/m ; *P*—test pressure, MPa.

According to Eq. (3), it is obtained by extrapolation: when the interfacial tension is zero, the test pressure is 29.4 MPa. The shape of the pendant drop when the actual test pressure reaches 29.4 MPa is shown in Fig. 9. It can be seen that when the system pressure reaches 29.4 MPa, the formation oil cannot form a complete oil drop in the carbon dioxide and diffuse quickly after the two phases of contact. A stable interface cannot be formed between the oil and gas, indicating that the interfacial tension disappears, and the formation of oil and carbon

Table 1: The experimental data for testing the interfacial tension by the pendant drop method.

Test Pressure (MPa)	Interfacial Tension (mN/m)	Formation Oil Density (g/cm^3)	CO_2 Density (g/cm^3)
10.06	8.15	0.7778	0.1780
11.22	7.40	0.7791	0.2066
12.17	6.84	0.7800	0.2321
13.55	6.15	0.7815	0.2665
16.14	5.05	0.7840	0.3349
17.19	4.55	0.7851	0.3645
18.51	4.03	0.7863	0.3958
19.81	3.57	0.7876	0.4300
21.42	3.01	0.7891	0.4701
22.56	2.62	0.7902	0.4979
24.24	2.03	0.7916	0.5370
25.22	1.79	0.7926	0.5578
26.48	1.33	0.7935	0.5847
27.52	0.93	0.7945	0.6050
28.57	0.48	0.7954	0.6265

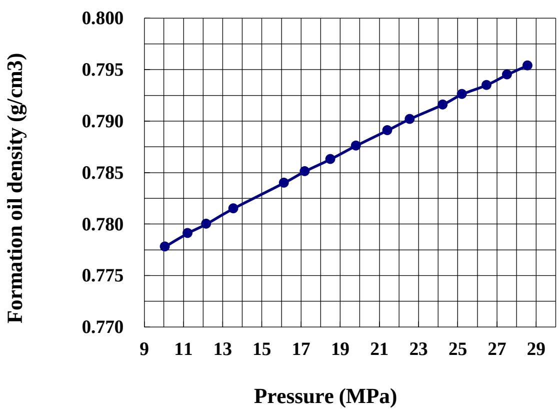

Fig. 6: The change curve of formation oil density with pressure at the formation temperature.

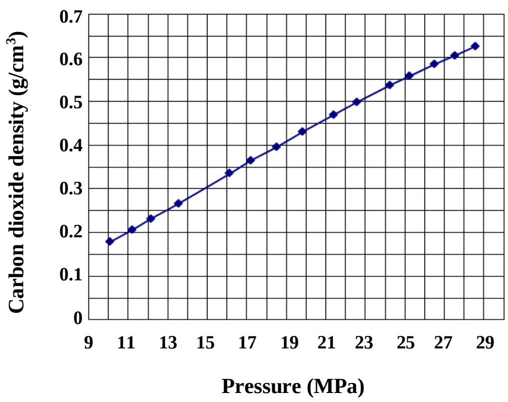

Fig. 7: The change curve of carbon dioxide density with pressure at the formation temperature.

dioxide reaches contact miscibility, and 29.4 MPa is the minimum pressure to reach the first contact miscibility.

CONCLUSIONS

As a high application value method of interfacial tension method, the pendant drop method is applied to determine the interfacial tension between the supercritical carbon dioxide and the formation of oil. In the process of determination, the miscibility between the supercritical carbon dioxide and the formation of oil can be observed clearly. The experimental process of testing the interfacial tension between oil and gas by the pendant drop method is easy to operate and feasible.

The interfacial tension data between the supercritical carbon dioxide and the formation oil under simulated formation temperature at 111.5 °C and different test pressures were determined by the pendant drop method. The experimental results show that the change of interfacial tension tends to decrease linearly with the increase of pressure. As the test pressure increased

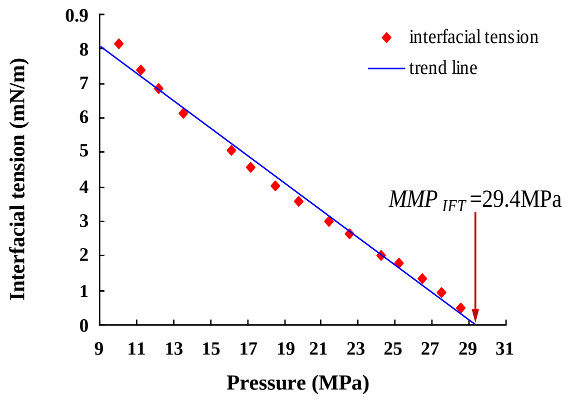

Fig. 8: The change trend curve of the interfacial tension with the test pressure.

Fig. 9: The oil drop shape image at the pressure 29.4MPa (111.5 ℃).

from 10.06 MPa to 28.57 MPa, the interfacial tension decreased from 8.15 mN/m to 0.48 mN/m, indicating that the miscibility between the two phases of crude oil and carbon dioxide gradually forms with the increase of test pressure. According to the linear regression analysis of the relationship between different test pressure and interfacial tension, the mathematical relationship between the two is obtained. Then, based on the extrapolation method, the pressure value when the interfacial tension disappears is 29.4 MPa, and it is verified by the pendant drop method. The experiment results show that under the pressure the formation of oil cannot form a complete oil drop in the carbon dioxide and diffuse quickly after the two phases of contact. A stable interface cannot be formed between the crude oil and carbon dioxide, indicating that the interfacial tension disappears, and the formation of oil and carbon dioxide reach the first contact miscibility, and 29.4 MPa is the minimum pressure to reach contact miscibility.

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