Study on Oil and Gas Amphiphilic Surfactants Promoting the Miscibility of CO₂ and Crude Oil

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ABSTRACT: In order to cope with the global climate crisis, carbon capture, utilization, and storage are the key technologies to achieve carbon neutrality, and it is an elegant geological utilization method for the oil and gas industry to improve the recovery rate of crude oil by using CO₂. However, in practical applications, the problem of low miscibility of CO₂ and crude oil, resulting in low oil displacement efficiency, cannot be avoided. Thus, finding an appropriate method to increase the utilization rate of CO₂ is a worth in-depth study. In light of this, this paper carries out the study on improving the CO₂ flooding efficiency by using oil and gas amphiphilic surfactants. First of all, according to the molecular structure theory and the solubility experiment of surfactants in CO₂, five kinds of surfactants and two kinds of additives with good performance of oil and gas were selected. Then, three experiments were conducted to explore the mechanism of the selected surfactants. The main mechanism of promoting the miscibility of CO₂ and crude oil is to reduce the interfacial tension of the oil and gas phases, followed by increasing the volume expansion of crude oil and reducing the viscosity of crude oil. Finally, through the slim tube displacement experiment, the oil displacement efficiency effect of adding the compound systems of SPO5/n-pentanol was simulated. The results show that the oil displacement efficiency is significantly higher than that of pure CO₂ flooding, and the pressure of miscibility reduces at the same time. The selected reagents have a good effect of promoting miscibility. Therefore, this is an effective method to improve the geological utilization of CO₂.

1. INTRODUCTION

Global climate change is a common crisis facing human society. In order to cope with the increasingly severe climate situation, the 2016 Paris Agreement proposed to limit the increase in global average temperature to within 2 °C.1 In order to achieve the goal of the agreement, between 2020 and 2030, global carbon emissions need to be reduced by about 1 to 2 billion tons per year. In 2019, the emissions reached 33.1 billion tons.2 In 2020, global carbon emissions had been reduced by 5.8% due to the pandemic, but they rebound at the end of 2020, increasing by 2% compared to the same period in 2019. To achieve net zero carbon emissions and the goal of “carbon neutrality” is exceedingly arduous.

The International Energy Agency (IEA) released the “Energy Technology Perspectives 2020” report which pointed out that carbon capture, utilization, and storage (CCUS) technology will play a leading role in reducing greenhouse gas emissions and is one of the key technologies to deal with global climate change. By 2070, the world needs to store at least 15% of total carbon emissions by CCUS, which is approximately 5 billion tons.3 CCUS is composed of capture, transportation, geological utilization, chemical utilization, biological utilization, and geological storage. In 2020, the “CO₂ Storage Resource Catalogue” released by the Oil and Gas Climate Initiative shows that the global carbon dioxide storage potential is 12.27 trillion tons. The Intergovernmental Panel on Climate Change assessment report believes that without CCUS, most climate models will not be able to achieve deep carbon emission reduction targets, and the cost of achieving the targets of the Paris Agreement will increase by an average of 138%.5 It is imperative to vigorously develop and promote the application of CCUS technology.

Since the proposal of using CO₂ as the displacement medium for crude oil exploitation in the 1930s, practice and research have proved that CO₂ flooding is an effective method to improve oil recovery. Because of its small molecule, strong diffusion ability, and excellent property of mixing with crude
oil, CO₂ is increasingly being used for low-permeability reservoir development. The petroleum industry has the advantages of capital, technology, experience, and professional teams in the fields of geological evaluation, geological storage, and engineering construction in the CCUS business process. The IEA and the International Renewable Energy Agency issued reports on the transformation and development of the oil and gas industry in January 2020 and February 2021, respectively, and both listed CCUS as one of the future strategic choices for the oil and gas industry. With CO₂ flooding, geological storage is realized in the form of bound gas, free gas, and dissolved gas at the same time, which not only realizes the geological storage of CO₂ but also brings economic benefits. It can be seen that the use of CO₂ to improve oil recovery is an excellent geological utilization method.

CO₂ utilization efficiency is restricted by the geological characteristics of the reservoir and fluid properties. For marine sedimentary reservoirs, the heterogeneity of the reservoir is weak. The crude oil has good properties, and the content of light components is high. The miscible pressure is generally lower than 10 MPa, and the miscibility can be realized under the formation pressure. However, in China, the oil reservoirs are dominated by continental deposits. The reservoir is characterized by strong reservoir heterogeneity with more paraffin-based crude oil which has high crude oil viscosity. Besides, it has high temperature, which is basically not lower than 60 °C, resulting in a high miscible pressure of CO₂ and crude oil. The low viscosity of CO₂ produces viscous fingering, and serious gas channeling leads to low sweep efficiency, which ultimately results in low miscibility and low oil displacement efficiency. The displacement effect of miscible and immiscible phases differs by 2~5 times. In the 1990s, alternate water and gas injection and CO₂ foam flooding were proposed to increase the displacement resistance and expand the sweep volume of the displacement fluid. To a certain extent, the degree of crude oil recovery has been improved, but the problem of low miscibility has not been effectively solved.

Finding a suitable method to increase the degree of miscibility of CO₂ and crude oil is of great significance for the oilfield to improve the oil recovery. From the 1970s to the 1980s, many methods were discovered to reduce the temperature of local reservoirs and inject oil. Light hydrocarbons, and low carbon alcohol to promote the miscibility of CO₂ and crude oil. Field tests have been conducted, but there are problems of large injection volume and high cost. In the past 10 years, the use of chemical reagents to improve the degree of miscibility has become the focus of research. In order to improve the extraction capacity of CO₂ for polar compounds in crude oil and enhance the solubility of CO₂ in crude oil, chemically modified solvents are usually used to increase the polarity of CO₂. Research reagents that have been reported include low carbon alcohol, toluene, benzene, DYM, methyl carbonate, dimethyl carbonate, diethyl carbonate, sec-butyl acetate, and so on. The most obvious effect is the injection of high concentration of preslug toluene (29 wt %), which can increase the oil displacement efficiency by 25%. The study found that after adding a chemically modified solvent, the CO₂ extraction capacity was increased 3 times. In addition, the use of surfactants to change the properties of oil and gas in the process of CO₂ flooding has gradually become an important research direction. Existing research shows that isobutyl citrate (TIBC), ethylene glycol butyl ether, mixed benzene, isopropyl citrate, span80, alkylphenol polyoxyethylene ether, sodium huang succinate, ME 1-6, peracetyl glucose lauryl ester, lauryl alcohol polyoxypropylene ether (C₃₃H₆₅O₄), TX45, and cetyl acetyl octaer X surfactants have excellent performance in promoting the miscibility of CO₂ and crude oil. Statistics show that the minimum miscible pressure range can be reduced by 7~24%. The range of interfacial tension (between oil and CO₂) reduction is 8.55~25.51% by adding a chemical reagent according to Wu’s research. The slim tube displacement experiment shows that by injecting 0.003 PV isobutyl citrate or 0.1 PV QHB oil, the displacement efficiency increased by 13 and 10%, respectively. In the core-flood experiment, the compound system of CO₂/TX45/ethanol improves the oil recovery rate by 13.8% compared to the pure CO₂ system.
The surfactant is composed of a polar head group and a nonpolar tail chain. The polar head group can form a reverse micelle and a microemulsion structure (Figure 2) with CO₂, water, and crude oil. To form a reverse micelle and a microemulsion structure, there are certain requirements for the surfactants. (1) The surfactant polar head group and water can form a hydrogen bond to provide aggregation power. (2) The interaction between the molecular tail chains is weak or the cohesive energy density is low. (3) There are functional groups with multiple modes of action of CO₂. The reverse micelle is composed of a binary system of a surfactant and oil or water, with a stable thermodynamic property. The microemulsion is usually composed of a surfactant, water, oil, and other components, at least a ternary system. It has stable thermodynamic and good dispersibility properties.

The polar head group and the polar components in the crude oil aggregate to form the inner core through hydrogen bonding. Polar macromolecules such as colloid and asphalt are wrapped in it. The highly branched hydrophobic tail chain extends into the nonpolar CO₂. The accumulation of van der Waals force is macroscopically manifested as the solubilization effect of CO₂ on crude oil and the two phases achieve miscibility. When the surfactant forms reverse micelles in CO₂, water molecules will enter the reverse micelles, and when the number of water molecules reaches a certain number, a microemulsion will be formed. The microemulsion core contains bound water and free water. The bound water and the polar head group of the surfactant interact closely through hydrogen bonds. Free water exists in the center of the microemulsion core, and its water molecules are highly hydrogen-bonded. The water in the core of the microemulsion is polar, forming polar microdomains, which can solubilize fat-soluble organics and water-soluble polar compounds.

The chemical composition of fatty alcohol polyoxypropylene ether is the polymer of fatty alcohol and propylene oxide. The molecular structure contains CO₂-philic polyoxypropylene group, and the carbon chain serves as the lipophilic end, which has oil and gas amphiphilic properties. Fatty acid ester compounds are compounds in which one end of the ester group is connected to short-chain alkanes and the other end is connected to long-chain alkanes. Short-chain alkanes and CO₂ have a similar polarity and have good compatibility. Long-chain alkanes have good compatibility with crude oil, which has oil and gas amphiphilic properties. The acetylene alcohol gemini surfactants, such as polyethoxycetylene glycol and dodecene glycol polyoxyethylene ether, contain acetylene alcohol in the molecular structure, and gemini surfactants are more easily adsorbed on the surface of the gas and liquid. It can also produce a synergistic effect with other surfactants, which is an excellent substitute for fluorocarbon surfactants and silicone surfactants. The molecular structure of the selected surfactants is shown in Figure 3.

2.2. Additive Selection. In the chemical industry, in order to increase the polarity of CO₂ and improve the solvation
ability of CO₂, chemically modified solvents are usually added to expand the extraction range. Commonly used CO₂ additives include alcohols, short-chain alkanes, and methylene chloride. Among these additives, low carbon alcohol has the characteristics of codissolving with CO₂ and crude oil, which can not only improve the ability of CO₂ to extract polar substances such as asphaltenes but also increase the solubility of surfactants in CO₂. At the same time, it is cheap and environmentally friendly. What kind of effect will be produced when it is used in combination with surfactants is worth exploring. The selection of low carbon alcohols should also consider the impact of crude oil type and reservoir water content. Low carbon alcohols are mainly divided into water-soluble alcohols (methanol, ethanol, and propanol) and oil-soluble alcohols (hexanol and heptanol). Different additives change the interface performance differently according to the crude oil components. Match the interaction between the additives and the crude oil and CO₂. Select short-chain ethanol and medium-long-chain short-chain ethanol and medium-long-chain n-pentanol as additives.

2.3. Evaluation of CO₂-Philic Performance. 2.3.1. Principle of the Experiment. The solubility of surfactants in CO₂ under different pressure conditions is measured and used as the evaluation index of their CO₂-philic performance. The cloud point curve method is selected for measurement.37 A certain quality of surfactant is accurately measured and put into the high-pressure visual kettle, and slowly the pressure of CO₂ is increased until the surfactant is completely dissolved. The pressure at the moment is called cloud point pressure. According to the solubility of the surfactant obtained in the experiment at a certain temperature and pressure, the solubility of the surfactant in CO₂ can be calculated. The solubility calculation method is as follows

\[ x\% = \frac{m_1}{m_1 + \rho_o v_o} \times 100\% \]  

(1)

\( x\% \) is the mass fraction of the solute in the binary system; \( m_1 \) is the mass of the solute, \( g \); \( \rho_o \) is the CO₂ density at the temperature and pressure, \( g/cm^3 \); \( v_o \) is the CO₂ volume at the temperature and pressure, \( cm^3 \).

2.3.2. Materials and Apparatus. The CO₂ purity used in the experiment was 99.9%, and it was provided by Beijing Hepu Beifen Gas Co., Ltd. The surfactants used are listed in Figure 1. The required experimental devices are a sapphire visible kettle provided by Beijing Century Senlang Co., Ltd. (model: LC-100; fixed volume: 100 mL; pressure sensor accuracy: ±0.001 MPa; temperature control accuracy of intelligent digital temperature controller: ±1 °C), a constant speed and constant pressure displacement pump (model: ISCO-260D; volume: 266 mL; pressure range: 10−7500 psi), a Mettler electronic balance (model: ME 204; accuracy: 0.1 mg), a precision digital pressure instrument (model: Drucker DPI 104; accuracy: 0.05% full scale; pressure ranges to 20,000 psi), and an electron microscope (model: RS-10M-500C-60; eyepiece magnification: 130 times).

2.3.3. Experimental Procedure. The experimental process is shown in Figure 4. First of all, according to the principle of the differential method, an electronic balance is used to weigh a certain mass (0.05−0.15 g) of the surfactant and place it in the visible reaction kettle. After vacuuming, a small amount of CO₂ is injected and heated up to 76 °C. Then, an ISCO displacement pump is used to add CO₂ slowly, increasing the pressure by 0.5 MPa at 15−20 min intervals until the surfactant is completely dissolved. Under the temperature and pressure conditions at this time, the density and volume of CO₂ are fixed values. The solubility of the surfactant in CO₂ can be calculated. CO₂ density is obtained from REFPROP software of the Institute of Standards and Technology Database.

2.3.4. Analysis of Results. During the experiment, a microscope is installed in the window of the reaction kettle and connected to a computer to observe the gas−liquid two-phase reaction state in real time. CO₂ is a solvent that easily reaches a supercritical state. As the density increases, its solvation ability increases, whereas the density of CO₂ is greatly affected by the temperature and pressure. The experimental phenomenon is shown in Figure 5. As the pressure of CO₂ increases, the volume of the surfactant at the bottom of the kettle gradually decreases until it completely disappears, indicating that the surfactant has completely dissolved into CO₂.

The higher the solubility of the surfactant in CO₂, the better its CO₂-philic performance. When the surfactant meets with CO₂ and crude oil in the porous media, it is more likely to...
accumulate on the two-phase interface. The nonpolar tail chain of the surfactant interacts with CO$_2$, and the polar head group combines with crude oil, so that the gravitational difference between the two phases of oil and gas is extremely low. The interfacial tension difference between the phases is reduced, thereby promoting themiscibility of CO$_2$ and crude oil into one phase. When the degree ofmiscibility of CO$_2$ and crude oil is higher, then correspondingly, the oil displacement efficiency will be significantly improved. If the solubility of the surfactant in CO$_2$ is very low, it indicates that the degree of binding with CO$_2$ is low. The effect of promoting the miscibility of CO$_2$ and crude oil is weak. In the end, even with the addition of the surfactant, CO$_2$ flooding still will be difficult to achieve with good results.

According to the experimental and calculation results, the curve of the solubility of the surfactant in CO$_2$ is fitted as shown in Figure 6. Under high-pressure conditions, the solubility of surfactants in CO$_2$ has a linear relationship with pressure. From the slope of the fitted trend line, the solubility of different types of surfactants varies with the increase in pressure.

Under the same condition, the solubilities of SW320 and DY604 are much higher than those of the other three surfactants, indicating that these two surfactants have good CO$_2$ affinity. The two sides of the alkynyl group are connected to the same hydrophobic alkane chains, and the alkane chains contain ethoxy groups. Its molecule contains acetylenic alcohol and CO$_2$ to produce Lewis acid–base effect, and its completely consistent symmetrical structure makes this effect stronger. In addition, the polymethyl branch chain contained in the molecule has a small contact area at the molecular tail, which weakens the interaction between the molecular tails and is not easy to aggregate and precipitate each other. The high surface energy of methyl groups is beneficial to enhance the solubility of CO$_2$ on the tail chain of surfactant molecules and increase the dissolution of surfactant molecules in CO$_2$.

SPOS contains multiple polyoxypropylene groups to interact with CO$_2$. The LAE4 molecule contains a carbonyl group. As a Lewis base, it has a strong Lewis acid–base effect with Lewis acidic CO$_2$. The strength of the force is equivalent to half of the hydrogen bond force between water molecules. At the same time, the weaker interaction between carbonyl molecules makes it soluble in CO$_2$ at a lower pressure, which improves the solubility of surfactant molecules in CO$_2$. SPOS and LAE4 are linear surfactants with long hydrophobic tail chains, which are prone to bend. There is less overlap between hydrocarbon tail chains, and their solubility in CO$_2$ is better. The molecular structure of TBC contains multiple carbonyl groups, which interact strongly with CO$_2$, but for the multibranched surfactant TBC, the molecular tail chains have a strong mutual attraction force and a large degree of overlap, which is prone to flocculation, resulting in poor solubility in CO$_2$.

### 3. SURFACANT ACTION MECHANISM

#### 3.1. Materials and Apparatus.

The experimental surfactants are listed in Figure 3. CO$_2$ and N$_2$ are provided by Beijing Hepu Beifen Gas Co., Ltd. Petroleum ether is provided by Beijing Jinxing Chemical Plant. The experimental oil is ground degassed crude oil in QS8 oilfield block, prepared according to the gas–oil ratio of associated gas (gas–oil ratio is 39.8 m$^3$/m$^3$; viscosity of 3.57 mPa·s and density of 0.775 g/cm$^3$ at 76 °C). The main instrument used in the solubilization experiment is the high-pressure physical property analyzer PVT (model: Ruaka 2730; maximum working pressure: 70 MPa; maximum working temperature: 150 °C; PC kettle and FPC kettle volume: 340 and 300 mL; visible kettle thickness: 5 mm; maximum pressure is 40 MPa; temperature resistance: 150 °C). Viscosity test experiment instrument includes a rotary viscometer provided by Shanghai Shuangxu Electronics Co., Ltd. (model: DV-III; measuring range: 0.1–92,160 cps; accuracy: ±1%), a constant temperature water bath (model: CS601; maximum temperature: 100 °C; accuracy: 0.01 °C), and a constant temperature magnetic stirrer (model: 85-2; maximum temperature: 100 °C; speed range: 2400 rpm). The...
interfacial tension test instrument mainly includes a high-
temperature and high-pressure interfacial tension meter
provided by Sanchez Technologies company (model: HTHP-IFT/CA; maximum working pressure: 30 MPa;
maximum working temperature: 180 °C; the video camera
comes with the system), a precision digital pressure meter
(model: DPI 104), a Mettler electronic balance (model: ME
2024), a high precision displacement pump (model: ISCO-
260D), and a high-pressure intermediate piston container
(volume: 1000 mL).

3.2. Solubilization Experiment. \( \text{CO}_2 \) is similar in polarity
to the light hydrocarbon components of crude oil and can be
miscible, with the formation of crude oil under certain
conditions. As the amount of \( \text{CO}_2 \) dissolved increases,
the volume of crude oil will expand to varying degrees. In order to
quantitatively evaluate the degree of expansion, the expansion
coefficient is defined as the ratio of the volume of crude oil
after dissolving \( \text{CO}_2 \) to the volume before dissolving under the
same temperature and pressure conditions.\(^{42} \) In order to
evaluate whether the addition of the surfactant has an effect on
the dissolution of \( \text{CO}_2 \) in the crude oil, the crude oil volume is
chosen at the saturation pressure to calculate its expansion
coefficient. The experimental schematic diagram is shown in
Figure 7.

First, 0.5% mass concentration of the surfactant is added to a
PVT main kettle. Then, the prepared crude oil is imported and
stirred, setting the test pressure value until the temperature
and pressure in the kettle are stable, and the crude oil volume
and pressure are recorded. After that, the pressure is decreased step
by step, reducing the pressure by 1–2 MPa each time, and
then the volume and pressure of the crude oil are recorded
after the pressure in the kettle is stable. After being fully
balanced, the pressure is lowered again, and the volume of
crude oil at various pressures is sequentially measured.

After completing one measurement, 10% mol \( \text{CO}_2 \) is
injected, pressurizing to dissolve all of it in crude oil. The
same above-mentioned experimental operation is repeated four
times. According to the corresponding pressure and volume
data, a \( P−V \) relationship graph can be drawn. The volume
corresponding to the inflection point of the curve in the figure
is the volume of crude oil under saturation pressure \( (P_{b3}, P_{b2}) \)
and \( P_{b1} \) represent the saturation pressure under different
experimental conditions.

3.3. Viscosity Test Experiment. A DV-III rotary
viscometer was used to measure the viscosity of crude oil
at different temperatures. At first, 100 g of dehydrated crude oil
with the sample bottles is weighed. Meanwhile, 0.5% mass
concentration of the surfactant is added to the crude oil and
stirred with a magnetic stirrer, keeping the temperature
constant at 76 °C for more than 2 h. Then, it is put into a
high-temperature tube and placed in a constant temperature
bath. After that, the rotor is installed and put into the
crude oil. Last, the speed is set and measured. When the
viscosity value displayed on the screen is stable, the value is
recorded. Gradually, the temperature of the water bath is
increased, and the viscosity change of the crude oil is
measured. Every time the temperature is changed, it must be
kept constant for more than 20 min.

3.4. Interfacial Tension Test Experiment. According to
the definition of miscibility, when the interfacial tension
between the injected gas and the crude oil decreases to 0, it can
be considered that the miscibility is reached. By measuring the
shape parameters of the hanging drop at the probe in a high-
pressure visual kettle, the interfacial tension of \( \text{CO}_2 \)–crude oil
under different pressure conditions is obtained by using the
calculation formula of the interfacial tension proposed by
Andreas. The schematic diagram of the principle of interfacial
tension testing by the pendant drop method is shown in Figure
8.

The formula for calculating the interfacial tension of the
pendant drop is

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

\[ 1/H = f(d_e/d_d) \]

Here, \( \gamma \) is the interfacial tension, N/m; \( d_e \) is the diameter of the
widest part of the hanging drop, m; \( g \) is the gravitational
acceleration, m/s\(^2\); \( \Delta \rho \) is the density difference of the two-
phase fluid in contact, kg/m\(^3\); \( H \) is the modified shape factor,
which is related to the shape factor \( S \). Shape factor \( S = d_e/d_d \),
where \( d_e \) is the diameter of the droplet’s cross-section in the
plane and \( d_d \) is the vertical distance from the top of the hanging
drop. The predecessors summarized the relationship between \( S \) and \( H \) applicable to liquids and established the empirical value
of the corresponding relationship between \( S \) and \( H \). In the
experiment, after the image is collected by the computer, the
interfacial tension can be calculated only by measuring \( d_e \) and
\( d_d \) of the droplet.

The experimental process of interfacial tension test is shown in
Figure 9. First, all experimental instruments and pipelines
are cleaned with petroleum ether, \( \text{N}_2 \), and \( \text{CO}_2 \), and the system
is heated to 76 °C. Next, the pressure of \( \text{CO}_2 \) in the high-
pressure kettle and the pressure of the oil sample prepared in
the PVT are boosted. Then, a drop of crude oil is slowly
pressed into the probe at the kettle and the oil drop that can be
stably suspended is selected; the shape is chosen as large as
possible, which reaches equilibrium with \( \text{CO}_2 \). The camera
system shoots and records oil drop images. At the same time,
the software system automatically calculates the value of the
interfacial tension between \( \text{CO}_2 \) and crude oil. Finally, the
experimental pressure is adjusted, and the above operation
steps are repeated to measure the interfacial tension of the
\( \text{CO}_2 \)–crude oil system under different pressure conditions.
The series of interfacial tension data are fitted and processed. The miscible pressure when the interfacial tension is zero can be calculated by extrapolation.

In order to test the influence of the selected surfactants on the interfacial tension of CO₂−crude oil, 0.5% mass concentration of the surfactant was added to the prepared oil sample, and the change of the interfacial tension of CO₂−crude oil was also measured by the Method 3.4. On the basis of this experiment, a surfactant that has a better effect in reducing the interfacial tension of oil and gas was selected and then mixed with ethanol and n-pentanol, respectively, with a mass concentration of 0.25%. Finally, it was added to the prepared oil sample to test the CO₂−crude oil interfacial tension change.

3.5. Results and Analysis. 3.5.1. Effect of Surfactants on the Solubility of CO₂. The crude oil volume expansion coefficient curve is shown in Figure 10. By comparing the volume expansion coefficient of crude oil after adding pure CO₂ and adding surfactant-CO₂, it is found that under the same conditions, the volume expansion coefficient of the crude oil added with the surfactant is larger, and the surfactant increases the dissolved amount of CO₂ in crude oil. There are also obvious differences in the effect of different types of surfactants.
surfactants in increasing CO₂ dissolution, which is mainly determined by the properties of the surfactants. DY604 gemini surfactant increases the strong interaction between CO₂ and crude oil, which significantly increases the amount of CO₂ dissolved in crude oil, and the volume expansion coefficient of crude oil continues to rise.

3.5.2. Effect of Surfactants on Crude Oil Viscosity. The viscosity—temperature curve of the surfactant and crude oil is shown in Figure 11. After adding the surfactant, the viscosity of pure crude oil is reduced under the same temperature conditions. When the temperature is lower than 55 °C, the viscosity—temperature curve is steep and the slope is negative; moreover, it is relatively small. The viscosity decreases rapidly with the increase of temperature. When the temperature is higher than 55 °C, the viscosity—temperature curve is relatively flat. The slope is also negative but relatively large. The viscosity decreases slowly with the increase of temperature, indicating that the influence of temperature change on the viscosity of crude oil at low temperature is greater than that at high temperature. In the low-temperature zone, the increase of temperature promotes the rupture of the chemical bonds of paraffin molecules. The complex spatial network structure is destroyed. The surfactant can easily enter the crude oil spatial network structure, and the viscosity decreases rapidly. Therefore, within a certain temperature range, increasing the temperature is beneficial to promote the effect of surfactant to reduce oil viscosity.

Judging from the viscosity test experiment effect of the selected surfactant, TBC has the best viscosity-reducing effect. The viscosity of crude oil with a viscosity of 52.7 mPa s at 50 °C is reduced to 30.6 mPa s, and the viscosity-reducing rate is 41.94%. In general, the viscosity—temperature reaction of crude oil in the target block is sensitive. When the temperature is increased from 30 to 55 °C, the viscosity of the crude oil decreases by 93.3%. When it is greater than 55 °C, the sensitivity of crude oil to temperature is weakened, and temperature changes have little effect on the viscosity of crude oil. Therefore, the viscosity reduction effect on crude oil is mainly for crude oil below 55 °C.

3.5.3. Effect of Surfactants on the Interfacial Tension of Oil and Gas. The reaction of pure CO₂ with crude oil is shown in Figure 12. According to experimental phenomena, it can be divided into three processes. (1) Under low-pressure conditions, the oil droplets dripping into CO₂ mainly show the experimental phenomenon of the gradual decrease in size. As the pressure of CO₂ increases, the volume of the oil droplets is compressed. At the same time, CO₂ continuously enters the surface of the oil droplets. The density of the surface layer of the oil droplets decreases and is continuously extracted, dissolved by CO₂. (2) When the pressure rises to a higher value, a bright layer can be observed on the surface of the oil droplets. This layer is mainly the CO₂—crude oil mixed-phase transition zone. The surface layer substances continue to flow out and will soon be dispersed in the CO₂. The surface layer continuously dissolves in the CO₂ and gradually reacts with the inner hydrocarbon components. The higher the pressure, the more violent the surface layer reaction. (3) When the oil droplet cannot form a regular ellipse, but gradually becomes a columnar shape, the oil droplet can only hover on the probe for a few seconds before dripping. The CO₂ and crude oil have reached a nearly miscible state at this time, and then increasing the pressure can help reach complete miscibility.

The data fitting curve of the interfacial tension of the CO₂—crude oil system with the pressure of the system is shown in Figure 13. According to the fitting results, the interfacial tension of the CO₂—crude oil system generally decreases exponentially with the increase of system pressure, but there is...
an obvious pressure inflection point, which can be divided into two pressure ranges. In these two pressure intervals, the interfacial tension value almost decreases linearly with the increase of pressure. In the pressure range of 9−16 MPa, the interfacial tension drops rapidly. The decrease of the interfacial tension is mainly due to the increasing pressure which makes the solubility of CO 2 continue to increase, and the light hydrocarbon components in the crude oil are extracted. At this time, the two-phase reaction of oil and gas is relatively violent, and the properties of oil and gas are different. When the pressure is 16−24 MPa, the interfacial tension declines at a slower rate, and the properties of CO 2 and crude oil are close to each other, gradually reaching miscibility. When the interfacial tension is 0, CO 2 and oil reach a miscible state.

The interfacial tension of CO 2 and crude oil was measured after adding oil and gas amphiphilic surfactants, as shown in Figure 14. After the addition of surfactants, the interfacial tension of CO 2−crude oil became lower, indicating that the surfactant has better performance in promoting the miscibility of CO 2 and crude oil. Therefore, it is used as the main evaluation index for selecting an excellent surfactant. According to the experimental data curve, DY604 and SW320 have superior CO 2 affinity due to their special molecular structure. The interfacial tension reduction value of oil and gas after adding is lower than other types of surfactants, and the effect of reducing the minimum miscible pressure of CO 2−crude oil is extremely obvious. It also proved the good oil and gas amphiphilic properties of the gemini surfactant. The effect of SPO5 in reducing the interfacial tension of CO 2−crude oil is similar to those of the former two, while the amplitude of reducing the interfacial tension of LAE4 and TBC is obviously lower. Therefore, DY604, SW320, and SPO5 are considered to be surfactants with better performance in promoting the miscibility of CO 2−crude oil. However, considering that the effects of reducing the interfacial tension of these three are not much different, the prices of DY604 and SW320 are about 10−20 times that of SPO5. It is not feasible to achieve commercial large-scale application with a high cost, so SPO5 which has a better effect in reducing the interfacial tension and is also low in price is selected for follow-up research.

In order to further improve the effect of surfactant in reducing the interfacial tension of CO 2−crude oil, SPO5 was compounded with ethanol and n-pentanol, and the interfacial tension changes between CO 2 and crude oil after the addition of the surfactant and low carbon alcohol were measured as
shown in Figure 15. As the equilibrium pressure increases, the interfacial tension of CO₂−crude oil decreases exponentially. Under the same pressure conditions, compared with simply adding SPO5, the CO₂−crude oil interfacial tension is further reduced after adding ethanol and n-pentanol to the compound. The low carbon alcohol molecules are adsorbed between the oil and gas interface, distributing in the oil phase and the interface, changing the accumulation factor of the surfactant, increasing the curvature of the microemulsion, playing a synergistic effect, and reducing the interfacial tension. As small molecular amphiphiles gathered at the interface, due to their weak amphiphilicity, they cannot form aggregates alone, but they support the aggregation of surfactants, inserting between the hydrophobic tail chains of the surfactant molecules to reduce the interaction of tail chains and micelles, which is conducive to the formation of stable reverse micelles and a microemulsion structure. In addition, the effect of n-pentanol in reducing interfacial tension is better than that of ethanol, indicating that n-pentanol has better compatibility with crude oil in the target block and promotes the formation of reverse micelles and microemulsion structure of the surfactant. Therefore, the compound of SPO5 and n-pentanol is the best formula.

4. SLIM TUBE DISPLACEMENT EXPERIMENT

At the formation temperature, the simulated formation crude oil configured according to the oil−gas ratio was used to conduct the slim tube displacement experiment to test the CO₂ displacement efficiency after adding reagents under a certain pressure condition. Slim tube displacement experiment can simulate the dynamic process of injecting CO₂ into the porous media of the formation and multiple contacting miscible with oil.

4.1. Materials and Apparatus. The experimental CO₂, N₂, petroleum ether, experimental oil are the same as described in Section 2.1; the surfactant used is SPOS, and the auxiliary agent is n-pentanol provided by Shanghai Zhanyun Chemical Co., Ltd. The main experimental instruments used are a SYS-III multistage high-temperature two-phase displacement system, a sand-filled capillary (slim tube length: 1251 cm; inner diameter: 0.458 cm; pore volume: 70 cm³; porosity: 34%); total displacement system volume: 74.1 cm³), a high-precision displacement pump (model: ISCO-260D), a high-precision pressure instrument (model: DPI 104), a high-pressure intermediate container (volume: 1000 mL), a gas flow meter (model: JX132326LMF-1; flow range: 200 m³/h; maximum flow: 300 m³/h), a separator, a back pressure valve, and a six-way valve.

4.2. Experimental Steps. The experimental process is shown in Figure 16, and the experimental steps are as follows:

1. Clean the pipeline: keeping the thermostat at 76 °C, the petroleum ether will displace about 2 PV at a constant rate of 0.45 mL/min under low pressure to saturate the entire pipeline.
2. Saturate dead oil: under normal pressure, dead oil will displace petroleum ether about 1.2 PV at a constant rate of 0.45 mL/min. After cleaning, the back pressure valve is opened to increase the pressure to the set experimental pressure to establish a stable displacement system.
3. Saturate simulated formation oil: the crude oil displaces dead oil at a constant rate of 0.45 mL/min. When an oil−gas section appears at the outlet end, the oil−gas ratio is tested. When the calculated oil−gas ratio is 39.8 m³/m³, the saturation is complete.
4. CO₂ displaces crude oil: displacing crude oil at 0.25 mL/min with CO₂, and stopping when displacing 1.2 PV. When adding reagents, first, the compound system of SPO5 (0.5 wt %)/n-pentanol (0.25 wt %) is injected as a preslug. After injecting CO₂, recording the upstream and downstream pressure, cumulative oil displacement volume, oil, and gas production is done.

4.3. Results and Analysis. According to the experimental data of slim tube displacement, the trend of oil displacement efficiency in the fitted slim tube displacement experiment is shown in Figure 17. When performing pure CO₂ flooding, the total oil displacement efficiency is 63.88% under the condition of 10 MPa displacement pressure. With the increase of the displacement pressure, the CO₂ in the slim tube comes into contact with more crude oil, thus getting closer and closer to the miscibility. The final oil displacement efficiency also increases linearly, but it never reaches 90%, which means unmixed. When the displacement pressure increases to 25 MPa, the total oil displacement efficiency reaches 90.32%, and the oil displacement efficiency does not increase significantly with the increase of pressure. Therefore, it is believed that under the condition of 25 MPa displacement pressure, CO₂ and crude oil are already in a miscible state (Table 1).

After injecting the preslug of compound systems, on performing CO₂ flooding, the total flooding efficiency is 72.41% under the condition of 10 MPa flooding pressure. Compared with pure CO₂ flooding under the same conditions, the oil displacement efficiency is increased by 8.53%. When the displacement pressure is 20 MPa, the total oil displacement efficiency is increased from 79.16% of the original pure CO₂ flooding to 87.64%, which is very close to 90%. At this time, it has reached a near-miscible state, and the pressure is already very close to the miscible pressure.

It can be observed that after adding reagents, the pressure value at which CO₂ and crude oil reach miscibility is reduced, and it can be miscible with crude oil under lower pressure conditions. That is to say, when the pressure is lower than the miscible pressure, the injection of the reagents can increase the degree of miscibility of CO₂ and crude oil, and thus the oil displacement efficiency will also be improved. In addition,
during the experiment, it was found that after the reagents were injected, the time for mass gas production was significantly delayed, that is, the time for CO₂ to break through the leading edge was longer. The injected preslug reagents, on the one hand, promotes the miscibility of CO₂ and crude oil, and the gas intrusion speed along the dominant seepage channel slows down. On the other hand, it plays a blocking role, making CO₂ enter into smaller gaps, expanding the affected area, and reacting with more crude oil. By injecting SPO5 and n-pentanol compound reagents, the CO₂ utilization efficiency is effectively improved.

5. CONCLUSIONS

In this paper, a study on improving CO₂ flooding efficiency with oil and gas amphiphilic surfactants is carried out. The solubility experiment of surfactants in CO₂ is mainly carried out, and then three experiments are conducted to explore the mechanism of the selected reagents. Finally, the oil displacement efficiency effect after adding the selected reagents is simulated through the slim tube displacement experiment. According to the research results, the following conclusions are drawn:

1. Surfactants containing CO₂-phlic groups have good solubility in CO₂. Among them, gemini surfactants, such as DY604 and SW320, have higher solubility in CO₂ than other types of surfactants. Gemini surfactant has better CO₂ affinity.

2. In the exploration experiment of the mechanism of the surfactant, it was found through the solubilization experiment that the surfactant increased the dissolution of CO₂ in crude oil. Different types of surfactants also have obvious differences in increasing CO₂ dissolution. DY604 gemini surfactant has the strongest effect in increasing CO₂ dissolution.

3. Surfactants can also reduce the viscosity of crude oil to a certain extent. TBC has the highest viscosity reduction rate, reaching 41.94%. The viscosity reduction effect on crude oil is mainly aimed at lower-temperature crude oil.

4. Most importantly, surfactants can reduce the interfacial tension between CO₂ and crude oil, thereby promoting
the two phases to achieve miscibility. After adding low carbon alcohol, this effect will be further enhanced. The compound system of SPOS/n-pentanol has a good effect in reducing the interfacial tension of oil and gas than the others.

(5) Through the comparison of the slim tube displacement simulation experiment, it is found that at the corresponding pressure point before the miscibility, the oil displacement efficiency is increased more than 8% after the preslug of reagents are added. In addition, the pressure condition required to reach the miscibility is reduced by about 5 MPa, which indeed could improve the CO₂ utilization efficiency.

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