Petroleum Science 22 (2025) 4271–4281

Contents lists available at ScienceDirect

Petroleum Science

journal homepage: www.keaipublishing.com/en/journals/petroleum-science

Original Paper

Experimental investigation of surfactants and their ethanol blends for CO_2–oil miscibility enhancement in CO_2-EOR

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A R T I C L E I N F O

Article history:
Received 28 October 2024
Received in revised form
7 July 2025
Accepted 8 July 2025
Available online 11 July 2025

Edited by Yan-Hua Sun

Keywords:
Carbon capture
Utilization and storage (CCUS)
CO_2-EOR
Miscibility pressure
Surfactants
Ethanol

A B S T R A C T

As one promising CO_2 capture, utilization and storage (CCUS) technology, miscible CO_2-enhanced oil recovery (CO_2-EOR) significantly outperforms immiscible flooding in enhancing oil production and storing CO_2. However, achieving CO_2 miscible flooding is often hindered by the high minimum miscibility pressure of CO_2–oil system in many reservoirs. To address this issue, this study focuses on the mechanisms for enhancing CO_2–oil miscibility using different types of surfactants and their blends with ethanol. The effects of fatty alcohol polyoxyethylene ethers (EO), fatty alcohol polyoxypropylene ethers (PO), tributyl citrate (TC), and glyceryl triacetate (GT) on the CO_2–oil miscibility pressure are quantitatively analyzed, as well as their synergy with ethanol. Results demonstrated that all tested surfactant additives reduce the CO_2–oil miscibility pressure. For ether-based surfactant additives, an increase in the degree of polymerization (CO_2-philic groups) weakens the effectiveness to reduce miscibility pressure. Oxygen atoms in the functional group contribute more significantly to miscibility enhancement than carbon atoms. Among ester surfactants, GT achieved the best reduction effect of miscibility pressure (11.82% at 3.0 wt%), attributed to its symmetrical short side-chain structure and ester groups. Furthermore, ethanol exhibited a significant improvement for surfactants in enhancing miscibility. Notably, the reduction of CO_2–oil miscibility pressure increases to 27.9% by 3.0 wt% GT blended with 5.0 wt% ethanol. These findings demonstrate that blending surfactants with ethanol is a feasible and effective strategy to facilitate miscible CO_2 flooding. This study provides valuable insights and practical guidance for the field implementation of miscible CO_2-EOR.

1. Introduction

Low-carbon development of fossil fuels has emerged as a critical global priority in recent decades, balancing the energy demands of human society with the pursuit of carbon neutrality. Beyond conventional petroleum development technologies, there is an increasing need for innovative low-carbon solutions to meet the growing global demand for oil and gas (Yu et al., 2015). Additionally, to achieve carbon neutrality targets, carbon capture, utilization and storage (CCUS) technologies are gaining prominence for mitigating CO_2 emissions. Among the most effective and promising CCUS approaches, CO_2-enhanced oil recovery (CO_2-EOR) not only boosts oil recovery (Zhou et al., 2019) but also contributes to carbon emission reduction by sequestering CO_2 into underground formations (Saira et al., 2021), creating a synergistic outcome for both oil and gas development and carbon neutrality.

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Peer review under the responsibility of China University of Petroleum (Beijing).

https://doi.org/10.1016/j.petsci.2025.07.005

Consequently, extensive research on CO_2-EOR has been conducted over the past few decades (Moradkhani et al., 2023; Wang et al., 2022; Wei et al., 2020; Zhang W. et al., 2024; Zuo et al., 2023).

CO_2-EOR can be categorized into two displacement modes—miscible flooding and immiscible flooding—based on the relationship between displacing pressure and miscible pressure. In miscible displacement, the interfacial tension (IFT) between CO_2 and oil can be reduced to zero, resulting in a single-phase CO_2–oil system and significantly enhancing displacement efficiency. Compared to immiscible displacement, miscible displacement offers superior performance in both oil production and CO_2 storage. However, certain oil reservoirs exhibit high miscible pressures, rendering direct miscible flooding either infeasible or prohibitively expensive. Therefore, a critical objective in CO_2-EOR is to identify effective methods for enhancing the miscibility of the CO_2–oil system, while minimizing both the interfacial tension (IFT) and the minimum miscible pressure (MMP) to achieve miscible or near-miscible CO_2 flooding.

To reduce the miscible pressure of CO_2–oil, several researches were conducted to try chemical agents, such as light alkanes, surfactants and alcohols. Saira et al. (2020) reviewed the effects of the polymers, alcohols, surfactants, and other chemicals on the IFT and MMP of the CO_2–oil system, providing insights and approaches for reducing miscibility pressure. Almobarak et al. (2021) reviewed the impact of different solvents on MMP and concluded that chemical agents in conjunction with CO_2 can reduce the CO_2–oil MMP.

Initially, scholars studied the impact of light solvents such as light alkanes on the miscibility of the CO_2–oil system. Bon et al. (2005) investigated the effect of methane on the MMP of the CO_2–oil system, finding that increasing methane content raises the MMP. Zhang et al. (2013) systematically studied the miscibility enhancement effects of methanol, ethanol, hexane, octane, petroleum ether, and gasoline on the CO_2–oil system. Jeong and Lee (2016) and Cho and Lee (2016) examined the effect of LPG content on MMP, finding that C_4 in LPG is more effective than C_3 in reducing miscibility pressure. Hawthorne et al. (2017) analyzed the effect of ethane on MMP using a vanishing interfacial tension (VIT) and they found MMP decreased linearly with ethane concentration. Yang et al. (2019) studied the effect of alcohols (butanol, pentanol, hexanol) on the CO_2–oil MMP. And they revealed that alcohols can form hydrogen bonds with oil molecules, weakening the strong interactions between oil molecules, and facilitating CO_2 entry into the oil phase. Xu et al. (2021) investigated the effect of condensate oil on reducing the minimum miscibility pressure of CO_2. Lee et al. (2021) used numerical simulations to analyze the impact of dimethyl ether on enhancing CO_2 miscibility. Previous research preliminarily demonstrated that co-solvents such as light alkanes, petroleum ether and alcohols, are effective additives in reducing the MMP of the CO_2–oil system.

Due to the large quantities and low economic efficiency of using light alkanes as co-solvents, several researchers turned their attention to the efficient surfactants in recent years. Zhang et al. (2011) discovered a surfactant (TX-100) capable of significantly dissolving CO_2, and provided some guidance for surfactant selection. Liu et al. (2019) and Guo et al. (2022) summarized the surfactants to reduce CO_2–oil miscibility pressure and analyzed the advantages and disadvantages of CF, SIO, and CH type surfactants, proposing suggestions for the selection of surfactant groups.

Besides the effectiveness study of chemical agents on enhancing miscibility, several studies focused on the mechanism of enhancing the effect of CO_2–oil miscibility and CO_2-EOR. Kuang et al. (2020) analyzed the mechanisms of surfactants to reduce the MMP of CO_2–oil system for enhancing CO_2-EOR, including increasing CO_2 solubility in crude oil, enhancing intermediate hydrocarbon extraction, reducing crude oil viscosity, increasing crude oil solubility in CO_2, and lowering interfacial pressure.

Guo et al. (2012) conducted experiments to analyze the effects of CAE and CAF surfactants on solubility, viscosity reduction, and displacement. Luo et al. (2018) studied the impact of C_iPO_j (fatty alcohol polyoxypropylene ether) on MMP, suggesting that there exists a critical concentration of surfactant to reduce MMP due to the finite occupancy of surfactants at the interface. Lv et al. (2022) assessed the impact of C_iPO_j dosage and structure on first contact miscibility pressure (FCMP) by a new optical method for measuring miscibility pressure and the solubility of surfactants in CO_2. The results demonstrated that surfactants tend to enter the oil phase, forming reverse micelles, thus increasing CO_2 solubility in crude oil. Zhang H. et al. (2024) used hydrophilic, lipophilic and CO_2-philic surfactants to enhance CO_2 flooding, and found that $C_4EO_3PO_6$ demonstrates the best performance in reducing the interfacial tensions. Wu (2021) studied the effects of carbonyl liquids on system expansion of the CO_2–ethanol, and ultimately selected glyceryl triacetate to examine its impact on MMP. Zhao et al. (2021) studied the effects of isobutyl (amyl) citrate ester on CO_2–oil miscibility and oil recovery, and concluded that the isobutyl (amyl) citrate ester can reduce MMP of CO_2–oil system. Lv et al. (2023) studied the miscibility process of the CO_2–oil system with the C_iPO_j surfactant by molecular dynamics (MD) simulations. The results showed that, with the addition of surfactants, O atoms in CO_2 primarily distribute near the O atoms of the surfactant, while C atoms in crude oil mainly distribute near the C chain parts of the surfactant. Additionally, longer polyoxyethylene chains (PO) lead to molecular bending and wrapping, making O atoms less exposed.

In addition to the utilization of only one type of chemical agent, the combinations of different types of additives have come into the view of researchers. To further enhance the effect of surfactants on reducing miscibility pressure, the concept of blending surfactants with alcohols was introduced recently. Wang et al. (2016) discussed the impact of alcohols on fatty alcohol polyoxypropylene ether on MMP, and concluded that alcohols can increase the solubility and stability of surfactants in CO_2. Ding et al. (2019) conducted CO_2 extraction and displacement experiments, and found that TX-45 surfactant blended with alcohols improved the extraction rate and enhanced displacement efficiency. Zhang et al. (2020) studied the synergistic effect of ethanol and surfactants on MMP of CO_2–oil system, and concluded that ethanol can be inserted into the tail chains of surfactants, and thereby increase micelle stability in CO_2. However, the study of surfactant combined with co-solvent to enhance CO_2–oil miscibility is still in the early exploratory stages and remains insufficient.

In summary, although several previous studies tried to reveal the mechanisms of surfactants to enhance miscibility between CO_2 and oil, these investigations were limited to investigate only one type of surfactants in a single research and the comprehensive comparison of different types of surfactants is lacking. Consequently, it remains unclear which type of functional groups in surfactants are more effective in reducing miscibility pressure. Therefore, identifying suitable surfactant types to optimize miscibility and improve the efficacy of miscible CO_2-EOR continues to be a critical research direction. In addition, as one type of co-solvent, alcohol was preliminary proved the effect to reduce the miscibility pressure of CO_2–oil systems when combining with surfactants. However, the research on surfactant–alcohol blends for enhancing CO_2–oil miscibility are still in the preliminary stages. There is a clear need for more in-depth research to elucidate the mechanisms of surfactants and their blends with alcohols for enhancing miscibility in CO_2–oil systems. Therefore, the main objective of this work is to assess the capability of several typical types of surfactants to reduce the miscibility pressure in CO_2–oil systems and moreover the synergistic effect of different types of surfactants blended with ethanol on enhancing miscibility are investigated.

2. Methodology

2.1. Experimental materials

According to previous studies (Kuang et al., 2020; Liu et al., 2019; Yang et al., 2019), incorporating both lipophilic and CO_2-philic groups into surfactant molecules is more effective in enhancing the miscibility of CO_2–oil systems. The primary types of CO_2-philic groups include fluorine-containing, silicon-containing, carbonyl-containing (esters, ketones, amides), ether-containing, and hydroxyl-containing groups, while lipophilic groups typically consist of saturated or unsaturated hydrocarbons. However, fluorine- and silicon-containing surfactants are excluded from this study due to their toxicity and environmental impact. Instead, this work focuses on non-ionic surfactants with CO_2-philic groups such as ether and ester to evaluate their influence on the first contact miscibility pressure (FCMP) of CO_2–oil systems. Seven types of surfactants are selected for comparative analysis: three fatty alcohol polyoxyethylene ethers (EO_j), two fatty alcohol polyoxypropylene ethers (PO_j), tributyl citrate (TC), and glyceryl triacetate (GT). *n*-hexadecane (C_{16}) is chosen as the simulated oil in this work. The specific information about surfactant additive materials is shown in Table 1 and Fig. 1.

2.2. Experimental setups and procedures

This work employs a high-temperature and high-pressure visual PVT experimental system to measure the first contact miscibility pressure (FCMP) of the CO_2–oil (*n*-hexadecane) system. The method of visual PVT experimental system to measure FCMP was successfully used and verified in some literature, such as Lv et al. (2022) and Rommerskirchen et al. (2018). As shown in Fig. 2, the high-temperature and high-pressure visual PVT experimental apparatus consists of five main parts: an experiment vessel, a pressure control system, a visualization imaging system, a temperature control system, and an operation and data acquisition system. The experimental vessel is resistant to high temperatures (400 K, $\pm$0.01 K) and high pressures (250 MPa, $\pm$0.001 MPa), equipped with a visual sapphire window. The experimental vessel achieves the required pressure through movement of a piston by the pressure control system and is equipped with a magnetic stirrer to accelerate equilibrium. The visualization imaging system uses a high-speed camera to capture the entire vessel, transmitting the information to a computer for imaging. The temperature control system provides precise temperature control within the vessel via temperature feedback. The operation and data acquisition system issues commands to perform a series of PVT operations and collects the temperature, pressure, and other necessary data.

The specific experimental procedures for measuring FCMP of the CO_2–oil system are as follows:

(1) Set the system temperature to the predetermined experimental temperature (e.g., 323 K). Simultaneously, vacuum the experimental vessel.
(2) After the temperature of vessel is stabilized, inject a fixed amount of *n*-hexadecane (e.g., 7.73 g for Exp. 1) measured by quality measuring instrument into the PVT experimental vessel by an injection needle.
(3) Inject a fixed amount of CO_2 into the PVT experimental vessel (CO_2 accounts for approximately 94% of the molar fraction of the entire system, e.g., 23.5 g for Exp. 1). The molar composition of the hydrocarbon and CO_2 corresponding to the FCMP in the phase transition pressure–composition phase diagram was selected as the target system composition to be studied. And the amount of CO_2 can be calculated by the state equation, because of fixed temperature and volume of vessel.
(4) After the injection process, activate stirring and gradually increase the pressure of vessel to 20 MPa, where the oil–gas system becomes a clear single-phase system with no interface. Raising the pressure to 20 MPa facilitates rapid mixing; therefore a moderate pressure increase rate is sufficient.
(5) Gradually decrease the pressure with a gradient of 0.1 MPa (at each pressure point wait 1 min to determine whether the system is changing) until the system becomes turbid and an interface appears, indicating a transition from miscible to immiscible. This pressure point is near the FCMP.
(6) Repeat the operations to increase and decrease pressure for determining the FCMP point.

The above experimental procedure is repeated three times to get the measured FCMP by taking the average value.

The FCMP measurement experiments for CO_2–oil systems with added surfactants or surfactant with co-solvents (ethanol) follow a similar procedure. The difference is in step (2), where a certain amount of surfactant or surfactant–ethanol mixture is injected via an injection pump according to experimental requirements.

3. Results and discussion

3.1. Phase behavior changes in CO_2–oil systems under different pressures

This study conducted FCMP measurement experiments on the CO_2–oil system and analyzed phase behavior changes under different pressure conditions. As shown in Figs. 3 and 4, the phase behavior changes of the CO_2–oil system in Exp. 1 during the pressurization and depressurization process were analyzed.

Table 1
Non-ionic surfactants used in this work.

Chemical agent	Abbreviation	Molecular formula
Fatty alcohol polyoxyethylene ether	EO_j	$C_4O(CH_2CH_2O)_jH$, $j = 3, 6, 10$
Fatty alcohol polyoxypropylene ether	PO_j	$C_4O(CH_2CH_2CH_3O)_jH$, $j = 3, 6$
Tributyl citrate	TC	$C_{18}H_{32}O_7$
Glyceryl triacetate	GT	$C_9H_{14}O_6$
n-hexadecane	C_{16}	$C_{16}H_{34}$
Ethanol	Ethanol	C_2H_5OH

Note: *j* denotes degree of polymerization.

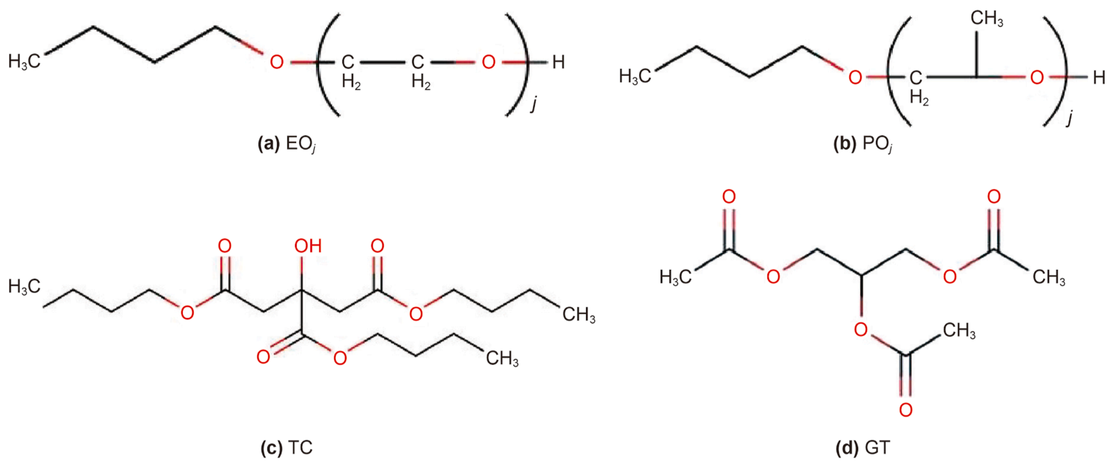


Fig. 1. Structure formulas of the non-ionic surfactants.

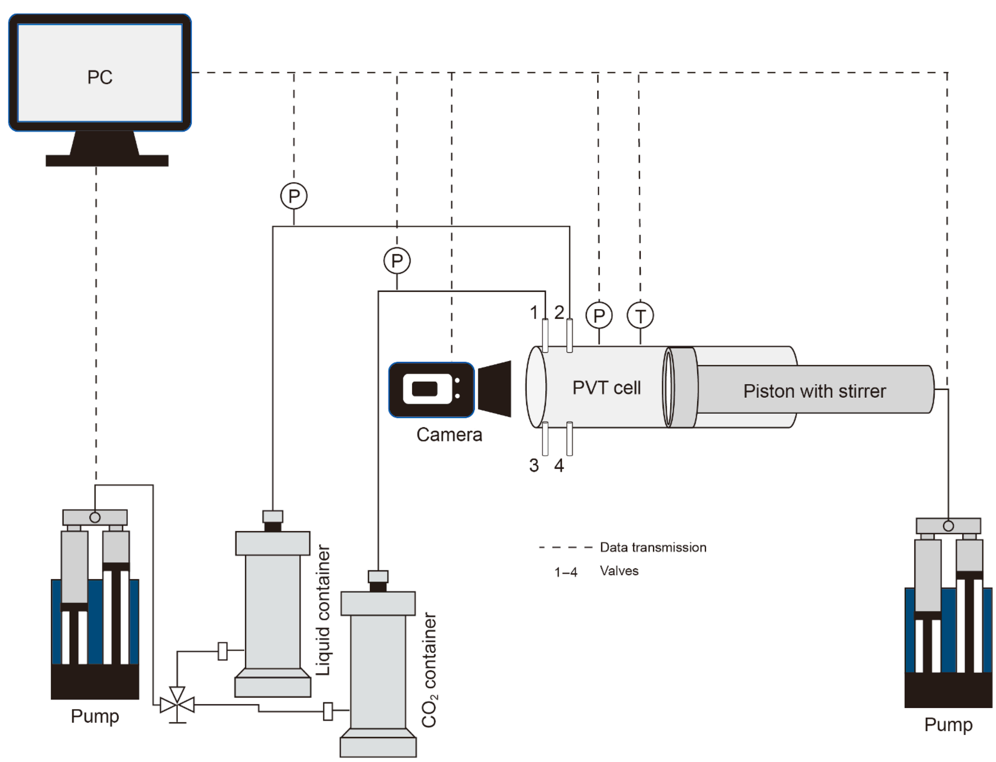


Fig. 2. Schematic diagram of high-temperature and high-pressure visual PVT experimental system.

As shown in Fig. 3(a)–(e), the location of the oil–gas interface rises but the interface state remains stable with the increasing pressure up to 15.3 MPa. The oil–gas interface begins to fluctuate violently at 16.6 MPa and is no longer stable, as shown in Fig. 3 (f). There is a phenomenon of CO_2 rapidly falling into the oil at the oil and gas interface (highlighted by the red circle), and several depressions appear on the liquid surface, indicating that the interfacial tension between oil and gas becomes very small as it approaches FCMP. As shown in Fig. 3(h), the intensity of the interface fluctuations further increases as the pressure continues to increase to 17.2 MPa, suggesting that the pressure likely exceeds the FCMP. At this point, the pressurization process is halted at 17.2 MPa, and stirring is initiated. Consequently, the CO_2–oil system transitions from an unstable interface with pronounced fluctuations (as seen in Fig. 3(h)) to a completely clear single-phase state after stirring (as shown in Fig. 4(a)), confirming a miscible state above the FCMP. The CO_2–oil system maintains this clear single-phase state without any changes as the pressure is reduced to 16.8 MPa, as depicted in Fig. 4(b). However, when the pressure is further decreased to 16.7 MPa, as shown in Fig. 4(c), the oil–gas system becomes highly turbid with a marked reduction in transparency. This turbidity is primarily attributed to the formation of CO_2 microbubbles within the CO_2–oil system. As illustrated in Fig. 4(d), these microbubbles rise to the top of the experimental vessel, forming a gas cavity and establishing a distinct macroscopic oil–gas interface after standing for 5 min. With further reduction in pressure, additional gas precipitates, causing the gas cavity at the top of

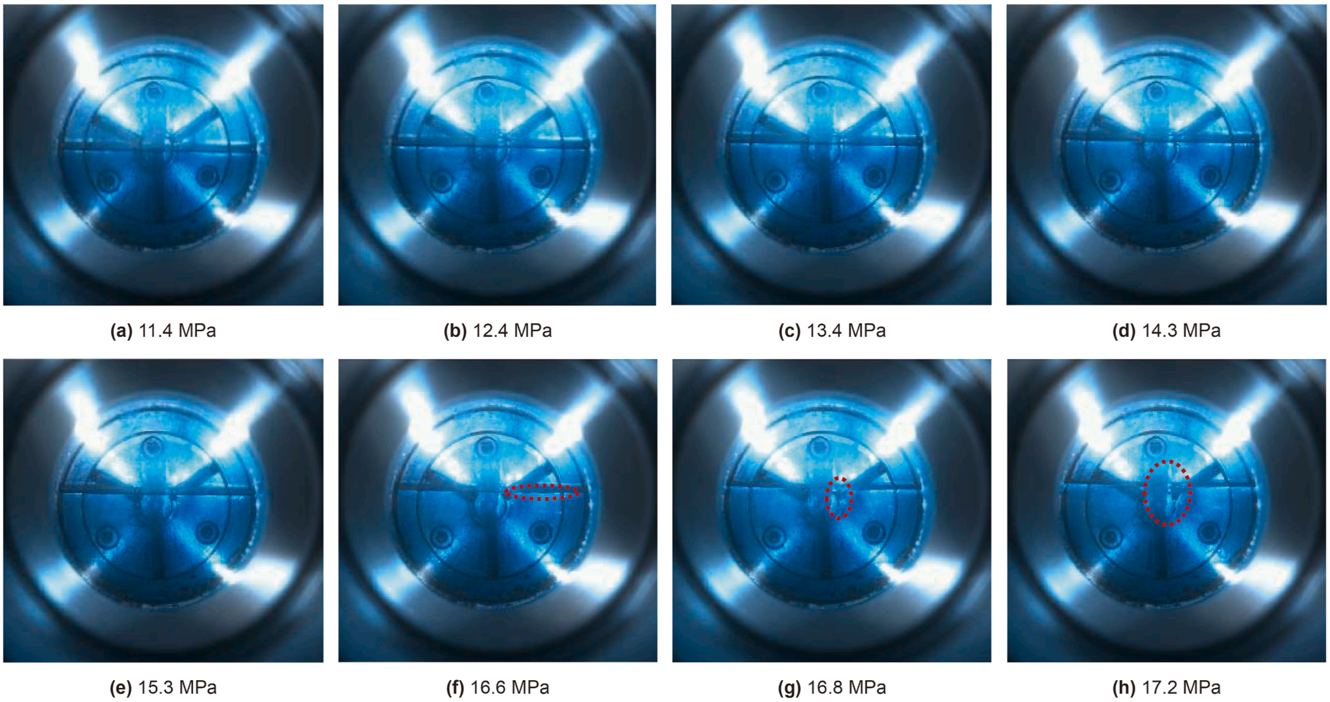


Fig. 3. Phase behavior changes of CO_2–oil system under different pressurization conditions.

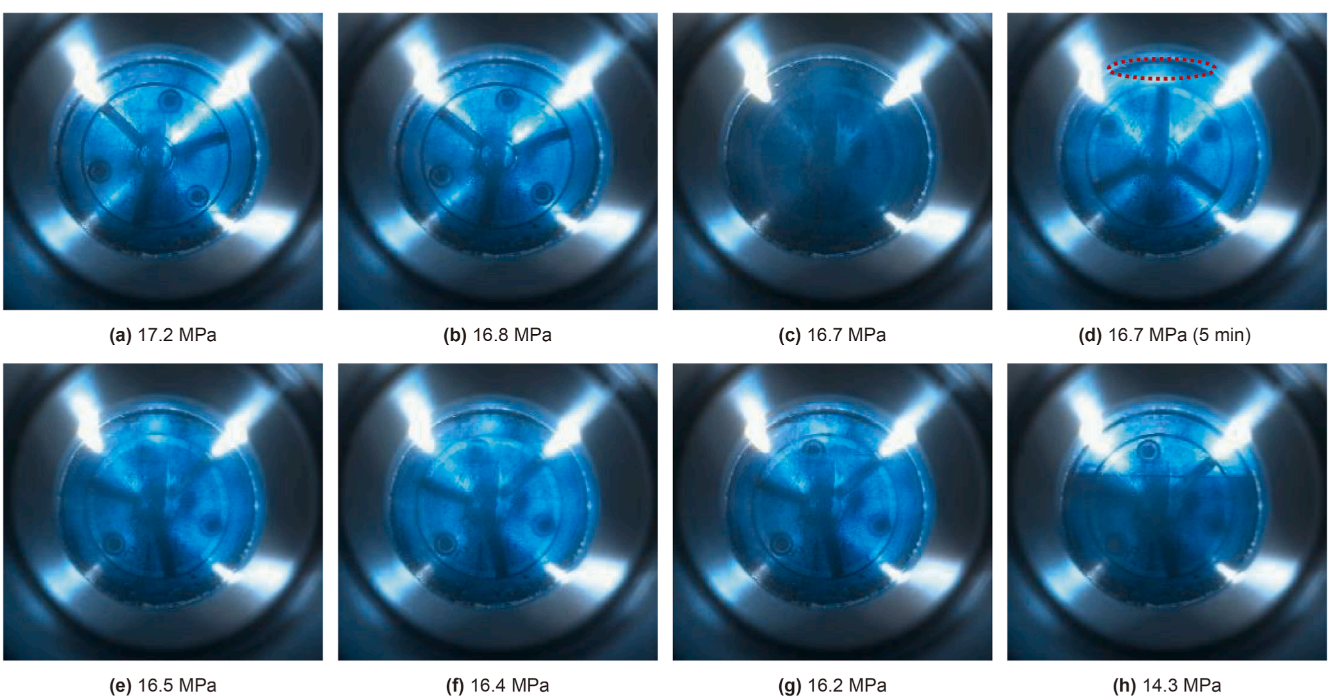


Fig. 4. Phase behavior changes of CO_2–oil system under different depressurization conditions.

the vessel to expand and the oil–gas interface to descend progressively.

As a result, the FCMP of the CO_2–oil system is determined to be 16.8 MPa under experimental conditions based on the phase behavior changes during the pressurization and depressurization processes. The FCMP of the CO_2–oil system was also measured using the interfacial tension disappearance method, whose details are provided in the Supplementary Material. The results obtained from the interfacial tension disappearance method align closely with those from this experimental approach, validating the accuracy of the procedure employed in this study. A comparable experimental method is applied to determine the FCMP of CO_2–oil systems with surfactants or surfactants combined with co-solvents in subsequent investigations. Further details are available in a recorded video that illustrates the changes in phase behavior under varying pressures, provided as Supplementary Material (video for FCMP measurement process).

3.2. Surfactants reducing FCMP of CO_2–oil systems

Certain non-ionic surfactants are believed to interact simultaneously with both oil and CO_2, which is beneficial for miscibility, as shown in Fig. 5. To investigate the effectiveness of non-ionic surfactants in reducing FCMP of the CO_2–oil system, this study selected seven types of surfactants for comparative analysis: three fatty alcohol polyoxyethylene ethers (EO_j), two fatty alcohol polyoxypropylene ethers (PO_j), tributyl citrate (TC), and glyceryl triacetate (GT). Surfactant concentration is typically controlled no more than 3.0 wt% for better economic efficiency. Therefore, this study evaluated the capability of these seven selected surfactants to reduce the FCMP of the CO_2–oil system at mass concentrations ranging from 1 to 3.0 wt%. The effects of surfactant concentration, the number of CO_2-philic groups (degree of polymerization), the length of the carbon chain, the type of functional groups, and the molecular structure on the FCMP reduction were systematically analyzed. As shown in Table 2, the FCMP and FCMP reduction effectiveness under different types of surfactants are discussed.

3.2.1. The effect of polymerization degree of ether surfactants on FCMP

The FCMP of the CO_2–oil system with the addition of five polyether surfactants, three fatty alcohol polyoxyethylene ethers (EO_3, EO_6 and EO_{10}) and two fatty alcohol polyoxypropylene ethers (PO_3 and PO_6), at mass concentrations of 1.0–3.0 wt% are measured to analyze the effect of the degree of polymerization of ether surfactants on the reduction of FCMP in the CO_2–oil system.

As shown in Fig. 6(a), the FCMP of the CO_2–oil system decreases continuously with the increase in the mass concentration (1.0–3.0 wt%) of the added fatty alcohol polyoxyethylene ethers. And fatty alcohol polyoxypropylene ethers have similar effect to reduce FCMP of the CO_2–oil system, as shown in Fig. 6(a). Furthermore, the FCMP of the CO_2–oil system still shows a trend of further reduction even at a concentration of 3.0 wt%, indicating that the surfactant only occupies part of the interface and has not reached the critical concentration.

As shown in Fig. 6, among the CO_2–oil systems with the addition of three fatty alcohol polyoxyethylene ethers, EO_3 exhibits a significantly stronger capability to reduce the FCMP than EO_6 and EO_{10}. Compared to no additive condition (16.8 MPa), the FCMP of the CO_2–oil system is reduced to 15.5 MPa by 3.0 wt% EO_3, and the reduction of FCMP achieves 7.8%. EO_6 reduces the FCMP to 15.7 MPa at 3.0 wt%, with a reduction of 6.66%. EO_{10} has the weakest effect to reduce FCMP, only 4.36% at 3.0 wt%. As shown in Fig. 7, a comparison of two fatty alcohol polyoxypropylene ethers reveals that PO_3 has a greater effect in reducing the FCMP than PO_6, and 3.0 wt% PO_3 reduces the FCMP to 15.7 MPa with a reduction of 6.66% compared to 16.0 MPa and 4.93% for 3.0 wt% PO_6.

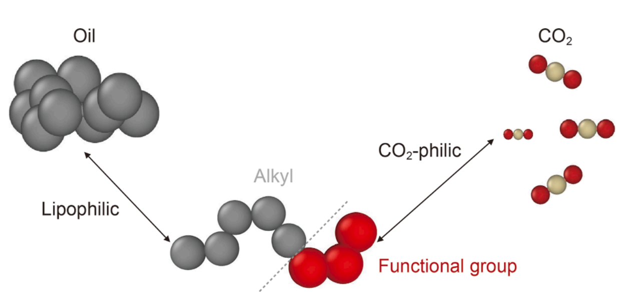


Fig. 5. The schematic diagram of simultaneous non-ionic surfactant interactions with CO_2 and oil.

It is commonly assumed that surfactants with a higher number of CO_2-philic groups should exhibit a greater ability to reduce the FCMP. However, the experimental results show different findings. The performance ranking of additives is EO_3 > EO_6 > EO_{10} and PO_3 > PO_6, with all five polyether surfactants possessing a 4-carbonalkyl chain (C_4). This indicates that the ability of polyether surfactants to reduce the FCMP decreases with an increase in the degree of polymerization at a constant C-chain length. In the polymer, macromolecules can interpenetrate and form topological entanglements, usually in the form of a loop of one macromolecule around another macromolecule (Krajenta, 2024). In another word, a macromolecule with long chain structure is easy to bend and entangle with other macromolecules. Therefore, this work proposed a reasonable speculation for this phenomenon that, the excessively long polyether chain structure leads to significant bending and entanglement of the surfactant molecules with an increase in the degree of polymerization (leading to greater molecular length). This result prevents some CO_2-philic groups from being exposed to the CO_2 phase, thereby reducing the overall interaction between CO_2 and the ether bonds, and ultimately diminishing the effectiveness of FCMP reduction. Several related studies also corroborate this observation (Lv et al., 2023).

By comparing polyoxyethylene ethers and polyoxypropylene ethers, such as EO_3 and PO_3, more carbon atoms in the CO_2-philic group result in weaker capability to reduce the FCMP of the CO_2–oil system. It indicates that the oxygen atoms in the group play the leading role in reducing the FCMP, while the influence of carbon atoms on reducing the FCMP is negligible.

3.2.2. The effect of ester surfactant type on FCMP

The GT and TC are selected to investigate the effects of different types of ester surfactants on the FCMP of the CO_2–oil system. As shown in Fig. 8, the effectiveness of both GT and TC surfactants in reducing the FCMP improves with the increase in mass concentration. When 3.0 wt% GT is added, the FCMP of the CO_2–oil system decreases to 14.8 MPa, achieving a reduction of 11.82%. With the same mass concentration of TC, the FCMP of the CO_2–oil system is 15.8 MPa, with a decrease of 6.08%.

GT demonstrates a significantly higher capability to reduce FCMP of the CO_2–oil system compared to TC with a similar functional group structure. The primary structural difference between these two surfactants is the length of their carbon chains. TC has a carbon chain length of 4 while that of GT is 1. It indicates that the surfactant capability to reduce the FCMP of CO_2–oil system decreases with the increase in carbon chain length.

3.2.3. The effect of functional group types of surfactants on FCMP

To further analyze the effect of functional group types on reducing the FCMP of the CO_2–oil system, this work selected GT and EO_3 to compare the changes in FCMP. The rationale for this selection is that GT has a total carbon number of 9, while EO_3 has a total carbon number of 10, resulting in similar total carbon counts. Additionally, both surfactants possess three functional groups and demonstrate the most effective reduction within their respective categories. As shown in Fig. 9, the FCMP of the CO_2–oil system with GT additive is significantly lower than that with EO_3 additive at the same mass concentration. The FCMP of the CO_2–oil system with 3.0 wt% GT is 14.8 MPa, while it is 15.5 MPa with 3.0 wt% EO_3. GT achieves a reduction of FCMP of 11.82%, clearly greater than EO_3 of 7.80%.

The underlying reasons for this phenomenon can likely be attributed to two primary factors. (1) As discussed in Section 3.2.1,

Table 2
FCMP of the CO_2–oil systems under different types of surfactant additives and the reduction effectiveness of FCMP.

Exp. No.	Surfactant	Surfactant concentration, wt%	FCMP, MPa	Reduction of FCMP, %
1	/	/	16.8	/
2	EO_3	1.0	16.4	2.64
3		2.0	16.0	4.93
4		2.5	15.7	6.66
5		3.0	15.5	7.80
6	EO_6	1.0	16.4	2.64
7		2.0	16.1	4.36
8		2.5	15.9	5.51
9		3.0	15.7	6.66
10	EO_{10}	1.0	16.6	1.49
11		2.0	16.4	2.64
12		2.5	16.2	3.78
13		3.0	16.1	4.36
14	PO_3	1.0	16.5	2.06
15		2.0	16.2	3.78
16		2.5	15.9	5.51
17		3.0	15.7	6.66
18	PO_6	1.0	16.6	1.49
19		2.0	16.4	2.64
20		2.5	16.2	3.78
21		3.0	16.0	4.93
22	TC	1.0	16.5	2.06
23		2.0	16.2	3.78
24		2.5	16.0	4.93
25		3.0	15.8	6.08
26	GT	1.0	16.1	4.36
27		2.0	15.4	8.38
28		2.5	15.1	10.10
29		3.0	14.8	11.82

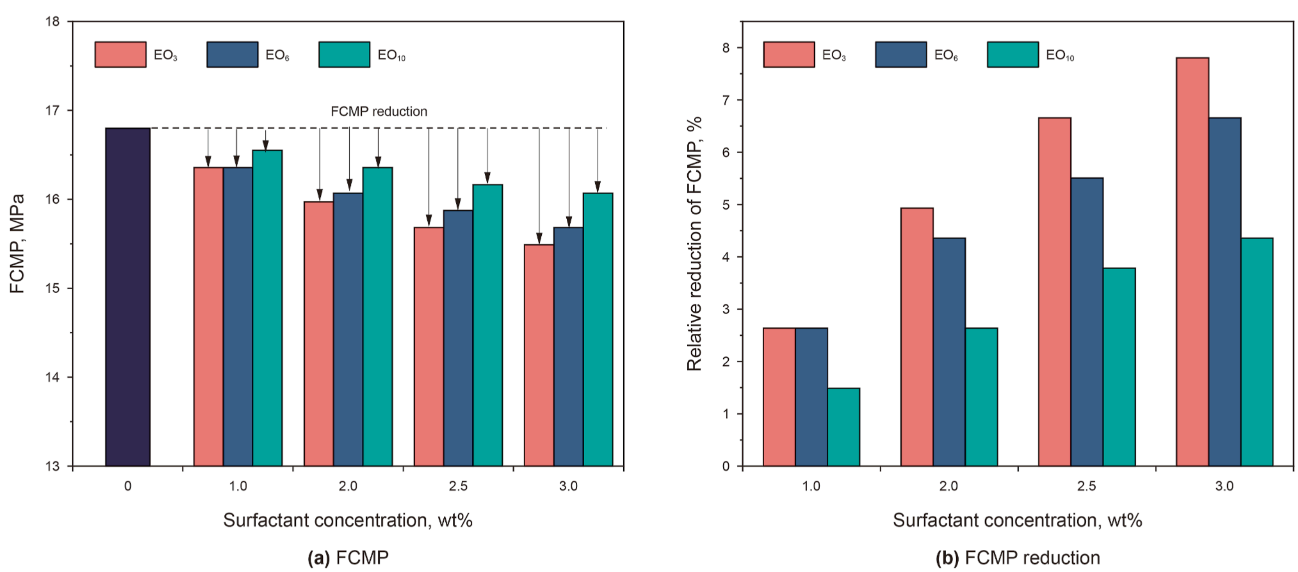
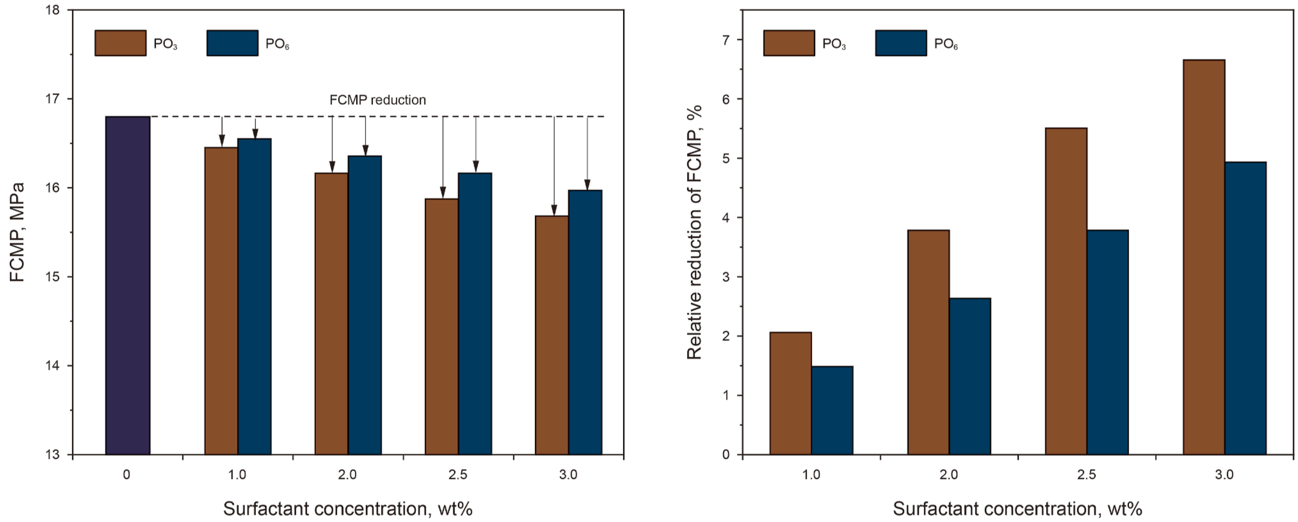


Fig. 6. Enhanced miscibility of CO_2–oil system by different polyoxyethylene ethers.

oxygen atoms within functional groups play a critical role in reducing miscibility pressure. Consequently, it can be reasonably inferred that the ester functional group in GT, which contains a C=O double bond in addition to the ether bond, further enhances the miscibility between CO_2 and oil. This observation also underscores that the presence of oxygen atoms in the functional groups of surfactants is a pivotal factor in lowering miscibility pressure. (2) The molecular structures of these two surfactants differ markedly. EO_3 possesses a linear structure, which is more susceptible to entanglement and bending, thereby impeding the effective exposure of oxygen atoms to the CO_2 phase and diminishing its ability to reduce the FCMP. In contrast, GT features a symmetrical structure with shorter branches, reducing the likelihood of surfactant molecules bending or entangling. This configuration allows for more effective exposure of oxygen atoms, thereby amplifying the surfactant capacity to promote miscibility between CO_2 and oil.

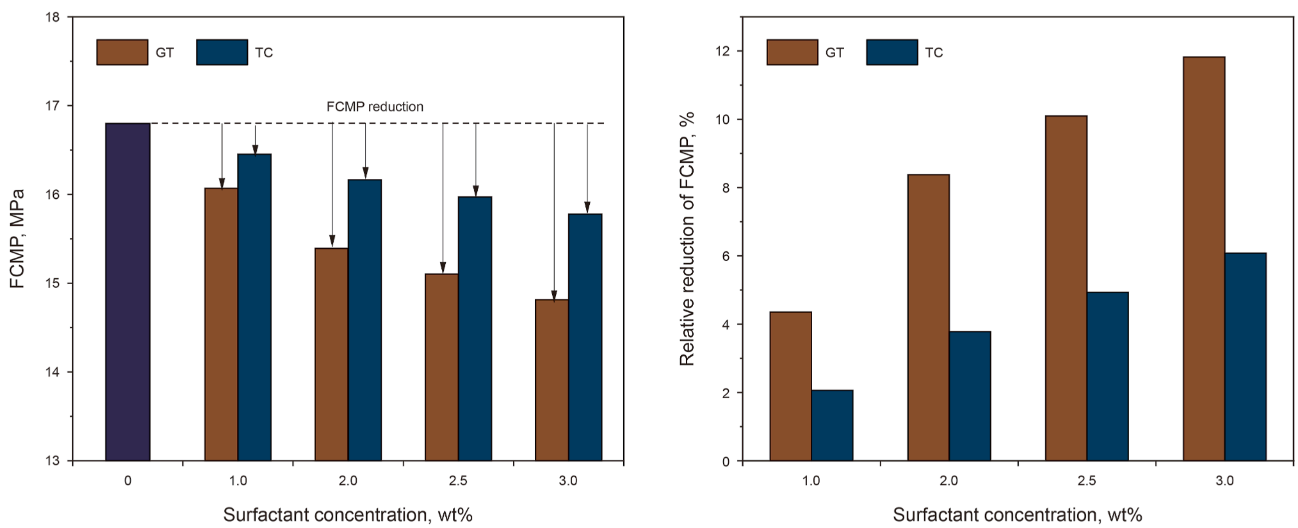
Overall, ester functional groups exhibit better reduction effects of miscibility pressure, and functional groups with shorter chains that are less prone to entanglement can better utilize the function



(a) FCMP

(b) FCMP reduction

Fig. 7. Enhanced miscibility of CO_2–oil system by different polyoxypropylene ethers.



(a) FCMP

(b) FCMP reduction

Fig. 8. Enhanced miscibility of CO_2–oil system by different types of esters.

of oxygen atoms to promote the miscibility of CO_2 and oil. Consequently, to more effectively reduce the FCMP of the CO_2–oil system, this type of surfactant should be a priority.

3.3. Reducing FCMP of CO_2–oil system by surfactant blended with ethanol

Previous research (Zhang et al., 2020) has preliminarily shown that alcohols, when used as co-solvents, enhance the ability of surfactants to reduce FCMP of CO_2–oil systems. Meanwhile, our recent work (Liu et al., 2025) clearly stated that ethanol exhibits better effect in enhancing CO_2–oil miscibility than other straight chain alcohol (*n*-pentanol) and branched chain alcohol (2-pentanol). Therefore, this work selected ethanol as a co-solvent to study its effect on polyether and ester surfactants reducing FCMP of CO_2–oil systems. Three types of surfactants, GT, EO_3, and PO_3, were selected based on their superior reduction capabilities as identified in the previous section. These surfactants were then blended with 5.0 wt% ethanol to perform FCMP measurement experiments for the CO_2–oil system. Table 3 presents the experimental design and results of the FCMP measurements for the CO_2–oil system with GT, EO_3, and PO_3 surfactants blended with 5.0 wt% ethanol.

Before conducting experiments on measuring the FCMP of the CO_2–oil system with additives of ethanol and surfactants, this work first tested the effect of ethanol on the FCMP of the CO_2–oil system. The FCMP of the CO_2–oil system is 13.9 MPa on the condition of 5.0 wt% ethanol additive, achieving a reduction of 17.26%.

As shown in Fig. 10, the capability of the surfactants blended with ethanol to reduce the FCMP of the CO_2–oil system continuously increases with the increasing surfactant concentration. Under the condition of 3.0 wt% GT blended with 5.0 wt% ethanol, the FCMP of the CO_2–oil system decreased to 12.1 MPa, with a high

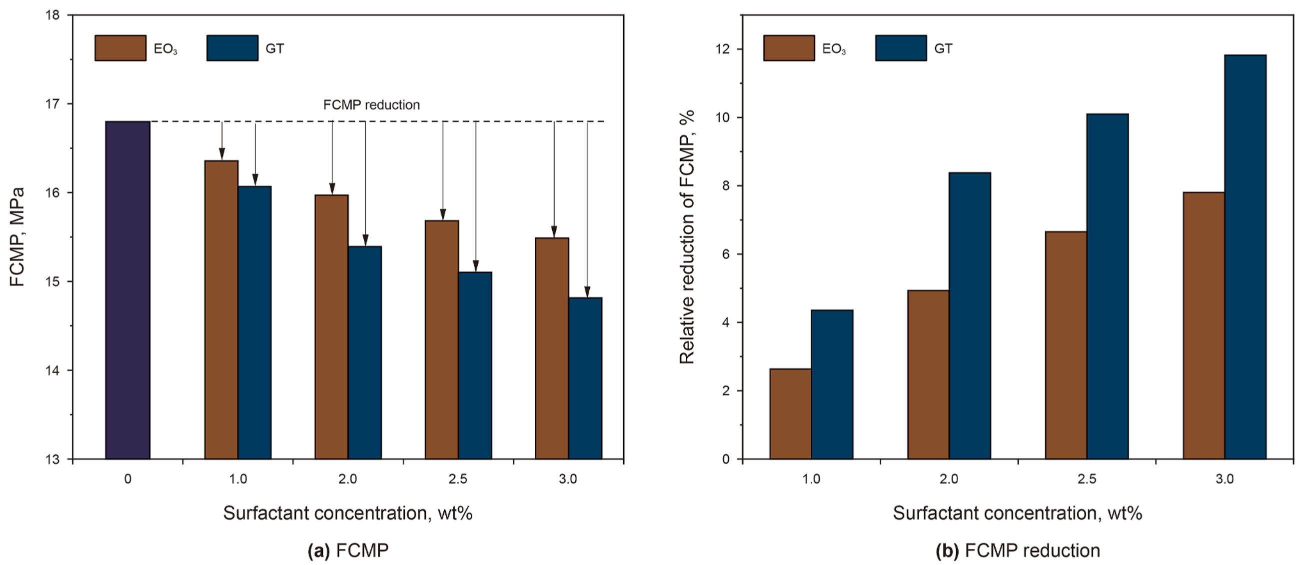


Fig. 9. Enhanced miscibility of CO_2–oil system by different types of functional groups.

Table 3
FCMP of the CO_2–oil systems with surfactants of GT, EO_3, and PO_3 blended with 5.0 wt% ethanol and the reduction effectiveness of FCMP.

Exp. No.	Surfactant	Surfactant concentration, wt%	FCMP, MPa	Reduction of FCMP, %
30	GT	1.0	13.3	21.01
31		2.0	12.7	24.45
32		2.5	12.4	26.18
33		3.0	12.1	27.90
34	EO_3	1.0	13.5	19.86
35		2.0	13.1	22.16
36		3.0	12.7	24.45
37	PO_3	1.0	13.6	19.29
38		2.0	13.2	21.58
39		3.0	12.9	23.31

reduction of 27.90%. The FCMP of the CO_2–oil system decreased to 12.7 and 12.9 MPa with addition of EO_3, and PO_3 blended with 5.0 wt% ethanol, respectively, achieving the reduction of 24.45% and 23.31%. Among these, the additives of GT blended with ethanol showed the best performance to reduce FCMP of the CO_2–oil system.

Fig. 11 illustrates the FCMP reduction effects of EO_3, PO_3, and GT when blended with ethanol. Compared to the use of a single surfactant, the combination of a surfactant with ethanol exhibits a significantly greater capacity to reduce the FCMP of the CO_2–oil system. For instance, with EO_3 surfactant, a 3.0 wt% concentration alone reduces the FCMP by 7.80%, whereas the addition of 3.0 wt% EO_3 blended with 5.0 wt% ethanol results in a substantially higher FCMP reduction of 24.45%. Ethanol demonstrates a similar enhancing effect in assisting PO_3 and GT to lower the FCMP of the CO_2–oil system. These results indicate that ethanol, as a co-solvent, significantly aids surfactants in reducing the FCMP of the CO_2–oil system, confirming that the strategy of blending surfactants with alcohol is both feasible and effective.

The results show that ethanol and surfactants (whether esters or ethers) have a synergistic effect in reducing the FCMP of the CO_2–oil system. On a molecular scale, ethanol modifies the polarity of CO_2, transitioning it from a non-polar to a partially polar state, thereby enhancing the solubility and stability of surfactants in CO_2. Zhang et al. (2020) also obtained a similar result. To verify the solubilizing effect of ethanol on the surfactant, this work conducted experiments to measure the solubility pressure of the CO_2-surfactant system with added ethanol, and the detail of the solubility experiment is shown in the Supplementary Material. After adding ethanol, the solubility pressure of 3.0 wt% surfactants in CO_2 decreased significantly from 9.9 to 9.2 MPa for GT, and from 13.6 to 12.6 MPa for PO_3, respectively. This indicates that, with ethanol as a co-solvent, CO_2 can dissolve a greater amount of surfactant at the same pressure. In other words, the same quantity of surfactant requires a lower pressure to dissolve when ethanol is present as an additive. Consequently, this approach offers an effective solution for oil fields where formation pressure is insufficient to reach the surfactant solubility pressure.

Another aspect, as discussed earlier, ethanol can independently lower the FCMP of the CO_2–oil system. Under the condition of 3.0 wt% surfactant blended with 5.0 wt% ethanol, the surfactant does not fully occupy the CO_2–oil interface, leaving space for ethanol to occupy the remaining interface. Consequently, the combination of surfactant and ethanol more effectively reduces interfacial tension and lowers the FCMP of the CO_2–oil system compared to using surfactants alone. As shown in Fig. 11, the curve slope of FCMP reduction with increasing surfactant concentration for the additive of surfactant blended with ethanol is similar to that for the single surfactant system. The difference in FCMP reduction between the additive of surfactant blended with ethanol and additive of single surfactant shows minimal variation with changes in mass concentration. Specifically, the average enhancement in FCMP reduction due to blended ethanol is 17.10%, 17.23%, and 16.43% for EO_3, PO_3, and GT, respectively, at

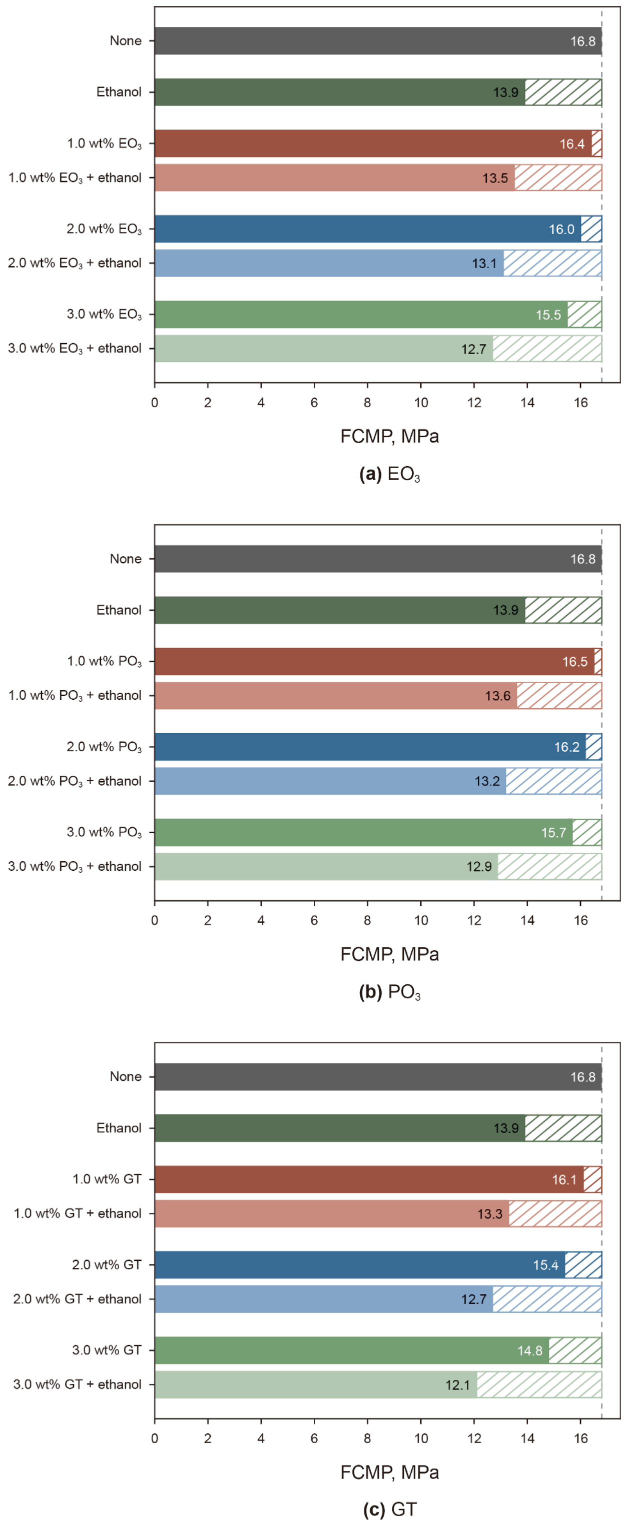


Fig. 10. FCMP of CO_2–oil system with the surfactants blended with 5.0 wt% ethanol.

concentrations ranging from 1 to 3.0 wt%. This enhancement closely aligns with the inherent FCMP reduction of 17.26% achieved by ethanol alone as a single additive, with the maximum difference being no greater than 0.83%. It demonstrates that the FCMP reduction capability of the blended ethanol largely comes from the ethanol itself. This result highlights an obvious synergistic effect of the combined system on enhancing CO_2–oil miscibility: the

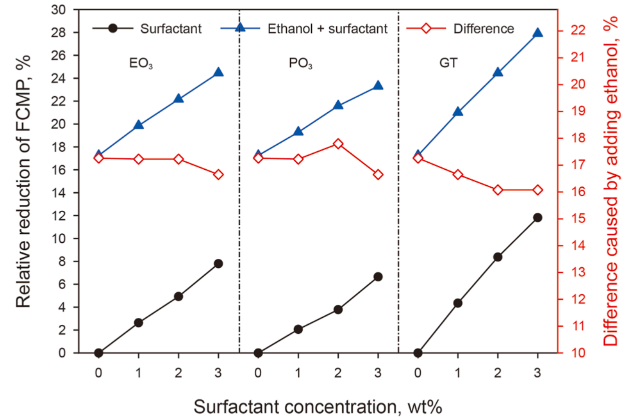


Fig. 11. Relative reduction of FCMP of CO_2–oil system by EO_3, PO_3, and GT blended with 5.0 wt% ethanol.

abilities of ethanol and surfactants to lower FCMP are not only fully additive but also independent of mutual interference or diminution. In this combined system, both components maintain their individual functions efficiently, without competition or weakening.

4. Conclusions

This work innovatively investigated the effect of different types of surfactants and their blends with ethanol on the miscible pressure of CO_2–oil (C_{16}) system by measuring the first contact miscibility pressure. Two fatty alcohol polyoxyethylene ethers (EO_j), three fatty alcohol polyoxypropylene ethers (PO_j), tributyl citrate (TC), and glyceryl triacetate (GT) were employed in the experiments. And then the effect of surfactants blended with ethanol on lowering the CO_2–oil FCMP was further studied from experiment and theory. The main conclusions are drawn as follows:

(1) A measurement method of the miscibility pressure of the CO_2–oil system by using a high-temperature and high-pressure visual PVT apparatus was proposed. Near the miscibility pressure point, significant changes in the CO_2–oil phase behavior can be clearly observed in the experiments enabling accurate measurement of the miscibility pressure.
(2) The capability of ether to reduce the FCMP weakens with increasing polymerization degree. The reason is that the length of the polyether molecules increases with an increase in polymerization degree, and a longer polyether chain structure leads to significant bending and entanglement of the surfactant molecules. These structural changes sterically hinder CO_2-philic groups from accessing the CO_2 phase.
(3) The results of GT and TC indicate that a longer carbon chain weakens the capability of surfactants to reduce the FCMP of the CO_2–oil system.
(4) The type of functional group and molecular structure significantly impact the capability of surfactants in reducing the CO_2–oil FCMP. Ester-based functional groups exhibit better FCMP reduction effects, while short-chain functional groups, being less prone to entanglement, can better utilize the FCMP-reducing effect of oxygen atoms. Therefore, ester surfactant with compact molecular architectures should be prioritized for effective CO_2–oil FCMP reduction.
(5) Surfactant–ethanol blends exhibit superior FCMP reduction capability in CO_2–oil systems compared to individual

components. As a co-solvent, ethanol synergistically enhances surfactants performance in reducing FCMP. It demonstrates that blending surfactants with ethanol is a feasible and effective strategy for enhancing CO_2–oil miscibility.

CRediT authorship contribution statement

Shu-Yang Liu: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Min-Feng Li:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Jia-Yu Chen:** Validation, Supervision, Resources, Formal analysis, Data curation. **Ying Teng:** Validation, Supervision, Resources, Formal analysis, Data curation. **Peng-Fei Wang:** Validation, Resources, Funding acquisition, Formal analysis, Data curation. **Jun-Rong Liu:** Writing – original draft, Validation, Supervision, Funding acquisition, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research is supported by the National Natural Science Foundation of China (52374063, 52204065 and 52304098), the Shandong Provincial Natural Science Foundation (ZR2023ME049), the Fundamental Research Funds for the Central Universities (25CX07004A), State Key Laboratory of Intelligent Construction and Healthy Operation and Maintenance of Deep Underground Engineering (SDGZK2429), and Shenzhen Science and Technology Program (JCYJ20220818095605012).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petsci.2025.07.005.

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