Article

Influence of Supercritical CO$_2$ Fracturing Fluid on the Permeability of Shale Reservoir and Mechanism Analysis

Qing Guo,* Ze Li, Xuanxiang Zeng, Dan Li, Huiming An, Li Zhao, Liang Tao, and Qiang Li

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Reduction of the reservoir permeability during supercritical CO$_2$ fracturing caused significant reservoir damage, which directly affects the crude oil recovery rate. This investigation explored a novel thickener for supercritical CO$_2$ fracturing fluid, this CO$_2$ thickener not only effectively improves the viscosity and rheological properties of CO$_2$ fracturing fluid but also contributes to reduce reservoir damage and improve permeability. The research results indicated that the synthesized CO$_2$ thickener (3 wt %) can increase the apparent viscosity of supercritical CO$_2$ fracturing fluid to 7 mPa·s, and a 9% matrix permeability damage rate and a 0.5 mD permeability decrease value are shown in a 3% CO$_2$ fracturing fluid. However, 3 wt % of commercial CO$_2$ thickener only increases the apparent viscosity of supercritical CO$_2$ fracturing fluid to 3 mPa·s, while the reservoir damage rate increases to 13%. Two thickeners exhibit completely different damage capabilities to the reservoir, and the synthesized CO$_2$ thickener shows excellent characteristics of reducing reservoir permeability and is also conducive to protecting shale reservoirs. Furthermore, supercritical CO$_2$ fracturing fluid containing synthetic thickeners has better temperature and shear resistance compared with commercial thickeners. This may be because the synthesized thickener and the micro grid formed by supercritical CO$_2$ reduce the adsorption in shale crevices, but a large amount of commercial thickeners can adsorb on the surface of shale.
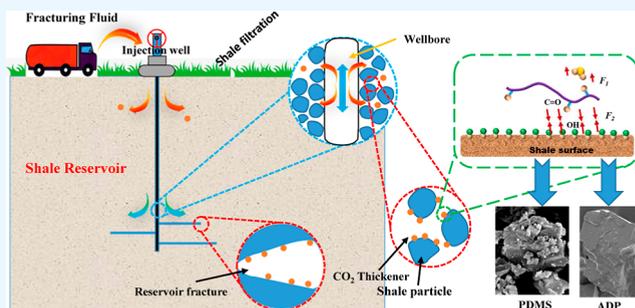
1. INTRODUCTION

Economic development has promoted the continuous enrichment of human material life and the improvement of life quality, but this is based on the consumption of a large amount of fossil fuels such as oil and gas.[1,2] Nevertheless, conventional energy sources such as oil, as nonrenewable energy sources, continue to decrease with significant consumption.[3] The unconventional resources such as shale oil and gas as alternative energy sources has become a research hotspot for petroleum engineers.[4] Reservoir stimulation is used to improve the crude oil recovery rate of reservoirs and can also achieve unconventional oil exploration in reservoirs.[5] As an important component of reservoir stimulation, fracturing operations can significantly improve the extraction capacity of crude oil.[6] However, the differences in fracturing operations show different advantages and disadvantages for different reservoir conditions. As a fracturing type that can be applied to most reservoirs, water-based fracturing can easily form a water sensitivity effect on shale reservoirs.[7] A poor stability and safety prevent oil-based fracturing fluid and foam fracturing fluid from being used in shale reservoir additionally. Therefore, an effective fracturing method should be explored by petroleum engineers to enhance oil and gas recovery in shale reservoirs.[8−10]

CO$_2$ fracturing technology is gradually receiving attention and being proposed due to the greenhouse effect and the urgent demand for unconventional energy.[11,12] CO$_2$ at 31.26 °C and 7.38 MPa exhibits a supercritical state, which can greatly change the CO$_2$ property greatly. Numerous advantages (minimal water sensitivity effect, weak water pollution, and mitigating greenhouse effects) can be achieved by applying supercritical CO$_2$ fracturing technology to energy extraction in shale reservoirs.[13−15] However, some shortcomings of supercritical CO$_2$ fracturing technology are constantly exposed as research deepens. Crack propagation and gravel transport cannot be achieved according to the extremely low CO$_2$ viscosity (>0.04 mPa·s).[16] The addition of oilfield chemicals such as fluorides, hydrocarbons, and siloxanes were considered as an effective measure to improve CO$_2$ fracturing fluids. Fluoroacrylate−styrene random copolymers caused a 3−10 fold increase in CO$_2$ viscosity (0.12−0.4 mPa·s) with 1 wt %
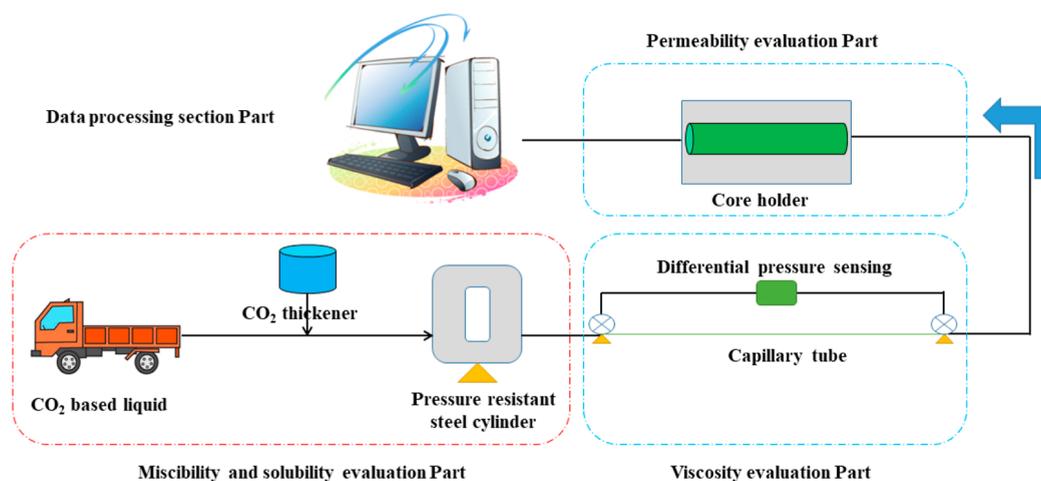
Figure 1. Performance evaluation device for the CO_2 fracturing fluid.

fluoropolymer at 25 °C and 35 MPa.[17] A 1.2−1.5 times (0.1−0.16 mPa·s) than that of pure CO_2 was shown after CO_2 dissolving the acetoxyl-terminated propylene oxide homopolymer.[18] 2 mPa·s of CO_2 viscosity was shown with a 2 wt % siloxane thickener at 303 K and 12 MPa, siloxane presented a more excellent thickening property than that of fluorides and hydrocarbons.[19] Furthermore, silicone thickeners exhibit 12% reservoir damage,[15] but the reservoir damage of supercritical CO_2 fracturing fluids containing fluorides or hydrocarbons has not yet been explored. Although fluorinated substances can effectively improve CO_2 viscosity, their inherent drawbacks such as high cost and groundwater pollution also hinder their practical application.[20] Hydrocarbon compounds cannot satisfy the fracturing conditions of oilfield sites due to the low solubility and thickening of hydrocarbon compounds in the CO_2 fracturing fluids. Although the addition of cosolvents can improve solubility, the thickening ability remains unchanged by cosolvents.[18] Silicone-based thickeners can avoid certain defects of fluorinated and hydrocarbon-based fluids and become potential thickeners for CO_2 fracturing fluids. Therefore, chemists and petroleum engineers actively embellish the chemical structure of siloxanes to ameliorate limited thickening, reservoir damage, and sand carrying capacity.[21]

In the present investigation, a novel silicone thickener containing functional groups was prepared according to the molecular interactions between siloxanes and the CO_2 molecules. In addition, the effect of thickener content, reservoir temperature, reservoir pressure, and shear rate on the apparent viscosity of supercritical CO_2 fracturing fluid was first investigated. Subsequently, the influence of the CO_2 fracturing fluid under different conditions on the fracture permeability continues to be analyzed. Finally, the microscopic mechanisms of apparent viscosity and permeability of the CO_2 fracturing fluid affected by different thickeners are revealed from a molecular perspective. Novel thickeners can provide basic theoretical references for shale reservoir protection and performance improvement of the CO_2 fracturing fluid.

2. MATERIALS AND METHODS

2.1. Experimental Materials. Analytical grade experimental materials were used for this investigation, and all chemicals were dried (100 °C) before use. Octamethylcyclotetrasiloxane (99.5%), tetramethyltetraphenylsiloxane (99.8%), and tetramethyltetrahydrosiloxane (99.5%) are donated by Nanjing Chemical Reagent Company. Acrylic acid-3-(trimethoxysilyl) propyl ester, chloroplatinic acid, concentrated sulfuric acid, and sodium bicarbonate were purchased from Aladdin Reagent Co., Ltd. Ultrapure water is self-made in the laboratory, and the rock core is taken from the Gulong Shale Block in Daqing Oilfield, CNPC.

2.2. Experimental Instruments. The experimental equipment used in this experiment was self-designed and assembled by the laboratory, and the entire experimental device is mainly used to measure the apparent viscosity and reservoir permeability changes of the supercritical CO_2 fracturing fluid. It is divided into four parts (Figure 1) based on the properties and device functions of CO_2 fracturing fluid. The mixing part of the CO_2 fracturing fluid mainly consists of a base fluid tank, a CO_2 thickener tank, and a pressure resistant steel cylinder with a transparent window. The evenly mixed CO_2 fracturing fluid is pressed into a pressure resistant steel cylinder containing a transparent window to observe the solubility and miscibility of the CO_2 thickener in the fracturing fluid. The apparent viscosity of the CO_2 fracturing fluid is mainly measured using a capillary viscometer, and different diameters of capillaries can be replaced for different viscosity characteristics of the fracturing fluid. The permeability evaluation of CO2 fracturing fluid on underground reservoirs is mainly measured through the core permeability measurement of the core holder, but the fracturing fluid needs to be pressurized before entering the core to meet the actual pressure requirements. The data inside the capillary and permeability data are ultimately transmitted to the data processing terminal for analysis.

2.3. Apparent Viscosity of CO_2 Fracturing Fluid. The rheological characteristics of CO_2 fracturing fluid follow the relevant data of laminar fluid, therefore a viscosity calculation formula for laminar fluid is used to evaluate the thickening ability of CO_2 thickeners (eq 1).[22]

$$\eta = \frac{\tau_w}{\gamma_w} = \frac{\frac{D\Delta p}{4L}}{\frac{8v}{D}} \tag{1}$$

where η is the apparent viscosity of CO_2 fracturing fluid, mPa·s. Shear stress and shear rate could be presented from τ_w and γ_w. D and L are the diameter and length of a capillary tube, m.
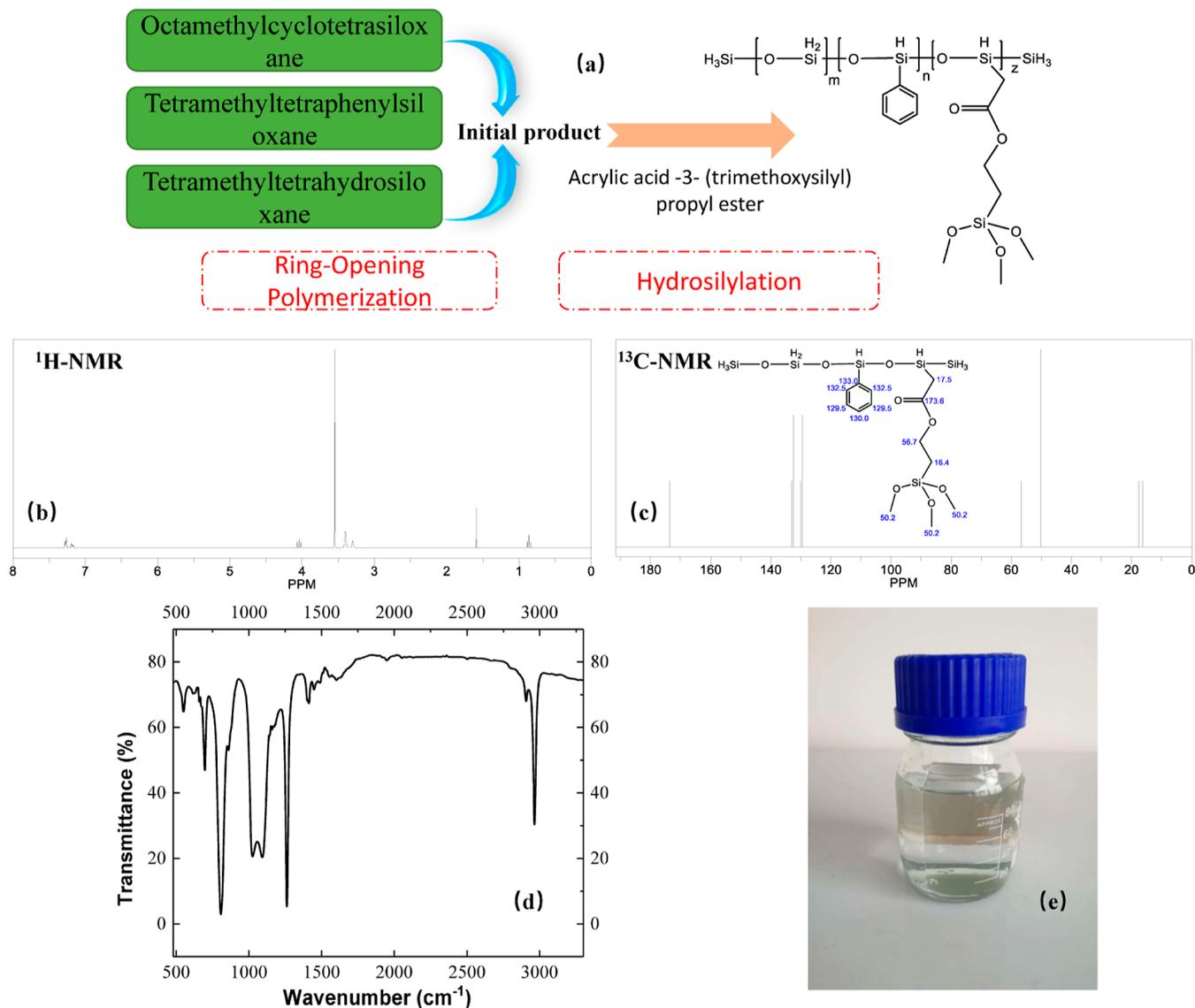
Figure 2. Preparation process and chemical characterization of thickeners. (a) Synthesis process. (b) ^1H NMR spectrum of ADP. (c) ^{13}C NMR spectrum of ADP. (d) FT-IR spectrum of ADP. (e) Physical picture of ADP.

Δp and v present the pressure difference and flow rate at both ends of the capillary tube, MPa and m/s.

In addition, the rheological index n and consistency coefficient K, used to characterize the rheological properties of fluids, can also be calculated and analyzed (eq 2). n and K also evaluate the thickening ability of CO_2 thickeners on CO_2 fracturing fluids.[23]

$$\lg \tau_w = \lg K \left(\frac{3n+1}{4n} \right)^n + n \lg \left(\frac{8v}{D} \right) \quad (2)$$

2.4. Analysis of Reservoir Permeability. The flow ability and oil recovery of crude oil in the formation are determined by the reservoir permeability, and a high permeability can allow CO_2 fracturing fluid to flow along reservoir fractures toward deep reservoirs. Additionally, a large oil recovery rate also increases with the increase of reservoir permeability. Therefore, the reservoir sealing by chemical agents such as CO_2 thickeners directly affects crude oil production and reservoir pollution.[24]

$$\alpha = \frac{Qvl}{A(P_1 - P_2)} \quad (3)$$

where α is the reservoir permeability, D. Q presented the volume flow rate of CO_2 fracturing fluid, m^3/s. A is the cross-sectional area, m^3. P_1 is the inlet pressure of drill-core, MPa. P_2 is the outlet pressure of drill-core, MPa.

3. RESULTS AND DISCUSSION

3.1. Synthesis of CO_2 Thickener. 50 mL of ethanol, 19 mL of octamethylcyclotetrasiloxane, 15 mL of tetramethylte-traphenylsiloxane, and 10 mL of tetramethyltetrahydrosiloxane were added into a 250 mL single ended flask, and these chemicals are stirred evenly at 70 °C and oxygen free conditions. Subsequently, 2.5 mL of sulfuric acid was added to the mixed liquid and the reaction continued for 5.5 h. 30 ppm chloroplatinic acid and 10.3 mL acrylic acid-3-(trimethoxysilyl) propyl ester were further added to the initial product and subjected to a hydrosilylation reaction for 2.5 h and 50 °C. Chemicals with small molecules and low boiling in
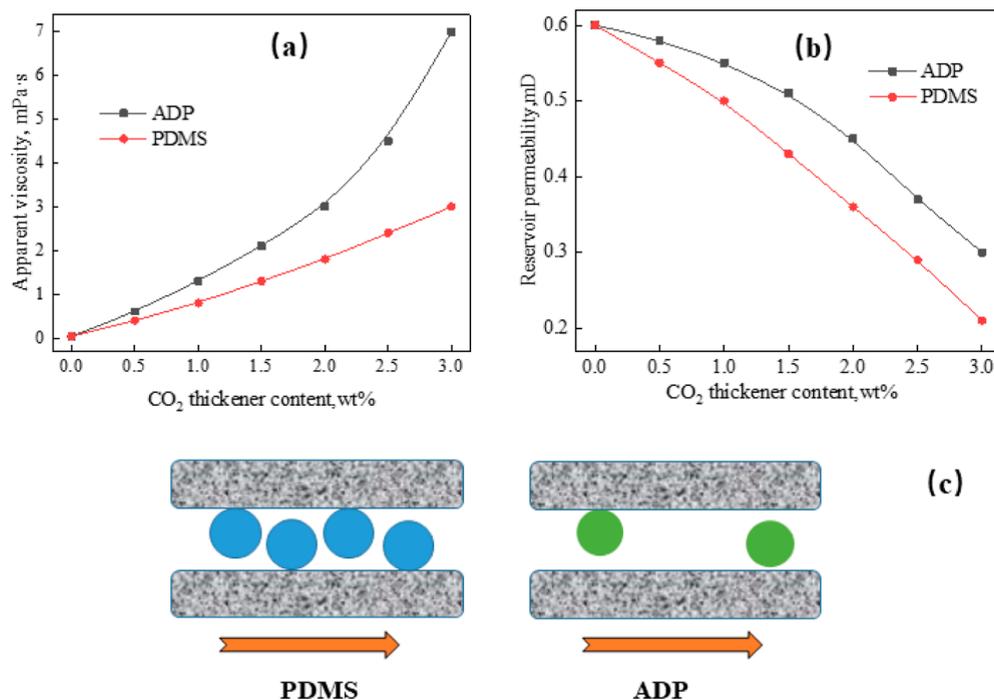
Figure 3. Effect of the thickener content on the apparent viscosity and reservoir permeability. (a) Relationship between thickener content and viscosity. (b) Relationship between thickener content and permeability. (c) Commercial products for sealing in cracks. (d) ADP for sealing in cracks.
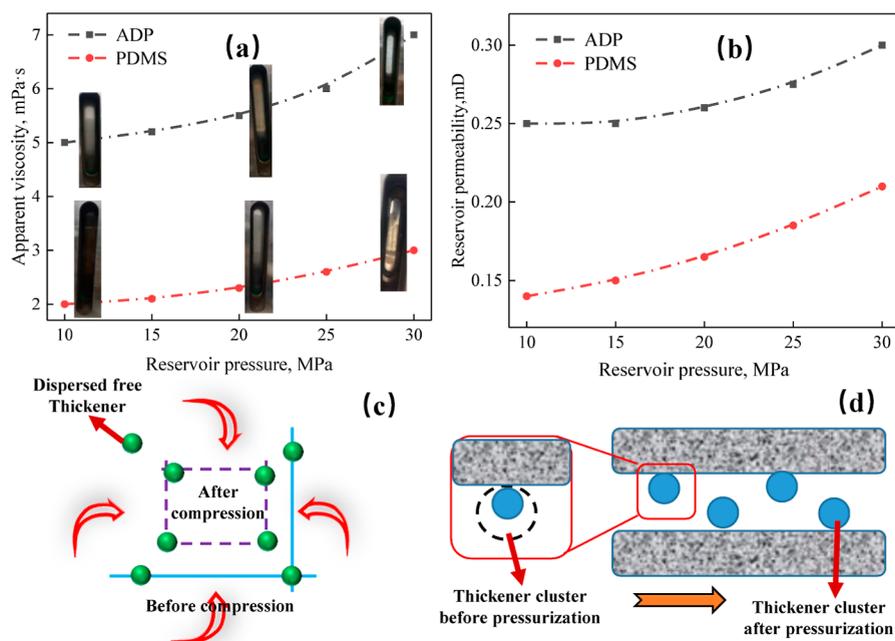
Figure 4. Effect of the reservoir pressure on the apparent viscosity and reservoir permeability. (a) Relationship between reservoir pressure and viscosity. (b) Relationship between reservoir pressure and permeability. (c) Interaction between thickener and CO_2. (d) Shape of thickener affected by pressure in cracks.

the final product were eliminated at 140 °C, and a polymer named ADP with a light green transparent liquid is the CO_2 thickener synthesized in this investigation. The synthesis process and chemical characterization of CO_2 thickener is shown in Figure 2. In addition, Ester group, carbonyl group, and phenyl group as functional groups showed a great influence on the solubility of thickener in supercritical CO_2, reservoir permeability CO_2 viscosity.

3.2. Effect of CO_2 Thickener Types and Content on the Apparent Viscosity and Permeability.
The influence of the thickener type and thickener content on the apparent viscosity of CO_2 fracturing fluid and reservoir permeability is shown in Figure 3 at 333 K and 30 MPa. In addition, a commercially available polydimethylsiloxane (PDMS) was considered as a reference material for comparing the performance differences of the prepared CO_2 thickeners. It
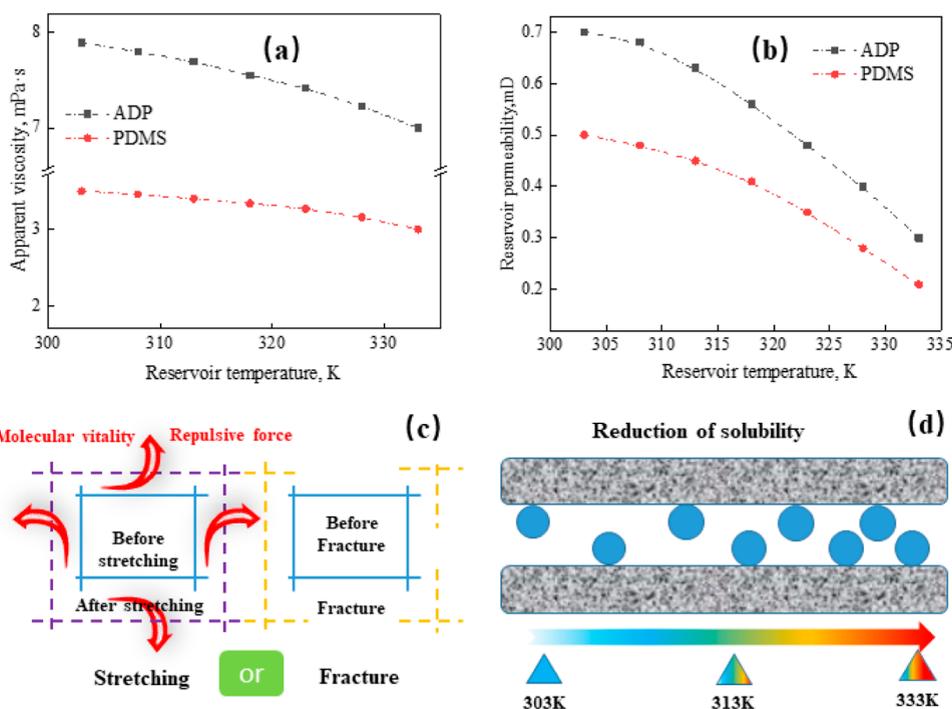
Figure 5. Effect of the reservoir temperature on the apparent viscosity and reservoir permeability. (a) Relationship between reservoir temperature and viscosity. (b) Relationship between reservoir temperature and permeability. (c) Interaction between thickener and CO_2. (d) Shape of thickener affected by temperature in cracks.

can be seen from Figure 3a that the thickened CO_2 fracturing fluid showed a bigger viscosity than the pure supercritical CO_2 (0 wt % thickener), and the increase in apparent viscosity of the CO_2 fracturing fluid implied an appropriate thickening and a potential application capability. Therefore, ADP represented a better thickening ability than that of commercial CO_2 thickener (PDMS) at the same content, and a completely different growth trend is presented between ADP and PDMS when the thickener content changed from 0 to 3 wt %. 1 wt % ADP (1 wt %) can increase the apparent viscosity of the CO_2 fracturing fluid to 1.5 mPa·s, while PDMS at this concentration can only reach an apparent viscosity of 0.9 mPa·s. In addition, 3 wt % ADP can increase the apparent viscosity of CO_2 from 0.04 to 7 mPa·s, while PDMS can only increase the apparent viscosity of the CO_2 fracturing fluid by 2.96 mPa·s. The apparent viscosity improvement occurred because of the inter-reaction among CO_2, thickener, and cosolvent (cyclohexane), and the interactions among molecules can form a dense grid structure.[15,16] Furthermore, the grid structure could be more dense with increasing the thickener content, and the apparent viscosity increases with the increase of thickener content macroscopically.[25] However, ADP at the same concentration exhibits a more excellent thickening ability compared to PDMS, mainly because CO_2-philic group of ADP such as ester and carbonyl group could contribute to construct the intermolecular chemical bond, but the construction of chemical bonds was hindered due to the lack of functional groups in PDMS.[26,27]

Figure 3b showed the effects of thickener content on the reservoir permeability at 330 K and 30 MPa. As can be seen from Figure 3b that an increasing thickener content resulted in a decreasing reservoir permeability, and the 0.6 mD of pure CO_2 fracturing fluid (containing 0 wt % PDMS) is significantly higher than the 0.5 mD of CO_2 containing 1 wt % PDMS. In

addition, a similar permeability change was exhibited for the CO_2 fracturing fluid containing ADP, a reduced reservoir permeability was demonstrated with increasing the ADP content. A decrease in permeability of 0.05 mD is shown when the ADP content increases from 0 to 1 wt %. Relatively small solubility of polymer in CO_2 causes free thickener molecules to remain in reservoir fractures, resulting in a large number of fractures being blocked. The dissociative thickening molecules increase with the increase of thickener content, which directly caused more severe sealing of reservoir fractures. In addition, PDMS lacking functional groups is prone to plugging reservoir fractures, but a large number of ester groups enhance the solubility and interaction of ADP in CO_2. Thus, the little dissociative ADP not only increased the viscosity of CO_2 fracturing fluid but also reduced the sealing of reservoir fractures (Figure 3c).

3.3. Effect of Reservoir Pressure on the Apparent Viscosity and Permeability. Figure 4a presents the variation trend of apparent viscosity of CO_2 fracturing fluid under reservoir pressure, and the effect of CO_2 fracturing fluid under different reservoir pressures on reservoir permeability has also been explored (Figure 4b). As shown in Figure 4a, a slowly rising apparent viscosity of CO_2 fracturing fluid (3 wt % thickener) was emerged as reservoir pressure increases from 10 to 30 MPa, which indicated that reservoir pressure was conducive to improve the rheological property of CO_2 fracturing fluid. It can be given from Figure 4a that a similar trend of apparent viscosity was showed between reservoir pressure and thickener content, but the thickened fracturing fluid (containing 3 wt % ADP) only grew the viscosity difference of 2 mPa·s when reservoir pressure increased from 10 to 30 MPa. Namely, a significantly smaller effect of reservoir pressure on the CO_2 viscosity occurred than that of the thickener content from 0 to 3 wt %.[28] In addition, ADP at the
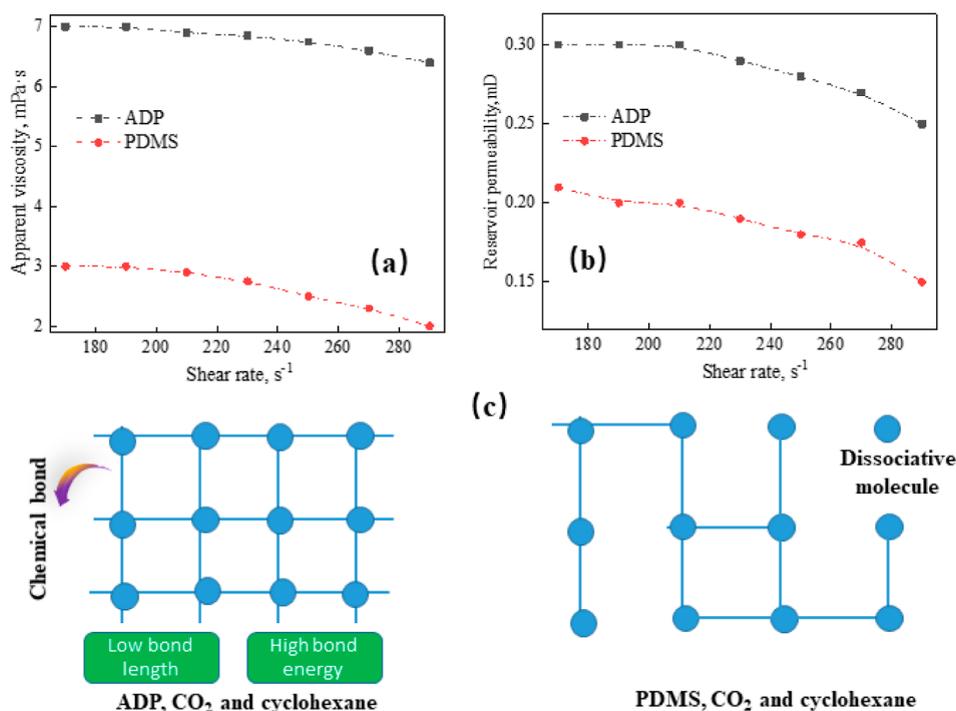
Figure 6. Effect of shear rate on the apparent viscosity and reservoir permeability. (a) Relationship between the shear rate and viscosity. (b) Relationship between shear rate and permeability. (c) Interaction between ADP and CO_2. (d) Interaction between PDMS and CO_2.

same content exhibited a greater influence of reservoir pressure on apparent viscosity than PDMS, and the CO_2 fracturing fluid containing 3 wt % PDMS only increased from 2 mPa·s at 10 MPa to 3 mPa·s at 30 MPa. Although the microgrid formed by PDMS, CO_2, and cyclohexane could reduce the same area within the pressure range of 10 to 30 MPa, the minimal density of the microgrid limited the influence of reservoir pressure on fracturing fluids containing PDMS (Figure 4c). The reservoir pressure compresses the microgrid, resulting in a decrease in the area and an increase in density of individual microgrids. The increase in microgrid density caused by reservoir pressure is still the microscopic reason for the increase in the apparent viscosity of CO_2 fracturing fluid.[29,30]

This investigation continued to analyze the effect of the CO_2 fracturing fluid on reservoir permeability under different reservoir pressures. It can be given from Figure 4b that the CO_2 fracturing fluid containing 3 wt % ADP could increase reservoir permeability from 0.25 mD at 10 MPa to 0.3 mD at 30 MPa, a significant increase in permeability trend is exhibited with an increase in the elevated reservoir pressure, and the effect of reservoir pressure on permeability is significantly opposite to the effect of thickener content in Figures 3b and 4b. In addition, the increasing trend of the CO_2 fracturing fluid containing PDMS on reservoir permeability is significantly higher than that of ADP, and the reservoir permeability can increase from 0.14 mD at 10 MPa to 0.21 mD at 30 MPa. Two reasons can explain the above phenomenon: ① Reservoir pressure reduced the microscopic distance between dissociative molecules, which was instrumental in enhancing the interaction between the thickener and supercritical CO_2. The dispersed thickeners are soluble in supercritical CO_2 easily due to the enhanced intermolecular forces, which avoided or reduced the sealing of fractures by undissolved thickener.[15] ② The undissolved PDMS sealed in reservoir fractures was also compressed and reduced due to the increase in reservoir

pressure; more voids in reservoir fractures alleviate the sealing effect of thickeners, and more fracturing fluid can pass through the fractures more smoothly and enter deeper reservoirs (Figure 4).

3.4. Effect of Reservoir Temperature on the Apparent Viscosity and Permeability. Figure 5 showed the effect of reservoir temperature on the apparent viscosity and reservoir permeability by a CO_2 fracturing fluid at 3 wt % thickener at 30 MPa and 170 s^{-1}. As shown in Figure 5a, a viscosity change trend completely different from the thickener content and reservoir pressure is presented when the reservoir temperature increased from 303 to 333 K. The apparent viscosity of the CO_2 fracturing fluid gradually decreased with an increase in the reservoir temperature, and a relatively slight effect of the reservoir temperature below 313 K on apparent viscosity was displayed. A reduction interval of 0.3 mPa·s for apparent viscosity was observed with increase in the reservoir temperature from 303 to 313 K. However, when reservoir temperature was higher than 313 K, a rapidly decreasing apparent viscosity change occurs. The apparent viscosity of the CO_2 fracturing fluid decreased from 7.6 mPa·s at 313 K to 7 mPa·s at 333 K. It can be analyzed from the curve trend in Figure 5a that the higher the reservoir temperature, the greater effect on the apparent viscosity of the CO_2 fracturing fluid. In addition, Figure 5a also indicated that the influence of reservoir temperature on the apparent viscosity of CO_2 fracturing fluid containing PDMS is much lower than that of ADP, and the apparent viscosity decreased from 3.5 mPa·s at 303 K to 3 mPa·s at 333 K. Although PDMS exhibits a smaller decrease in the apparent viscosity than that of ADP, a basically consistent decreasing trend is showed between these two CO_2 fracturing fluid.[31] In brief, the reservoir temperature is not conducive to the maintenance and enhancement of apparent viscosity. Above all, The Arrhenius equation has already shown that the molecular energy increased significantly because of the

increasing reservoir temperature (eq 4), and an improving intermolecular repulsion was bespoken as the reservoir temperature gradually elevated. The chemical bond between two molecules will elongate due to these two forces, or the chemical bond would break as the force reaches a certain value. Broken chemical bonds, resulting from the increase in the reservoir temperature, formed more dissociated molecules. The unbroken chemical bonds also resulted in a sparse grid density. The decrease in microgrid density caused by broken or elongated chemical bonds is an important reason for the influence of reservoir temperature on apparent viscosity. Besides that, CO_2 fracturing fluid containing ADP contains more chemical bonds that can be cut or stretched, resulting in a greater decrease in grid density (Figure 5b).[32]

$$\omega = A \exp\left(\frac{E_f}{R_g T}\right) \tag{4}$$

where molecular activation energy and frequency factor are represented by E_f and A. R_g is a molar constant, and A and R_g are considered as a constant value. w is the molecular motion velocity.

As given in Figure 5c, the variation of reservoir permeability with reservoir temperature is similar to the apparent viscosity curve; a gradually decreasing permeability occurs as the reservoir temperature increases. A decrease in reservoir permeability of 0.4 mD is shown for the CO_2 fracturing fluid containing 3 wt % ADP at 30 MPa, and PDMS only exhibited a decrease in reservoir permeability of 0.3 mD. The increasing reservoir temperature will induce the elongation or fracture of chemical bonds, while few chemical bonds among PDMS, CO_2, and cyclohexane are broken. The low solubility of PDMS in CO_2 has sealed off many reservoir fractures, and almost no PDMS is released from CO_2 although the reservoir temperature increases.[33] However, The high solubility of ADP in CO_2 at a low temperature cannot seal reservoir fractures, but the low solubility of ADP in CO_2 at high temperatures can aggravate the sealing of fractures (Figure 5d).

3.5. Effect of Shear Rate on the Apparent Viscosity and Permeability. As seen in Figure 6a,b, a decreasing apparent viscosity of the CO_2 fracturing fluid and reservoir permeability were shown with an increase in shear rate between 170 and 270 s^{-1}. It should be noted that this data evaluation was carried out at the pressure of 30 MPa at the temperature of 333 K and 3 wt % thickener content. Commercial PDMS is still used as a reference material for CO_2 thickeners to explore the effects of shear rates under different thickener type. When the shear rate was lower than 210 s^{-1}, a reduction amplitude of 0.1 mPa·s of CO_2 fracturing fluid (containing 3 wt % ADP) was presented. However, a shear rate greater than 210 s^{-1} will cause a significant decrease in apparent viscosity, and the apparent viscosity decreased from 6.9 mPa·s of 210 s^{-1} to 6.6 mPa·s of 270 s^{-1}. However, a greater impact on apparent viscosity is exhibited in CO_2 fracturing fluids containing 3 wt % PDMS. The apparent viscosity of the fracturing fluid will decrease to 2.3 mPa·s of 270 s^{-1}, which is 0.7 mPa·s lower than 3 mPa·s of 170 s^{-1}. Shear force can cause damage or fracture of chemical bonds, which can reduce the density microgrid and apparent viscosity. ADP exhibited a superior shear resistance of the CO_2 fracturing fluid than that of PDMS, which is attributed to the functional groups contained in ADP. CO_2-philic group of ADP (ester group) not only was conducive to improve the

interaction with CO_2 and cyclohexane but also form stable and short chemical bonds.[34] The stable chemical bonds with a strong bond energy can withstand large shear forces. However, the absence of functional groups in PDMS reduces the interaction and weak chemical bond formation among PDMS, CO_2, and cyclohexane, and these chemical bonds with smaller energy are easily sheared off under shear action (Figure 6c).[35]

It can be seen from Figure 6b that a decreased reservoir permeability was shown with an increase in the shear rate from 170 to 270 s^{-1}, and the effect of ADP on reservoir permeability is significantly smaller than that of PDMS under different shear rates. CO_2 fracturing fluid containing 3 wt % ADP can achieve a reservoir permeability of 0.3 mD at 170 s^{-1}, and the reservoir permeability of 0.27 mD is shown with 270 s^{-1} of shear rate. However, the CO_2 fracturing fluid containing 3 wt % PDMS can decrease reservoir permeability by 0.06 mD when the shear rate changed from 170 to 270 s^{-1}, and ADP demonstrated a superior shear resistance of the CO_2 fracturing fluid than that of PDMS. ADP can form stable chemical bonds with CO_2 and cyclohexane, which avoids the formation of dissociative ADP molecular clusters. The weaker chemical bonds between PDMS and CO_2 are quickly sheared off under shear action, and more dissociative PDMS can be blocked in reservoir fractures.

4. CONCLUSIONS

A novel branched siloxane was synthesized Ring-opening polymerization and hydrosilylation, and the prepared siloxane thickener (ADP) for CO_2 fracturing exhibited an excellent thickening ability for CO_2 fracturing fluid than that of commercial PDMS. The increasing thickener content and reservoir pressure contributed to promote the fluid viscosity and rheological ability, but an increasing reservoir temperature and shear rate was adverse to the apparent viscosity of CO_2 fracturing fluid. In addition, the addition of ADP can effectively alleviate reservoir permeability and exhibit less reservoir damage than that of PDMS. A shorter and stronger chemical bond is formed among ADP, CO_2, and cyclohexane, and CO_2 fracturing fluid containing ADP can form a denser microgrid than PDMS. The microgrid density is considered as an important reason for the performance changes of CO_2 fracturing fluids.

■ AUTHOR INFORMATION

Corresponding Author

Qing Guo − *BaiLie School of Petroleum Engineering, Lanzhou City University, Lanzhou 730070, China; Xi'an Key Laboratory of Tight Oil (Shale Oil) Development (Xi'an Shiyou University), Xi'an 710065, China;* ● orcid.org/0009-0004-5657-4326; Email: guoqing2310@126.com

Authors

Ze Li − *The First Oil Production Plant of PetroChina Changqing Oilfield Branch, Yan'an 716000, China*

Xuanxiang Zeng − *The First Oil Production Plant of PetroChina Changqing Oilfield Branch, Yan'an 716000, China*

Dan Li − *Changqing Downhole Technology Operation Company, CNPC Chuanqing Drilling Engineering Co., Ltd., Xi'an 710018, China*

Huiming An − *BaiLie School of Petroleum Engineering, Lanzhou City University, Lanzhou 730070, China*

Li Zhao − *BaiLie School of Petroleum Engineering, Lanzhou City University, Lanzhou 730070, China*

Liang Tao − *Oil and Gas Technology Research Institute Changqing Oilfield Company, PetroChina Company Limited, Xi'an 710018, China*

Qiang Li − *School of Engineering, China University of Petroleum Beijing at Karamay, Karamay 834000, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c09728

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Liu, Y.; Tang, Y.; Chang, Q.; Ma, C.; He, S.; Yuan, Li. Development of a novel heat- and shear-resistant nano-silica gelling agent. *Nanotechnol. Rev.* **2022**, 11 (1), 2786−2799.

(2) Lv, Q.; Li, Z.; Li, B.; Zhang, C.; Shi, D.; Zheng, C.; Zhou, T. Experimental study on the dynamic filtration control performance of N_2/liquid CO_2 foam in porous media. *Fuel* **2017**, 202, 435−445.

(3) Wang, S.; Qin, C.; Feng, Q.; Javadpour, F.; Rui, Z. A framework for predicting the production performance of unconventional resources using deep learning. *Appl. Energy* **2021**, 295, 117016.

(4) Li, Q.; Liu, J.; Wang, S.; Guo, Y.; Han, X.; Li, Q.; Cheng, Y.; Dong, Z.; Li, X.; Zhang, X. Numerical insights into factors affecting collapse behavior of horizontal wellbore in clayey silt hydrate-bearing sediments and the accompanying control strategy. *Ocean Eng.* **2024**, 297, 117029.

(5) Zhao, L.; Chen, X.; Zou, H.; Liu, P.; Liang, C.; Zhang, N.; Li, N.; Luo, Z.; Du, J. A review of diverting agents for reservoir stimulation. *J. Pet. Sci. Eng.* **2020**, 187, 106734.

(6) Kim, J.; Moridis, G. J. Numerical analysis of fracture propagation during hydraulic fracturing operations in shale gas systems. *Int. J. Rock Mech. Min. Sci.* **2015**, 76, 127−137.

(7) Wu, G.; Pan, J.; Anwaier, M.; Wu, J.; Xiao, P.; Zheng, T.; Wang, W.; Meng, X.; Wang, P.; Liu, J.; et al. Effect of nano-SiO_2 on the flowback-flooding integrated performance of water-based fracturing fluids. *J. Mol. Liq.* **2023**, 379, 121686.

(8) Wanniarachchi, W. A. M.; Ranjith, P. G.; Perera, M. S. A. Shale gas fracturing using foam-based fracturing fluid: a review. *Environ. Earth Sci.* **2017**, 76, 91.

(9) Gaurina-Medimurec, N.; Brkić, V.; Topolovec, M.; Mijić, P. Fracturing fluids and their application in the Republic of Croatia. *Appl. Sci.* **2021**, 11 (6), 2807.

(10) Sun, X.; Gao, Z.; Zhao, M.; Gao, M.; Du, M.; Dai, C. Development and evaluation of a novel seawater-based viscoelastic fracturing fluid system. *J. Pet. Sci. Eng.* **2019**, 183, 106408.

(11) Nianyin, L.; Jiajie, Y.; Chao, W.; Suiwang, Z.; Xiangke, L.; Jia, K.; Yuan, W.; Yinhong, D. Fracturing technology with carbon dioxide: A review. *J. Pet. Sci. Eng.* **2021**, 205, 108793.

(12) Liu, H.; Wang, F.; Zhang, J.; Meng, S.; Duan, Y. Fracturing with carbon dioxide: Application status and development trend. *Pet. Explor. Dev.* **2014**, 41 (4), 513−519.

(13) Zhang, C. P.; Liu, S.; Ma, Z. Y.; Ranjith, P. Combined micro-proppant and supercritical carbon dioxide (SC-CO_2) fracturing in shale gas reservoirs: A review. *Fuel* **2021**, 305, 121431.

(14) Wilkins, R.; Menefee, A. H.; Clarens, A. F. Environmental life cycle analysis of water and CO2-based fracturing fluids used in unconventional gas production. *Environ. Sci. Technol.* **2016**, 50 (23), 13134−13141.

(15) Li, Q.; Wang, F.; Forson, K.; Zhang, J.; Zhang, C.; Chen, J.; Xu, N.; Wang, Y. Affecting analysis of the rheological characteristic and reservoir damage of CO_2 fracturing fluid in low permeability shale reservoir. *Environ. Sci. Pollut. Res.* **2022**, 29 (25), 37815−37826.

(16) Li, Q.; Wang, Y.; Wang, F.; Li, Q.; Kobina, F.; Bai, H.; Yuan, L. Effect of a modified silicone as a thickener on rheology of liquid CO_2 and its fracturing capacity. *Polymers* **2019**, 11 (3), 540.

(17) Zhang, Y.; Zhu, Z.; Tang, J. Investigation on modified polyether as an efficient CO_2 thickener. *New J. Chem.* **2021**, 45 (2), 651−656.

(18) Zhang, Y.; Zhu, Z.; Tang, J. Research on polyether-based hydrocarbon thickener for CO_2. *Fluid Phase Equilib.* **2021**, 532, 112932.

(19) Li, Q.; Wang, Y.; Li, Q.; Wang, F.; Bemardo, J.; Zhang, Y.; Bai, B.; Liu, F. Performance Improvement of Thickened Liquid CO2 by Introducing a Philic-CO_2 Silicone Polymer. *SPE Asia Pacific Oil and Gas Conference and Exhibition*; SPE, 2020..

(20) Keating, E. H.; Fessenden, J.; Kanjorski, N.; Koning, D. J.; Pawar, R. The impact of CO 2 on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration. *Environ. Earth Sci.* **2010**, 60, 521−536.

(21) Li, Q.; Wang, Y.; Wang, Y.; San, J.; Li, Q.; Foster, G. Synthetic process on hydroxyl-containing polydimethylsiloxane as a thickener in CO_2 fracturing and thickening performance test. *Energy Sources, Part A* **2018**, 40 (9), 1137−1143.

(22) Aycaguer, A. C.; Lev-On, M.; Winer, A. M. Reducing carbon dioxide emissions with enhanced oil recovery projects: A life cycle assessment approach. *Energy Fuels* **2001**, 15 (2), 303−308.

(23) Sun, X.; Liang, X.; Wang, S.; Lu, Y. Experimental study on the rheology of CO_2 viscoelastic surfactant foam fracturing fluid. *J. Pet. Sci. Eng.* **2014**, 119, 104−111.

(24) Sander, R.; Pan, Z.; Connell, L. D. Laboratory measurement of low permeability unconventional gas reservoir rocks: A review of experimental methods. *J. Nat. Gas Sci. Eng.* **2017**, 37, 248−279.

(25) Li, Q.; Wang, F.; Wang, Y.; Forson, K.; Cao, L.; Zhang, C.; Zhou, C.; Zhao, B.; Chen, J. Experimental investigation on the high-pressure sand suspension and adsorption capacity of guar gum fracturing fluid in low-permeability shale reservoirs: factor analysis and mechanism disclosure. *Environ. Sci. Pollut. Res.* **2022**, 29 (35), 53050−53062.

(26) Talebian, S. H.; Sagir, M.; Mumtaz, M. An integrated property-performance analysis for CO_2-philic foam-assisted CO2-enhanced oil recovery. *Energy Fuels* **2018**, 32 (7), 7773−7785.

(27) Miller, M. B.; Chen, D. L.; Xie, H. B.; Luebke, D. R.; Karl Johnson, J.; Enick, R. M. Solubility of CO2 in CO2-philic oligomers; COSMOtherm predictions and experimental results. *Fluid Phase Equilib.* **2009**, 287 (1), 26−32.

(28) Li, Q.; Wang, Y.; Wang, F.; Ning, X.; Chuanbao, Z.; Zhang, J.; Zhang, C. Factor analysis and mechanism disclosure of supercritical CO_2 filtration behavior in tight shale reservoirs. *Environ. Sci. Pollut. Res.* **2022**, 29, 17682−17694.

(29) Baysal, C.; Erman, B.; Chu, B. Conformational features of poly (1, 1-dihydroperfluorooctyl acrylate) and poly (vinyl acetate) diblock oligomers in supercritical carbon dioxide. *J. Chem. Phys.* **2001**, 114 (12), 5444−5449.

(30) Li, Q.; Han, Y.; Liu, X.; Ansari, U.; Cheng, Y.; Yan, C. Hydrate as a by-product in CO2 leakage during the long-term sub-seabed sequestration and its role in preventing further leakage. *Environ. Sci. Pollut. Res.* **2022**, 29 (51), 77737−77754.

(31) Li, Q.; Wang, Y.; Wang, F.; Wu, J.; Usman Tahir, M.; Li, Q.; Yuan, L.; Liu, Z. Effect of thickener and reservoir parameters on the filtration property of CO_2 fracturing fluid. *Energy Sources, Part A* **2020**, 42 (14), 1705−1715.

(32) Tamm, L.; Mcconnell, H. Supported phospholipid bilayers. *Biophys. J.* **1985**, 47 (1), 105−113.

(33) Li, Q.; Wang, F.; Wang, Y.; Zhang, J.; Yu, X.; Zhao, M.; Zhou, C.; Forson, K.; Shi, S.; Zhao, Y.; et al. Influence of organoboron cross-linker and reservoir characteristics on filtration and reservoir residual of guar gum fracturing fluid in low-permeability shale gas reservoirs. *Environ. Sci. Pollut. Res.* **2022**, *29* (55), 82975−82985.

(34) Luo, X.; Wang, S.; Wang, Z.; Jing, Z.; Lv, M.; Zhai, Z.; Han, T. Experimental investigation on rheological properties and friction performance of thickened CO_2 fracturing fluid. *J. Pet. Sci. Eng.* **2015**, *133*, 410−420.

(35) Li, Q.; Wang, F.; Wang, Y.; Bai, B.; Zhang, J.; Lili, C.; Sun, Q.; Wang, Y.; Forson, K. Adsorption behavior and mechanism analysis of siloxane thickener for CO_2 fracturing fluid on shallow shale soil. *J. Mol. Liq.* **2023**, *376*, 121394.