

Interfacial Characterization and Minimum Miscible Pressure Study of CO₂ Flooding Based on Molecular Dynamics

Bochao Qu, Xinle Ma, and Zhenzhen Dong*, Xi'an Shiyou University, Xi'an, China

Abstract

CO₂ flooding can not only effectively improve the recovery of oil reservoirs, but also permanently store CO₂ underground to alleviate the greenhouse effect. In the process of CO₂ flooding, CO₂ is injected into the oil reservoirs to affect the properties of crude oil through adsorption on oil interface, which reduces the interfacial tension and the density of the crude oil, thereby enhancing the recovery factor. Conventional core flooding experiments can only observe the oil displacement effect from a macroscopic perspective, but it is difficult to characterize the interface of CO₂ flooding from a microscopic perspective. Furthermore, the experiment to obtain the minimum miscible pressure (MMP) usually requires a long time and high cost.

In this study, an all-atom molecular dynamics simulation method was used to establish a CO₂ model and a crude oil model. Using the CO₂ force field of ZHU and the alkane force field of NERD, the interface interaction, interface characteristics, and minimum miscible pressure between CO₂ and crude oil were analyzed. The research results show that when CO₂ mixes with the crude oil, CO₂ accumulates at the interface to form an adsorption layer; with the increase of system pressure, the phase interface and the CO₂ adsorption layer gradually become thicken, and the interfacial tension (IFT) between CO₂ and crude oil decreases linearly. The addition of the light hydrocarbon component allows CO₂ to be more readily miscible with crude oil. At a low pressure, IFT decreases with increasing temperature, while at a high pressure, IFT increases with increasing temperature and MMP increases with increasing temperature as well. The MMP calculated using linear extrapolation of the interfacial tension was in good agreement with the experiment measurements.

The main innovations of this study was the use of molecular dynamics analysis to simulate the interfacial properties of a system composed of CO₂ and n-alkanes, and it is applicable to apply the simulated MMP in real oilfields. This study can significantly reduce the human, material and financial resources of the experiment in estimating MMP and also provide constructive suggestions on the practical application of CO₂ flooding on oil reservoirs.

Introduction

In domestic and international reservoir development, CO₂ flooding can not only enhance oil recovery, but also achieve CO₂ sequestration and reduce the greenhouse effect. When the pressure is high enough, the ability of the crude oil to dissolve bitumen and paraffin decreases after CO₂ precipitates the lighter

components in the crude oil, and the heavy components precipitate out of the crude oil, the crude oil viscosity decreases significantly and the oil flow ability is improved to achieve the purpose of mixed-phase oil drive.

Under certain temperature and pressure conditions, when the crude oil is miscible with CO₂, the interfacial tension of the crude oil is eliminated, and the pressure at this point is the minimum miscible pressure (MMP) for CO₂ miscible flooding. Therefore, understanding the interfacial properties of processes, such as the dissolution of CO₂ into crude oil, is particularly important for CO₂ miscible flooding technology. The MMP is the minimum pressure at which the interfacial tension between oil and gas disappears. The most commonly used experiments for determining MMP are the fine tube test method, the bubbler method, and the vanishing interfacial tension method.

The fine tube experiments is a standard method widely used and accepted in the petroleum industry to measure MMP and usually the measured MMP is reliable (Elsharkaw1996; Flock and Nouar 1984). Yelling et al. (1980) used sand-filled long fine tubes to simulate the CO₂ repulsion process in real reservoirs to determine MMP, and investigated the effect of reservoir temperature and oil compositions on MMP. Nouar and Flock(1984) performed a parameter analysis of the MMP determination using a thin-tube test and suggested that increasing the length of the thin-tube could result in more accurate MMP values. However, the fine tube test is very expensive and time consuming (Zhang and Gu 2015). The bubble-lift method is an relative cheap and fast method for determining MMP. The movement of CO₂ bubbles in oil is observed through a high-pressure window, and the oil-gas miscible state is determined by the change in appearance of the bubbles as they move at different pressures. However, the method relies on human observations and is subjective (Elsharkaw 1996; Dong 2001). The vanishing interfacial tension method was used to determine the interfacial tension between the injected gas and oil at constant temperature and pressure, and the pressure at which the interfacial tension is zero is obtained by extrapolation, i.e. the MMP (Rao 1997; Rao and Lee 2002; 2003). Ayirala and Rao demonstrated that the MMP determined using the vanishing interfacial tension method was similar to that was determined by the fine tube experiment and the bubble lifter method. The experiment results clearly supported that the use of vanishing interfacial tension for the rapid and economical determination of MMP (Ayirala and Rao 2011).

Due to the complex composition of crude oil, there are too many influencing factors if the properties of the system composed of CO₂ and crude oil are studied directly in the CO₂ flooding process. Therefore, researchers generally take the major components of oil to represent crude oil, such as n-alkanes, cycloalkanes aromatic hydrocarbons, etc. Shaver et al. (2001) experimentally measured the phase fraction, phase density and interfacial tension of CO₂ and n-decane in the pressure range of 1~13MPa at 344 K. Hsu et al.(1985) measured the oil composition, oil density, and interfacial tension of CO₂ and n-butane system at the temperature of 319K~378K until the pressure achieved the MMP. Spee and Schneider (1991) measured the change of oil composition with pressure in a CO₂/dodecane system and CO₂/1,8-octanediol system at 393 K and 10~100 MPa.

In recent years, molecular simulations have been widely applied to study the CO₂ and crude oil systems. Makimura et al. (2012) investigated two characteristics of CO₂-EOR based on molecular simulations, including interfacial properties and phase equilibrium. Neyt et al. (2011) used Gibbs Ensemble Monte Carlo and two-phase Monte Carlo to calculate the interfacial tension between CO₂ and water, the interfacial tension between CO₂ and n-butane system. The calculated results were in good agreement with the experiment results. Müller et al .(2009) used molecular dynamics to calculate the oil composition, oil density, interfacial tension and interfacial structure of n-hexane and n-decane system, CO₂ and n-decane system, and ethane and n-eicosane system. The simulation results agreed well with the experiments. De

Lara et al. (2012) used molecular dynamics to investigate the interfacial properties of brine/light oil, CO₂/light oil, N₂/light oil and CH₄/light oil systems. They showed that the CO₂/light oil system had the advantage of lower interfacial tension and enhancing diffusion of CO₂ in the oil phase. The diffusion coefficients of n-alkanes from methane to tetradecane in CO₂ at infinite dilution were calculated by Feng et al. (2013). The results obtained from the simulations were reliable.

Compared to experimental methods, molecular simulations can be used to calculate the interfacial tension between CO₂ and crude oil, to reveal the interfacial properties of CO₂ and oil, and to observe microscopic mixing processes. These are difficult or impossible to be observed and measured using experimental methods. In addition, molecular dynamics simulations can be used to predict the interfacial properties of CO₂ and oil with low cost and fast calculation time.

In this study, the molecular dynamics simulation method was proposed to study the miscibility characteristics of injected CO₂ and oil in a block of Yanchang Oilfield. The paper is structured as follows: Section 2 describes the proposed methodology in details, including force field and MMP calculation methods; Section 3 describes the model used for the molecular simulations; Section 4 presents the main results of the study.

Methodology

Force Field. The potential energy function describing the forces interacting between atoms in a system is called the force field. Constructing an accurate potential energy function for a system is an important step in molecular dynamics calculations. In general, molecular force fields mainly include bond stretching potential energy, bond angle bending potential energy, dihedral angle distortion potential energy, and non-bonding potential energy. Non-bonding potential energy includes van der Waals potential energy and Coulomb electrostatic potential energy.

Force fields have been developed for each system and are basically suitable for molecular dynamics simulation studies in various fields. Different force fields include different atom types, so before selecting a force field one should first check the list of atom types for the force field and whether the force field covers the atom types in the simulated system.

The available CO₂ molecular force fields are mainly divided into a rigid force field containing the TraPPE force field, a semi-flexible force field with the EPM2 force field and a flexible force field with the ZHU force field (Potoff and Siepmann 2001; Harris and Yung 1995; Zhu 2009). The molecular force fields of n-alkanes can be divided into two categories: joint atomic force fields and all-atomic force fields. Joint atomic force fields are those that equate CH₃ and CH₂ of n-alkanes as one atom, such as OPLS-UA, TraPPE-UA and NERD (Jorgensen 1984; Martin and Siepmann 1998; Nath 1998). All-atomic force fields are those all atoms expressed in n-alkanes explicitly, such as OPLS-AA and CHARMM (Jorgensen 1996; Price 2001; Davis 2008).

The ZHU force field was proposed by Zhu et al. (2009), which can accurately predict the saturated gas-liquid phase density, critical point properties, while taking into account the molecular structure properties of supercritical CO₂, and is therefore suitable for the simulation of systems containing supercritical CO₂. The calculated gas-liquid equilibrium curves from the NERD force field are in good agreement with experimental data for both shorter chain alkanes and longer chain alkanes (Müller 2009; Nath 1998). Therefore, the ZHU CO₂ force field and the NERD n-alkane force field were used in this study. The NERD molecular force field defines the total potential energy function of an alkane as shown in Eq. 1.

$$\begin{aligned}
V_{\text{total}} = & \sum_{\text{bonds}} \frac{k_{ij}^b}{2} (r_{ij} - b_{ij})^2 + \sum_{\text{angles}} \frac{k_{ijk}^\theta}{2} (\theta_{ijk} - \theta_{ijk}^0)^2 \\
& + \sum_{\text{dihedrals}} V_0 + V_1(1 + \cos \psi) + V_2[1 - \cos(2\psi)] + V_3[1 + \cos(3\psi)] \\
& + \sum_{\text{nonbonded}} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}} \dots\dots\dots(1)
\end{aligned}$$

The ZHU CO₂ force field function takes the form shown in **Eq. 2**.

$$\begin{aligned}
V_{\text{total}} = & \sum_{\text{bonds}} \frac{k_{ij}^b}{2} (r_{ij} - b_{ij})^2 + \sum_{\text{angles}} \frac{k_{ijk}^\theta}{2} (\theta_{ijk} - \theta_{ijk}^0)^2 \\
& + \sum_{\text{nonbonded}} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}} \dots\dots\dots(2)
\end{aligned}$$

Van der Waals interactions between atoms describe the interactions between atoms that are caused by non-covalent and non-hydrostatic forces that attract or repel each other. The Lennard-Jones potential function is a function that describes the Van der Waals interactions between atoms and has the form shown in **Eq. 3**.

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \dots\dots\dots(3)$$

The sums between the different atoms are obtained by means of a mixing rule, the common Lorentz-Berthelot mixing rule, as shown in **Eq. 4 and 5**, respectively.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \dots\dots\dots(4)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \dots\dots\dots(5)$$

Simulation method. In this study, Lammmps molecular simulation software was used for the simulations. During the molecular dynamics (MD) simulations, periodic boundary conditions were used, the equations of motion were solved for integration using the Velocity-verlet method. The long-range force electrostatic interactions used the particle-particle-particle-mesh (PPPM) summation method with an accuracy of 1.0×10^{-4} . The non-bonded van der Waals forces used the 12-6 Lennar-Jones potential function with a truncation radius of 2 nm and a time step of 1 fs. The temperature coupling was performed using the Nosé-Hoover algorithm. The entire simulation time was 10 ns of relaxation time, 30 ns of calculation time, with data collected at 0.1 ps intervals. Finally, the IFT of the system was calculated.

There are many ways to obtain the MMP, the most common ones are to calculate the number of CO₂ and alkanes that cross the phase interface at the same temperature and different pressures as a percentage of the total number of CO₂ and alkanes, and to obtain the MMP when the number of ratios drops to a stable pressure. There are also methods to obtain the MMP by the disappearance of interfacial tension.

In this study, the MMP was obtained by the disappearance of interfacial tension, as the method has a clear definition of parameters. When the interfacial tension is zero, the interface between the two phases disappears, then the two phases can completely become a miscible phase. The Gibbs interfacial tension equation was used to calculate the variation of the two-phase interfacial tension with pressure, from which MMP is indirectly calculated. The specific expression is given as **Eq. 6**.

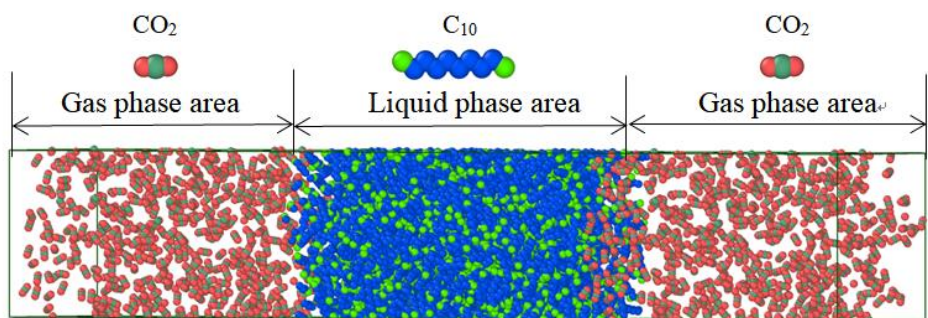
$$\gamma = \frac{1}{2} \int_0^{L_z} (P_N(z) - P_T(z)) dz = \frac{1}{2} \left[P_{zz} - \frac{(P_{xx} + P_{yy})}{2} \right] L_z \dots\dots\dots(6)$$

where γ is the interfacial tension, and $P_N(z)$ and $P_T(z)$ represents the normal and tangential pressures, $P_{\alpha\alpha}$ is the amount on the diagonal of the pressure tensor, and L_z is the length in the z-direction of the simulated system.

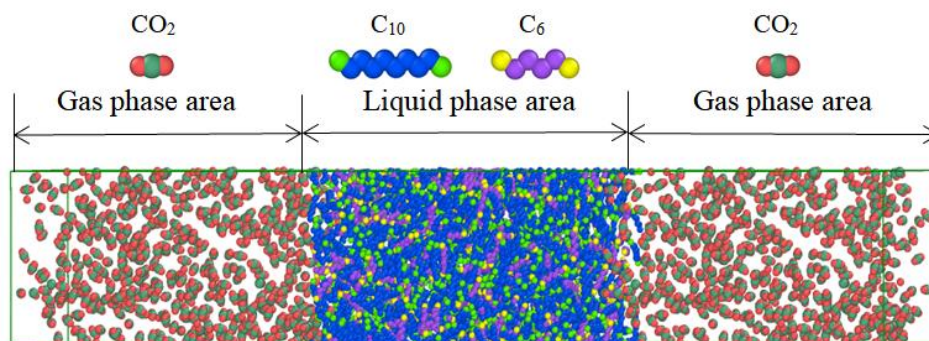
Modeling. The force field parameters for this study are shown in **Table 1**. The initial systems of two cases are given in **Figure 1**, with a oil (liquid phase) in the middle and CO₂ (gas phase) in the two side. The oil phase consists of alkanes of different chain lengths, depending on the case. For the CO₂/n-decane system, the oil contains 800 n-decane molecules. The system pressure was varied with the number of CO₂ molecules in the gas phase on both sides. The size of the simulated system was taken to be 5×5×30 nm³.

Table 1—Force field parameters.

Atom	σ (nm)	ϵ_{ij} (KJ/mol)		
CT_CH ₃	0.3910	0.8647		
CT_CH ₂	0.3930	0.3808		
C	0.2800	0.23397		
O	0.3028	0.66824		
Bond	r_0 (nm)	k_b (kJ/(mol/nm ²))		
CH ₃ _CH ₂	0.1540	80235.0280		
CH ₂ _CH ₂	0.1540	80235.0280		
C-O	0.1162	60000.0000		
Angle	θ_0 (deg)	K_θ (kJ/mol/rad ²)		
CH ₃ _CH ₂ _CH ₂	114	519.657		
CH ₂ _CH ₂ _CH ₂	114	519.657		
C-O-C	180	110.000		
Torsion	V_0 (kJ/mol)	V_1 (kJ/mol)	V_2 (kJ/mol)	V_3 (kJ/mol)
CH ₃ _CH ₂ _CH ₂ _CH ₂	0.0000	5.9038	-1.1339	13.1590
CH ₂ _CH ₂ _CH ₂ _CH ₂	0.0000	5.9038	-1.1339	13.1590



(a) Case 1



(b) Case 2

Figure 1—Initial structure of the two systems.

Results and Discussion

Interfacial Tension and MMP. The disappearance of interfacial tension method was used in the MD simulation to indirectly calculate the MMP of CO₂ with n-decane at 334K. Because Shaver (2001) experimentally measured the phase fraction, phase density and interfacial tension of CO₂ and n-decane in the pressure range of 1~13MPa at 344 K, the simulation results in this section are compared with the experimental values. As shown in **Figure 2(a)**, the calculated IFTs by this work were in very good agreement with Shaver (2001) method. The interfacial tension decreases with increasing pressure and displays a linear relationship, which indicates that the interface between CO₂ and alkane becomes increasingly blurred and gradually tends to a miscible phase. In addition, the linear relationship enables a reliable extrapolation to obtain the pressure when the interfacial tension is zero. Thus, the MMP was determined to be 11.89 MPa when IFT equal 0. The estimated MMP is very close to that measured MMP (12.74 MPa) by Shaver et al (2001).

As can be seen from **Figure 2(b)**, the relationship between interfacial tensions and pressure obtained by Müller and Mejía (2009) using the EPM2 CO₂ model and the NERD n-decane model were in good agreement with the experiments. Mejia et al. (2014) used coarse-grained molecular model to simulate CO₂/n-decane system. But the estimated interfacial tensions were slightly higher than the measured values. The estimated IFTs by this work agreed well with the measured values. Therefore, ZHU CO₂ model and the NERD n-alkane model used in this paper are an effective, convenient and low-cost method for predicting the MMP for CO₂ and alkane systems compared to coarse-grained simulations.

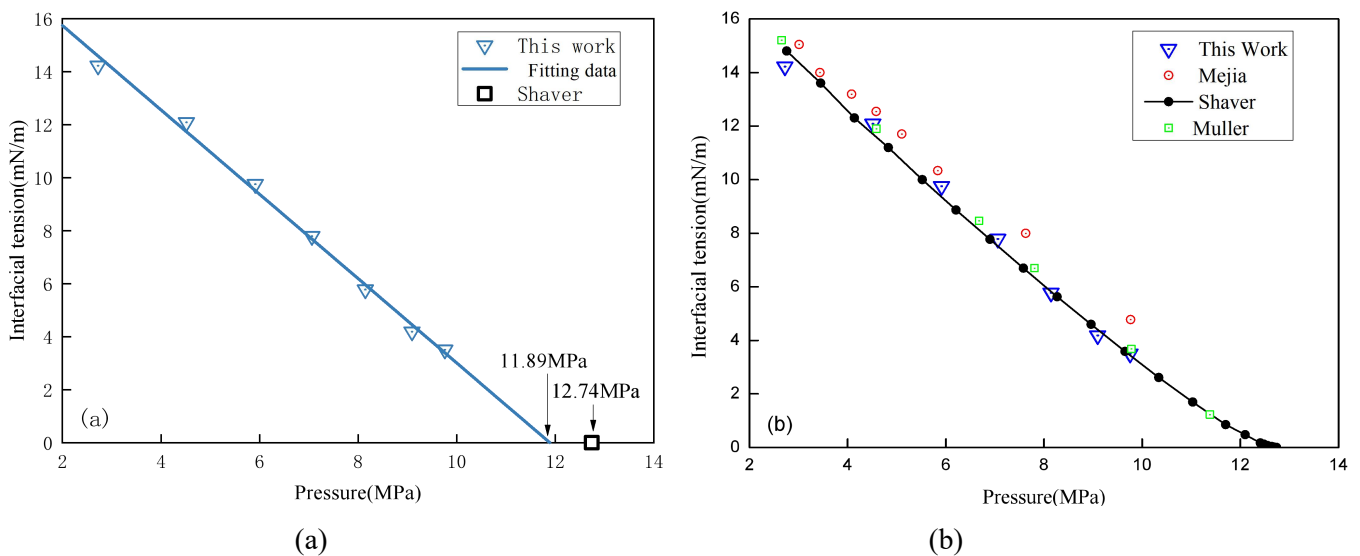


Figure 2—Interfacial tension between carbon dioxide and n-decane with pressure.

To validate the effectiveness of the proposed method in estimating MMP, the proposed method was compared to the empirical formulas. The comparison results are shown in **Table 2**. The National Petroleum Council (NPC) empirical equation estimates MMP roughly, mainly by using API and temperature as parameters, and obtains results with large errors. Yellig and Metcalfe (1980) proposed a method to predict MMP according to the temperature, which is one of the most common methods. The temperature is the only parameter in the formula:

$$MMP=1833.7217+2.2518055(T-460)+0.01800674(T-460)^2 - \frac{103949.93}{T-460} \dots\dots\dots(7)$$

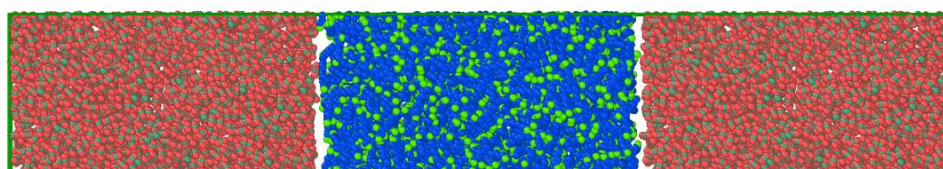
As can be seen from Table 2, the results of the NPC empirical formula approach are poor. The molecular simulation used in this study has a higher prediction accuracy than the Yellig-Metcalfe model.

It indicates that the empirical formula has certain limitations, such as the composition of different oil fields, the composition of the injected gas, and the range of working conditions. Thus, the results obtained by the empirical formulas are difficult to be generalized. In contrast, the working conditions of the molecular simulation method proposed in this study is easy to set, and the calculated values agree well with the experimental values, so it has a wider applications.

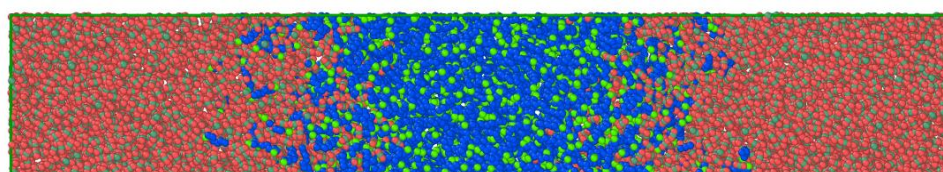
Table 2—Comparisons between the proposed method and the empirical formulas.

MMP from experiment (MPa)	NPC		Yellig-Metcalf (1980)		This study	
	MMP (MPa)	Error (%)	MMP (MPa)	Error (%)	MMP (MPa)	Error (%)
12.74	10.69	2.05	13.78	1.04	11.89	0.85

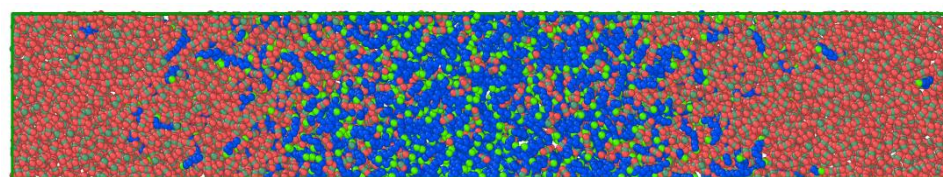
Phase Interface Properties. The phase interface properties of CO₂ and n-decane systems, such as interfacial structure and interfacial thickness, are difficult or impossible to be measured by experiments. However, molecular dynamics has the advantage of being intuitive and convenient for this purpose. In this section, the mixing process, interfacial structure and interfacial thickness of the CO₂ and n-decane system at 344 K were investigated. The dynamic mixing process of the CO₂/n-decane system at 344 K are shown in **Figure 3**. A small amount of decane molecules were extracted by CO₂ and moved towards the CO₂ phase, and the phase interface gradually disappeared; a large number of CO₂ molecules formed clusters around the decane molecules, and the two gradually miscible, and finally the phase interface disappeared and reached the mixed-phase state after 40ns.



(a) 0ns



(b) 5ns



(c) 15ns

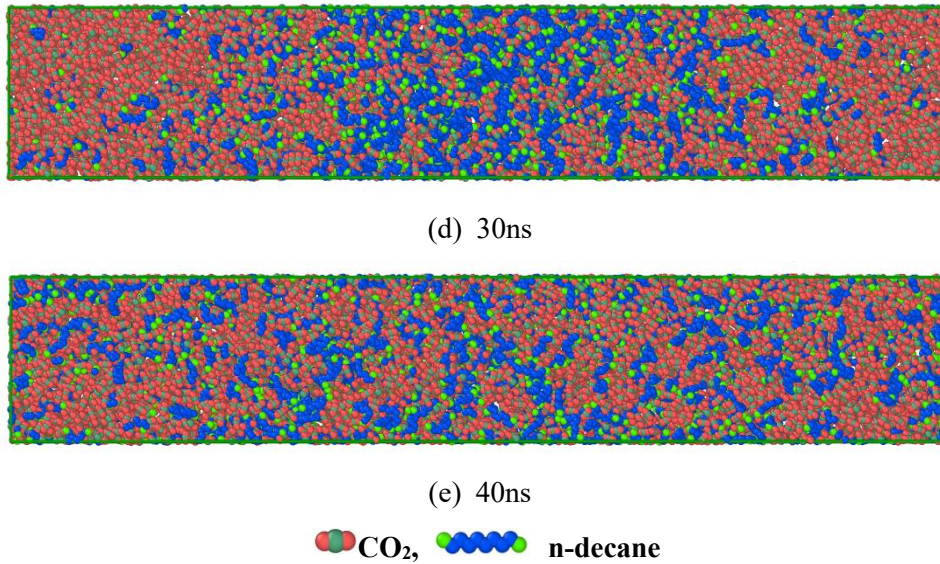


Figure 3—CO₂/n-decane mixed-phase microscopic processes.

The variation of the gas-liquid phase density with pressure for the CO₂ and n-decane system at 344 K is shown in **Figure 4**. As the pressure of the system increases, the system in the liquid phase area gradually expands, the gas-liquid phase density also increases and the phase interface gradually becomes thicker.

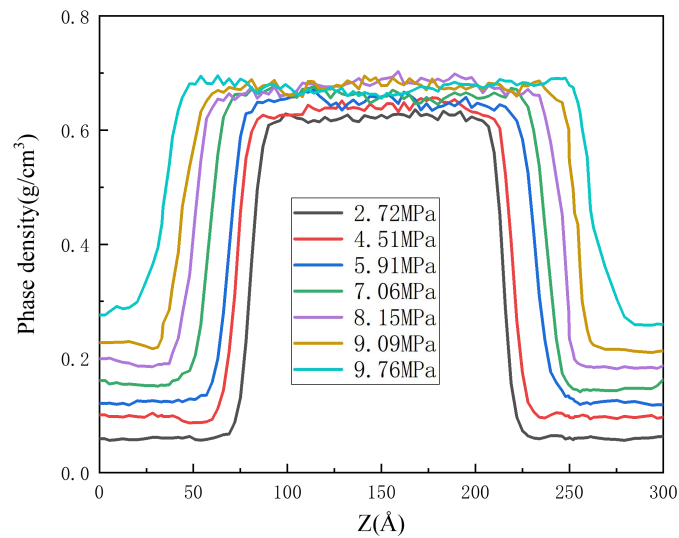


Figure 4—Variation of gas-liquid phase density with pressure of CO₂/n-decane system.

The density distribution of CO₂ and n-decane in the system at different pressures is shown in **Figure 5**. As the pressure of the system increases, the density of n-decane decreases and the density of CO₂ increases. Part of the CO₂ in the system gathered at the interface to form a CO₂ adsorption layer, and the adsorption layer gradually became thicker as the pressure increased, which surface more and more CO₂ gathered at the interface as the pressure increased.

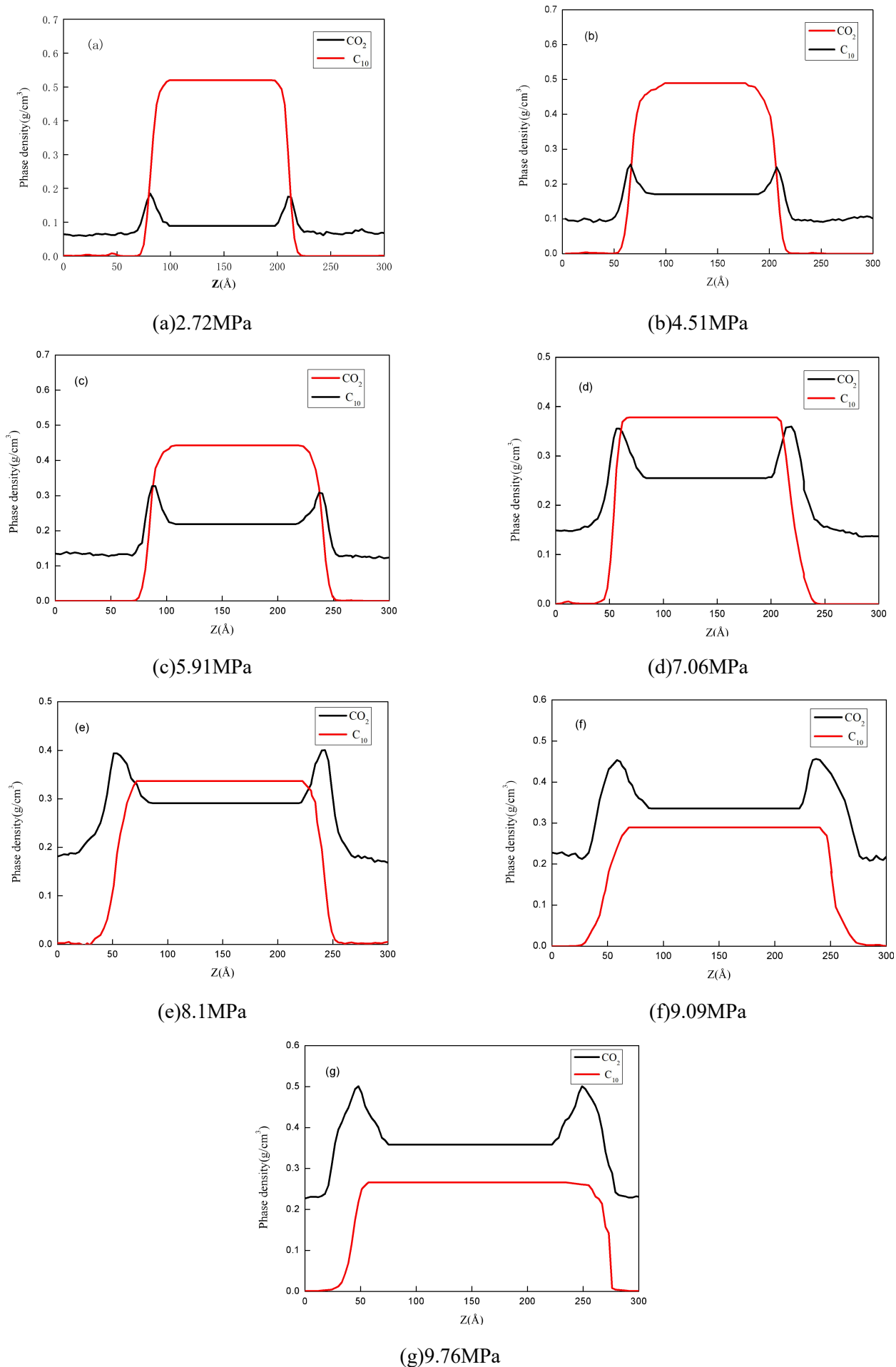


Figure 5—Density distribution of components of CO₂/n-decane system at different pressures.

Base on the above analytical simulations, a mixture of n-decane and n-hexane was used to replace the oil from the Yanchang field and the MMP was determined. The results are shown in **Figure 6**, which shows an MMP of 11.4 MPa at 344 K. And the effect of the oil components on the MMP can also be illustrated with Figure 6, which shows that the addition of n-hexane has a significant effect on the MMP of n-decane and CO₂. The addition of n-hexane makes the MMP decrease, because the light hydrocarbon components can be extracted from oil phase by CO₂, when CO₂ contacts with the oil, while the light components originally were dissolved in the oil. As a result, it makes CO₂ become hydrocarbon rich. The enriched CO₂ then contacts with the oil to further extract the light components. The process repeats until CO₂ extracts enough alkanes. In contrast, when n-hexane is dissolved in the oil to contain more light components, so CO₂ can be more easier to extract enough light hydrocarbons to accelerate enrichment and make CO₂ be more easy miscible with the oil.

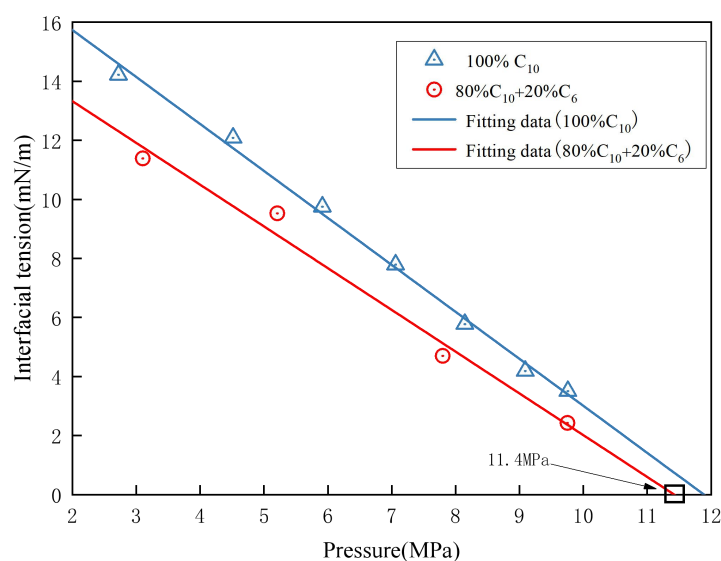


Figure 6—Effect of oil composition on MMPs.

The Effects of Temperature on MMP. It has been proven by numerous experiments that reservoir temperature has a significant effect on MMP and it is an important variable affecting MMP (Zolghadr 2013). The variation of MMP with temperature for the CO₂/n-decane system is shown in **Figure 7**. At a low pressure, IFT decreases with increasing temperature. But at a high pressure, IFT increases with increasing temperature and MMP increases with increasing temperature. This is because the density of CO₂ is controlled by temperature and pressure.

As can be seen in **Figure 8**, at a constant pressure, the density of CO₂ decreases with increasing temperature, leading to a decrease in the solubility of CO₂ and in the extraction ability of light hydrocarbons. Thus, to give CO₂ sufficient solubility to achieve a mixed phase, it is necessary to increase the density of CO₂ by increasing pressure, so the MMP increases with increasing temperature.

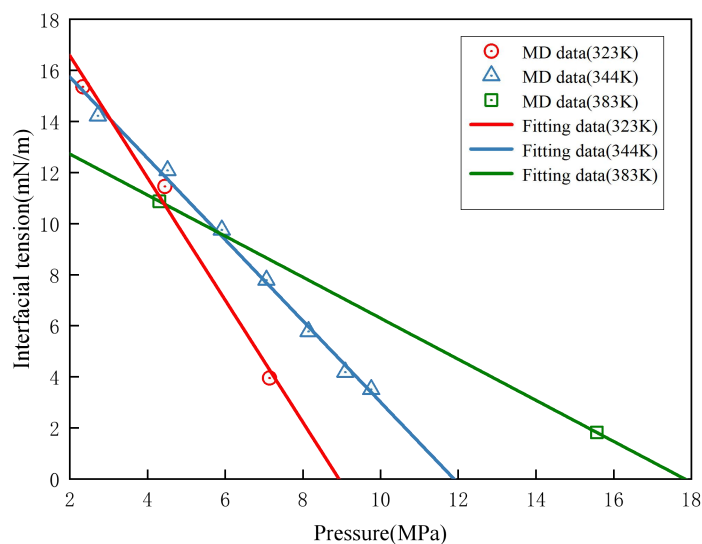


Figure 7—Effect of temperature on MMPs.

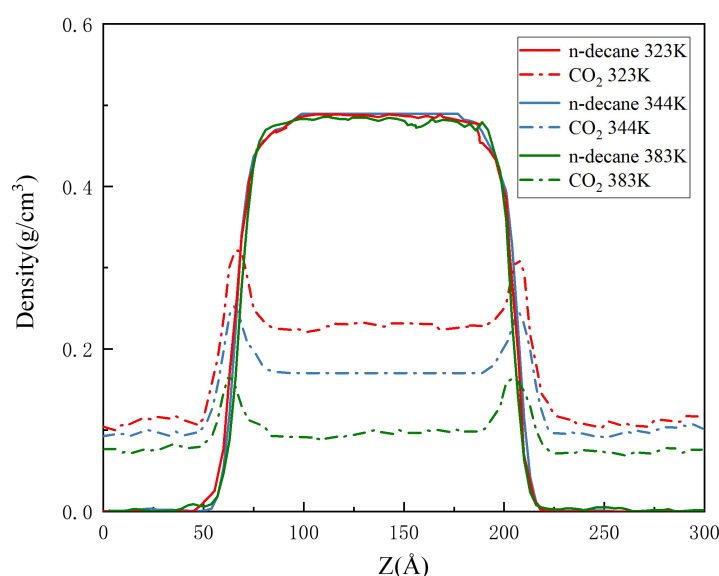


Figure 8—The density distribution of CO₂/n-decane at 4.5 MPa.

Conclusions

In this paper, we simulated the phase density and interfacial tension of the CO₂ and n-decane system at 334 K under different pressures using molecular dynamics methods, analyzed the interfacial characteristics of the system, and investigated the effect of the addition of hexane on the minimum miscibility pressure of the CO₂ and n-decane system, and the main conclusions are as follows.

1. The MMP of CO₂ with n-decane at 334 K was predicted to be 11.89 MPa using the molecular simulation method, which has the advantage of being less costly and more efficient than the experimental methods, and the prediction is more realistic and reliable than the theoretical equations.
2. The proposed molecular dynamics simulation displayed the mixing process of CO₂/n-decane system. In the process, CO₂ is dissolved into n-decane, while n-decane is continuously extracted by CO₂. The interface between CO₂ and n-decane gradually disappears and the interfacial tension gradually decreases, and finally reaches the miscible state.

- As the pressure of the system increases, the thickness of the phase interface between CO₂ and n-decane increases, and the CO₂ adsorption layer on the interface also gradually becomes thicker, and the density of n-decane decreases with the increase of pressure, while the density of CO₂ is the opposite.
- When a certain amount of hexane is dissolved to the system of CO₂ and n-decane, the MMP of the system decreases. At a low pressure, the IFT decreases with increasing temperature; while at a high pressure, both the IFT and MMP increases with increasing temperature.

Conflicts of Interest

The author(s) declare that they have no conflicting interests.

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Bochao Qu, is a master candidate in Petroleum Engineering department at Xi'an Shiyou University. He has focused his research in areas involving reservoir simulation, well testing, and production analysis. Tian holds a BS degree in Petroleum Engineering from Xi'an Shiyou University.

Xinle Ma, is a master candidate in Petroleum Engineering department at Xi'an Shiyou University. He has focused his research in areas involving reservoir simulation, well testing, and production analysis. Tian holds a BS degree in Petroleum Engineering from Xi'an Shiyou University.

Zhenzhen Dong is a Professor in the Petroleum Engineering Department at Xi'an Shiyou University. She worked as a reservoir engineer with Schlumberger from 2012 to 2016. Her research interests include unconventional resources/reserves estimates, reservoir simulation, well testing, and production analysis.

Dong holds a bachelor's degree in mathematics from Northeast Petroleum University, China; a master's degree in petroleum engineering from Research Institute of Petroleum Exploration and Development, China; and a PhD degree in petroleum engineering from Texas A&M University.