The miscible behaviors and mechanism of crude oil and mixing gas of CO_2/N_2 (CO_2/H_2S): a molecular dynamic simulation study

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Abstract. Considering the low cost and no corrosion of N_2 and the inevitability of H_2S generation, CO_2/N_2 or CO_2/H_2S injection is seen as a promising approach for enhanced oil recovery. The miscible behaviors of gas mixture and crude oil are studied by molecular dynamic simulations. The results indicate that H_2S shows better miscibility with C_7H_{16} than CO_2 and N_2, which is a method for rational utilization of H_2S produced in the reservoirs. In addition, there exists an optimal proportion of gas mixture for high miscibility. Specially, the gas mixture consisting of 50% H_2S and 50% CO_2 has great miscibility with polar crude oil. These findings show that CO_2/N_2 injection could be applied for the reservoirs with high apolar crude oil while CO_2/H_2S could be appropriate for the reservoirs with both polar and apolar crude oil. These findings could provide guidance for enhanced oil recovery in the development of deep and ultra-deep reservoirs and gas sequestration.

Keywords: Miscibility, Gas mixture, Molecular Dynamics Simulation.

1 Introduction

CO_2 flooding could significantly increase oil recovery in the carbonate reservoirs[1], but there are some drawbacks, such as carbonate precipitation, wellbore and ground oil pipeline corrosion and CO_2 shortage. Combining the advantages of two gases, CO_2/N_2 and CO_2/H_2S mixtures have been applied in some reservoirs to improve oil recovery. N_2, a kind of sufficient source, has higher compression coefficient and expansion coefficient than CO_2. In addition, N_2 has the characteristics of no corrosion and maintenance of formation energy[2]. Considering the high minimum miscibility pressure (MMP) of N_2 and crude oil, the solubility of N_2 in crude oil is low. CO_2/N_2 mixture could better dissolve in crude oil than N_2.

Recently, CO_2/H_2S injection has also attracted attention. H_2S produced in the reservoirs is inevitable[3]. The injection of acid gases (CO_2 + H_2S) into the reservoir could reduce atmospheric emissions. Additionally, H_2S has been demonstrated to enhance oil

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recovery in muscovite and MgO nanopores[4]. However, there are few studies about CO_2/H_2S injection for EOR in calcite nanoslits.

This work intends to explore the best proportion of CO_2/N_2 and CO_2/H_2S for EOR, which is finished by Molecular dynamics (MD) method. Because it is difficult and costly to carry out experiments at the molecular scale under high temperatures and pressures. MD simulation is an effective method for investigating fluid flow in nanoslits[5]. The miscible mechanism and behavior of different gas and crude oil in calcite nanopores are investigated at 90 MPa and 453 K. Firstly, the miscible mechanisms between C_7H_{16} and pure gas (CO_2, N_2 and H_2S) are explored. Then, the influence of N_2/H_2S proportion on the miscibility between gas and crude oil is investigated. Finally, the impact of crude oil polarity on the miscibility of gas mixture and crude oil is discussed.

2 Models and methods

In this paper, all MD simulations were conducted in Materials Studio software. The simulation process was performed under NVT (constant volume and temperature) ensemble. The MD simulation time was 4 ns with a fixed time step of 1fs.

The MD system with a pore width of 7 nm is illustrated in Fig. 1. The proportion of N_2 and H_2S in the mixture was 0%, 30%, 50%, 70% and 100%, respectively. The calcite surface was cleaved along the (104) crystal plane with sizes of 140 × 30 × 15 Å^3. The part of calcite surface and He nanosheets were fixed.

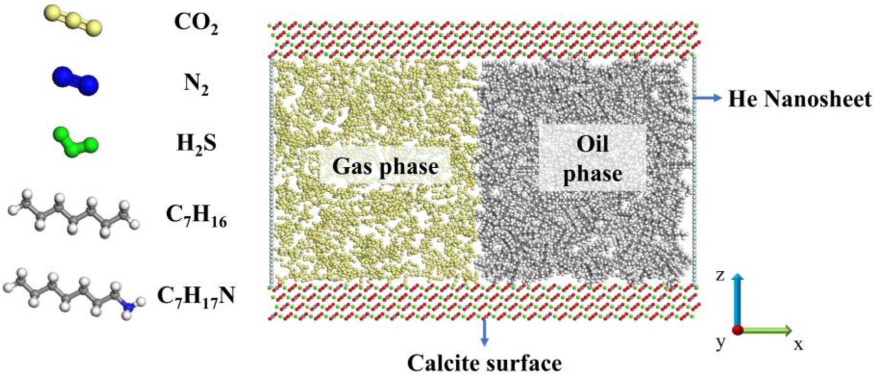

Fig. 1. The molecule models and miscible system.

3 Results and discussions

3.1 The miscibility of crude oil and pure gas

Fig. 2 presents the equilibrium configurations of crude oil and pure gas. CO_2 and H_2S adsorb on the rock surface and C_7H_{16} could dissolve into the bulk phase while C_7H_{16} adsorb on the calcite surface for N_2/C_7H_{16} system. Additionally, C_7H_{16} molecules tend to gather for N_2/C_7H_{16}. To describe the miscible ability, the miscibility (M) of gas and crude oil is calculated by equation (1).

$$M = \frac{N_1}{N_2} \tag{1}$$

where N_1 represents the number of oil molecules unabsorbed on the rock, N_2 represents the number of oil molecules dissolved in the initial range of gas phase. Fig. 3a illustrates that the M values of C_7H_{16} in different gas phases follow the order of H_2S flooding (0.480) > CO_2 flooding (0.422) > N_2 flooding (0.384). It could be concluded that H_2S shows better miscibility with C_7H_{16}.

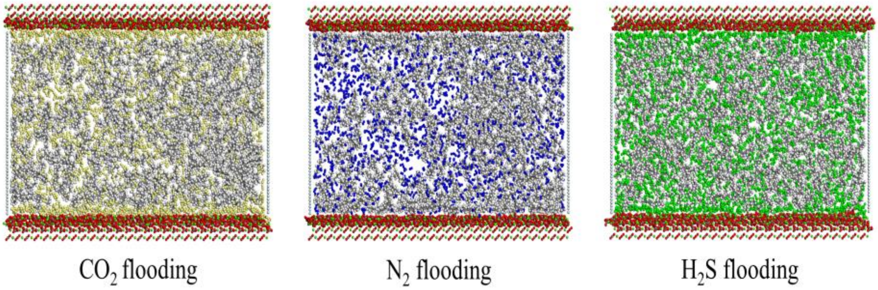

Fig. 2. The equilibrium configurations of C_7H_{16} and pure gas. (Yellow: CO_2; Bule: N_2; Green: H_2S).

To confirm the above analysis, the interaction energy between C_7H_{16} and gas and the interaction energy between gas and rock are computed by equations (2) and (3), as presented in Fig. 3b,

$$E_{C_7H_{16}/gas} = \frac{E_{C_7H_{16}+gas} - (E_{C_7H_{16}} + E_{gas})}{N_{C_7H_{16}}} \tag{2}$$

$$E_{gas/rock} = \frac{E_{gas+rock} - (E_{gas} + E_{rock})}{N_{gas}} \tag{3}$$

where $E_{C_7H_{16}/gas}$ is the interaction energy between C_7H_{16} and gas, $E_{C_7H_{16}+gas}$ is the total energy of C_7H_{16} and gas, $E_{gas/rock}$ is the interaction energy between gas and rock, $E_{gas+rock}$ is the total energy of gas and rock, $E_{C_7H_{16}}$, E_{gas} and E_{rock} are the energy of C_7H_{16}, gas and rock, respectively, $N_{C_7H_{16}}$ and N_{gas} represent the number of C_7H_{16} and gas molecules, respectively. Obviously, the order of $E_{C_7H_{16}/gas}$ is H_2S > CO_2 > N_2, which is consistent with that of M values, indicating that high miscibility between C_7H_{16} and H_2S could be caused by strong interaction energy. $E_{co_2/rock}$ is significantly higher than $E_{H_2S/rock}$, which demonstrates that the CO_2 absorption concentration on calcite surface is larger than that of H_2S, which could also well explain that $E_{C_7H_{16}/H_2S}$ is stronger than $E_{C_7H_{16}/co_2}$ (Fig.3c and 3d). Thus, it is possible to conclude that H_2S injection is appropriate for reservoirs with high apolar crude oil.

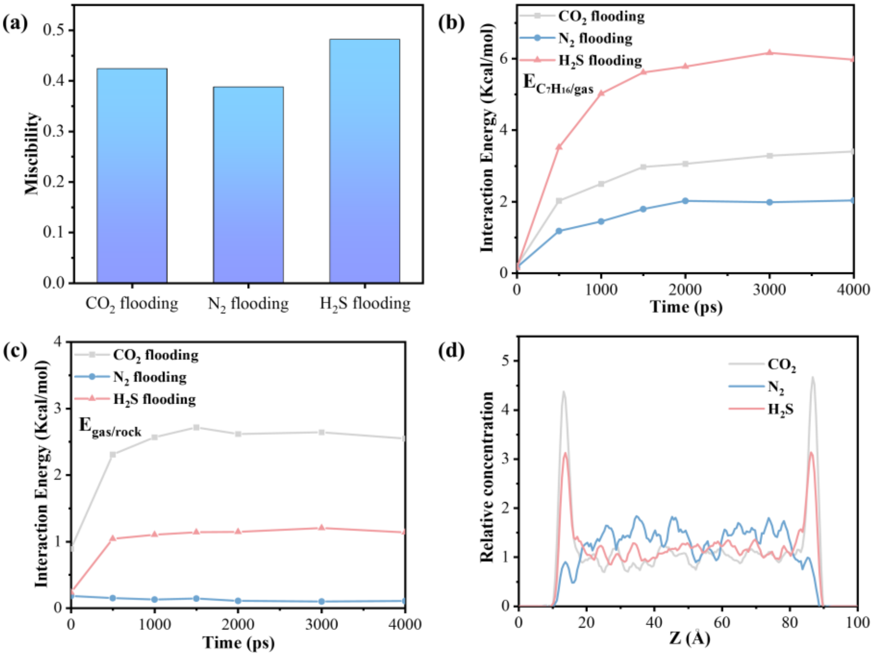

Fig. 3. (a) The M values of gas and C_7H_{16}; (b) The interaction energy between gas and C_7H_{16}; (c) The interaction energy between gas and rock; (d) The relative concentration of gas along the Z direction.

3.2 The miscibility between crude oil and gas mixture with different proportions of N_2/H_2S

Based on the above simulations, it could be assumed that N_2/H_2S combined with CO_2 is possible to improve oil-gas miscibility. The content of N_2/H_2S in the gas mixture was 0%, 30%, 50%, 70% and 100%, respectively. Fig. 4 shows the equilibrium configurations of C_7H_{16} and gas mixture. It could be found that C_7H_{16} could be evenly dissolved in the gas phase when the proportion of N_2 is low, while C_7H_{16} molecules tend to aggregate when the proportion of N_2 is high. In addition, the solubility of C_7H_{16} in the gas phase could be increased for CO_2/H_2S injection. Fig. 5a exhibits the M values of C_7H_{16} and gas mixture with different N_2 content. It could be observed that the miscibility of C_7H_{16} and "CO_2 + N_2" is greater when the proportion of N_2 is less than 50%. The gas mixture with 30% N_2 and 70% CO_2 shows the best miscibility with C_7H_{16} owing to stronger interaction energy between gas and C_7H_{16} and faster diffusion velocity of C_7H_{16} (Fig. 5b and 5c). The M values of C_7H_{16} and "CO_2 + H_2S" are illustrated in Fig. 5d. It could be discovered that gas mixture with 50% H_2S and 50% CO_2 shows the best miscibility because $E_{C_7H_{16}/rock}$ is smaller (Fig. 5e), indicating more C_7H_{16} molecules are dissolved in the gas phase rather than absorbed on the rock surface. Additionally, the diffusion coefficient of C_7H_{16} is large (Fig. 5f). The aforementioned analysis demonstrates that the gas mixture injection with optimal proportion has better miscibility with C_7H_{16} than pure gas injection.

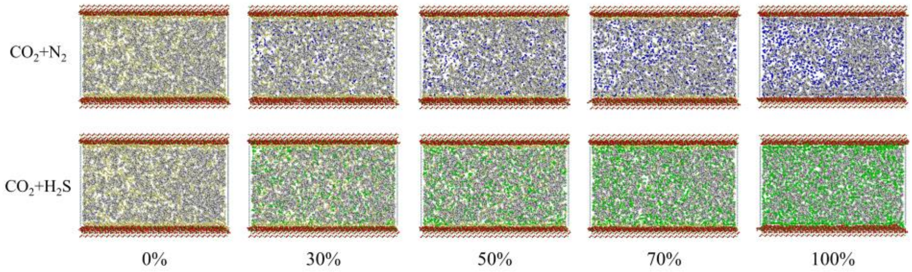

Fig. 4. The equilibrium configurations of C_7H_{16} and gas mixture with different content of N_2/H_2S.

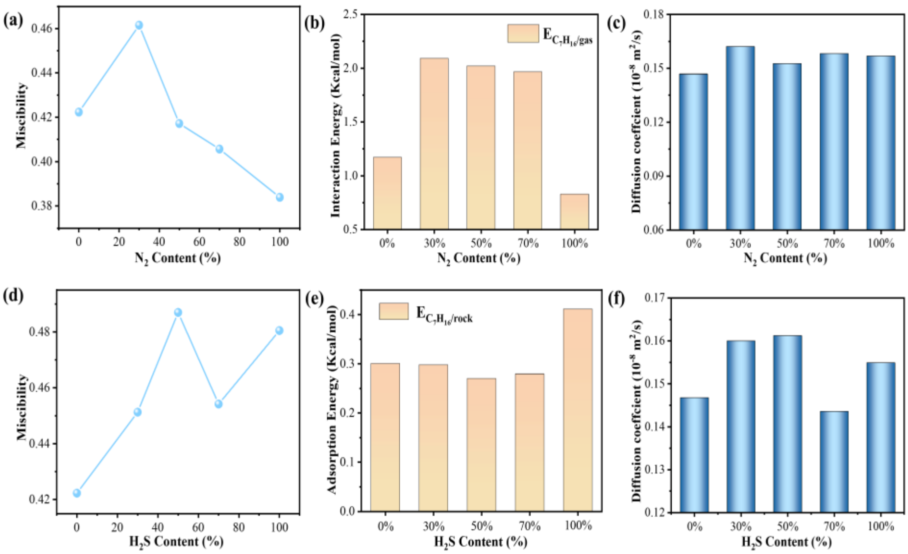

Fig. 5. The M value of C_7H_{16} and gas mixture different content of (a)N_2 and (d)H_2S; (b) The interaction energy between gas and C_7H_{16} and (c) diffusion coefficient of C_7H_{16} when gas is composed of CO_2 and N_2; (e) The interaction energy between C_7H_{16} and rock surface and (f) diffusion coefficient of C_7H_{16} when gas is composed of CO_2 and H_2S.

3.3 The impact of crude oil polarity on the miscibility between crude oil and gas

$C_7H_{17}N$ is selected to investigate the influence of crude oil polarity on the miscibility between crude oil and gas. Compared with pure CO_2, few $C_7H_{17}N$ molecules are dissolved in 30% N_2 and 70% CO_2 phase and $C_7H_{17}N$ aggregates highly, while more $C_7H_{17}N$ molecules are dissolved in 50% H_2S and 50% CO_2 phase, as shown in Fig. 6. To further analyze the impact of crude oil polarity on the miscibility between crude oil and gas, the M values are calculated in Fig. 7a. It could be seen that M values follow the order of 50% H_2S and 50% CO_2 (0.356) > pure CO_2 (0.289) > 30% N_2 and 70% CO_2 (0.262), indicating 30% N_2 and 70% CO_2 has better miscibility with polar crude oil than pure CO_2. Furthermore, we also compute the interaction energy between $C_7H_{17}N$ and gas, following the order of 50% H_2S and 50% CO_2 > pure CO_2 > 30% N_2 and 70% CO_2 (Fig. 7b), which could explain well the above phenomenon. Therefore, it comes to a conclusion that CO_2/H_2S injection could be more feasible for the reservoir containing polar crude oil compared with CO_2/N_2 injection.

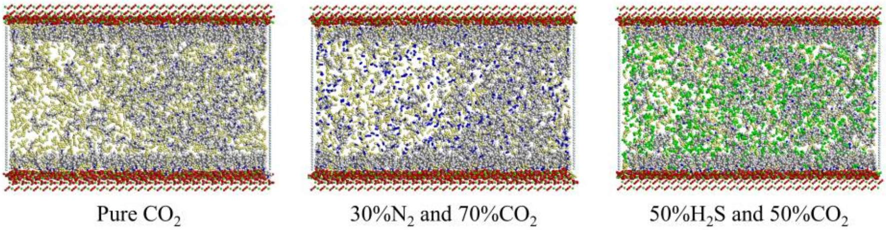

Fig. 6. The equilibrium configurations of $C_7H_{17}N$ and gas.

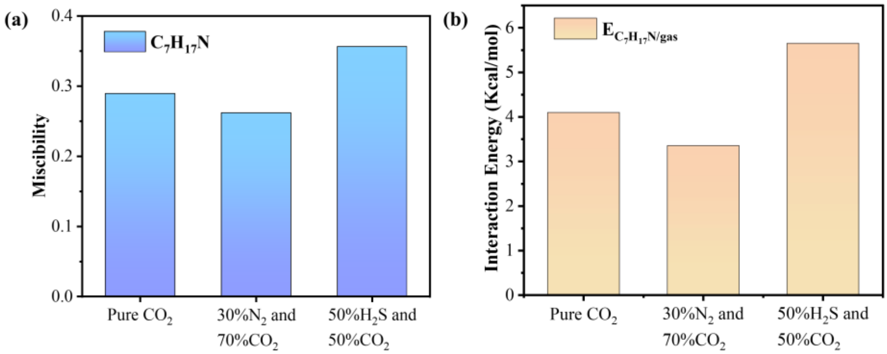

Fig. 7. (a) The M values of gas and $C_7H_{17}N$; (b) The interaction energy between $C_7H_{17}N$ and gas.

4 Conclusions

The MD simulations are adopted to explore the potential of CO_2/N_2 and CO_2/H_2S injection for improving the miscibility between crude oil and gas. These findings show that the order of miscibility with C_7H_{16} is $H_2S > CO_2 > N_2$. Additionally, the gas mixture composed of 30% N_2 and 70% CO_2 shows better miscibility with C_7H_{16} than pure CO_2, illustrating the gas mixture composed of 30% N_2 and 70% CO_2 could be more applicable in the reservoirs with high apolar oil. The miscibility between $C_7H_{16}/C_7H_{17}N$ and gas mixture consisting of 50% H_2S and 50% CO_2 is significantly higher than that of $C_7H_{16}/C_7H_{17}N$ and pure CO_2. Therefore, CO_2/H_2S injection for EOR is promising.

References

1. Wang P, Li X, Tao Z, Wang S, Fan J, Feng Q, et al. The miscible behaviors and mechanism of CO_2/CH_4/C_3H_8/N_2 and crude oil in nanoslits: A molecular dynamics simulation study. Fuel 2021;304:121461. https://doi.org/10.1016/j.fuel.2021.121461.
2. Nguyen P, Carey JW, Viswanathan HS, Porter M. Effectiveness of supercritical-CO_2 and N_2 huff-and-puff methods of enhanced oil recovery in shale fracture networks using microfluidic experiments. Applied Energy 2018; 230:160–74. https://doi.org/10.1016/j.apenergy.2018.08.098.
3. Alizadeh B, Telmadarreie A, Shadizadeh SR, Tezhe F. Investigating Geochemical Characterization of Asmari and Bangestan Reservoir Oils and the Source of H_2S in the Marun Oilfield. Petroleum Science and Technology 2012; 30:967–75. https: //doi. org/ 10. 1080/ 10916466.2010.493914.
4. Badmos SB, Bui T, Striolo A, Cole DR. Factors Governing the Enhancement of Hydrocarbon Recovery via H_2S and/or CO_2 Injection: Insights from a Molecular Dynamics Study in Dry Nanopores. J Phys Chem C 2019; 123: 23907–18. https: //doi. org/ 10. 1021/ acs. jpcc. 9b04247.
5. Sun S, Liang S, Liu Y, Liu D, Gao M, Tian Y, et al. A review on shale oil and gas characteristics and molecular dynamics simulation for the fluid behavior in shale pore. Journal of Molecular Liquids 2023; 376:121507. https://doi.org/10.1016/j.molliq.2023.121507.