

Research Article

Effect of Contact Time and Gas Component on Interfacial Tension of CO₂/Crude Oil System by Pendant Drop Method

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Pendant drop method has been used to measure the equilibrium interfacial tension and dynamic interfacial tension of CO₂/crude oil system under the simulated-formation condition, in which the temperature is 355.65 K and pressure ranges from 0 MPa to 30 MPa. The test results indicated that the equilibrium interfacial tension of CO₂/crude oil systems decreased with the increase of the systematic pressure. The dynamic interfacial tension of CO₂/original oil, CO₂/remaining oil, and CO₂/produced oil systems is large at the initial contact and decreases gradually after that, and then finally it reaches dynamic balance. In addition, the higher the pressure is, the larger the magnitude of changing of CO₂/crude oil interfacial tension with time will reduce. Moreover, by PVT phase experiment, gas-oil ratio, gas composition, and well fluid composition have been got, and different contents of light components in three oil samples under reservoir conditions have also been calculated. The relationship between equilibrium interfacial tensions and pressures of three different components of crude oil and CO₂ system was studied, and the higher C₁ is, the lower C₂-C₁₀ will be, and the equilibrium interfacial tension will get higher. Therefore, the effect of light weight fractions on interfacial tension under formation conditions was studied.

1. Introduction

The EOR technology of gas injection is theoretically better than water injection in the enhancement of oil recovery. Gas injection has developed rapidly in recent years overseas, and it has become the most important EOR method besides thermal recovery [1–3]. There are a variety of gases that can be injected, and CO₂, for its wide sources and good flooding effect, has been widely put into practical application in oil fields [4–7]. When CO₂ is in a supercritical state, at the temperature above the critical temperature of 31.26°C and the pressure higher than the critical pressure of 7.2 MPa, its property will change. The density of CO₂ is close to liquid, and the viscosity of it is close to gas at this condition; moreover, the diffusion coefficient of the CO₂ is 100 times higher than liquid. Therefore, CO₂ has a great ability to dissolve in liquid [8–15]. This is helpful in improving the overall mass transfer rate when supercritical solubility increases and the reservoir

structure is conducive to increase inner diffusion and external diffusion, in order to increase the opportunity of the contact of CO₂ with oil and make them easier to mix. Therefore, CO₂ miscible flooding can meet the requirements for injected solvent in many oil fields [16–22].

The data of gas and crude oil interfacial tension under conditions of formation has very important theoretical and practical value, and the key of miscible flooding technology is to determine the minimum miscibility pressure of injection agent and crude oil [23–27]. The phenomenon that the interfacial tension changes with pressure significantly affects the reservoir fluid transfer behavior [28–31]. Miscible flooding technology is considered as one of the most cost-effective methods of EOR [32–35].

Pendant drop has been used to measure the relationship between the equilibrium interfacial tension and the pressure of CO₂/crude oil system under the condition of the stratum temperature. Changes of interfacial tension with time

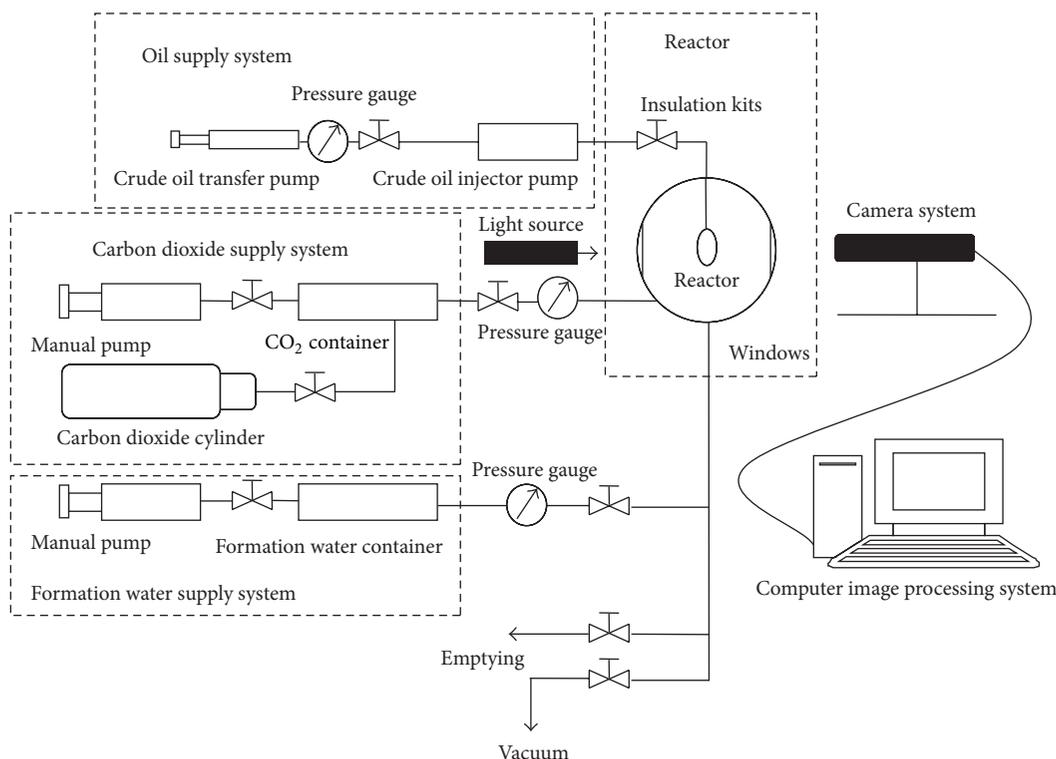


FIGURE 1: The schematic for the determination of interfacial tension by pendant drop method.

and pressure were measured by this method. By PVT phase experiment, the gas-oil ratio, gas composition, and well fluid composition have been measured. And the effect of light weight fractions on the interfacial tension under formation conditions was also calculated.

2. Experiment

2.1. Experimental Apparatus. High temperature and pressure interfacial tension meter has been used in the experiments, made by a French production company ST. The core of the device is a reactor with a window, which has an operating temperature of 0~200°C and a maximum working pressure of 70 MPa. Diameter of the needle used in the experiment is 0.81 mm, which is used for hanging droplets and using PVT analyzer for routine analysis.

Pendant drop method technology is the most accurate method to measure the interfacial tension under high temperature and high pressure conditions. First, the pump is used to form droplets on stainless steel needle department, and then the droplets shape photos are shot by amplifying camera system; after that the computer image processing systems are used to get the outer contour of the oil droplets. Ultimately calculated the interfacial tension, by using corrected image magnification, the density of light phase and heavy phase. The apparatus is shown in Figure 1.

2.2. Experimental Samples. Crude oil was provided by Zhongyuan oilfield, and formation temperature was 355.65 K. Experiment with CO₂ gas was produced by Beijing Hua

Yuan Co. with a purity of 99.995% and petroleum ether was produced by Sinopharm Chemical Reagent Company.

3. Experimental Phenomena and Results Analysis

3.1. CO₂/Oil Equilibrium Interfacial Tension

3.1.1. Experimental Phenomena

(1) *The Dissolution and Extraction Effect.* The experimental temperature is 82.5°C, and the pressure ranged from 0 MPa to 30 MPa. During the experiment, there is a medium exchange as the oil drop from the tip of the needle interacts with the CO₂ from the reactor on the condition that the experiment pressure is higher than the bubble point pressure [16–18]. CO₂ has been dissolved into the oil droplets constantly, and the light group of oil droplets also spread to CO₂ [19–22]. At the beginning of the contact of oil and CO₂, the reaction is much stronger, and the light component of crude oil has been dissolved by supercritical CO₂ constantly [23–25], as shown in Figure 2. After some dissolution and extraction, the heavy component of crude oil will be left behind, and the crude oil and CO₂ will eventually reach equilibrium state as shown in Figure 3. The interfacial tension of this time can be seen as the equilibrium interfacial tension.

(2) *The Effect of Pressure on the Dissolution and Extraction.* It can be seen from the picture that, with the increase of the pressure, the extraction of crude oil increases, and the



FIGURE 2: The initial phase.



FIGURE 3: The equilibrium phase.

interface between CO_2 and crude oil becomes unstable. A small amount of light components can be extracted out at the pressure of 16 MPa, but the extraction effect becomes more significant when the pressure reaches 30 MPa, as shown in Figure 4, taken at the initial state. At this time, the oil droplets gravity is equal to the CO_2 /oil interfacial tension, so that the oil droplets could suspend on the needle without dripping.

3.1.2. The Experimental Curve. The relationship between interfacial tension and pressure is shown in Figure 5. The equilibrium interfacial tension between crude oil and CO_2 decreases with the increase of pressure. The minimum miscibility pressure of the system calculated by extrapolation method is 18.97 MPa. When the pressure is lower than 18.97 MPa, the interfacial tension decreased rapidly; but while the pressure reaches 18.97 MPa, the reduction of interfacial tension will get slower.

3.2. The Dynamic Interfacial Tension between Crude Oil and CO_2 . The experiment showed that the interaction between CO_2 and crude oil is strong at the early stage, but with the extraction of light weight fractions of crude oil by CO_2 and the dissolution of CO_2 into the oil, the interfacial tension between them changes. In order to study the effect of this process on the interfacial tension, the contact time's effect on the interfacial tension between crude oil and CO_2 should also be tested.

TABLE 1: The equilibrium interfacial tension of three CO_2 /crude oil systems.

Oil sample	Equilibrium interfacial tension/MPa
Original oil	18.9744
Remaining oil	19.4748
Produced oil	20.5144

Figures 6, 7, and 8 show how the three oil samples' interfacial tension changes with time. The oil samples include original oil, remaining oil, and produced oil. It can be seen from the figure that the interfacial tension of CO_2 and oil is large at the initial contact; but as the contact time is getting longer, the interfacial tension decreases gradually and eventually reaches dynamic balance.

Figures 9 and 10 compared the curves of CO_2 /crude oil interfacial tension change with time in two different pressures. It can be seen from the figure that the higher the pressure is, the larger the magnitude of CO_2 /crude oil interfacial tension changing with time will reduce. The value of equilibrium interfacial tension under 12 MPa is more than 90% of the initial interfacial tension, but it turns to 80% at the pressure of 21 MPa. Obviously, the interaction between CO_2 and oil is stronger, and the change of interfacial tension is bigger at a higher pressure. This phenomenon is due to the fact that more lightweight components are extracted out and the dynamic mass transfer is getting active at high pressure. The actual reservoir CO_2 flooding belongs to multicontact miscible flooding, it's a process that after the contact of CO_2 and oil, and many times extraction and dissolution, the oil and CO_2 eventually get miscible. This leads to the interfacial tension between crude oil and CO_2 which becomes an inevitable result of dynamic change.

3.3. Effects of Gas Composition on CO_2 /Oil Interfacial Tension. Using PVT phase experiment, gas-oil ratio, gas composition, and well fluid composition have been got as shown in Figures 11, 12, and 13. And calculate different contents of light weight fractions in the three oil samples under reservoir condition. Contents of C_1 , C_2-C_{10} , and C_{11+} of three oil samples are shown in Figure 14.

As can be seen from Figure 13, the higher the C_1 is, the lower its corresponding C_2-C_{10} will be, and the C_{11+} content of the three oil samples is relatively at a low level.

Using extrapolation method, calculate the equilibrium interfacial tension of CO_2 /original oil system, CO_2 /remaining oil system, and CO_2 /produced oil system. The equilibrium interfacial tension of three different systems is shown in Table 1.

It can be seen from Figure 13 and Table 1 that the content of C_1-C_{10} component is continually increasing. The higher C_1 is, the lower C_2-C_{10} will be, and the equilibrium interfacial tension is getting higher. On the contrary, the lower C_1 is, the higher C_2-C_{10} will be, and the equilibrium interfacial tension becomes lower. In other words, C_1 is negative for CO_2 and oil miscibility, and C_2-C_{10} promotes the miscibility of CO_2 and oil system. Therefore, factors that affect the CO_2 and crude oil system interfacial tension are pressure, gas composition,

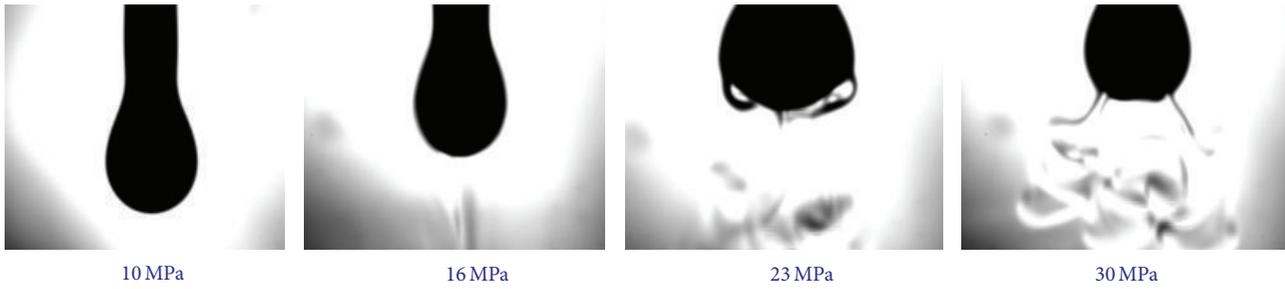


FIGURE 4: Images of the pendant oil drop in CO₂/crude oil system under different pressure.

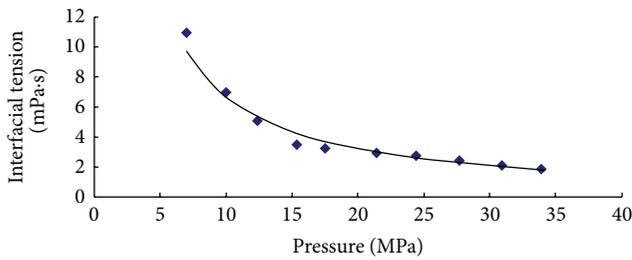


FIGURE 5: Interfacial tension of CO₂/crude oil system under different pressure.

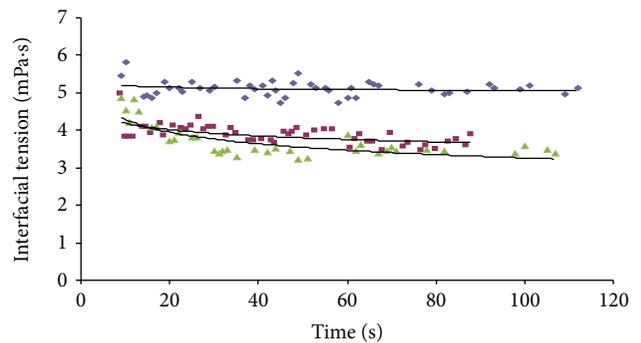


FIGURE 7: The relationship between interfacial tension and time of CO₂/remaining oil system.

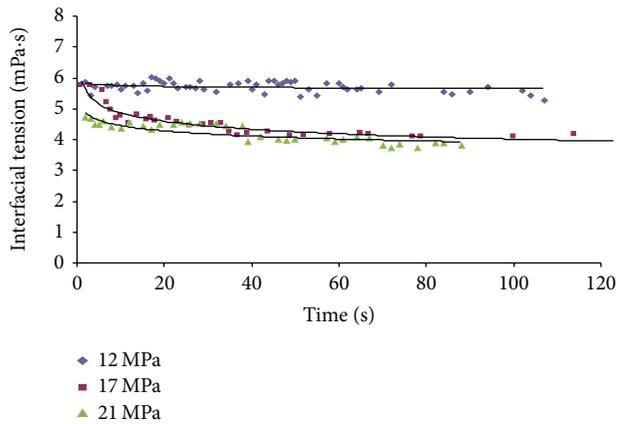


FIGURE 6: The relationship between interfacial tension and time of CO₂/original oil system.

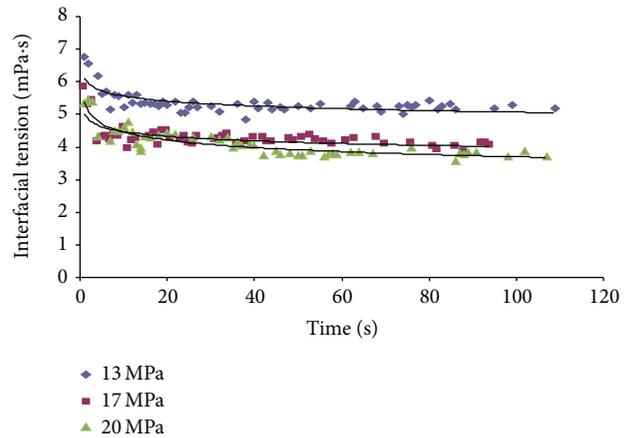


FIGURE 8: The relationship between interfacial tension and time of CO₂/produced oil system.

and time. In hydrocarbons and CO₂ compound flooding process, the selection of C₂-C₁₀ and CO₂ as a composite system will achieve better results in flooding.

Recent studies mostly focused on the research and application of equilibrium interfacial tension, and the study of dynamic interfacial tension is rare. But the actual reservoir CO₂ flooding belongs to multicontact miscible flooding, and this leads to the interfacial tension between crude oil and CO₂ becoming an inevitable result of dynamic change. So the dynamic interfacial tension can better simulate the situation under reservoir conditions and is more valuable. Historical studies do not mention hydrocarbons and CO₂ compound flooding, but the data from the experimental measurements are conducive to the development of hydrocarbons and

CO₂ compound flooding technology. The findings not only provide experimental evidence for indoor hydrocarbons and CO₂ compound flooding but also make it not just stick to a single CO₂ flooding. The experimental results provide a broad prospect for CO₂ flooding and opened up new areas for hydrocarbons and CO₂ compound flooding technology.

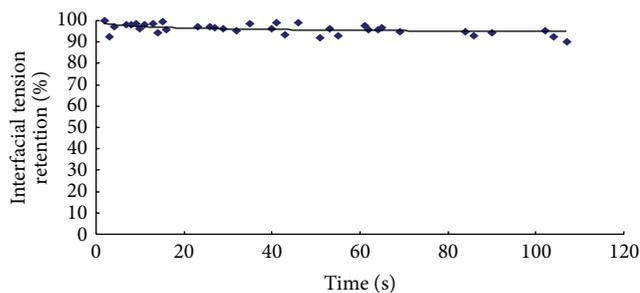


FIGURE 9: The curve of CO₂/crude oil system interfacial tension change with time under 12 MPa.

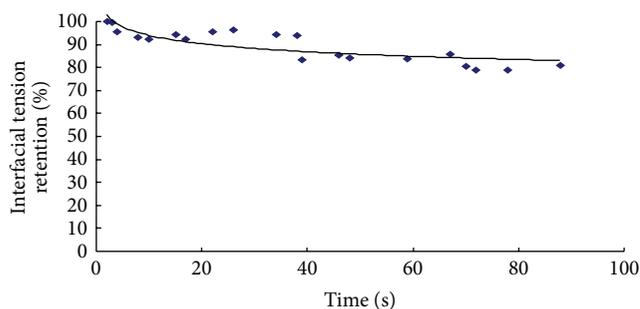


FIGURE 10: The curve of CO₂/crude oil system interfacial tension change with time under 21 MPa.

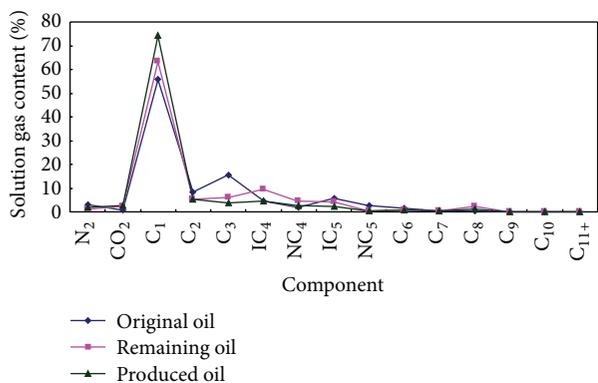


FIGURE 11: Gas phase composition of crude oil.

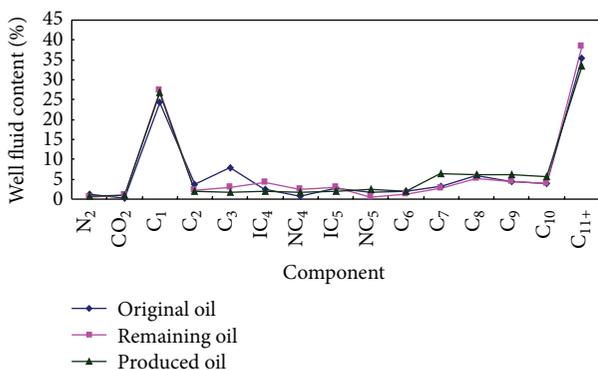


FIGURE 12: Well fluid composition of crude oil.

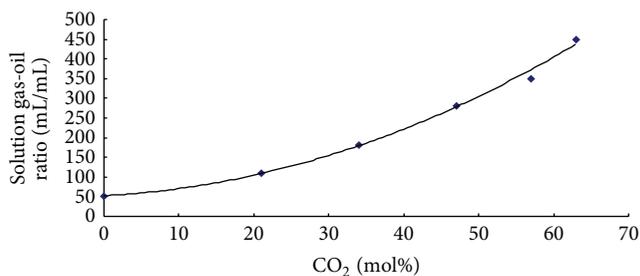


FIGURE 13: Gas-oil ratio of crude oil.

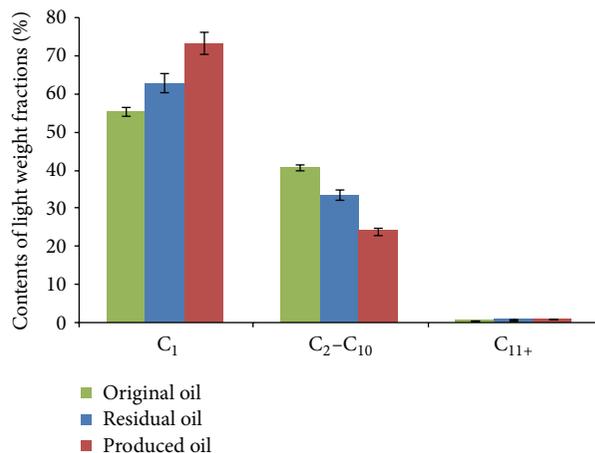


FIGURE 14: Content of different light weight fractions of original oil, remaining oil, and produced oil.

4. Conclusions

(1) Using the pendant drop method, the interaction between CO₂ and crude oil can be seen through the reactor under simulated-formation conditions of temperature and pressure. There is a strong mutual diffusion at the beginning of the contact of CO₂ and crude oil, and as the pressure goes higher, the dissolution and extraction become easier.

(2) Data of CO₂ and crude oil interfacial tension under conditions of the temperature of 355.65 K and the pressure ranging from 0 MPa to 30 MPa were measured by experiment. Experimental results show that CO₂/crude oil equilibrium interfacial tension decreases with the increasing of pressure.

(3) The interfacial tension of CO₂ and oil is large at the initial contact, and as time is getting longer, the interfacial tension decreases gradually and eventually reaches dynamic balance. Moreover, the higher the pressure is, the more the magnitude of changing of CO₂/crude oil interfacial tension with time will reduce.

(4) The higher the content of C₁ in crude oil is, the lower the content of C₂-C₁₀ will be, and the equilibrium interfacial tension will get higher. On the contrary, the lower the content of C₁ is, the higher the content of C₂-C₁₀ will be, and the equilibrium interfacial tension will become lower. In other words, C₁ is negative for the miscibility of CO₂ and oil, and C₂-C₁₀ can promote the miscibility of CO₂ and crude oil system.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] L. Mengtao, S. Wenwen, L. Xiangui, and S. Genhua, "Laboratory study on miscible oil displacement mechanism of supercritical carbon dioxide," *Acta Petrolei Sinica*, vol. 27, no. 3, pp. 80–83, 2006.
- [2] T. W. Teklu, N. Alharthy, H. Kazemi, X. Yin, and R. M. Graves, "Vanishing interfacial tension algorithm for MMP determination in unconventional reservoirs," in *Proceedings of the SPE Western North American and Rocky Mountain Joint Meeting (SPE-169517-MS)*, 2014.
- [3] M. Stukan and W. Abdallah, "Interfacial tension (IFT) and surface alteration interplay," in *Abu Dhabi International Petroleum Exhibition and Conference—Sustainable Energy Growth: People, Responsibility, and Innovation (ADIPEC '12)*, Proceedings of the SPIE, pp. 1155–1164, Abu Dhabi, UAE, November 2012.
- [4] D. Makimura, M. Kunieda, Y. Liang, T. Matsuoka, S. Takahashi, and H. Okabe, "Application of molecular simulations to CO₂-enhanced oil recovery: phase equilibria and interfacial phenomena," *SPE Journal Paper*, vol. 18, no. 2, pp. 319–330, 2013.
- [5] V. Mirchi, S. Saraji, L. Goual, and M. Piri, "Dynamic interfacial tensions and contact angles of surfactant-in-brine/oil/shale systems: implications to enhanced oil recovery in shale oil reservoirs," in *Proceedings of the SPE Improved Oil Recovery Symposium (169171-MS SPE Conference Paper)*, 2014.
- [6] S. Shehbaz and B. T. Hoffman, "CO₂ flooding the elm coulee field," in *Proceedings of the SPE Rocky Mountain Petroleum Technology Conference*, Society of Petroleum Engineers, Denver, Colorado, April 2009.
- [7] J. Phirani and K. K. Mohanty, "Kinetic simulation of CO₂ flooding of methane hydrates," in *Proceedings of the SPE Annual Technical Conference and Exhibition*, 2010.
- [8] R. M. Brush, H. J. Davitt, O. B. Aimar, J. Arguello, and J. M. Whiteside, "Immiscible CO₂ flooding for increased oil recovery and reduced emissions," in *Proceedings of the Improved Oil Recovery Symposium*, Tulsa, Okla, USA, April 2000.
- [9] D. S. Sequeira, S. C. Ayirala, and D. N. Rao, "Reservoir condition measurements of compositional effects on gas-oil interfacial tension and miscibility," in *SPE Symposium on Improved Oil Recovery*, Tulsa, Okla, USA, 2008.
- [10] Y.-X. Zuo, J.-Z. Chu, S.-L. Ke, and T.-M. Guo, "A study on the minimum miscibility pressure for miscible flooding systems," *Journal of Petroleum Science and Engineering*, vol. 8, no. 4, pp. 315–328, 1993.
- [11] B.-G. Liu, P. Zhu, Z.-Q. Yong, and L.-H. Lu, "Pilot test on miscible CO₂ flooding in Jiangsu oil field," *Acta Petrolei Sinica*, vol. 23, no. 4, pp. 56–61, 2002.
- [12] Y. Daoyong and G. Yongan, "A new experimental technique for studying gas mass transfer in the crude oil by analysis of the measured dynamic and equilibrium interfacial tensions," in *Proceedings of the SPE Annual Technical Conference and Exhibition*, Society of Petroleum Engineers, San Antonio, Tex, USA, September 2006.
- [13] T. W. Teklu, N. Alharthy, H. Kazemi, X. Yin, and R. M. Graves, "Vanishing interfacial tension algorithm for MMP determination in unconventional reservoirs," in *SPE Western North American and Rocky Mountain Joint Meeting*, Denver, Colo, USA, 2014.
- [14] B. Peng, H. Luo, G. Chen, and C. Sun, "Determination of the minimum miscibility pressure of CO₂ and crude oil system by vanishing interfacial tension method," *Acta Petrolei Sinica*, vol. 28, no. 3, pp. 93–95, 2007.
- [15] C. Y. Sun, W. Q. Wang, G. J. Chen, and C. F. Ma, "Interfacial tension experiment of oil and water, oil and gas for CO₂ injected reservoir fluid system," *Journal of China University of Petroleum*, vol. 30, no. 5, pp. 109–112, 2006.
- [16] Y. Daoyong and Y. Gu, "Visualization of interfacial interactions of crude Oil-CO₂ systems under reservoir conditions," in *Proceedings of the SPE/DOE Symposium on Improved Oil Recovery*, Society of Petroleum Engineers, Tulsa, Okla, USA, April 2004.
- [17] A. M. Elsharkawy, F. H. Poettmann, and R. L. Christiansen, "Measuring CO₂ minimum miscibility pressures: slim-tube or rising-bubble method?" *Energy and Fuels*, vol. 10, no. 2, pp. 443–449, 1996.
- [18] D. B. Bennion and S. Bachu, "correlations for the interfacial tension between supercritical phase CO₂ and equilibrium brines at in situ conditions," in *Proceedings of the Annual Technical Conference and Exhibition*, Denver, Colo, USA, September 2008.
- [19] K. Jessen and F. M. Orr, "On interfacial-tension measurements to estimate minimum miscibility pressures," *SPE Reservoir Evaluation & Engineering*, vol. 11, no. 5, pp. 933–939, 2008.
- [20] M. Dong, S. Huang, S. B. Dyer, and F. M. Mourits, "A comparison of CO₂ minimum miscibility pressure determinations for Weyburn crude oil," *Journal of Petroleum Science and Engineering*, vol. 31, no. 1, pp. 13–22, 2001.
- [21] D. N. Rao, "A new technique of vanishing interfacial tension for miscibility determination," *Fluid Phase Equilibria*, vol. 139, no. 1-2, pp. 311–324, 1997.
- [22] D. Yang and Y. Gu, "A new experimental technique for studying gas mass transfer in the crude oil by analysis of the measured dynamic and equilibrium interfacial tensions," in *Proceedings of the SPE Annual Technical Conference and Exhibition (ATCE '06)*, Paper SPE 95844, pp. 2081–2094, Dallas, Tex, USA, September 2006.
- [23] S. Siregar, P. Mardisewojo, D. Kristanto, and R. Tjahyadi, "Dynamic interaction between CO₂ gas and crude oil in porous medium," in *Proceedings of the Asia Pacific Improved Oil Recovery Conference*, Kuala Lumpur, Malaysia, October 1999.
- [24] U. W. R. Siagian and R. B. Grigg, "The extraction of hydrocarbons from crude oil by high pressure CO₂," in *SPE/DOE Improved Oil Recovery Symposium*, Tulsa, Okla, USA, 1998.
- [25] A. Y. Zekri, S. A. Shedid, and R. A. Almehaideb, "An experimental investigation of interactions between supercritical CO₂, asphaltene crude oil, and reservoir brine in carbonate cores," in *Proceedings of the International Symposium on Oilfield Chemistry*, Society of Petroleum Engineers, Houston, Tex, USA, 2007.
- [26] D. N. Rao and J. I. Lee, "Determination of gas-oil miscibility conditions by interfacial tension measurements," *Journal of Colloid and Interface Science*, vol. 262, no. 2, pp. 474–482, 2003.
- [27] R. A. DeRuiter, L. J. Nash, and M. S. Singletary, "Solubility and displacement behavior of a viscous crude with CO₂ and hydrocarbon gases," *SPE Reservoir Engineering*, vol. 9, no. 2, pp. 101–106, 1994.
- [28] D. Yang, P. Tontiwachwuthikul, and Y. Gu, "Interfacial tension phenomenon and mass transfer process in the reservoir brine-CO₂ system at high pressures and elevated temperatures," in

Proceedings of the International Green Energy Conference (IGEC-1), Waterloo, Canada, 2005.

- [29] Q.-Y. Ren, G.-J. Chen, W. Yan, and T.-M. Guo, "Interfacial tension of (CO₂ + CH₄) + water from 298 K to 373 K and pressures up to 30 MPa," *Journal of Chemical and Engineering Data*, vol. 45, no. 4, pp. 610–612, 2000.
- [30] C.-Y. Sun, G.-J. Chen, and L.-Y. Yang, "Interfacial tension of methane + water with surfactant near the hydrate formation conditions," *Journal of Chemical and Engineering Data*, vol. 49, no. 4, pp. 1023–1025, 2004.
- [31] R. Ghez, *Diffusion Phenomena: Cases and Studies*, Kluwer Academic & Plenum, New York, NY, USA, 2001.
- [32] C. A. Grattoni and R. A. Dawe, "Gas and oil production from waterflood residual oil: effects of wettability and oil spreading characteristics," *Journal of Petroleum Science and Engineering*, vol. 39, no. 3-4, pp. 297–308, 2003.
- [33] D. Yang and Y. Gu, "Visualization of interfacial interactions of crude oil-CO₂ systems under reservoir conditions," in *SPE/DOE Symposium on Improved Oil Recovery*, Tulsa, Okla, USA, 2004.
- [34] J. Zappe, A. Wesch, and K. H. Ebert, "Measurement of the mass transfer into single drops in the system of water/supercritical carbon dioxide," *Journal of Colloid and Interface Science*, vol. 231, no. 1, pp. 1–7, 2000.
- [35] D. Yang and Y. Gu, "Interfacial interactions between crude oil and CO₂ under reservoir conditions," *Petroleum Science and Technology*, vol. 23, no. 9-10, pp. 1099–1112, 2005.



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