Energy Proceedings
Vol 35, 2023
ISSN 2004-2965

Experimental Investigation of Factors Influencing PVT Behavior in CO_2-Oil-Brine System

Danchen Li [1*], Jinghua Wang [2], Wei Fan [3]

1, 2, 3 Research Institute of Exploration and Development, PetroChina Changqing Oilfield Company

(*Danchen Li: ldchen_cq@petrochina.com.cn)

ABSTRACT

To clarify the driving mechanisms of carbon capture, utilization, and storage (CCUS), phase behaviors in bulk CO_2-oil-brine system is inevitably foundational investigation. In this study, we conducted pressure-volume-temperature tests under single-variable control in laboratory with in-situ crude oil and synthetic brine samples. First, constant composition expansion tests were designed to examine saturation pressure between CO_2 and oil phases with varied CO_2 mole concentration and temperature, respectively. Meanwhile, as a major mechanism for carbon storage, CO_2 solubility in brine and oil was then measured with changing pressures at a specific reservoir temperature. Growth of the saturation pressure was constantly detected with increasing CO_2 mole concentration and temperature, respectively. With sufficient CO_2 guaranteed during the tests, we found that CO_2 solubility in tested liquids was strengthened by the pressure increase as expected. Moreover, within the same pressure range, incremental CO_2 solubility in oil was about ten times larger than that in the brine, which indicated potentially underestimated CO_2 storage capacity in depleted oil reservoirs..

Keywords: CCUS, PVT, CO_2 solubility, Phase behavior, Constant composition expansion

NONMENCLATURE

Abbreviations

CCUS	Carbon capture, utilization, and storage
CCE	Constant composition expansion
EOR	Enhanced oil recovery
EWR	Enhanced water recovery
PVT	Pressure-Volume-Temperature
SF	Swelling factor

Symbols

m	Weight
s	Saturation
S	Solubility
X	Mole fraction
P	Pressure

1. INTRODUCTION

For the synergistic energy and environmental benefits, carbon capture, utilization, and storage (CCUS) application in oil reservoirs has been globally concerned [1], [2], [3], [4], [5]. Its target objects cover saline aquifers and oil reservoirs for enhanced water/oil recovery (EWR/EOR), respectively [5], [6], [7], [8]. Due to depletion of conventional petroleum resources, CCUS in unconventional reservoirs, especially tight reservoirs with considerable petroleum reserves was then developed [9], [10], [11]. Multi-scale investigations (from pore to reservoir scale) were designed and conducted through various methods mainly including laboratory experiments and numerical modeling [12], [13], [14], [15], [16]. Such investigations contributed to effective injection strategies, accurate evaluation systems, and reliable predictions [13], [17], [18], [19]. However, the diversification of analysis methods focused on intuitive reflection of CCUS performances resulting in unexpected neglect of underlying mechanisms and inter-phase behaviors.

As main objects, CO_2, oil, brine, and rock media are dominant elements in the CCUS research system [20]. Eliminating the complexity from different physical media, behavior between fluid flows is the driving foundation for CCUS projects [20], [21]. Solidified understanding of the basic driver provides flexibility to deal with characteristic reservoirs and provides a

This is a paper for International CCUS Conference 2023 (ICCUSC2023), April 14-15, 2023, Beijing, China.

baseline to further emphasize behavior caused by medium differences.

Pressure-volume-temperature (PVT) experiment is a commonly-used method for phase behavior investigation through the quantification of PVT relationships between tested phases [22], [23]. For CCUS, the combination of CO_2 enhanced oil recovery (EOR) and CO_2 sequestration, CO_2 saturation and solubility in reservoir liquids are required to be clarified [24], [25]. Correspondingly, constant composition expansion (CCE) test is adopted to measure CO_2 saturation pressure (Ps) in oil and swelling factor (SF) under different test conditions [22], [26], [27]. CO_2 solubility in oil and brine can also be measured using PVT equipment (ResFluid Solutions Inc., Canada) with sufficient CO_2 supplies to reach interaction equilibrium. In the same process, test parameters were varied to examine their influences on the fluid properties and interactions. However, some existing PVT studies were conducted based on single- or finite-component liquids [27], [28], [29]. Such simplified design is advantageous for accurate operation and precise representation of the underlying mechanism, while it risks the reliability to reflect the phase behaviors in a real reservoir.

In this study, we used the crude oil sample collected from Yanchang Formation in the Ordos Basin, China. The brine was synthesized according to ion compositions from the same-source brine analysis. The reservoir oil and brine samples guaranteed the accuracy and practicability of experimental results. We designed and conducted four CCE tests with total volume recorded at different pressures to calculate Ps. Then CO_2 solubility in the oil and brine was also measured within a pressure range. CCE and solubility tests were designed for investigating CO_2 EOR and sequestration mechanisms, which are key contents of CCUS projects in oil reservoirs. Moreover, we examined influences of varied CO_2 mole percent (mol%) and temperature on Ps under single-variable control. Relationship between pressure and CO_2 solubility was also obtained throughout the solubility measurements. The experimental setup, procedures, results, and conclusions are described and discussed in the following sections.

2. EXPERIMENTAL SETUP AND PROCEDURES

2.1 Fluid samples

The crude oil for the PVT tests was collected from the Yanchang Formation in the Ordos Basin. The synthesized brine was made following the ion compositions and total dissolved solids of the reservoir brine. Their specific compositions and properties (density and viscosity) can be found in previous works [13]. High-purity CO_2 was supplied by Rocky Mountain Air Solution.

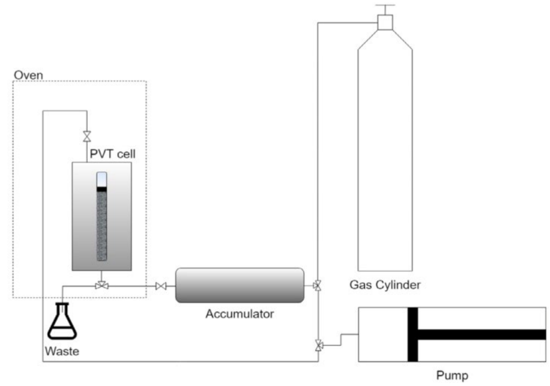


Fig. 1. PVT schematic diagram.

2.2 PVT apparatus

CCE and solubility tests were both completed by the PVT equipment (ResFluid Solutions Inc., Canada) as shown in **Fig. 1**. The tested liquids (crude oil and brine) and CO_2 were stored in an accumulator and a gas cylinder, respectively. Pressurization of samples can be reached separately through controls of three-way valves. Samples were then injected into PVT cell for the tests. Combined with an attached camera system, effective heights of the tested mixture can be observed and recorded through the window on the PVT cell. Unit volume of the PVT cell was measured to calculate the total volumes based on the height observations. Dead volumes of tubes and the glass cell were measured and calibrated before the tests.

2.3 Designs and procedures

2.3.1 Constant composition expansion test

CCE tests were designed in two sets with varied CO_2 mole percents (mol%) and temperature separately. The first set were conducted at the reservoir temperature (T_{res}=60℃) with varied CO_2 concentrations (40 mol%, 60 mol%, and 80 mol%). Then a test was added with the same 60 mol% CO_2 but at 70℃. In each CCE test, pressurized CO_2 and oil were injected into the PVT cell and mixed at a high pressure until reaching an one-phase mixture. The equivalent pressure in the PVT cell during the test can be further adjusted by the pump. Then the pressure was reduced step by step and the total volume of the mixture was measured and recorded at each pressure point. At a point of the pressure decrease, the one-phase mixture was separated into two phases (liquid and gas phases). The liquid volume can be calculated according to the liquid height for each measurement. Total volumes at different pressures can be plotted in two curves for one-phase and two-phase conditions, separately. The cross-point of two curves indicates P_s and the first bubble appearance during the pressure drop.

2.3.2 CO_2 solubility test

We used 60 mol% and 80 mol% CO_2 to measure CO_2 solubility in the brine and oil, respectively. CO_2 was mixed thoroughly (~2000 rpm for about 20 minutes) with the tested liquid at each pressure point. The gas and liquid volumes were calculated through height observations. Before each measurement, we added a 30-minute equilibrium period for the stable heights of CO_2 and the tested liquid in both CCE and solubility tests, which confirmed an accurate identification of the gas phase and accurate solubility guaranteed by sufficient CO_2 supplies.

2.4 Metrics

Saturation pressure (also called bubble-point pressure: P_s) was indicated by the corresponding pressure at the cross-point of two pressure-volume curves of single- and two-phase conditions. CCE test can further estimate swelling factor (SF) using **Eq. 1**:

$$SF = \frac{V_{oc}(T_b,P_b)}{V_{oil}(T_b,P_o)} \times \frac{1}{1-X_{CO_2}} \qquad \textbf{Eq. 1}$$

where T is temperature, P is pressure, and V is volume. Subscript b is the bubble point. V_{oc} is molar volume of the CO_2-oil mixture, P_o is the atmospheric pressure, and X_{CO2} is mole fraction of CO_2 in the mixture.

CO_2 solubility (S: %) was calculated by **Eq. 2**:

$$S = \frac{\Delta m_c}{m_l} \qquad \textbf{Eq. 2}$$

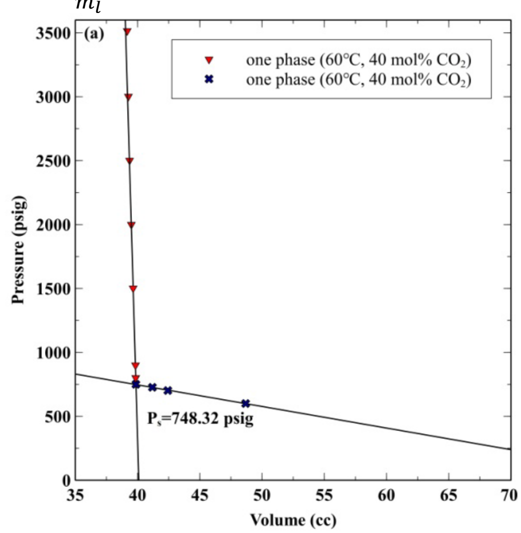
where Δm_c is the weight of the dissolved CO_2, and m_l is the weight of the tested liquid (crude oil or brine). Δm_c was calculated by the gas-phase volume loss during the pressure increase and calibrated to the same pressure.

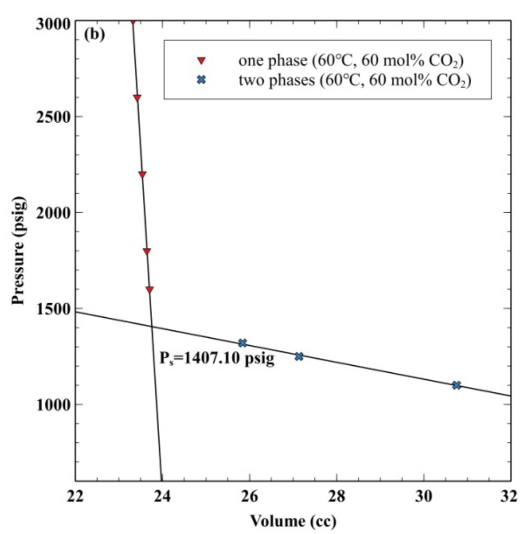
3. RESULTS AND DISCUSSIONS

3.1 CCE tests

The first set of CCE tests with the varied CO_2 concentration from 40 mol%, 60 mol%, to 80 mol% were conducted within pressure ranges of 3500~600 psig, 3000~1100 psig, 4500 ~1100 psig, respectively. The matched Ps increased from 748.32 psig to 1407.10 psig, and then 1907.55 psig (**Fig. 2a-c**). Then another test using 60 mol% CO_2 was conducted at 70℃ (**Fig. 2d**). Such temperature growth resulted in 151.39 psig to 1558.49 psig. The obtained results revealed positive relationships between CO_2 concentration-P_s and temperature-P_s. The swelling factor in the first CCE test with 40 mol% CO_2 was estimated at 1.34 in previous results, which provided an observation of volume expansion in the CO_2-oil interactions [13].

P_s indicates the first appearance of the gas bubble when tested pressure was dropped from a high pressure (one-phase condition). Its high value means that the CO_2 has a high probability to exist as an independent phase at the same pressure condition. The high temperature and the high CO_2 concentration will both result in low CO_2 solubility and thus challenging CO_2 dissolution, which also explains the tendency of the independent gas phase.





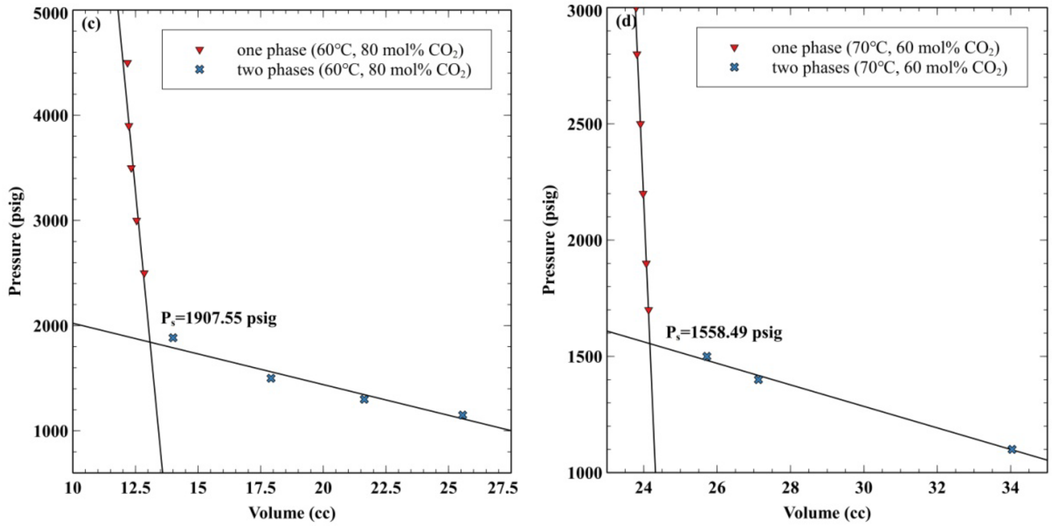


Fig. 2. CCE tests under single-variable control: (a) 40 mol% CO_2, 60℃ (b) 60 mol% CO_2, 60℃; (c) 80 mol% CO_2, 60℃; (d) 60 mol% CO_2, 70℃.

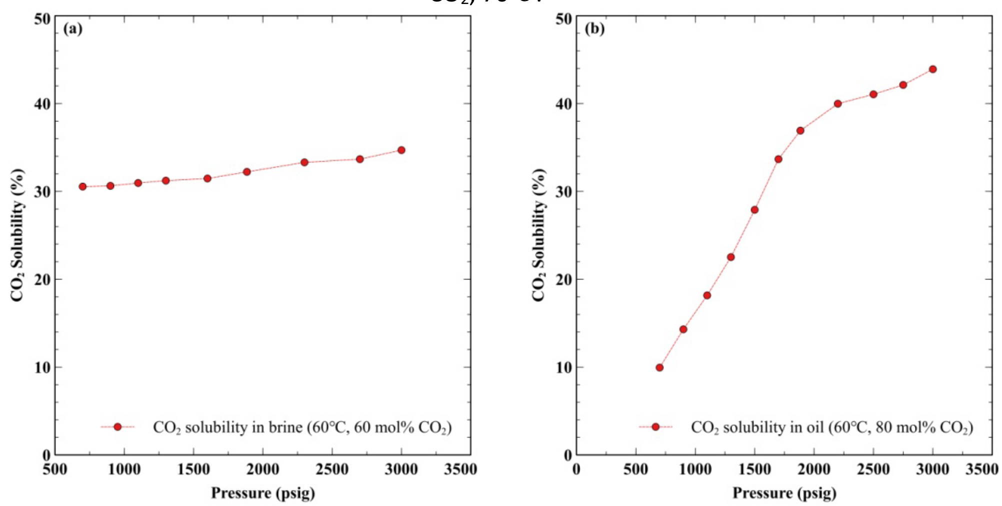


Fig. 3. CO_2 solubility in (a) brine (60 mol% CO_2, 60℃); (b) crude oil (80 mol% CO_2, 60℃).

3.2 CO2 solubility tests

CO_2 solubility was measured from 700 psig to 3000psig. It increased from 30.55% to 34.70 and 9.95% and 43.91% in brine and oil (**Fig. 3**), respectively. This test also quantified solubility at the specific target reservoir pressure (P_{res}=1885 psig), where 32.22% CO_2 was dissolved in the brine and 36.92% in the crude oil. Although they are similar at the P_{res}, a greater increase was detected within the test range between CO_2 and oil compared with that between CO_2 and brine. **Fig. 3** represents that the pressure has a larger influence on CO_2 solubility in the oil than in the brine. The solubility measurement will provide a reference for CO_2 sequestration design and prediction in CCUS projects.

4. *C*ONCLUSIONS

In this study, four CCE tests were conducted to clarify the influences of temperature and CO_2 concentration on Ps. Meanwhile, to assist quantification of carbon storage in CCUS, CO_2 solubility was measured in the crude oil and the brine, which was collected from the reservoir and synthesized according to the same-source brine compositions.

1. According to the CCE tests, Ps between oil and CO_2 has a positive correlation with the temperature and the CO_2 concentration, which reveals the tendency of the independent gas phase in the gas-oil mixture at high pressure or in a high-concentration CO_2 environment.

2. At the reservoir condition (Tres=60℃, Pres=1885 psig), CO_2 solubility in the crude oil (36.92%) and the brine (32.22%) were detected at the same level, which

implies the potential carbon storage caused by CO_2 dissolution in reservoir liquids.

3. Compared with CO_2 solubility in the brine, the pressure change performs a larger influence on the solubility in the oil. Such quantification can serve as evaluation and prediction references for reaching an objective sequestration in a specific CCUS project.

DECLARATION OF INTEREST STATEMENT

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

REFERENCE

[1] Y. oil Field, "CCS : A China Perspective Yanchang Petroleum Report 2 : CO_2 storage and EOR in ultra-low permeability reservoir in the Yanchang Formation ," p. 46, 2020.

[2] X. Wang *et al.*, "Cleaner coal and greener oil production: An integrated CCUS approach in Yanchang Petroleum Group," *Int. J. Greenh. Gas Control*, vol. 62, no. October 2016, pp. 13–22, 2017.

[3] S. Mishra, J. Hawkins, T. H. Barclay, and M. Harley, "Estimating CO_2-EOR potential and co-sequestration capacity in ohio's depleted oil fields," *Energy Procedia*, vol. 63, pp. 7785–7795, 2014.

[4] Q. M. Malik and M. R. Islam, "CO_2 injection in the Weyburn field of Canada: Optimization of enhanced oil recovery and greenhouse gas storage with horizontal wells," *SPE - DOE Improv. Oil Recover. Symp. Proc.*, 2000.

[5] B. T. F. Gozalpour, S.R. Ren, "CO_2 EOR and Storage in Oil Reservoirs," *Oil Gas Sci. Technol.*, vol. 60, no. 3, pp. 537–546, 2005.

[6] R. Vivek and G. S. Kumar, "Numerical investigation on effect of varying injection scenario and relative permeability hysteresis on CO_2 dissolution in saline aquifer," *Environ. Earth Sci.*, vol. 75, no. 16, pp. 1–14, 2016.

[7] S. Li, Y. Zhang, X. Zhang, and C. Du, "Geologie modeling and fluid-flow simulation of acid gas disposal in western Wyoming," *Am. Assoc. Pet. Geol. Bull.*, vol. 96, no. 4, pp. 635–664, 2012.

[8] Y. Tang, R. Yang, and X. Bian, "A review of CO_2 sequestration projects and application in China," *Sci. World J.*, vol. 2014, 2014.

[9] Z. Song, Y. Song, Y. Li, B. Bai, K. Song, and J. Hou, "A critical review of CO_2 enhanced oil recovery in tight oil reservoirs of North America and China," *Fuel*, vol. 276, no. May, p. 118006, 2020.

[10] B. Jia, J. S. Tsau, and R. Barati, "A review of the current progress of CO_2 injection EOR and carbon storage in shale oil reservoirs," *Fuel*, vol. 236, no. July 2018, pp. 404–427, 2019.

[11] A. Wilson, "Experimental and Numerical Studies of CO_2 EOR in Unconventional Reservoirs," *J. Pet. Technol.*, vol. 69, no. 01, pp. 45–47, 2017.

[12] Z. Li *et al.*, "Evaluation of CO_2 storage of water alternating gas flooding using experimental and numerical simulation methods," *Fuel*, vol. 311, no. October 2021, p. 122489, 2022.

[13] D. Li, S. Saraji, Z. Jiao, and Y. Zhang, "CO_2 injection strategies for enhanced oil recovery and geological sequestration in a tight reservoir : An experimental study," *Fuel*, vol. 284, no. August 2020, p. 119013, 2021.

[14] A. Ghanizadeh, C. Song, H. Hamdi, and C. R. Clarkson, "Experimental and computational evaluation of cyclic solvent injection in fractured tight hydrocarbon reservoirs," *Sci. Rep.*, vol. 11, no. 1, pp. 1–12, 2021.

[15] P. Tahmasebi, F. Javadpour, M. Sahimi, and M. Piri, "Multiscale study for stochastic characterization of shale samples," *Adv. Water Resour.*, vol. 89, pp. 91–103, 2016.

[16] S. Afzali, N. Rezaei, and S. Zendehboudi, "A comprehensive review on Enhanced Oil Recovery by Water Alternating Gas (WAG) injection," *Fuel*, vol. 227, no. April, pp. 218–246, 2018.

[17] F. I. Syed, T. Muther, A. K. Dahaghi, and S. Neghabhan, "CO_2 EOR Performance Evaluation in an Unconventional Reservoir through Mechanistic Constrained Proxy Modeling," *Fuel*, vol. 310, no. PA, p. 122390, 2022.

[18] M. Sahimi and P. Tahmasebi, "Reconstruction, optimization, and design of heterogeneous materials and media: Basic principles, computational algorithms, and applications," *Phys. Rep.*, vol. 939, pp. 1–82, 2021.

[19] M. Andrew, "Permeability Prediction using multivariant structural regression," *E3S Web Conf.*, vol. 146, pp. 1–7, 2020.

[20] A. Rezaei, H. Abdollahi, Z. Derikvand, A. Hemmati-Sarapardeh, A. Mosavi, and N. Nabipour, "Insights into the effects of pore size distribution on the flowing behavior of

carbonate rocks: Linking a nano-based enhanced oil recovery method to rock typing," *Nanomaterials*, vol. 10, no. 5, pp. 1–22, 2020.

[21] Y. Tang *et al.*, "Review on Phase Behavior in Tight Porous Media and Microscopic Flow Mechanism of CO_2 Huff-n-Puff in Tight Oil Reservoirs," *Geofluids*, vol. 2020, 2020.

[22] A. Habibi, M. R. Yassin, H. Dehghanpour, and D. Bryan, "Experimental investigation of CO_2-oil interactions in tight rocks: A Montney case study," *Fuel*, vol. 203, pp. 853–867, 2017.

[23] R. P. Sutton, "Fundamental PVT calculations for associated and gas/condensate natural-gas systems," *SPE Reserv. Eval. Eng.*, vol. 10, no. 3, pp. 270–284, 2007.

[24] B. Wei *et al.*, "Interactions and phase behaviors between oleic phase and CO_2 from swelling to miscibility in CO_2-based enhanced oil recovery (EOR) process: A comprehensive visualization study," *J. Mol. Liq.*, vol. 232, pp. 277–284, 2017.

[25] A. Abedini and F. Torabi, "On the CO_2 storage potential of cyclic CO2 injection process for enhanced oil recovery," *Fuel*, vol. 124, pp. 14–27, 2014.

[26] H. Han, S. Yuan, S. Li, X. Liu, and X. Chen, "Dissolving capacity and volume expansion of carbon dioxide in chain n-alkanes," *Pet. Explor. Dev.*, vol. 42, no. 1, pp. 97–103, 2015.

[27] H. Wang, F. Zeng, and X. Zhou, "Study of the non-equilibrium PVT properties of methane- and propane-heavy oil systems," *Soc. Pet. Eng. - SPE Canada Heavy Oil Tech. Conf. 2015, CHOC 2015*, pp. 1386–1408, 2015.

[28] E. C. Morris, "Accurate measurements of the PVT properties of methane from -20 to 150 °C and to 690 MPa," *Int. J. Thermophys.*, vol. 5, no. 3, pp. 281–290, 1984.

[29] N. R. Kim, P. R. Ribeiro, and P. A. Pessôa-Filho, "PVT behavior of methane and ester-based drilling emulsions," *J. Pet. Sci. Eng.*, vol. 135, pp. 360–366, 2015.