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Review Article

An Investigation of the Robustness of Physical and Numerical Vanishing Interfacial Tension Experimentation in Determining CO_2 + Crude Oil Minimum Miscibility Pressure

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Different experimental and theoretical methods are used for predicting the minimum miscibility pressure (MMP) of complex CO2 + reservoir crude oil systems that are of particular interest to petroleum industry. In this paper, published physical and numerical vanishing interfacial tension (VIT) experimentations are critically examined for identifying best practices to reliably predict the CO_2 + crude oil MMP. Some of the reported physical VIT experimentation studies appear to follow a portion of full scale VIT experimentation (i.e., a combination of the pendent drop method and the capillary rise technique). The physical VIT experimentation method in which the IFT measurements are made at varying pressures but with the same initial load of live oil and gas phases in the optical cell seems to be the most robust mechanistic procedure for experimentally studying the pressure dependence of IFT behaviors of complex CO_2 + crude oil systems and thus determining the MMP using the VIT technique. The results presented here suggest that a basic parachor expression based on numerical VIT experimentation can reasonably follow the physical VIT experimentation in low IFT region, provided measured input data such as equilibrium phase densities and compositions are used in calculations.

1. Introduction

Accurate knowledge of MMP is crucial for designing and implementing successful miscible CO_2 flooding based enhanced oil recovery (EOR) projects. For this reason, operating companies spend significant time and resources to reliably determine the MMP. Various experimental as well as theoretical methods are available for determining the MMP between injected CO_2 and reservoir crude oils (Table 1). A brief description of these methods and discussion on their accuracy and limitations can be found elsewhere [1–7].

According to Nagarajan et al. [8], near-critical region where interfacial tension (IFT) between injected CO_2 and reservoir crude oil approaches zero is of particular interest in EOR applications, since improved efficiency of oil displacement by CO_2 occurs when the IFT becomes low. According to Hsu et al. [9], existing data shows that, at sufficiently low IFT values (less than 0.1 mN/m (0.1 dyne/cm) and perhaps as low as 0.001 mN/m), displacement efficiencies under immiscible conditions can approach those for miscible floods. Nagarajan and Robinson Jr. [10], who measured the IFT for CO_2 + hydrocarbon (n-decane) system at various pressures and temperatures, suggested that a better understanding of the effects of temperature, pressure, and composition on the IFT in such systems could also lead to improved understanding of the process of miscible (or near-miscible, low IFT) displacement of reservoir oils by CO_2 injection. In their US patent, Christiansen and Kim [11] correlated the observed behavior of pure CO_2 bubbles in CO_2-saturated n-decane with independently determined IFT data for demonstrating the operability of RBA for determining the MMP.

Rao [12] developed a new experimental technique, namely, the vanishing interfacial tension (VIT) technique, that relies on studying the pressure dependence of the IFT behavior of CO_2 + crude oil system at several pressures steps and by making a plot of the IFT against the pressure. The MMP is then obtained by extrapolating the observed pressure versus IFT curve to zero IFTs.

Table 1: List of various experimental and theoretical CO_2-crude oil MMP determination methods reported in the published literature.

(A) Experimental methods
Slim-tube test[1]
Micro slim-tube test[1]
Rising bubble apparatus[1]
Single bubble injection technique[1]
Vanishing interfacial tension (VIT) method [12]
Vapor-liquid equilibrium-interfacial tension test[1]
Vapor density of injected gas versus pressure[1]
High-pressure visual sapphire cell[1]
PVT multicontact experiments[1]
(B) Other experimental methods
Fluorescence-based microfluidic approach [20]
(C) Theoretical methods
Various empirical correlations[2,3,4]
Key tie-line approach and the Method of Characteristics (MOC)[5]
Mixing cell methods[5]
Vanishing tie-line approach[6]
Response surface based model [21]
Least-Squares Support Vector Machine (LSSVM) model [2]
Multiple Linear Regression (MLR) technique [22]
Neural network model [1]
1D slim-tube simulation models[7]
Parachor models[8]
Mechanistic parachor models[9]
Linear gradient theory (LGT) model [19]

[1] After methods and references given in Alomair and Garrouch [1].
[2,3,4] After methods and references given in Alomair and Garrouch [1], Alomair and Iqbal [22], and Mogensen et al. [5].
[5] After methods and references given in Mogensen et al. [5].
[6] After methods and references given in Ahmadi et al. [4].
[7] After methods and references given in Mogensen et al. [5]; Bui et al. [23]; Ju et al. [24].
[8] After methods and references given in Teklu et al. [25].
[9] After methods and references given in Ayirala and Rao [14, 26]; Ashrafizadeh and Ghasrodashti [27].

The VIT technique reported by Rao and coworkers [13–17] uses a combination of the pendant drop (or falling-drop) technique and the capillary rise technique for experimentally studying the pressure dependence of IFT behaviors of complex CO_2 + crude oil systems. This combination of the two abovementioned techniques is particularly useful to measure low values of gas/oil IFT because, in the low IFT region, use of the pendant drop method alone due to irregular shapes of the pendant oil drops and the oil drops disappearing into the gas phase as the miscibility pressure is approached makes the IFT measurements very difficult.

Ayirala and Rao [3] have discussed the VIT technique developed by Rao and coworkers in detail. Rao and coworkers [13–17] have used physical VIT experimentation for experimentally measuring the MMP for different CO_2 + crude oil systems.

Tathed et al. [18] conducted experiments to measure gas-oil IFT at varying pressures at reservoir temperature using pendant drop technique for three different injection gases including CO_2 and two different Alaska North Slope (ANS) heavy oil samples. They used the experimental VIT technique to determine MMP of the respective injection gas-oil pairs. Nobakht et al. [19] measured the equilibrium IFTs of a crude oil + CO_2 system under different equilibrium pressure and at 27°C (80.6°F) by applying the ADSA (axisymmetric drop shape analysis) technique for the pendant drop case and used the measured equilibrium IFT versus equilibrium pressure data to determine the MMP of the crude oil + CO_2 system by applying the so-called VIT technique.

Wang et al. [30] measured the equilibrium IFT between crude oil and CO_2 as a function of the equilibrium pressure and used the experimental VIT technique to determine the MMP (they used the term "so-called MMP") of three different CO_2 + crude oil systems. The measured equilibrium IFT was found to reduce linearly with equilibrium pressure in three distinct pressure ranges for the two CO_2 + light crude oil systems and in two different pressure ranges for the CO_2 + medium crude oil system. Saini and Rao [17] reported the MMP for two recombined live oil samples and CO_2 at reservoir temperature of 142.7°C (289°F) using the experimental VIT technique.

Recently, Al-Siyabi [32] used experimental VIT approach to estimate the MMPs of CO_2 + n-decane in the pressure of impurities and the pure CO_2. Awari-Yusuf [31] conducted the pendant drop IFT experiments for estimating first-contact MMP (FCMP) of several crude oil + gas (CO_2 and N_2) systems using the experimental VIT technique.

In parallel to the use of measured IFT data for determining the MMP for CO_2 + crude oil systems, pressure dependence of CO_2 + crude oil IFTs has been also been studied and modeled using parachor based IFT prediction methods for deducing useful information about the MMP. Schechter and Guo [33] developed new pure-component parachors, parachor correlations, and oil-cut parachors and tested them for IFT predictions for six reservoir oil/CO_2 mixtures. According to them, using the new parachors and correlations with parachor method, IFTs of reservoir fluids can be predicted with the Peng-Robinson equation of state (PREOS) with an acceptable error.

Ayirala and Rao [14, 26] proposed a mass transfer enhanced mechanistic parachor model to predict gas-oil IFT at reservoir conditions. They tested the performance of the proposed mechanistic model for two reservoir crude oil-gas systems and claimed to find an excellent match between the experiments and the mechanistic model predictions. They used the predicted IFT data for determining MMP using the VIT approach.

Orr Jr. and Jessen [34] presented a numerical analysis of VIT experimentation by studying the pressure dependence of IFT behaviors of several CO_2 + standard hydrocarbon mixtures and CO_2 + crude oil mixtures. They concluded that the VIT approach to determine the MMP for multicomponent gas-oil displacements should be used with caution given the potential for significant errors in the resulting estimate of the MMP.

Nobakht et al. [19] used the parachor model and linear gradient theory (LGT) model for predicting the equilibrium IFT versus equilibrium pressure data of a crude oil-CO_2 system. The predicted equilibrium IFT data from each model were used to determine the MMP. According to them, comparison of the MMPs determined from the two equilibrium IFT prediction models and that determined from the measured equilibrium IFTs shows that the LGT model is suitable for determining the MMP of the CO_2 + crude oil system.

Ashrafizadeh and Ghasrodashti [27] presented a comparative study on five representative EOSs for predicting MMP using the mechanistic parachor model together with the criterion of zero IFT at the miscibility conditions. According to them, all of the studied EOSs can predict MMP using the mechanistic parachor model within an acceptable range of accuracy; however the model might be found nonsuitable for scenarios which incorporate considerable amounts of polar components. In such cases, they suggested the use of more complicated EOSs such as electrolyte models.

Teklu et al. [25] reported the development of a computational approach to determine the MMP which mimics the VIT experiment. In their approach, they used parachor model [35] for modeling the VIT trend of equilibrium gas-oil with increasing pressure. They mentioned that other parachor models such as mechanistic parachor model [14] can also be used for obtaining VIT trend.

2. Different Versions of Physical VIT Experimentation

As evident from the review of the abovementioned published literature, various researchers have used the experimental VIT technique to determine the MMP of CO_2 + reservoir crude oil systems. These studies also demonstrate the increasing popularity of the use of both experimentally measured and theoretically determined IFT data for estimating MMP using the VIT approach. Table 2 provides a summary of experimental apparatus, system(s) investigated (CO_2, hydrocarbon gas, and live/dead crude oil), IFT measurement methods used, and results obtained (MMP, FCMP) in various physical VIT studies reported in the published literature. However there appear to be significant variations in experimental procedures used in such studies which are highlighted and discussed here.

2.1. Rao [12]. The first published study to report on the experimental VIT technique is Rao's [12]. In that study, gas/oil IFTs were measured by applying the ADSA technique to pendant crude oil drops immersed in the gas phase of desired composition at reservoir temperature and varying pressures. According to Rao, gas and crude oil were preequilibrated in the high-pressure optical cell before commencing the acquisition of pendant drop profile images on the computer. The solvents used in the study include ethane, propane, and gas mixtures representative of lean and rich gases available in the field. The density of live and stock-tank oils, required in the calculation of interfacial tension, was measured using a density meter. It is worth mentioning here that one of the objectives of the study was to determine minimum miscibility composition (MMC) of injection gas using the VIT technique. Hence, the density of the gas phase, at each enrichment level, was calculated using a commercial phase behavior calculation package assisted by chromatographic compositional analysis of gas sample collected during the IFT experiments.

Rao noted that, including the cleaning of the optical cell and its accessories (which is essential for obtaining accurate IFT measurements), each determination of MMP for one crude oil with one solvent gas (or gas mixture) took about 4–6 h to complete. This experimental duration is indicative of performing IFT measurements at various pressure steps in a single experiment. The next study that is worth mentioning here is Yang and Gu [28].

2.2. Yang and Gu [28]. Yang and Gu [28] used pendant drop or falling-drop method for studying crude oil-CO_2 interactions at reservoir conditions. In the experimental procedure followed by them, a pendant oil drop is formed in the CO_2 bulk phase present inside a see-through windowed high-pressure cell. The digital image of pendant drop is acquired and analyzed by the ADSA program (pendant drop case) to determine the dynamic IFT of the pendant oil drop. According to Yang and Gu, the IFT measurement and visualization are conducted for at least six pendant oil drops to ensure satisfactory repeatability at specified pressure and temperature. After each test, the pressure cell and the whole system are cleaned. For the tested crude oil, Yang and Gu [28] noted that the oil density variations with dissolved CO_2 concentration at high pressures were small. Hence they considered constant oil density values in their work. The density of CO_2 was calculated from a standard property table at different pressures and temperatures. They found no ultralow or zero IFTs between crude oil and CO_2, regardless of the operating pressures and temperatures. Based on the measured constant low IFT and the observed interfacial interactions, they concluded that only partial miscibility between crude oil and CO_2 can be achieved for most reservoirs.

2.3. Ayirala [13]; Ayirala and Rao [14]. In addition to the use of pendant drop method in the VIT technique developed by Rao [12], Ayirala [13] and Ayirala and Rao [14] adopted the capillary rise technique for performing the IFT measurements in low IFT region. In their studies, a combination of the pendant drop method with the capillary rise technique facilitated the measurement of IFT up to 0.04 mN/m. It is noted here that such low IFT was measured for the live decane + CO_2 system. Similar to Rao [12], all IFT measurements were made at varying pressures but with the same initial load of live oil and gas phases in the optical cell. Their experimental procedure also differed from Rao [12] in another aspect. The densities of both fluid phases (equilibrated oil and gas phases) were measured using a density meter compared to Rao [12] where the equilibrated gas phase density was calculated from a phase behavior calculation package.

Table 2: Summary of experimental apparatus, system(s) investigated, IFT measurement methods used, and results obtained in various physical VIT studies reported in the published literature.

Reported physical VIT experimentation study	Experimental apparatus used	System investigated	IFT measurement technique(s) employed	Method(s) used for measuring gas and oil phase densities	Results obtained
Rao [12]	High-pressure high-temperature optical cell	Hydrocarbon gas + live crude oil; hydrocarbon gas + dead crude oil	Pendant drop	Oil and gas: equation of state	MMP, FCMP, MMC
Yang and Gu [28]	See-through windowed high-pressure cell	CO_2 + dead crude oil	Pendant drop	Gas: standard property table Oil: atmospheric dead oil density	FCMP
Ayirala [13]; Ayirala and Rao [14]	High-pressure high-temperature optical cell	CO_2 + n-decane; CO_2 + live decane	Pendant drop Capillary rise method	Oil and gas: density meter	MMP
Sequeira [15]; Sequeira et al. [16]	High-pressure high-temperature optical cell	CO_2 + live crude oil	Pendant drop Capillary rise method	Oil and gas: density meter	MMP, FCMP
Nobakht et al. [19]	See-through windowed high-pressure cell	CO_2 + dead crude oil	Pendant drop	Gas: equation of state Oil: atmospheric dead oil density	FCMP
Patil et al. [29]	High-pressure optical cell	CO_2, CH_4, or viscosity reducing injectant + ANS crude oil	Pendant drop	Oil and gas: equation of state	MMP
Wang et al. [30]	See-through windowed high-pressure cell	CO_2 and three different crude oils	Pendant drop	Gas: equation of state Oil: N/A	The "so-called MMP", the "so-called FCMP"
Saini and Rao [17]	High-pressure high-temperature optical cell	CO_2 + live crude oil	Pendant drop Capillary rise method	Oil and gas: density meter	MMP
Awari-Yusuf [31]		CO_2 + dead crude oil	Pendant drop	Gas: equation of state Oil: Pycnometer	FCMP

2.4. Sequeira [15]; Sequeira et al. [16]. Sequeira [15] and Sequeira et al. [16] used a combination of the pendant drop method and the capillary rise technique to conduct the IFT measurements at elevated pressures and reservoir temperature. In the experiments, the image of the first pendant drop of live crude oil at the tip of capillary tube in the optical cell as soon as it contacts the gas phase through was captured. Using the densities of the pure fluid phases, the first-contact gas-oil IFT was determined with the help of commercial drop shape analysis (DSA) software. After acquiring first-contact pendant drop, previously determined amount of live oil was added to this optical cell for performing multiple-contact IFT measurements. After allowing the fluids to reach equilibrium in the cell at the experimental conditions (approximately 6 h), a pendant drop of the fresh recombined reservoir fluid at the tip of capillary tube in the optical cell in the gas phase that has already interacted with the oil residing at the bottom of the cell was introduced. The image was captured and the procedure was repeated for about 8–10 pendent oil drops. This step facilitated obtaining the equilibrium IFT from the pendant drop shape analysis technique.

After completing the pendant drop IFT measurements, approximately 24 h was allowed for the fluids to reach equilibrium in the cell at the experimental conditions. After that, the capillary rise observed in the capillary tube placed in the optical cell was recorded. The samples of equilibrium fluid phases (gas and oil) were collected to measure the equilibrium fluid phase densities. The collected samples were also analyzed for compositions and the molecular weight of the stock-tank oil was also measured. The optical cell was thoroughly cleaned at the end of each pressure test, evacuated, and reloaded with fresh recombined reservoir fluid and CO_2 to start the test at the next pressure. The same procedure was repeated at different experimental pressure steps and reservoir temperature. This procedure was distinctly different from the procedure of previously conducted experimental studies [13, 14] wherein all IFT measurements were made at varying pressures but with the same initial load of live oil and gas phases in the optical cell.

It is worth mentioning here that the equilibrated gas and oil phase densities needed to determine the "multiple-contact" IFT from both the capillary rise technique and the pendant drop shape analysis techniques were experimentally measured. This experimental procedure facilitated the measurements of both the FCMP and the multiple-contact miscibility pressures (or MMP) for the CO_2 + live crude oil system investigated in the study. The measured FCMP was distinctly higher than the MMP which agrees well with the general trend of higher FCMP compared to the MMP for CO_2 + live crude oil systems. Using the capillary rise technique, Sequeira [15] was also able to measure the IFT as low as 0.01 mN/m.

2.5. Nobakht et al. [19]. Nobakht et al. [19] used a see-through windowed high-pressure cell for measuring the equilibrium IFT between the crude oil and CO_2 by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. The experimental procedure used by Nobakht et al. appears to be a "first-contact" IFT measurement procedure. It is noted here that the PREOS was used for calculating the densities of CO_2 at different pressures and 27°C (80.6°F). It appears that they used the measured density of crude oil sample at atmospheric pressure and 27°C in the IFT calculations because it is unlikely that crude oil density will change significantly in the tested pressure range. The use of atmospheric crude oil density may also be justifiable due to the "first-contact" nature of the experimental procedure. As can be seen in the measured IFT behaviors presented in Figure 4 of their paper, Nobakht et al. extrapolated the trend shown by IFT data points in high IFT region to zero IFT condition to determine the system MMP. However, their experimental procedure does not appear to incorporate the "multiple-contact" gas-oil interactions. In the absence of multiple-contact interactions, pressure obtained from the extrapolation of the equilibrium IFT data to the VIT condition does not correspond to the MMP. However, an extrapolation of the low IFT trend to the VIT condition may provide an estimate of the FCMP not the MMP.

2.6. Patil et al. [29]. Patil et al. [29] used the experimental VIT technique to determine the MMP of different gas (CO_2, CH_4, or viscosity reducing injectant) + ANS crude oil systems. They used the ADSA technique for pendant drop analysis which was used to measure the dynamic and equilibrium IFT between the oil/gas systems. In their experimental procedure, a gas at a selected pressure was allowed to enter the optical cell. Then, the pendant oil drops were allowed to form in the optical cell at a slow flow rate. The image of the first pendant drop of crude oil at the tip of the needle in the optical cell was captured with the digital camera as soon as it contacted the gas phase. Using the initial fluid phase densities, the first-contact miscibility was determined. The fluids were then allowed to equilibrate for about 2 hours at the experimental conditions. A pendant drop of the crude oil was allowed to form at the tip of the needle in the optical cell in the gas phase that had already interacted with the oil residing at the bottom of the cell. This image was captured and drop shape analysis was performed. The density was determined by using commercial phase behavior software and the IFT was calculated. The same procedure was repeated for about 8–10 pendant oil drops. The pressures of the oil and gas phases were increased to repeat the abovementioned procedure at subsequent high-pressure steps.

Patil et al. used experimentally measured densities of pure fluid phases to tune the EOS parameters in two-phase flash simulations. Using the two-phase flash calculations, densities were determined at different pressures of oil-gas interactions. They also noted that it was difficult to measure the drop shape factor at higher pressures. It is noted here that the drop shape factor determines the axisymmetric nature of the pendant drop shape while determining the IFT from the drop shape profile. Therefore, in all the cases the values of IFT where the drop shape factor equaled 1 were used to extrapolate to "zero" IFTs. The pressure corresponding to the extrapolated "zero" IFTs was termed MMP.

2.7. Wang et al. [30]. Wang et al. [30] used an experimental procedure similar to Yang and Gu [28] for experimentally

studying the mutual interactions between each of three different crude oils and CO_2. It is noted here that they used the terms so-called "MMP" and so-called "FCMP" while discussing the experimental results. Wang et al. inferred the so-called "MMP" and so-called "FCMP" by extrapolating different linear IFT versus pressure trends. They distinguished that those trends on the basis of distinct pressure ranges have provided a detailed discussion on the mechanisms responsible for such trends. They found that the measured equilibrium IFT is reduced almost linearly with the equilibrium pressure in three distinct pressure ranges.

As discussed earlier, their experimental procedure which is similar to Yang and Gu [28] seems to follow a "first-contact" IFT measurement approach. Being a "first-contact" experiment signifies the absence of "multiple-contact" interactions. This appears to be a reason that they used the terms so-called "MMP" and so-called "FCMP" for the pressures that corresponded to the VIT conditions in their experiments. It is noted here that the densities of CO_2 were at different pressures and 27°C (80.6°F) and were calculated by using the CMG WinProp module (Computer Modelling Group (CMG) Limited, Canada) with the PREOS.

2.8. Saini and Rao [17]. Saini and Rao [17] used a combination of the capillary rise technique and the pendant drop method equipped with commercial drop shape analysis software to conduct the IFT measurements for a live (recombined) reservoir crude oil + CO_2 system at various pressures and reservoir temperature of 142.7°C (289°F) for determining the MMP. This study was undertaken to find the suitability of CO_2 as an injection gas for implementing the miscible gas injection process as part of comprehensive reservoir management plan to maximize oil recovery in a newly discovered oil field. They used an experimental procedure similar to Ayirala [13] and Ayirala and Rao [14], in which all IFT measurements are made at varying pressures but with the same initial load of live oil and gas phases in the optical cell. Including the cleaning of the optical cell and its accessories and other preparation time (rocking the heated crude oil sample, generating high CO_2 pressure prior to filling the optical cell with it, and, to increase the pressure during experiments, assembling of the various equipment components after cleaning, equilibration time, etc.), each determination of MMP for one oil sample took about 3 days to complete which is definitely rapid and cost-effective compared to costly and time-consuming slim-tube testing.

It is worth mentioning here that it was the first reported study that conducted the physical VIT experiments for an actual live (recombined) reservoir crude oil and pure CO_2 using the experimental procedure described by Ayirala [13] and Ayirala and Rao [14]. The measured VIT MMP was found to be little lower (~4%) compared to the estimated MMP obtained in a separate and independent EOS simulation study based on the vanishing tie-line method.

2.9. Awari-Yusuf [31]. Awari-Yusuf [31] used the VIT technique to estimate the FCMP of the different gas + crude oil systems from the measured IFT data. In the experimental procedure used by Awari-Yusuf, the view cell was filled with gas (CO_2 or N_2) until the predetermined pressure was reached. Then, a crude oil pendant drop was formed in the gas phase. A digital image of each drop was taken and stored on the computer hard drive. The DSA software was used for determining the IFT from the pendant drop profile. The IFT of each crude oil drop was measured and the drops were replaced five times as old drops were withdrawn from the capillary and new drops were created to ensure repeatability and accuracy of the data. The measurements were done within five to ten seconds of contact with the gas phase. At the end and the beginning of each test, the entire system was cleaned. Awari-Yusuf used a laboratory Pycnometer for determining the crude oil density at desired temperatures. The densities of gas phases (CO_2 or N_2) at the pressure and temperature conditions of interest, that is, 0.7–4.1 MPa (100–600 psia) and 22°C (71.6°F) and 60°C (140°F), were calculated by using commercial software. Awari-Yusuf appropriately defined the pressure that corresponds to the zero IFT condition (obtained from the linear extrapolation of the measured IFT data) as the FCMP. However, use of the measured IFT data points that fall in the high IFT region (>5 mN/m) for determining the FCMP may significantly underestimate its value.

3. Discussion

3.1. Analysis of Published Physical VIT Experimentation Studies. Some of the experimental VIT studies used only the pendant drop method whereas others used a combination of the capillary rise technique and the pendant drop method. The experimental procedure employed by Yang and Gu [28] resembles to the procedure that was termed "first-contact" by Rao [12]. The use of an experimental procedure similar to a "first-contact" experiment led Yang and Gu [28] to conclude that there always exists a constant low equilibrium IFT as long as the pressure is higher than a threshold value. However their experimental procedure, being a "first-contact" experiment, signifies the absence of "multiple-contact" interactions.

According to Patil et al. [29], the VIT technique is not applicable for measuring very low IFT values. As miscibility or the critical point between fluid/fluid phases is approached, due to rapid diffusion of drops into the surrounding gas, it is difficult to measure the drop shape factor accurately. Though the experimental procedure used by Patil et al. [29] was similar to the VIT experimental procedure described by Ayirala [13] and Ayirala and Rao [14], the use of pendant drop technique restricted the IFT measurements in low IFT region. The use of the measured IFT data that is limited to high IFT region to determine the MMP is justifiable if the measured IFT continues to follow the same trend in low IFT region. As discussed by Yang and Gu [28], some CO_2 + hydrocarbon systems tend to exhibit two distinct IFT trends. Hence the reliance on the extrapolation of the measured IFT data that is limited to high IFT region may result in erroneous estimates of the miscibility condition (the FCMP or the MMP).

In case of pendant drop technique, both "first-contact" and "multiple-contact" IFT measurements are possible; however an optical cell fitted with one needle cannot provide good

IFT measurements in low IFT range due to irregular drop profiles. In light of two distinct IFT trends exhibited by some CO_2 + hydrocarbon systems, extrapolation of the measured IFT data limited to high IFT region may result in erroneous estimates of the MMP if a different trend is present in low IFT region.

As mentioned earlier, in addition to the pendant drop technique, the full scale VIT technique also uses the capillary rise technique for performing the IFT measurements in low IFT region. The capillary rise technique is by default a "multiple-contact" IFT measurement technique as it requires some liquid phase at the bottom of the optical cell for observing capillary rise. However use of the capillary rise technique alone still will require introduction of fresh oil and fresh gas into the system (e.g., use of separate entry ports) which is essential for covering the entire range of gas-oil interaction occurring in the displacement of reservoir oil by injection gas.

As demonstrated by Hsu et al. [9], limitation of single needle pendant drop IFT optical cell in measuring ultralow IFT (<0.01 mN/m) was overcome by mounting several needles of varied diameters on a rotating turret. In a similar fashion, both the accuracy of the IFT measurements in low IFT region and the range of the IFT measurements (e.g., 10 mN/m to 0.001 mN/m) can be further increased by placing multiple capillary tubes at the bottom of the optical cell. A combination of the pendant drop technique and the capillary rise technique, as demonstrated by Sequeira [15], also facilitates both types (i.e., the FCMP and the MMP) of VIT tests in a single experiment.

The physical VIT experimentation studies use the IFT versus pressure curves to determine the MMP. However, direct measurements of equilibrium phase densities of both liquid and vapor phases are needed to calculate the IFT values needed for obtaining such curves. In case of the FCMP, pure phase densities are needed to perform similar calculations. The pure phase densities are relatively easy to measure; however, measurement of the equilibrium liquid and vapor phase densities adds another level of experimental complexity and uncertainties to the physical VIT experimentation.

In the early 60s, Stegemeier et al. [36] experimentally determined the IFT divided by the difference in density between the liquid and the vapor phases (normal decane-methane system) by directly determining the IFT versus density difference term from the shape of pendant drop. This approach was adopted to eliminate the need to measure the phase density values for calculating the IFT. In a similar manner, can the measured height obtained from the images of capillary rise (e.g., Figures 6 and 7 of Saini and Rao [17]) be used for plotting capillary height versus pressure curve? This can potentially eliminate the need of measurement of the equilibrium phase densities for deducing the MMP from the IFT versus pressure curve. However, the robustness of such approach needs to be tested first.

3.2. Applicability of the Height of Capillary Rise versus Pressure Curves in Determining the MMP. The equations governing the capillary rise in a circular glass tube are well known. The force balance in a capillary is given by

$$2\pi r\gamma\cos\theta = \pi r^2 h\left(\rho_l - \rho_v\right) g. \tag{1}$$

Solving for interfacial tension (γ) gives

$$\gamma = \frac{rh\left(\rho_l - \rho_v\right) g}{2\cos\theta}, \tag{2}$$

where γ is the interfacial tension (mN/m) between oil and gas phase and ρ_l and ρ_v are the densities (g/cm^3) of liquid and gas phase, respectively. r is the internal radius of capillary tube (cm), h is height of capillary rise (cm), $\cos\theta$ is the equilibrium contact angle in degrees, and g is acceleration due to gravity.

On rearranging (2), we can get

$$\frac{\gamma}{\left(\rho_l - \rho_v\right)} = h\frac{rg}{2\cos\theta}. \tag{3}$$

As can be seen in (3), the left hand side term (i.e., "IFT/density difference") is directly proportional to the height of capillary rise observed in a given size capillary tube as the rest of the terms appearing on the right hand side of (3) are constant. Hence, if the height of capillary rise versus pressure data is plotted and extrapolated to zero IFTs, the corresponding value of the pressure (MMP) should be similar to the value determined from the extrapolation of the conventional IFT versus pressure. The applicability of such scheme is tested below using the published data [16, 17].

In the first case (Figure 3), the MMP value obtained from the height of capillary rise versus pressure curve and the value obtained from the conventional IFT versus pressure plot reasonably matched. A difference of 1.6% was observed between the two values. However in another case (Figure 4) the difference between the two values was found to be 12%. In this case, due to nonlinear nature of the IFT versus pressure data, the conventional IFT versus pressure data was plotted in terms of IFT versus 1/pressure and the resultant linear trend was then extrapolated to zero IFTs (Figure 4(a)) whereas the height of capillary rise versus pressure data did not need such manipulation (Figure 4(b)). These observations suggest that the use of capillary height rise versus pressure curve can result in significant errors in the prediction of the MMP. The results suggest that such approach may not necessarily eliminate the need of measured phase densities data in the VIT experimentation.

3.3. Analysis of Published Numerical VIT Experimentation Studies. As far as the numerical VIT experimentation studies reported in the published literature are concerned, the majority of these studies [19, 25, 27, 34, 37] rely on the equilibrium phase compositions and densities data generated by performing equation of state (EOS) based phase equilibrium calculations not on experimentally measured equilibrium phase densities and composition data. Use of EOS for predicting densities of the equilibrium liquid and vapor phases, needed for parachor modeling, may not necessarily predict the measured densities with sufficient accuracy, even for simple and well characterized multicomponent standard

CO_2 + hydrocarbon systems (e.g., Figure 12 of Orr Jr. and Jessen [34]). A significant deviation between the experimentally measured and the calculated IFT versus pressure trends even for standard CO_2 + hydrocarbons mixtures has also been observed (e.g., Figure 13 of Orr Jr. and Jessen [34]; Figure 61 of Ayirala [13]).

Hsu et al. [9], Nagarajan and Robinson Jr. [10], Nagarajan et al. [8], and Gasem et al. [38] were among early researchers who used the experimentally measured input data (phase compositions and densities of the equilibrium liquid and vapor phases) to model the experimental IFT behaviors of complex but standard CO_2 + hydrocarbons systems using a basic parachor expression. Ayirala and Rao [26] proposed a mechanistic parachor model to include mass transfer effects for predicting gas-oil IFT in complex CO_2 + hydrocarbon systems. However, Orr Jr. and Jessen [39] stressed that the difference between the VIT estimated MMP and the MMP obtained in Zick's experiments, for example, arises from the fact that, for some mixture compositions, two phases with nonzero IFT persist to pressure far above the MMP, not from inaccuracy in the calculated IFT.

On the other end, mechanistic parachor model based MMP estimates for Zick's Oil A + Gas A system presented by Ashrafizadeh and Ghasrodashti [27] indicate that the mechanistic parachor model can predict MMP within an acceptable range of accuracy. However, due to the formation of saturated mixtures at the reservoir temperature, Ashrafizadeh and Ghasrodashti were not able to do flash calculations for certain feed mixture compositions. It resulted in the termination of IFT calculations at either the bubble point pressure or the dew point pressure of the feed mixture. In view of the numerical constraint, Ashrafizadeh and Ghasrodashti [27] used a mixture consisting of 10 mol% of Zick's Oil 1 (Oil A) and 90 mol% of Gas 1 (Gas A) to calculate the IFT behavior using the PREOS and mechanistic parachor model. The predicted VIT MMP was found to be 15.4 MPa (2233.5 psia) which is in excellent agreement with the measured slim-tube MMP.

It is interesting to note that, in case of 20 + 80 system, use of the PREOS coupled basic parachor expression results in a saturation pressure (the termination point) of 12.8 MPa (1862 psia) and a calculated IFT around 14 mN/m, whereas use of the PREOS coupled mechanistic parachor model results in a saturation pressure of 14.8 MPa (2146.5 psia) and an IFT value close to 2 mN/m. In case of 50 + 50 system, parachor model prediction is terminated at a saturation pressure of 17.7 MPa (2572 psia) with an IFT value around 3.5 mN/m whereas mechanistic parachor model prediction is terminated at a saturation pressure of 14.4 MPa (2088.5 psia) with an IFT value of 1 mN/m. A reasonable agreement between mechanistic parachor model predictions of the saturation pressures (termination points) of 20 + 80 and 50 + 50 systems, again, substantiates the experimental observations made by Sequeira et al. [16] that the IFTs for different feed mixtures vary with the gas/oil ratio; all of them would eventually converge nearly to the same point of the zero IFTs yielding similar VIT MMP.

The abovementioned results of Ashrafizadeh and Ghasrodashti [27], again, highlight the common limitation of cubic EOS that the cubic EOSs either are not able to perform flash calculations for certain mixtures or are not able to predict the equilibrium fluid phase densities in the near-critical region. The same observation can be made for the results (Figure 24) reported by Schechter and Guo [33] where the computation algorithm in the PREOS did not converge. A comparison between the results of Ashrafizadeh and Ghasrodashti [27] and Orr Jr. and Jessen [34] presented above also suggests that significant error may occur in the prediction of the VIT condition from an VIT approach that employs a cubic EOS coupled with basic parachor expression for modeling the IFT behaviors of complex CO_2 + hydrocarbon systems.

Based on the numerical analysis of pressure dependence of IFT behaviors of several complex CO_2 + reservoir crude oil systems (i.e., numerical VIT experimentation), Jessen and Orr Jr. [37] concluded that additional experimental information would be required to select the optimal cell-mixture composition that would give a reasonably accurate estimate of the MMP by extrapolated CO_2 + oil IFT versus pressure curve to zero IFTs. Their results appear to suggest that composition of CO_2/oil mixture is a priori if measured pressure dependence of CO_2 + oil IFT behaviors is to be used for determining MMP with confidence. In their analyses of numerical VIT experiments for ternary and quaternary systems using the EOS coupled basic parachor expression, Orr Jr. and Jessen [34] were intrigued by reported measurement of IFT [14] at pressures above the bubble point pressure of a CO_2 + hydrocarbon mixture for which simulated VIT curve was terminated at bubble point pressure.

As suggested by Ashrafizadeh and Ghasrodashti [27], it appears that the formation of saturated mixtures that make it impossible to perform flash calculations results in termination of calculations at saturation pressures. In contrast to the calculation procedures, it is the formation of saturated fluid phases that facilitates the IFT measurements in physical VIT experiments. Unlike the calculated IFT behaviors that may be terminated at the bubble point/dew point pressures of the feed mixture compositions, results (Figure 24) reported by Ayirala and Rao [14] suggest that the experimental IFT measurements can be performed for any chosen feed mixture composition.

Sequeira et al. [16] experimentally examined the compositional path effects on CO_2 + oil IFT and miscibility. According to them, the gas-oil IFT measured at various gas-oil ratios at reservoir temperature, although displaying different relationships with pressure, converged to almost the same end-point pressure at zero IFTs. In spite of the large variations in the initial mixture compositions, only negligible changes in VIT miscibility pressures were observed.

Unfortunately, for complex CO_2 + crude oil systems of petroleum engineering interest, experimentally measured data needed to perform parachor expression based numerical modeling are not readily available in the published literature. Sequeira [15] and Sequeira et al. [16] reported the equilibrium phase densities and compositions, pure phase densities, crude oil composition, and molecular weight of the equilibrium liquid phase for various feed mixtures while inferring the MMP of a complex supercritical CO_2 + live crude oil system from the observed trends of pressure dependence of IFT behaviors.

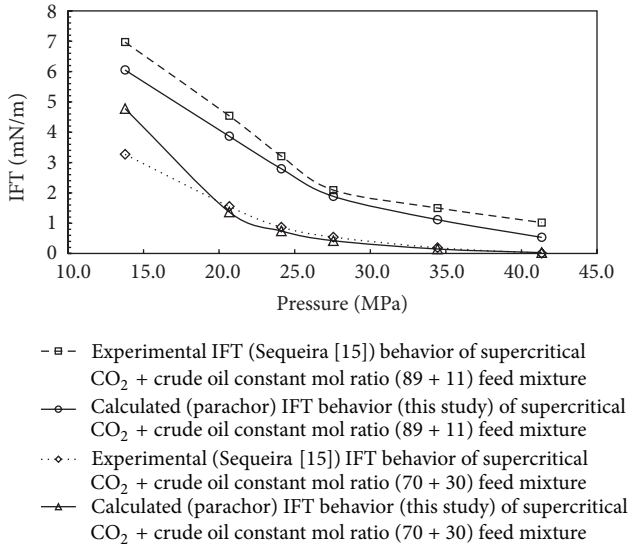

Figure 1: Comparison of the calculated IFT behaviors (parachor based, this study) with the experimental IFT [15, 16] at 114.4°C (238°F) for two CO_2 + crude oil constant mol ratio (89 + 11, 70 + 30) feed mixtures of CO_2 + crude oil system reported by Sequeira [15]; Sequeira et al. [16].

In this study, basic parachor expression based modeling of pressure dependence of experimental IFT behaviors of the systems reported by Sequeira [15] and Sequeira et al. [16] has been performed.

3.4. Use of Experimentally Measured Input Data for Modeling of the Experimental IFT Behaviors. As can be seen in Figure 1, though calculated IFT behaviors show significant deviation from the experimental IFT behaviors in high IFT region, difference between the calculated and the experimental behaviors appears to vanish in low IFT region (<1 mN/m) and the calculated behaviors follow the experimental behaviors more closely. A comparison of the deviations observed between the VIT MMPs obtained from linear extrapolation of the calculated IFT behaviors and the experimental VIT MMP is given in Table 3. As can be seen in Table 3, the parachor VIT MMPs obtained from extrapolation of the curve consisting of IFT data points with value <1 mN/m reasonably match with the experimental VIT MMPs. These modeling results also demonstrate the compositional independence of the VIT MMP. Secondly, these results also suggest that the parachor model based calculated IFT behavior trends consisting of low IFT region (<1 mN/m) data points may provide a reasonable estimate of the MMP if measured phase densities and compositions are utilized.

Gasem et al. [38] mentioned that, in gas EOR processes, such as CO_2 injection, sufficiently low IFT levels (less than approximately 0.04 dyne/cm (mN/m)) occur only when the CO_2/oil mixtures that develop during the displacement process approach the mixture critical composition at reservoir temperature and pressure conditions. In case of feed mixtures tested by Sequeira [15] and Sequeira et al. [16], at least one feed mixture (89% CO_2 + 11% oil, constant mol ratio) appears

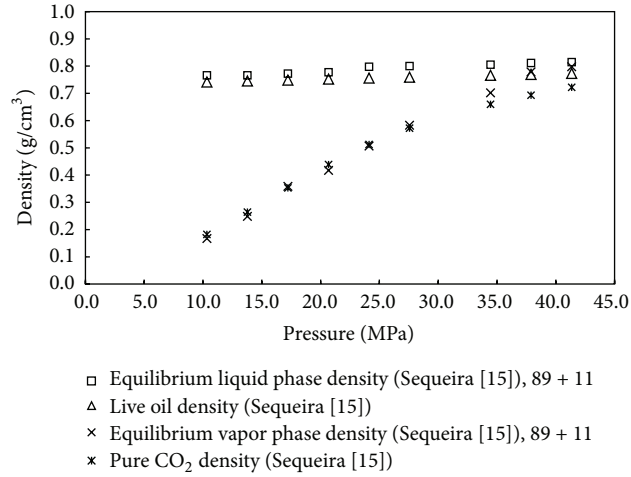

Figure 2: Measured equilibrium and pure phase densities at 114.4°C (238°F) for constant mol ratio (89 + 11) feed mixture of CO_2 + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

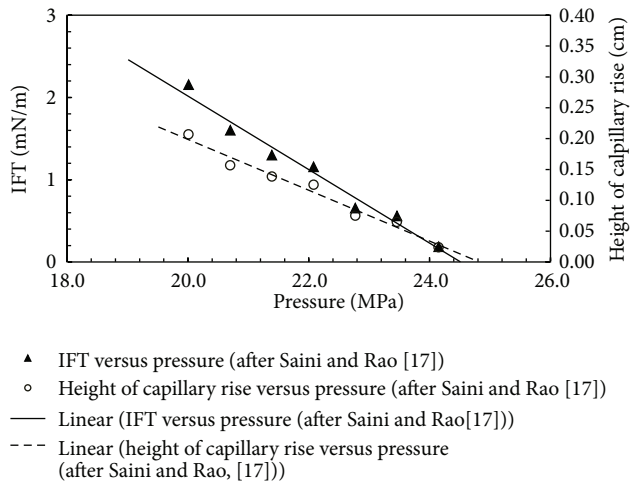

Figure 3: Comparison of the conventional IFT versus pressure curve with the height of capillary rise curve for a CO_2 + crude oil system investigated by Saini and Rao [17].

to attain critical composition at the highest experimental pressure of 41.3 MPa as evident from negligible difference between the equilibrium liquid and vapor phase densities (Figure 2).

As can be seen from the results shown in Table 4, despite the fact that the equilibrium liquid and vapor phase densities for the rest of the tested feed mixtures did not reach a single value at the highest experimental pressure, both measured and calculated IFTs for two of the feed mixtures were still fairly low and close to the IFT values shown by the mixture that seemed to attain critical composition. The calculated IFT trends for all of the feed mixtures converged to almost the same end-point pressure at zero IFTs as evident from little deviation in the measured and the calculated VIT MMPs (Table 4). These observations also reinforce the compositional independence of the VIT experimentation whether physical or numerical.

Table 3: Deviation of the experimental VIT MMP [15, 16] and the calculated (parachor based, this study) VIT MMP at 114.4°C (238°F) for constant and variable mol ratio feed mixtures of CO_2 + live crude oil system reported by Sequeira [15] and Sequeira et al. [16].

System	System type	Highest experimental pressure (MPa)	Deviation of the calculated (parachor) VIT MMP from the measured VIT MMP (%) IFT data points in low IFT region (<1 mN/m)
89 + 11	Constant mol ratio	41.3	−1.0
70 + 30	Constant mol ratio	41.3	−8.3
88–95 mol% CO_2	Variable mol ratio (constant volume ratio: 85 + 15)	34.5	+5.5
53–74 mol% CO_2	Variable mol ratio (constant volume ratio: 45 + 55)	41.3	−3.7

Table 4: Comparison of the experimental IFT [15, 16] at the highest experimental pressure with the calculated (parachor) IFT values (this study) at 114.4°C (238°F) for constant and variable mol ratio feed mixtures of CO_2 + live crude oil system reported by Sequeira [15] and Sequeira et al. [16].

Mol ratio of supercritical CO_2 + live crude oil in feed mixture	Type	Highest experimental pressure (MPa)	Measured IFT value (mN/m) [15, 16]	Calculated IFT value (mN/m) (this study)
89 + 11	Constant mol ratio	41.3	0.01	0.018
70 + 30	Constant mol ratio	41.3	0.01	0.029
88–95 mol% CO_2	Variable mol ratio (constant volume ratio: 85 + 15)	34.5	0.65	0.177
53–74 mol% CO_2	Variable mol ratio (constant volume ratio: 45 + 55)	41.3	0.02	0.030

3.5. Potential Alternatives to Physical and Numerical VIT Experimentation Procedures. Recently reported comparison [40] of experimental VIT measurements with slim-tube test for discussing the accuracy of both tests at various scenarios especially when both tests rely on very different principle seems to be another important step towards evaluating the robustness of VIT experimentation for determining the MMP. On the other hand, there are some attractive experimental alternatives to physical VIT experimentation that have recently been reported in the published literature.

Nguyen et al. [20] used a microfluidic approach for measuring CO_2-in-oil MMP at reservoir-relevant temperatures and pressures in which mixing of continuously generated CO_2 bubbles within a microchannel embedded in silicon is observed quantitatively, leveraging the inherent fluorescence of crude oil sample. According to them, as the pressure was increased to MMP, the interfacial tension decreased and the injected CO_2 bubbles deformed readily in response to flow induced stresses. Specifically, round nose-shaped bubbles were formed with trailing boundaries that were rapidly eroded as they mixed with the continuous oil phase, unimpeded by interfacial tension. Above MMP, mixing is rapid, and the two phases are largely indistinguishable at the downstream location. At the injector, distinct phases are observed at pressures moderately above MMP and progressively less so as interfacial tension vanishes with increasing pressure. The formation of two distinct phases at injector even at pressures higher than MMP makes perfect sense as continuous flow of fresh oil and continuous injection of fresh CO_2 at injector will always replicate the "first-contact" conditions. However, at the downstream location, the two phases become largely indistinguishable due to "multiple-contact" because incoming fresh CO_2 continually interacts with residual live crude oil and CO_2 mixed oil moves forward to contact fresh live oil.

The method used by Nguyen et al. [20] provides visual evidence of attainment of zero IFT condition (i.e., disappearance of two distinct phases) as two phases become largely indistinguishable at the downstream location. The mixing of the two phases enhanced by flow induced stresses in microchannel also seems to replicate the gas-oil interactions that are critical at the MMP in a displacement in a porous medium and are expected to occur in standard slim-tube tests. However, use of this technique needs to be further evaluated for the systems that may exhibit condensing or mixed (condensing + vaporizing) drive mechanisms for attaining complete multicontact miscibility. Their method also eliminates the need of direct density measurement as it relies on change in system's fluorescence for quantitative measurement of MMP.

Recently, Georgiadis et al. [41] used a density functional theory (DFT) based on the statistical associating fluid theory-variable range (SAFT-VR) equation of state (EOS) for modeling the experimental IFT behaviors of standard CO_2 + hydrocarbon systems. The use of a density functional theory (DFT) based on the statistical associating fluid theory-variable range (SAFT-VR) EOS appears to provide a good description of the bulk fluid phases for standard CO_2 + hydrocarbon systems. The results are encouraging; however capability of the DFT-SAFT-VR EOS for modeling of the IFT

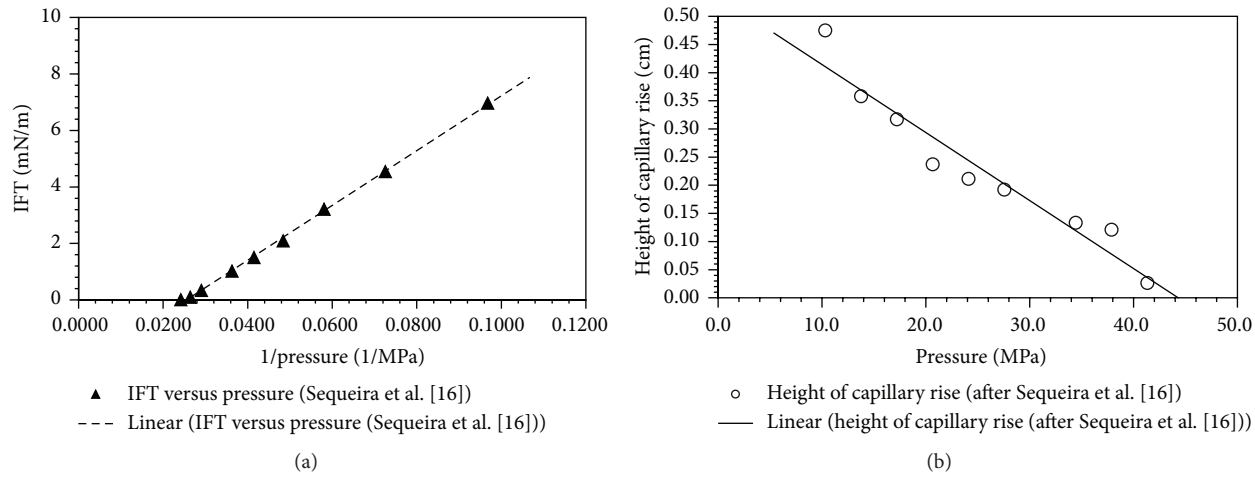

Figure 4: Comparison of the IFT versus 1/pressure curve (a) with the height of capillary rise curve (b) for a CO_2 + crude oil system at 114.4°C (238°F) investigated by Sequeira [15]; Sequeira et al. [16].

behaviors of complex CO_2 + hydrocarbon systems still needs to be evaluated.

4. Summary, Conclusions, and Recommendations

Some of the reported physical VIT experimentation studies appear to follow a portion of full scale VIT experimentation (i.e., a combination of the pendent drop method and the capillary rise technique). The use of the pendant drop method for measuring the gas-oil IFT without placing a small amount of initial oil appears to be a "first-contact" experiment and signifies the absence of "multiple-contact" interactions. Hence the measured IFT versus pressure trend observed is more correlatable to the FCMP compared to the MMP.

Also, some CO_2 + crude oil systems tend to exhibit two distinct trends and the reliance on pendant drop method alone for making interfacial tension (IFT) measurements may limit data acquisition in low IFT (<1 mN/m) region. The reliance on the extrapolation of the measured IFT data that is limited to high IFT region (>1 mN/m) may result in erroneous estimates of miscibility conditions (first-contact or multiple-contact).

Some of the physical VIT experimentation studies have used the equation of state- (EOS-) calculated fluid phase densities which is well justified for the "first-contact" VIT experiments; however, for the "multiple-contact" VIT experiments, use of measured fluid phase densities (especially the equilibrium vapor phase densities) makes more sense as the EOS models may not predict the equilibrium fluid phase densities very well in the neighborhood of a critical point.

In some reported physical VIT experimentation studies, IFT measurements at various pressure steps were conducted in a single experiment compared to other studies in which individual IFT data points at various pressures were obtained by means of individual experiment at a given pressure step.

The physical VIT experimentation method in which the IFT measurements are made at varying pressures but with the same initial load of live oil and gas phases in the optical cell seems to be the most robust mechanistic procedure for experimentally studying the pressure dependence of IFT behaviors of complex CO_2 + crude oil systems and thus determining the MMP using the VIT technique. A combination of the pendant drop method and the capillary rise technique also facilitates the measurements of both the FCMP and the MMP in a single VIT experiment.

The results presented here suggest that basic parachor expression based calculated IFT behaviors can reasonably follow the experimental IFT behaviors of complex supercritical CO_2 + live crude oil systems in low IFT region, if measured input data such as equilibrium phase densities and compositions are used in calculations. Despite the large variations in the feed mixtures' compositions, both the calculated and the experimental IFT behaviors show low IFT values (ranging from 0.01 mN/m to 0.03 mN/m) and converged to almost the same end-point pressure at zero IFTs resulting in a reasonable match between the measured and the calculated VIT MMP. These results also reinforce the compositional independence of physical VIT experimentation.

Recently reported fast fluorescence-based microfluidic method and DFT-SAFT-VR EOS appear to be attractive alternatives to physical and numerical VIT experimentation, respectively. The microfluidic method also eliminates the need of direct density measurement required for IFT experiments as it relies on change in system's fluorescence for quantitative measurement of MMP. However, robustness of these methods in determining the MMP of complex CO_2 + hydrocarbon systems, especially the systems exhibiting condensing or mixed (condensing + vaporizing) drive mechanisms, for attaining complete multicontact miscibility is yet to be tested.

Lastly, collection of a variety of experimentally measured data such as phase densities, phase compositions, and molecular weight in physical VIT experiments appears to be necessary for reliable estimates of MMP by the physical VIT

experimentation as well as for obtaining MMP by means of numerical VIT experimentation.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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