Modeling of Pressure Dependence of Interfacial Tension Behaviors of a Complex Supercritical CO₂ + Live Crude Oil System Using a Basic Parachor Expression

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Abstract

Parachor based basic expressions are often used to model the experimentally observed pressure dependence of interfacial tension (IFT) behaviors of complex supercritical CO₂ + crude oil (dead or live) mixtures at elevated temperatures. However, such modeling requires compositions and densities of the equilibrium liquid and vapor phases and molecular weights of various components present in the system. In the absence of measured data, often phase behavior packages are used for obtaining these input data for performing calculations. Very few researchers have used experimentally measured input data for performing parachor based modeling of the experimental IFT behaviors of complex supercritical CO₂ + live crude oil systems.

This study presents the results of a basic parachor model based modeling of pressure dependence of IFT behaviors of a complex supercritical CO₂ + live crude oil system for which experimentally measured input data is available in public domain. Though the calculated IFT behaviors showed significant deviation from the experimentally measured behaviors at a given pressure, calculated IFT versus pressure trends appeared to follow the experimental observed trends closely. Also, despite a large variation in the compositions of feed supercritical CO₂ + live crude oil mixtures, both trends (calculated and experimental) converged rapidly to attain a near zero IFT condition at more or less same pressure.

Keywords: Super-critical; Crude oil; Parachor

Introduction

In the CO₂ injection based enhanced oil recovery (EOR) operations; injected supercritical CO₂ interacts with reservoir crude oil in a multiple-contact fashion to develop a low IFT condition between the two phases that plays a crucial role in achieving low residual oil saturation. In case of oil reservoirs, depending on the pressure, temperature, and composition of the gas and oil, injection of supercritical CO₂ can be under either immiscible or miscible modes. As described by Al-Mjeni et al. [1], “in an immiscible flood, gas and oil remain distinct phases. Gas invades the rock as a nonwetting phase, displacing oil from the largest pores first. However, when they are miscible, gas and oil form one phase. This mixing typically causes the oil volume to swell while lowering the IFT between the oil phase and water. Displacement by miscible-gas injection can be highly efficient for recovering oil”. Wallace et al. [2] state that “as reservoir pressure enters the near-miscible range (0.8 to 0.95 of minimum miscibility pressure), the vaporization of light hydrocarbon components from the crude oil into the CO₂ vapor phase begins, the mixing of CO₂ and oil phases progresses, and the IFT of the system is lowered, all contributing to improved oil recovery efficiency”. It had prompted researchers to experimentally investigate and theoretically model the pressure dependence of complex supercritical CO₂ + crude oil systems at elevated pressures and temperatures.

Hsu et al. [3], Nagarajan and Robinson [4], Nagarajan et al. [5], and Gasem et al. [6] are 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 supercritical CO₂ + hydrocarbon systems using a basic parachor expression. Based on Modern physics and an experimental database, Schechter and Guo [7] suggested the use of a critical scaling exponent 3.88 in the parachor equation. The also obtained new parachors of pure substances commonly encountered in petroleum fluids. They tested newly developed pure-component parachors, paracrhal correlations, and oil-cut parachors for IFT predictions with six reservoir oil/CO₂ mixtures. They used the Peng-Robinson equation of state (PREOS) for computing vapor- and liquid-phase densities of the six fluids. They noted that only for one system measured density data was available. Comparison between the measured and PREOS-computed densities for oil VI + CO₂ system (recombined oil plus 55.55 mol.% CO₂) indicated that the difference between them increases as pressure increases. It is important to note that above certain pressure (14.9 MPa (2,160 psia) in case of oil VI system) the computation algorithm in the PREOS did not converge. According to them, using the new parachors and correlations with parachor method, IFT’s of reservoir fluids can be predicted with the PREOS with an acceptable error.

Ayirala and Rao [8,9] proposed a mass transfer enhanced mechanistic parachor model to predict gas-oil IFT at elevated pressures and temperatures. 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 experimentally observed pressure dependence of IFT behaviors and the mechanistic model predictions. Nobakht et al. [10] 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. According to them, the comparison of the predicted equilibrium IFTs from the paracho model and the measured data shows that, in general, the paracho model poorly predicts the equilibrium IFTs between the crude oil and CO$_2$ in the equilibrium pressure range tested. On the other hand, the predicted equilibrium IFTs from the LGT model are in excellent agreement with the measured data.

Recently, Georgiadis et al. [11] carried out interfacial tension measurements for three (n-alkane + supercritical CO$_2$) systems for temperatures ranging from 298 K (24.9°C) to 443 K (170.9°C) and pressures up to the critical points of each system and 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. The DFT based SAFT-VR EOS based IFT estimates in high IFT region are in excellent agreement with the experimental measurements. However, it is not clear if such analyses have also been extended to low IFT region and more complex supercritical CO$_2$ + hydrocarbon systems.

It is worth to mention here that there are several studies (both the experimental [9,12-19] and the paracho expression based modeling [7-10, 20-23]) which have used the pressure dependence of IFT behaviors of CO$_2$ + crude oil systems to infer the minimum miscibility pressure (MMP). However, present study is only limited to perform basic paracho expression based modeling for predicting pressure dependence of IFT behaviors of complex supercritical CO$_2$ + live crude oil systems.

Unfortunately, in case of complex supercritical CO$_2$ + live crude oil systems, experimentally measured data needed to perform paracho expression based modeling or any other modeling methods such as mechanism paracho model or LGT are not readily available in the published literature. Sequeira [13]; Sequeira et al. [14] 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. The present study uses the experimental data reported by Sequeira [13]; Sequeira et al. [14] for predicting the pressure dependence of IFT behaviors of this complex supercritical CO$_2$ + live crude oil system. The experimental IFT behaviors of various feed mixtures tested by Sequeira [13] are predicted using a version of the paracho model described by Schechter and Guo [7]. The paracho model described by Schechter and Guo [7] uses a scaling exponent of 3.88. The results are presented and discussed next.

The Calculated IFT Behaviors of Supercritical CO$_2$ + Live Crude Oil System Tested by Sequeira [13]; Sequeira et al. [14]

Sequeira [13], Sequeira et al., [14] performed physical measurements for a supercritical CO$_2$ gas + live crude oil system to examine the effect of feed mixture composition on the pressure dependence of IFT behaviors. The experiments were conducted for two constant composition (i.e. 70 + 30, and 89+11 mol.% of CO$_2$ and live crude oil and two constant volume (i.e. 45 + 55, and 85 + 15 volume% of CO$_2$ and live crude oil) feed mixtures at reservoir temperature of 114.4°C. The constant volume feed mixtures tested by them correspond to variable composition (mol.) feed mixtures. In case of first variable composition feed mixture, CO$_2$ composition varied from 88 to 95 mol.% (i.e. 12 to 5 mol.% live crude oil). For second mixture, CO$_2$ composition varied from 52 to 74 mol.% (i.e., 48 to 26 mol.% live crude oil).

While performing physical IFT measurements, Sequeira also experimentally measured the equilibrium properties (gas and liquid phase compositions of various components, equilibrium gas and liquid phase densities, molecular weight of C7+ fraction in both liquid and gas phases). Readers are referred to Tables 1 and 2 of Sequeira et al. [14] for further details on above mentioned experimentally collected data.

However, apart from the equilibrium properties (phase compositions and densities), the paracho based modeling of pressure

| Mol Ratio of Supercritical CO$_2$ + Live Crude Oil in Feed Mixture | Type                          | Highest Experimental Pressure (MPa) | Measured IFT value (mN/m) (Sequeira [13]; Sequeira et al. [14]) | Calculated IFT value (mN/m) (This Study) | Absolute Deviation between the experimental and the calculated IFT (%) |
|---------------------------------------------------------------|-------------------------------|-----------------------------------|---------------------------------------------------------------|-----------------------------------------|---------------------------------------------------------------------|
| 89 + 11 Constant mol ratio                                    | 41.3                          | 0.01                              | 0.018                                                         | 84.7                                     |
| 70 + 30 Constant mol ratio                                    | 41.3                          | 0.01                              | 0.029                                                         | 186.9                                    |
| 88 -95 mol % CO$_2$ Variable mol ratio (constant volume ratio: 85+15) | 34.5                          | 0.65                              | 0.177                                                         | 72.7                                     |
| 53 -74 mol % CO$_2$ Variable mol ratio (constant volume ratio: 45+55) | 41.3                          | 0.02                              | 0.030                                                         | 50.2                                     |

Table 1: Comparison of the experimental IFT (Sequeira [13]; Sequeira et al. [14]) at highest experimental pressured with the calculated (paracho) 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 [13]; Sequeira et al. [14].

| Mol Ratio of Supercritical CO$_2$ + Live Crude Oil in Feed Mixture | Type                          | Highest Experimental Pressure (MPa) | Measured IFT value (mN/m) (Sequeira [13]; Sequeira et al. [14]) | Calculated IFT value (mN/m) (This Study) | Difference between measured densities of the equilibrium liquid and vapor phases, g/m$^3$ (Sequeira [13]; Sequeira et al. [14]) |
|---------------------------------------------------------------|-------------------------------|-----------------------------------|---------------------------------------------------------------|-----------------------------------------|---------------------------------------------------------------------|
| 89 + 11 Constant mol ratio                                    | 41.3                          | 0.01                              | 0.018                                                         | 0.0165                                  |
| 70 + 30 Constant mol ratio                                    | 41.3                          | 0.01                              | 0.029                                                         | 0.1014                                  |
| 88 -95 mol % CO$_2$ Variable mol ratio (constant volume ratio: 85+15) | 34.5                          | 0.65                              | 0.177                                                         | 0.1722                                  |
| 53 -74 mol % CO$_2$ Variable mol ratio (constant volume ratio: 45+55) | 41.3                          | 0.02                              | 0.030                                                         | 0.0788                                  |

Table 2: Difference between measured densities of the equilibrium oil and vapor phases at 114.4°C (238°F) for constant and variable mol ratio feed mixtures of CO$_2$ + live crude oil system reported by Sequeira [13]; Sequeira et al. [14].
dependence of IFT behaviors also requires pure and oil-cut (C7+ fraction) parachors. In the calculations presented here, C7+ fraction parachors were calculated using three different parachor correlations (Equations 10-12) discussed in Schechter and Guo [5]. The pure component parachors suggested by Schechter and Guo [7] were used in the calculations of C7+ fraction parachors. The equilibrium liquid phase (C7+ fraction) molecular weights measured at various pressures (Tables 1 and 2 of Sequeira et al. [14]) were used to determine C7+ fraction parachor. Among all correlations, Equation 11 of Schechter and Guo [7] provided the lowest parachor values. The same was used in the calculations.

Both the calculated and the experimental IFT behaviors of feed mixtures tested by Sequeira [13]; Sequeira et al., [14] are plotted in Figures 1, 3, 5, and 7. Corresponding densities of the equilibrium oil and vapor phases along with densities of pure live oil and pure supercritical CO2 at various pressures are shown in Figures 2, 4, 6 and 8. For a more close comparison between the calculated and the experimental IFT behaviors, IFT versus 1/Pressure plots were also generated (Figures 8-12). The results are compared next.
in the densities of the equilibrium phases (oil and vapor) from the densities of the pure phases is observed (Figures 2, 4, 6, and 8) in low pressure (high IFT) region. Despite densities of the equilibrium phases showed a little deviation from densities of corresponding pure phases, IFT declined rapidly in low pressure region. It signifies the role of intermolecular interactions that is responsible for sharp decline in IFT with a significant mass transfer between the equilibrium phases. This can be further explained by example of the phenomenon that is regularly observed in the case of oil/water system. A sharp decline in oil/water IFT can be observed only by adding a small amount of a surfactant. According to Schechter and Guo [7], if a single drop of alcohol is added to an oil/water system, the alcohol will rapidly adsorb at the interface. The IFT will be significantly reduced, but the density difference between the bulk phases will change very little (Fig. 6 of Schechter and Guo [7]). As shown in Figure 7 of Schechter and Guo [7], in low IFT region, difference between the densities of the bulk phases starts to diminish and basic parachor expression is able to reliably predict the IFT behavior of the system (alcohol/oil/water). Similarly, in cases of supercritical CO2 + live crude oil feed mixtures modeled here, difference between the equilibrium vapor and liquid phase densities rapidly starts to diminish in high pressure (low IFT) region and the trend in high pressure region compared to a sharp decline in IFT that was observed in low pressure (high IFT) region was observed.

The above mentioned behavior is very similar to the IFT behaviors of oil/water system that they typically show in the presence of surfactant. According to Schechter and Guo [7], if a single drop of alcohol is added to an oil/water system, the alcohol will rapidly adsorb at the interface. The IFT will be significantly reduced, but the density difference between the bulk phases will change very little (Fig. 6 of Schechter and Guo [7]). As shown in Figure 7 of Schechter and Guo [7], in low IFT region, difference between the densities of the bulk phases starts to diminish and basic parachor expression is able to reliably predict the IFT behavior of the system (alcohol/oil/water). Similarly, in cases of supercritical CO2 + live crude oil feed mixtures modeled here, difference between the equilibrium vapor and liquid phase densities rapidly starts to diminish in high pressure (low IFT) region and the trend in high pressure region compared to a sharp decline in IFT that was observed in low pressure (high IFT) region was observed.
IFT behaviors show low IFT values (in the range of 0.01 mN/m to 0.03 mN/m) near critical point and the calculated IFT behaviors are able to reasonably follow the experimental IFT behaviors.

As can be seen in Figures 8-12 (IFT versus 1/Pressure plots), compositional independence or irrelevance of path taken for attaining near critical (signified by very low IFT) compositions is clearly visible from the convergence demonstrated by IFT versus pressure trends (both the experimental and the calculated) in high pressure region (IFT < 1 mN/m). Though, absolute variation between the individual IFT value measured at the highest experimental pressure (41.3 MPa) and corresponding calculated IFT value ranged from 50% to 187% (Table 1), both the calculated and the experimental IFT behaviors (IFT versus 1/Pressure), converged to more or less a same pressure value when extrapolated to zero IFT condition. In this scenario, deviation between the calculated pressure and the experimental pressure values that corresponded to zero IFT condition ranged from +5.5% to -8.3%. The difference between measured densities of the equilibrium oil and vapor phases at highest experimental pressure (41.3 MPa) and corresponding IFT values (experimental and calculated) are given in Table 2. As evident from the data presented in Table 2, at least one feed mixture (89 + 11) showed the lowest density difference of 0.0165 gm/cm³ at

calculated IFT behaviors start to follow the experimental IFT behaviors more closely.

Schechter and Guo [7] also emphasized that, near critical point, parachor model can reasonably predict the IFT behavior regardless of the path taken to the critical point. In case of CO₂ + live crude oil system studied in the present study, it appears that the critical point lies around 41.3 MPa (5990 psi) and 114.4°C (238°F) as suggested by a very low density difference between the equilibrium liquid and vapor phases for 89 +11 feed mixture (Figure 2 and Table 2). Three out of four feed mixtures, at highest experimental pressure of 41.3 MPa, show low density (experimentally measured) difference ranging from 0.017 gm/cm³ to 0.079 gm/cm³ between the equilibrium liquid and vapor phases. The low density difference between the equilibrium liquid and vapor phases is also signified from low IFT values shown by both the experimental (in range from 0.01 mN/m to 0.02 mN/m) and the calculated (in range from 0.018 mN/m to 0.030 mN/m) IFT behaviors. These observations suggest that despite the large variation in feed mixtures’ compositions, both the experimental and the calculated
highest experimental pressure of 41.3 MPa suggesting the attainment of near critical point condition from thermodynamic point of view. In cases of other three feed mixtures, the equilibrium oil and vapor phases showed a density difference in the range from 0.0788 gm/cm³ (53 - 74 mol.% CO₂) to 0.1722 gm/cm³ (89 - 95 mol.% CO₂). However it did not change the end result i.e. convergence of both the calculated and the experimental IFT behaviors to more or less a same pressure value when extrapolated to zero IFT condition. It demonstrates that not only the experimental IFT behaviors, but also the calculated IFT behaviors using a basic parachor expression can show compositional independence for achieving near critical condition, provided quality input data is used for modeling the pressure dependence of IFT behaviors of complex supercritical CO₂ + live crude oil systems.

It is emphasized here that the calculated IFT behaviors presented here used experimentally measured input data (i.e. the equilibrium phase compositions, phase densities, and molecular weight of the equilibrium liquid phase). More details on experimental procedure used for generating input data can be found elsewhere (Sequeira [13]). Recently, Saini [25] has provided a critical analysis of the robustness of the physical experimentation used by various researchers for studying pressure dependence of interfacial tension behaviors of complex CO₂ + crude oil systems.

Summary and Conclusions

The results presented here demonstrate that a basic parachor expression based modeling of the IFT behaviors of complex supercritical CO₂ + hydrocarbon systems can reasonably predict the experimentally observed IFT behaviors. Though, a significant deviation between the calculated and the experimental IFT versus pressure trends may still be observed in low pressure (high IFT) region but the calculated IFT versus pressure trend can still reasonably follow the observed experimental IFT versus pressure trend in high pressure (low IFT) region.

Despite the large variations in the feed mixtures’ compositions, both the calculated and the experimental IFT converged to more or less a same pressure value when extrapolated to zero IFT condition. It demonstrates that not only the experimental IFT behaviors, but also the calculated IFT behaviors using a basic parachor expression appear to exhibit the compositional independence for reaching to an extrapolated zero IFT condition.

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