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

Saini Dayanand*

California State University, Bakersfield, CA, USA.

(Received 25 October 2015, Accepted 11 December 2015)

Abstract

Parachor based expressions (basic and mechanistic) are often used to model the experimentally observed pressure dependence of interfacial tension (IFT) behaviors of complex supercritical carbon dioxide (sc-CO₂) and crude oil mixtures at elevated temperatures. However, such modeling requires various input data (e.g. compositions and densities of the equilibrium liquid and vapor phases, and molecular weights and diffusion coefficients for 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 sc-CO₂ and crude oil systems that are of particular interest to CO₂ injection in porous media based enhanced oil recovery (EOR) operations.

This study presents the results of parachor based modeling performed to predict pressure dependence of IFT behaviors of a complex sc-CO₂ and crude oil system for which experimentally measured data is available in public domain. Though parachor model based on calculated IFT behaviors shows significant deviation from the measured behaviors in high IFT region, difference between the calculated and the experimental behaviors appears to vanish in low IFT region. These observations suggest that basic parachor expression based calculated IFT behaviors in low IFT region follow the experimental IFT behaviors more closely. An analysis of published studies (basic and mechanistic parachor expressions based on modeling of pressure dependence of IFT behaviors of both standard and complex sc-CO₂ and crude oil systems) and the results of this study reinforce the need of better description of gas-oil interactions for robust modeling of pressure dependence of IFT behavior of these complex systems.

Keywords

CO₂ injection in porous media;
CO₂-EOR and storage;
CO₂-oil interactions;
Gas-oil interfacial tension;
Parachor model;
Miscibility.

* Corresponding Author.

E-mail: dsaini@csb.edu (S. Dayanand)

1. Introduction

In the CO₂ injection in porous media based enhanced oil recovery (EOR) operations; injected supercritical CO₂ (sc-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 sc-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 (MMP)), 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 contribute to improved oil recovery efficiency. It had prompted researchers to experimentally investigate and theoretically model the pressure dependence of complex sc-CO₂ and crude oil systems at elevated pressures and temperatures.

The study of pressure dependence of IFT behaviors of complex sc-CO₂ and crude oil systems is not only of particular interest to petroleum industry but also a reliable knowledge of the confined behavior of injected sc-CO₂ at the pressure and temperature conditions of reservoir which is greatly influenced by the fluid phase interfacial interactions of IFT between injected sc-CO₂ and reservoir fluids, is critical for implementing CO₂ storage projects in geologic reservoirs (depleted hydrocarbon bearing formations and deep saline sedimentary formations).

Hsu et al. [3], Nagarajan and Robinson [4], Nagarajan et al. [5], and Gasem et al. [6] are among early researchers who not only experimentally studied the pressure dependence of IFT behaviors of complex but standard sc-CO₂ + hydrocarbons systems but also used measured input data (phase compositions and densities of the equilibrium liquid and vapor phases) to model the experimental IFT behaviors of these complex but standard systems using a basic parachor expression. Based on modern physics and an experimental database, Schechter

and Guo [7] concluded that the use of new parachor and correlations developed by them with parachor method, IFT's of reservoir fluids can be predicted with the Peng-Robinson equation of state (PREOS) with an acceptable error.

Ayirala and Rao [8] 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. [9] used the parachor model and linear gradient theory (LGT) model for predicting the equilibrium IFT versus equilibrium pressure data of a crude oil-CO₂ system. According to them, the comparison of the predicted equilibrium IFTs from the parachor model and the measured data shows that, in general, the parachor model poorly predicts the equilibrium IFTs between the crude oil and CO₂ 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.

Ashrafizadeh and Ghasrodashti [10] presented a comparative study on five representative equations of state (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 non-suitable for scenarios which incorporate considerable amounts of polar components. In such cases, they suggested the use of more complicated EOSs such as electrolyte models.

However, reported modeling studies (e.g. Schechter and Guo, [7]; Orr Jr. and Jessen, [11]; Jessen and Orr Jr. [12]; Ashrafizadeh and Ghasrodashti, [10]; Tecklu et al., [13]) have relied on the EOS based phase equilibrium calculations while modeling the fluid phase interfacial interactions of IFT for complex sc-CO₂ and crude oil systems. The use of available EOSs for describing interfacial interactions of gas-oil IFT often results in significant deviation between the experimentally measured and the calculated IFT versus pressure trends even for standard sc-CO₂ and hydrocarbons mixtures (e.g. Fig. 13 of Orr Jr. and Jessen, [11]; Fig. 61 of Ayirala, [14]).

In their mechanistic parachor model, Ayirala and Rao [8] used the ratio of diffusivities between the fluid phases raised to an exponent to incorporate mass transfer effects in basic parachor expres-

sion. Again, a significant difference between the calculated (mechanistic parachor model) and the experimental IFT behavior of complex but standard sc-CO₂ and hydrocarbon system (Fig. 61 of Ayirala, [14]) at low pressure is still observed. Ayirala [14] used empirical correlation for computing diffusivity ratios in multicomponent hydrocarbon systems.

One of the possible reasons for observed disagreements between the experimental and the calculated IFT behaviors may be the reliance of these studies on the use of equilibrium phase compositions and densities data generated by EOSs based phase equilibrium calculations not the experimentally measured input data. This practice not only limits our efforts to better understand the underlying mechanisms of gas-oil interactions responsible for observed experimental IFT behaviors but it also hinders the development of robust yet simple mathematical methods that are capable of depicting these interactions accurately.

As evident from the published studies of Nagarajan and Robinson [4], Nagarajan et al. [5], and Gasem et al. [6], using the experimental measured input data in basic parachor expression based modeling had resulted in excellent agreement between the experimental and the calculated pressure dependence of IFT behaviors of complex but standard sc-CO₂ and hydrocarbons mixtures. Unfortunately, in case of complex sc-CO₂ and actual crude oil systems, experimentally measured input data needed to perform basic parachor expression based modeling or any other modeling methods such as mechanistic parachor model or LGT are not readily available in the published literature. In this scenario, it would be interesting to test the ability of basic parachor expression in modeling of pressure dependence of complex sc-CO₂ and crude oil systems using the experimentally measured input data. Such exercise may shed new light on the underlying mechanisms of these complex gas-oil interactions. This study reports on such efforts.

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 sc-CO₂ and live crude oil system from the observed trends of pressure dependence of IFT behaviors. The experimental IFT behaviors of various feed mixtures tested by Sequeira [15] are predicted using a version of the parachor model described by Schechter and Guo [7] and the experimental input data reported by Sequeira [15] and Sequeira et al. [16]. The parachor model described by Schechter and Guo [7] uses a scaling ex-

ponent of 3.88. The results will be presented and discussed later.

2. The Calculated IFT Behaviors of Sc-CO₂ and Live Crude Oil System Tested by Sequeira [15] and Sequeira et al. [16]

Sequeira [15] and Sequeira et al. [16] performed physical measurements for a sc-CO₂ gas and 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 CO₂ and live crude oil and two constant volume (i.e. 45+55, and 85+15 volume% of CO₂ and live crude oil) feed mixtures at reservoir temperature of 114.4°C (238°F). The constant volume feed mixtures tested by them correspond to variable composition (molar composition) of feed mixtures. In case of variability of first composition feed mixture, CO₂ composition varied from 88 to 95 mol% (i.e. 12 to 5 mol% live crude oil). For second mixture, CO₂ 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). Tables 7, 8, 10, 11, 13, 14, 16, 17 of Sequeira et al. [16] contain all of the above mentioned data. However, apart from the equilibrium properties (phase compositions and densities), the parachor model also requires pure and oil-cut (C7+ fraction) parachors. In the calculations presented in this paper, C7+ fraction parachors were calculated using three different parachor correlations (Eqs. 10, 11, and 12) discussed in Schechter and Guo (1998) research. 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 8, 11, 14, and 17 of Sequeira et al., [16]) were used to determine C7+ fraction parachor. Among all correlations, Eq. 11 of Schechter and Guo [7] provided the lowest parachor values. The same procedure was used in the calculations.

Both the calculated and the experimental IFT behaviors of feed mixtures tested by Sequeira [15] and Sequeira et al. [16] are plotted in Figs. 1, 3, 5,

and 7. Corresponding densities of the equilibrium oil and vapor phases along with densities of pure live oil and pure sc-CO₂ at various pressures are shown in Figs. 2, 4, 6 and 8. The absolute variation between the individual IFT value measured at the highest experimental pressure (41.3 MPa or 5990 psi) and corresponding calculated IFT value ranged from 50% to 187% (Table 1). 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.

3. Comparison of the Calculated and the Experimental IFT Behaviors of SC-CO₂ and Live Crude Oil System Tested by Sequeira [15] and Sequeira et al. [16]

As evident from Figs. 1, 3, 5 and 7, both the experimental and the calculated IFT behaviors show two distinct trends, i.e. a rapid decline in IFT with pressure trend at low pressure region (IFT > 1 mN/m) and a moderate to low decline in IFT with pressure trend at high pressure region (IFT < 1 mN/m). In high IFT region, both the calculated and the experimental IFT behaviors for constant composition feed mixtures (89+11 and 70+30) show a sharp decline in IFT with pressure (Figs. 1 and 3). In case of 89+11 feed mixture, the calculated behavior more or less follows a trend similar to the experimental IFT behavior (Fig. 1). However

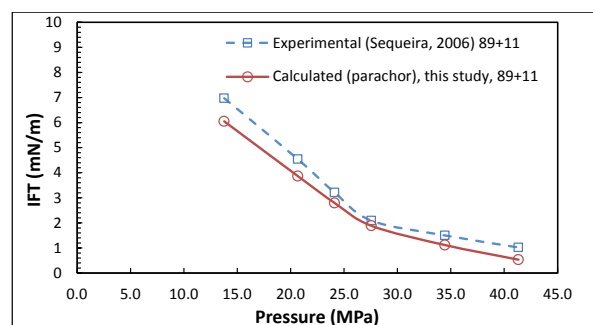


Figure 1. The experimental IFT (Sequeira, [15]) and the calculated (parachor) IFT behaviors (this study) at 114.4°C (238°F) for constant mol ratio (89 + 11) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

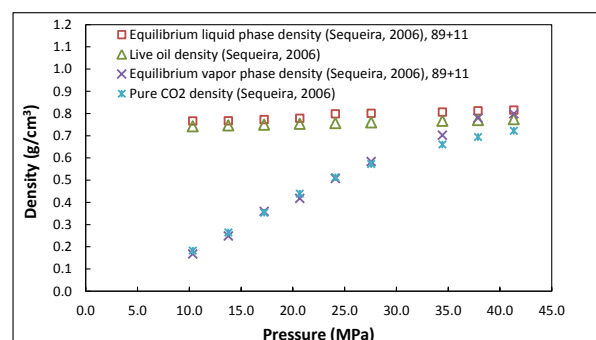


Figure 2. Corresponding measured equilibrium and pure phase densities (Sequeira, [15]) to the experimental IFT behavior at 114.4°C (238°F) for constant mol ratio (89 + 11) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

Table 1. Comparison of the experimental IFT (Sequeira [15]; Sequeira et al. [16]) at 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 sc-CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

Mol Ratio of sc-CO ₂ + Live Crude Oil in Feed Mixture	Type	Highest Experimental Pressure (MPa)	Measured IFT value (mN/m) (Sequeira, [15]; Sequeira et al., [16])	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

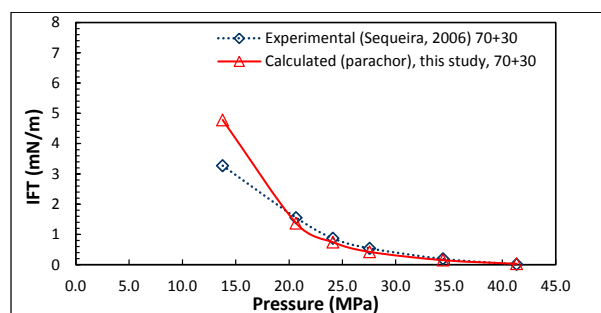


Figure 3. The experimental IFT (Sequeira, [15]) and the calculated (parachor) IFT behaviors (this study) at 114.4°C (238°F) for constant mol (70 + 30) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

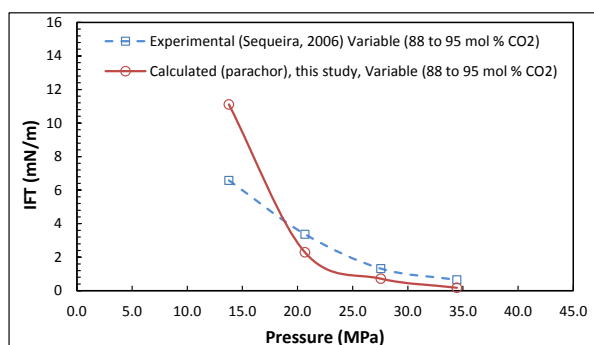


Figure 5. The experimental IFT (Sequeira, [15]) and the calculated (parachor) IFT behaviors (this study) at 114.4°C (238°F) for variable mol (88 to 95 mol % CO₂) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

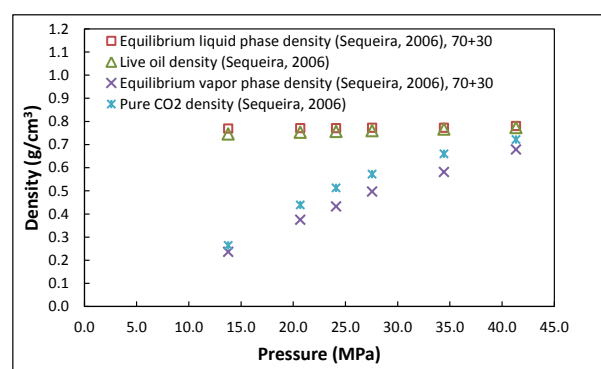


Figure 4. Corresponding measured equilibrium and pure phase densities (Sequeira, [15]) to the experimental IFT behavior at 114.4°C (238°F) for constant mol ratio (70 + 30) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

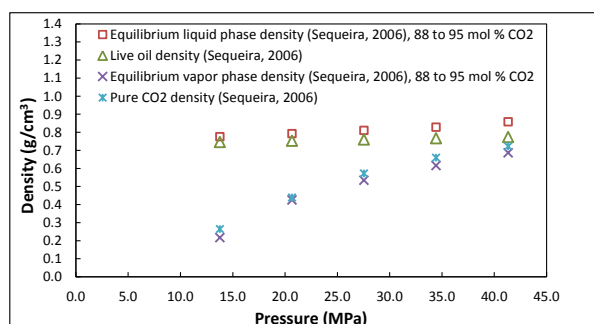


Figure 6. Corresponding measured equilibrium and pure phase densities (Sequeira, [15]) to the experimental IFT behavior at 114.4°C (238°F) for variable mol (88 to 95 mol % CO₂) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

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 sc-CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

Mol Ratio of sc-CO ₂ + Live Crude Oil in Feed Mixture	Type	Highest Experimental Pressure (MPa)	Measured IFT value (mN/m) (Sequeira, [15]; Sequeira et al., [16])	Calculated IFT value (mN/m) (This Study)	Difference between measured densities of the equilibrium liquid and vapor phases, gm/cm ³ (Sequeira, [15]; Sequeira et al., [16])
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

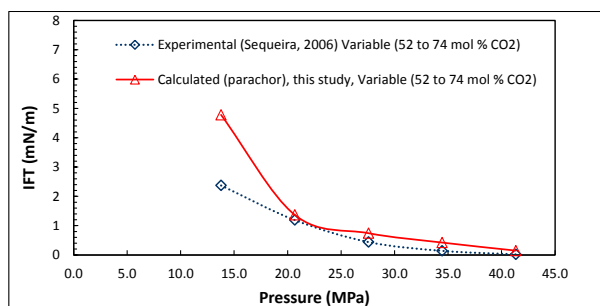


Figure 7. The experimental IFT (Sequeira, [15]) and the calculated (parachor) IFT behaviors (this study) at 114.4°C (238°F) for variable mol (52 to 74 mol % CO₂) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

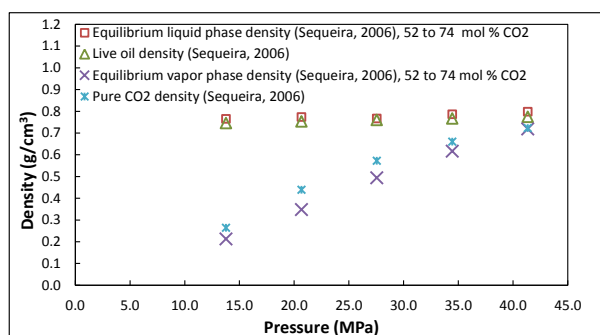


Figure 8. Corresponding measured equilibrium and pure phase densities (Sequeira, [15]) to the experimental IFT behavior at 114.4°C (238°F) for variable mol (52 to 74 mol % CO₂) feed mixture of CO₂ + live crude oil system reported by Sequeira [15]; Sequeira et al. [16].

in case of 70+30 feed mixture, the calculated IFT trend shows a sharper decline compared to the experimental IFT trend (Fig. 3).

In case of variable composition feed mixtures (i.e. 88 to 95 mol% CO₂ and 52 to 74 mol% CO₂), the calculated IFT trend in high IFT region shows a much steeper decline compared to the experimental IFT trends. For all four feed mixtures, the calculated IFT behavior in low IFT region shows more or less a similar decline with pressure trend that is shown by the experimental IFT behaviors. The difference between the calculated and the experimental IFT behaviors appears to diminish in low IFT region for all except one (89 + 11) feed mixtures (Figs. 1, 3, 5, and 7).

In high IFT region, both the calculated and the experimental IFT behaviors of all four feed mixtures show a rapid decline in IFT with pressure (Figs. 1, 3, 5, and 7) however a little deviation in

densities of the equilibrium phases (oil and vapor) from densities of the pure phases is observed (Figs. 2, 4, 6, and 8). It is noted here that the calculated IFT behaviors of 3 out of 4 feed mixtures show a sharper decline compared to the experimental IFT behaviors despite densities of the equilibrium phases show a little deviation from densities of corresponding pure phases. It is also worth to mention here that, in case of complex sc-CO₂ and crude oil systems, experimental conditions of pressure and temperature will also significantly affect on the equilibrium phase densities. Despite the fact that density difference between the equilibrium phases and the pure (live oil and sc-CO₂) phases remain large in high IFT region, all four feed mixtures show rapid decline in IFT. Similar observations can be made for the system investigated by Saini and Rao [17].

In low IFT region, where density difference between the two phases (equilibrium liquid and vapor or live oil and pure sc-CO₂) reduces very rapidly, the IFT behaviors starts to show a decline trend different from the trend shown in high IFT region. However the calculated IFT behaviors start to follow the experimental IFT behaviors more closely. This behavior is very similar to the IFT behaviors of oil/water system that they typically show in the presence of a surfactant. The IFT behavior of one of such surfactant/oil/water systems is discussed by Schechter and Guo [7].

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 Fig. 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 sc-CO₂ + crude oil feed mixtures evaluated here, difference between the equilibrium vapor and liquid phase densities rapidly starts to diminish in low IFT region and the calculated IFT behaviors start to follow the experimental IFT behaviors more closely.

Similarly, even for standard CO₂ and live decane system (Fig. 62 of Ayirala, [14]), there exists a significant difference between the calculated (mechanistic parachor model) and the experimental IFT behaviors in low pressure (high IFT region). Both the calculated (mechanistic and basic parachor models) and IFT behaviors were able to closely follow the experimental behaviors in low IFT region.

However the mechanistic parachor model based calculated IFT behavior started to follow the experimental IFT behavior well before the behavior of the basic parachor model based calculated IFT, could do so.

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 the case of CO₂ and live crude oil system studied in the present study, it appears that the critical point at 114.4°C lies around 41.3 MPa as suggested by a very low density difference between the equilibrium liquid and vapor phases for 89 + 11 feed mixture (Fig. 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 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.

It is emphasized here that the calculated IFT behaviors presented here use experimentally measured input data (i.e. the equilibrium phase compositions, phase densities, and molecular weight of the equilibrium liquid phase). However EOS coupled parachor calculations for modeling the IFT behaviors of complex sc-CO₂ and hydrocarbon systems that rely on the calculated input data often fail to predict the experimental IFT behaviors. This issue will be discussed in the next sections.

4. EOS Coupled Parachor Modeling Studies

It is interesting to note that EOS coupled basic parachor calculations often stop at either high IFT value (i.e. at feed mixture's saturation or bubblepoint pressure, e.g. Fig. 13 of Orr Jr. and Jessen, [11]; Fig. 1 of Ashrafizadeh and Ghasrodashti, [10]) or attain a low IFT value at very high saturation pressure (i.e. at feed mixture's dewpoint pressure, e.g. Fig. 3 of K. Jessen, F.M. Orr Jr, [12]). Such phenomena may not

necessarily be observed in the case of experimental IFT behaviors (e.g. experimentally measured IFT data reported by Ayirala and Rao [8] in Fig. 13 of Orr Jr. and Jessen, [11]).

The termination of the EOS coupled parachor calculations at the saturation pressures (bubblepoint pressure) of certain feed mixtures appears to arise from either non-convergence of the EOS algorithm (Schechter and Guo, [7]) or inability to perform the flash calculations for certain feed mixtures (Ashrafizadeh and Ghasrodashti, [10]). On the other hand, scenario of attaining a low IFT value at very high saturation pressure (i.e. at feed mixture's dewpoint pressure) appears to arise from the need of very high pressure for obtaining the condition of no density difference between the equilibrium liquid and vapor phases (near critical point region).

In case of mechanistic parachor calculations also, a significant difference between the calculated (mechanistic parachor model) and the experimental IFT behaviors in low pressure (high IFT region), even for standard sc-CO₂ and live decane system (Fig. 62 of Ayirala, [14]), can be observed. This may be attributed to the use of empirical correlation for computing diffusivity ratios in multicomponent hydrocarbon systems.

The extension of basic parachor expression for predicting the IFT behaviors of complex sc-CO₂ and hydrocarbon systems fundamentally relies on treating multicomponent mixtures as a single component and accounting the gas-oil interactions in terms of the mixture Parachor. It seems that the modification in the slope of IFT versus pressure curve will be equivalent to a modification to the Parachor if multicomponent mixture is treated as a single component system. These observations suggest that the mechanistic parachor model essentially modifies the mixture Parachor by taking an account of gas-oil interactions in terms of their diffusivity ratios. The use of diffusivity ratios appears to improve the predictions of the components' distribution and their concentrations in the equilibrium fluid phases that end up in a modified mixture Parachor compared to the mixture Parachor incorporated in the basic parachor expression.

Recently, Georgiadis et al. [18] 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 CO₂ and 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 CO₂ and hydrocarbon systems as shown by the reliable prediction of the experimental IFT behaviors for standard CO₂ and hydrocarbon system (Fig. 9). These results are encouraging however capability of the SAFT-VR-DFT EOS for modeling of the IFT behaviors of complex CO₂ and hydrocarbon systems still needs to be evaluated.

5. Summary and Conclusions

The results presented here suggest that a basic parachor expression based calculated IFT behaviors reasonably follow the experimental IFT behaviors of complex sc-CO₂ and crude oil systems in low IFT (< 1 mN/m) region. However, a significant deviation between the calculated and the experimental IFT behaviors may still be observed in high IFT region (> 1mN/m). 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) near critical point region.

The results suggest that the use of experimentally measured input data coupled parachor modeling may provide more robust predictions of the experimental IFT behaviors of complex sc-CO₂ and crude oil systems. An analysis of published studies (basic and mechanistic parachor expressions based modeling of pressure dependence of IFT behaviors of both standard and complex sc-CO₂ and crude oil systems) and the results of this study reinforce the need to better description of gas-oil interactions for robust modeling of pressure dependence of IFT behaviors of these complex systems.

References

- Al-Mjeni, R., Arora, S., Cherukupalli, P., van Wunnik, J., Edwards, J., Felber, B.J., Gurpinar, O., Hirasaki, G.J., Miller, A.C., Jackson, C., Kristensen, M.R., Lim, F., Ramamoorthy, R. (2011). "Has the time come for EOR?", *Schlumberger's Oilfield Review*, Winter 2010/2011, Vol. 22, no. 4.
- Wallace M, Kuuskraa VA, DiPietro P (2013) An In-Depth Look at "Next Generation" CO₂-EOR Technology. Available from http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Publications/Disag-Next-Gen-CO2-EOR_full_v6.pdf. Accessed June, 2015.
- Hsu Jack, J.C., Nagarajan, N., Robinson, J.R.L. (1985). "Equilibrium phase compositions, phase densities, and interfacial tension for CO₂ + hydrocarbon Systems. 1. CO₂ + n-butane.", *Journal of Chemical Engineering Data*, Vol. 30, No. 4, pp. 485-491.
- Nagarajan, N., Robinson, J.R.L. (1986). "Equilibrium phase compositions, phase densities, and interfacial tensions for CO₂ + hydrocarbon systems. 2. CO₂ + n-decane." *Journal of Chemical Engineering Data*, Vol. 31, No. 2, pp. 168-171.
- Nagarajan, N., Gasem, K.A.M., Robinson, J.R.L. (1990). "Equilibrium phase compositions, phase densities, and interfacial tensions for CO₂ + Hydrocarbon Systems. 6. Carbon dioxide + n-butane + n-decane." *Journal of Chemical Engineering Data*, Vol. 35, No. 3, pp. 228-231.
- Gasem, K.A.M., Dickson, K.B., Shaver, R.D., Robinson, R.L. (1993). "Experimental phase densities and interfacial tensions for a CO₂/synthetic-oil and a CO₂/reservoir-oil system." *Society of Petroleum Engineers*. DOI:10.2118/22216-PA.
- Schechter, D.S., Guo, B. (1998). "Parachors based on modern physics and their uses in IFT prediction of reservoir fluids." *Society of Petroleum Engineers*. DOI: 10.2118/30785-PA.
- Ayirala, S.C., Rao, D.N. (2004). "Application of a new mechanistic Parachor model to predict dynamic gas-oil miscibility in reservoir crude oil-solvent systems." *Society of Petroleum Engineers*. DOI: 10.2118/91920-MS.
- Nobakht M, Moghadam S, and Gu Y (2008) Determination of CO₂ Minimum Miscibility Pressure from Measured and Predicted Equilibrium Interfacial Tensions. *Ind. Eng. Chem. Res.*, 47 (22), pp. 8918-8925, DOI: 10.1021/ie800358g.
- Ashrafizadeh, S.N., Ghasrodashti, A.A. (2011). "An investigation on the applicability of Parachor model for the prediction of MMP using five equations of state." *Chemical Engineering Research and Design*, Vol. 89, pp. 690-696.
- Orr, J.F.M., Jessen, K. (2007). "An analysis of the vanishing interfacial tension technique for determination of minimum miscibility pressure." *Fluid Phase Equilibria*, Vol. 255, No. 2, pp. 99-109.

12. Jessen, K, Orr J.F.M. (2008). "On interfacial-tension measurements to estimate minimum miscibility pressures." *Society of Petroleum Engineers*. DOI: 10.2118/110725-PA.
13. Teklu T.W, Alharthy, N., Kazemi, H., Yin, X., Graves, R.M. (2014). "Vanishing interfacial tension algorithm for MMP determination in unconventional reservoirs." *Society of Petroleum Engineers*. DOI: 10.2118/169517-MS.
14. Ayirala, S.C. (2005). *Measurement and modeling of fluid-fluid miscibility in multicomponent hydrocarbon systems*. PhD Dissertation, Louisiana State University, Baton Rouge, Louisiana.
15. Sequeira, D.S. (2006). *Compositional effects on gas-oil interfacial tension and miscibility at reservoir conditions*. MS Thesis, Louisiana State University, Baton Rouge, Louisiana.
16. Sequeira, D.S., Ayirala, S.C., Rao, D.N. (2008). "Reservoir condition measurements of compositional effects on gas-oil interfacial tension and miscibility." *Society of Petroleum Engineers*. DOI: 10.2118/113333-MS.
17. Saini, D., Rao, D.N. (2010). "Experimental determination of minimum miscibility pressure (MMP) by gas/oil IFT measurements for a gas injection EOR project." *Society of Petroleum Engineers*. DOI: 10.2118/132389-MS.
18. Georgiadis, A., Llovel, F., Bismarck, A., Blas, F.J., Galindo, A., Maitland, G.C., Martin Trusler, J.P., Jackson, G. (2010). "Interfacial tension measurements and modelling of (carbon dioxide + n-alkane) and (carbon dioxide + water) binary mixtures at elevated pressures and temperatures." *Journal of Supercritical Fluids*, Vol. 55, pp. 743-754.