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SHORT COMMUNICATION - PRODUCTION ENGINEERING

New correlations for CO_2-Oil solubility and viscosity reduction for light oils

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Abstract This paper presents the development of new empirical correlations for (1) CO_2 solubility in dead oil and (2) oil viscosity reduction ratio due to CO_2 saturation. These correlations are specifically developed for light oils, i.e., with oil gravities less than 0.9 (greater than 26° API). The new correlations are developed to be simple equations and dependent only on reservoir temperature and pressure while maintaining a relatively high level of accuracy. The new correlations developed in this work can be used as a tool for better performance evaluation of CO_2 injection into depleted oil fields and/or CO_2 sequestration.

Keywords CO_2 · Solubility · Viscosity reduction · Empirical correlation

List of symbols

a, b, c, d	Coefficients
p	Pressure, MPa
sol	Solubility of CO_2 in oil, mole fraction
T	Temperature (°C)
γ_o	Stock-tank oil specific gravity
μ_{oCO2}	Viscosity of CO_2 saturated oil (mPa-s)
μ_{oi}	Initial oil viscosity (mPa-s)
μ_{oCO2}/μ_{oi}	Oil viscosity reduction ratio

Introduction

There is growing interest in the use of CO_2 for enhanced oil recovery, with the added benefit of co-sequestration of CO_2 towards greenhouse gas emissions reduction. Predicting reservoir performance and evaluating optimum injection conditions requires a variety of tools ranging from simple material balance to complicated field scale compositional reservoir simulations. In all of these approaches, pressure–volume-temperature (PVT) relationships for oil–gas-brine–CO_2 systems are required for modeling the effects of CO_2 injection and predicting the amount of oil recovered and sequestered CO_2. Two key variables in this context are CO_2 solubility in oil and the corresponding reduction in oil viscosity due to the added CO_2. Often, these properties are not measured in the laboratory because of time and/or cost considerations and have to be predicted from empirical correlations (e.g., Simon and Graue 1965; Emera 2006). The existing correlations often lack accuracy, are complicated, or are dependent on reservoir fluid properties such as molecular weight which are generally not available.

This paper describes the development of simplified correlations for (1) CO_2-oil solubility and (2) viscosity reduction for light oils, with oil gravities less than 0.9 (greater than 26° API). Light oils are typical of oil fields in the Appalachian Basin of the USA, many of which are operated by small and medium size operators that typically do not have the resources to develop full laboratory characterization of PVT properties. The results of this study will also be applicable to light oil reservoirs in other parts of the world where screening analyses and/or predictive modeling of CO_2 enhanced oil recovery and co-sequestration are being considered with limited PVT data.

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Experimental data

The data used to develop the new correlations are taken from several experimental data sources that were aggregated by Emera. As discussed in the introduction, the data used for the correlation development was limited to the data with oil gravities less than 0.9. Experimental data sets with oil gravities as low as 0.85 and 0.78 were used to develop the solubility and viscosity reduction correlations, respectively. These data sets are presented in Appendix Tables 5 and 6. A summary of the experimental data parameter value ranges is shown in Tables 1 and 2.

Many oil fields that are candidates for CO_2 enhanced oil recovery and co-sequestration are depleted and underpressured. Therefore, solubility measurements in dead oil rather than live oil are most relevant for developing this new correlation. Viscosity reduction measurements for data sets with oil gravities less than 0.9 were only available for live oil. However, in the available data sets, there were two live oil/dead oil data pairs that had similar temperature and oil gravity values, allowing for an isolation of the effect of live versus dead oil on the viscosity reduction. These two pairs of data sets are plotted in Fig. 1. The similarity of the viscosity reduction values within each pair of data seta sets demonstrates that oil viscosity reduction is much more dependent on temperature and solubility than it is dependent on whether the oil is live or dead.

Correlation for CO_2-oil solubility for dead oil

Existing correlations

Some prevailing existing correlations for CO_2 solubility in oil include:

- Welker and Dunlop: function of the saturation pressure and oil API gravity at 26.67 °C
- Simon and Graue: graphical model that is dependent on CO_2 fugacity and temperature or saturation pressure, temperature, and characterization factor
- Mehrotra and Svrcek: function of the pressure and temperature for pressures up to 6.38 MPa and temperatures 23.89 to 99.22 °C
- Chung et al.: function of temperature, pressure, and oil gravity.
- Emera: function of temperature, pressure, oil gravity, and oil molecular weight.

Table 1 CO_2-dead oil solubility experimental data sets summary

Parameter description	Parameter value range
Oil gravity (γ_o)	0.85–0.90
Temperature (T)	32.2–73.9 °C
Pressure (p)	1.81–27.4 MPa
CO_2 Solubility (Sol)	0.12–0.85 mol fraction

Table 2 CO_2-Oil viscosity reduction ratio experimental data sets summary

Parameter description	Parameter value range
Oil gravity (γ_o)	0.78–0.89
Temperature (T)	42.0–137.2 °C
CO_2 solubility (Sol)	0–0.68 mol fraction
Viscosity reduction ratio (μ_{oCO2}/μ_{oi})	0.188–1.0

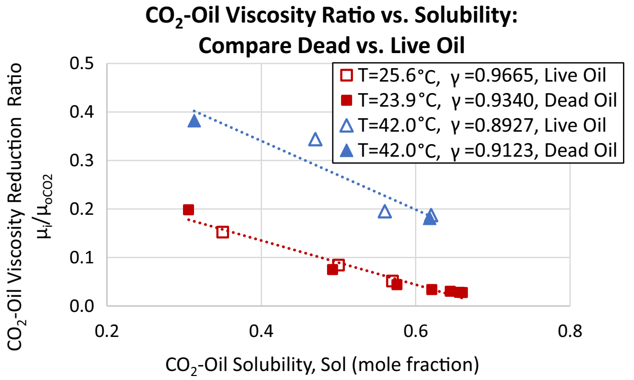


Fig. 1 Experiment data for CO_2-oil viscosity reduction ratio as a function of CO_2 solubility in oil with best fit lines for two pairs of data sets, each pair with one live oil and one dead oil data set. The first pair have temperatures of ~25 °C and oil gravities of ~0.95. The second pair have temperatures of ~42 °C and oil gravities of ~0.90

Emera found that his correlation resulted in errors that were quite small, while those of other literature correlations were larger. A summary of the error for the existing correlations reported in Emera (2006) is summarized in Table 3. The Emera correlation, while accurate, would not be useful for oil fields where oil gravity can only be generally characterized and molecular weight is unknown. Fortunately, as shown in Fig. 7–1 of Emera (2006), the correlation coefficients of oil gravity and molecular weight for CO_2 Solubility in dead oil are very small compared to the correlations coefficients of pressure and temperature. The goal of the current study was to develop simpler correlations, dependent only on temperature and pressure, but resulting in similar accuracy as the Emera correlation when applied to light oils with gravities less than 0.9.

Table 3 Existing correlations CO_2-dead oil solubility error detailed in Emera

Model	No. of data	Average error (%)	STDEV (%)	R^2
Emera	106	4.0	5.6	0.985
Simon and Graue	49	5.7	10.8	0.97
Mehrotra and Svrcek	106	32.6	36.6	0.756
Chung et al.	106	83.7	150.3	0.0096

New correlation

Initial plotting of solubility versus pressure for all of the available dead oil experimental data (106 data points) compiled in Emera (2006), showed a trend of increasing solubility with pressure. Additionally, when the data points were colored by temperature, a strong correlation between temperature and solubility became apparent as well, as shown in Fig. 2.

The next step was to plot each data set (each with a different temperature) individually to isolate the relationship between pressure and solubility. Because the focus was developing correlations for light oils, we limited this step to data sets with oil specific gravity less than 0.9. This left seven experimental data sets, each with three to six data points (29 total data points, see Appendix Table 5). Each data set was plotted with both a linear and natural logarithm best fit line. Based on the least squares regression coefficient of determination, R^2, for each fit, a logarithmic correlation proved a better fit for five of the seven experimental data sets. The plots of each of the seven data sets with their logarithmic best fit equations and R^2 values are shown in Fig. 3.

Once a logarithmic correlation was selected for the relationship between pressure and solubility, we sought to determine the correlation with temperature. Based on empirical observations, the form of $C_1 + C_2 \times T$ was selected as an appropriate form to use for both the slope and intercept coefficients, which upon testing seemed to be adequate for the purposes of the study. Using the Excel® *Solver* function, we determined the coefficients for the equation of the form

$$\mathrm{Sol} = (a + b \cdot T) \cdot Ln(p) + (c + d \cdot T) \tag{1a}$$

(p in MPa and T in °C) that provided the smallest error between the experimental data and correlation solubility values. The resulting coefficients were

$$a = 0.36913, b = -0.00106, c = 0.01280, \text{and } d = -0.00160 \tag{1b}$$

A plot of the correlation solubility values versus the experimental data is shown in Fig. 4. The best fit line for the new correlation has a slope of 0.99 with a relatively high R^2 value of 0.9825, showing the new correlation provides a strong fit for the experimental data. The correlation has an average error of 3.9 % with a standard deviation of 4.8 %. The new correlation gives a comparable level of accuracy as the Emera correlation which has an R^2 value of 0.9768 for the data sets with oil gravity less than 0.9; however, the new correlation has the advantage of requiring only temperature and pressure and not requiring the oil gravity and molecular weight parameters as needed by Emera.

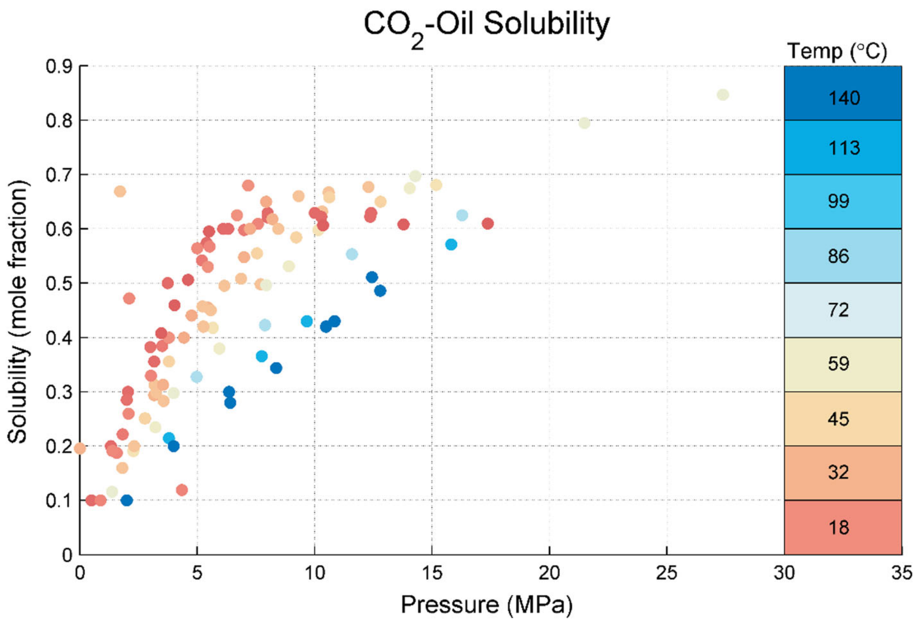
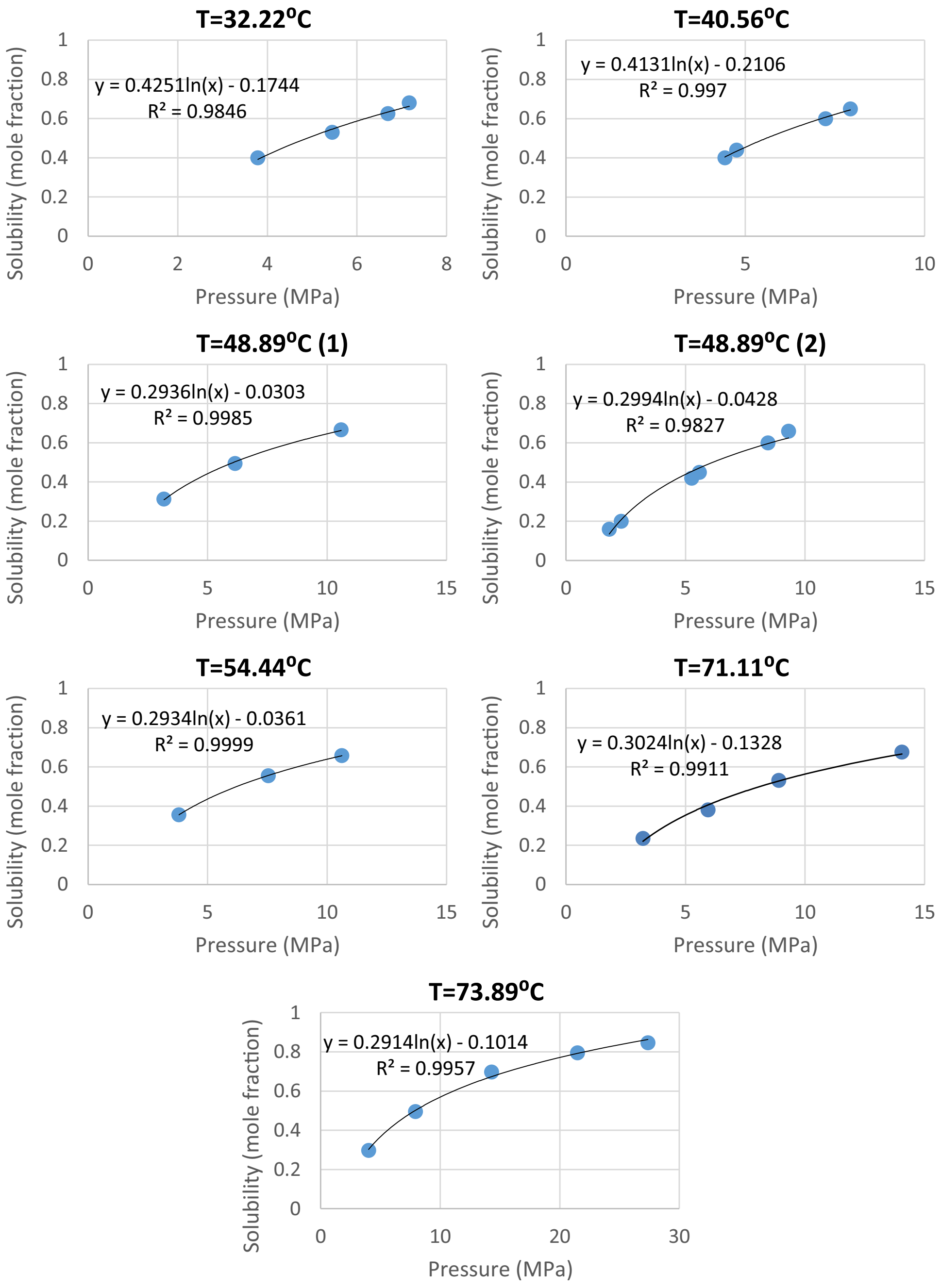


Fig. 2 Experimental CO_2-Dead Oil solubility as a function of pressure with data points colored by temperature

Fig. 3 Experimental CO_2-Dead Oil solubility as function of pressure with logarithmic best fit line for each data set



The new correlation was tested using a "one-off" validation procedure. This involves removing one point from the data set at random, determining the new corresponding correlation coefficients, a, b, c, and d, for the remaining data, and then comparing the single removed point experimental value to the new correlation value. This was repeated for a total of five times with random data points selected across the range of CO_2-oil solubility values. These five points are plotted in Fig. 5. The five points give an R^2 value of 0.9981 suggesting that the correlation is valid.

CO_2-oil viscosity ratio correlation development for live oil

Existing correlations

Some prevailing existing correlations for CO_2-Oil viscosity include:

- Welker and Dunlop, a graphical model dependent on saturation pressure and limited to a temperature of 26.67 °C

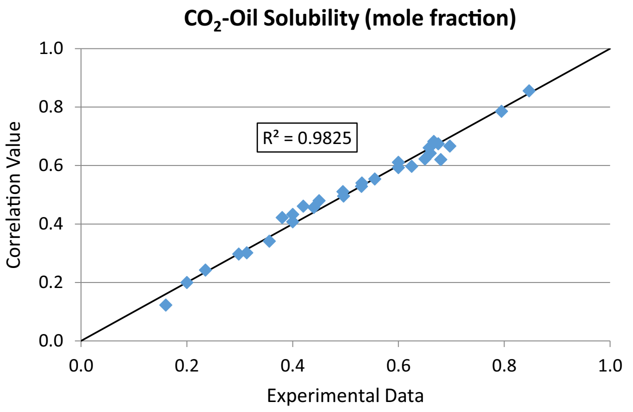


Fig. 4 CO_2-Dead Oil solubility correlation values versus experimental data for oil with gravities less than 0.9

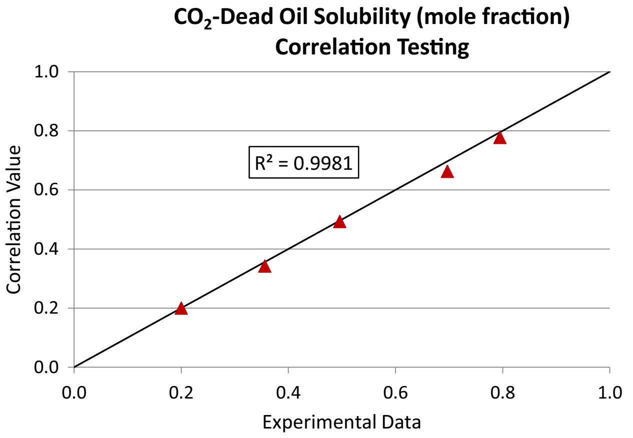


Fig. 5 CO_2-Dead Oil solubility correlation testing

- Lohrenz-Bray-Clark, function dependent on the density, molecular weight, critical pressure, critical temperature, and reservoir liquid composition
- Simon and Graue, a graphical model dependent on saturation pressure and CO_2 solubility
- Beggs and Robinson, function of temperature, dead oil viscosity, and oil gravity
- Emera, function of CO_2 solubility, temperature, pressure, and oil gravity

Emera found that his correlation resulted in errors that were substantially smaller than the other correlations in the literature. A summary of the error for the existing correlations found in Emera (2006) is summarized in Table 4. Again, the goal of this study was to develop correlations that are simpler, are dependent on less information about the reservoir fluid properties, and result in comparable accuracy to the Emera correlation when applied to light oils with gravities less than 0.9.

Table 4 Existing correlations CO_2-oil viscosity error detailed in Emera

Model	No. of data	Average error (%)	STDEV (%)	R^2
Emera	52	6.6	9.75	0.9996
Beggs and Robinson	52	56.25	91.4	0.8734
Mehrotra and Svrcek	52	65.1	79.5	0.4387

New correlation

The CO_2-oil viscosity ratio is a ratio of the viscosity of the oil with CO_2 dissolved at a given pressure and temperature compared to the initial oil viscosity prior to increasing the pressure and dissolving CO_2. A plot of the viscosity ratio versus CO_2-oil solubility for the experimental live oil data (39 points, see Appendix Table 6) with oil gravities less than 0.9 is shown in Fig. 6. The best fit lines (with a designated intercept of 1) for each data set are also shown. These data sets show a strong linear correlation between the solubility and the viscosity ratio but with varying slopes for the different temperatures. Figure 7 shows the slopes of these best fit lines plotted against temperature. This plot once again shows a strong linear correlation between the slope and temperature. These results combine to give a correlation for the viscosity reduction ratio of

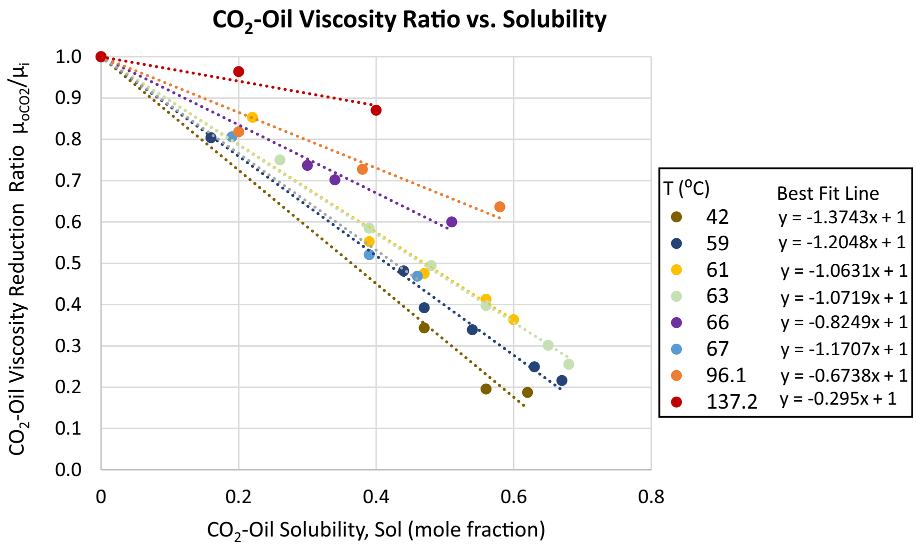
$$\mu_{oCO2}/\mu_{oi} = 1 + (0.01113T - 1.78210)\text{Sol} \quad (2)$$

(T in °C and Sol in mole fraction) for live oil with gravities less than 0.9.

A plot of the correlation viscosity ratio values versus the experimental data is shown in Fig. 8. The best fit line for this plot has a slope of 0.99 and an R^2 value of 0.9749, demonstrating the new correlation provides a very good fit using the independent parameters of temperature and solubility. The correlation has an average error of 6.3 % with a standard deviation of 7.8 %. Again, the Emera correlation has comparable accuracy with an R^2 value of 0.9805 for these data sets, but is also dependent on oil gravity and initial viscosity.

The new correlation was tested by the same "one-off" method as described earlier for the CO_2-oil solubility correlation. One point is removed from the data set, and new coefficients for the developed correlation are determined based on the remaining data. This adjusted correlation is used to predict the viscosity reduction for the single removed data point. This was repeated for a total of four times with random data points selected across the range of CO_2-oil solubility values and data set temperatures. These four points are plotted in Fig. 9. The four

Fig. 6 Experiment data for CO_2-oil viscosity reduction ratio as a function of CO_2 solubility in oil with best fit lines for different temperatures. Experimental data sets include live oil with gravities less than 0.9



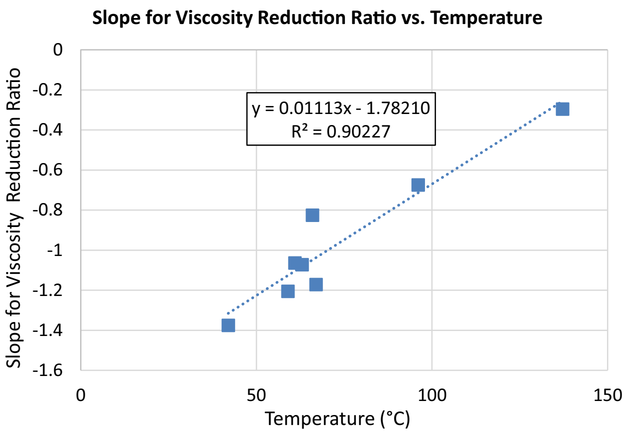


Fig. 7 Slopes of best linear fit lines determined for CO_2-Oil viscosity reduction ratio plotted against temperature

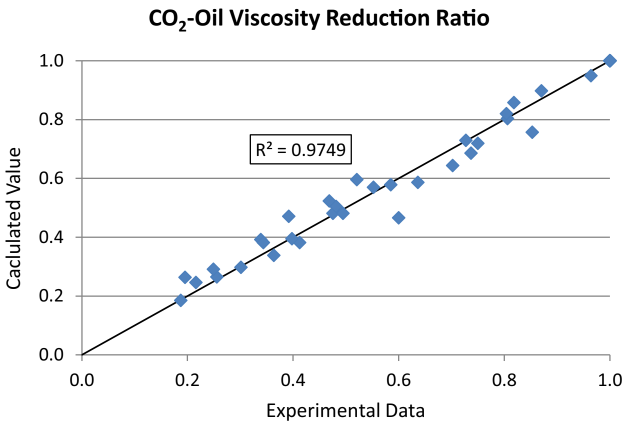


Fig. 8 CO_2-Oil viscosity ratio correlation calculation versus experimental values for live oil with oil gravities less than 0.9

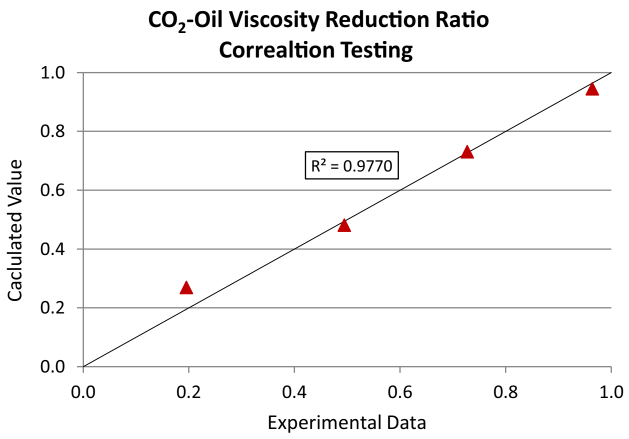


Fig. 9 CO_2-Oil viscosity ratio correlation testing

points give an R^2 value of 0.9770 suggesting that the correlation is valid.

Concluding remarks

We have presented the development of new correlations for CO_2-oil solubility and the corresponding viscosity reduction of CO_2 dissolved oil. The new correlations are simpler than existing literature correlations but retain comparable accuracy for application to light oils with gravities less than 0.9. Specifically, the new solubility correlation only requires temperature and pressure, and the new viscosity correlation only requires temperature and solubility. The previous leading correlations additionally require molecular weight and oil gravity. These new correlations can serve for better performance evaluation of enhanced oil recovery with CO_2 sequestration in light oil reservoirs typical of the Appalachian Basin in the USA as well as other regions of the world, where detailed PVT characterization of CO_2-oil systems is not available.

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Appendix

See Tables 5 and 6.

Table 5 Experimental data used for developing a correlation for CO_2 solubility in dead oil

Experiment source	Oil gravity, γ_o (−)	Temperature, T (°C)	Pressure, p (MPa)	Experiment CO_2-oil solubility, Sol (mole fraction)
Bou-Mikael	0.84985	73.89	4	0.298
	0.84985	73.89	7.93	0.496
	0.84985	73.89	14.28	0.697
	0.84985	73.89	21.48	0.795
	0.84985	73.89	27.38	0.847
Huang and Tracht	0.857576	32.22	3.79	0.4
	0.857576	32.22	5.45	0.53
	0.857576	32.22	6.69	0.625
	0.857576	32.22	7.17	0.68
Simon and Graue	0.858617	71.11	3.22	0.235
	0.858617	71.11	5.94	0.38
	0.858617	71.11	8.9	0.531
	0.858617	71.11	14.05	0.675
Simon and Graue	0.858617	48.89	3.18	0.313
	0.858617	48.89	6.15	0.495
	0.858617	48.89	10.59	0.667
Taylor	0.865443	40.56	4.43	0.4
	0.865443	40.56	4.76	0.44
	0.865443	40.56	7.24	0.6
	0.865443	40.56	7.93	0.65
Taylor	0.865443	48.89	1.81	0.16
	0.865443	48.89	2.31	0.2
	0.865443	48.89	5.26	0.42
	0.865443	48.89	5.58	0.45
	0.865443	48.89	8.45	0.6
	0.865443	48.89	9.31	0.66
Simon and Graue	0.899555	54.44	3.8	0.356
	0.899555	54.44	7.54	0.555
	0.899555	54.44	10.62	0.658

Table 6 Experimental data used for developing a correlation for CO_2-oil viscosity reduction ratio

Experiment Source	Oil Gravity [γ_o (−)]	Temp. T (°C)	CO_2-oil Solubility, Sol (mole Fraction)	Experiment Viscosity Reduction Ratio (μ_{oCO2}/μ_{oi})
Bon and Sarma	0.7796	137.2	0	1.000
	0.7796	137.2	0.2	0.964
	0.7796	137.2	0.4	0.871
Delany and Fish	0.8203	96.1	0	1.000
	0.8203	96.1	0.2	0.818
	0.8203	96.1	0.38	0.727
	0.8203	96.1	0.58	0.636
Dong et al.	0.8251	66	0	1.000
	0.8251	66	0.3	0.737
	0.8251	66	0.34	0.702
	0.8251	66	0.51	0.600
Dong et al.	0.8348	67	0	1.000
	0.8348	67	0.19	0.806
	0.8348	67	0.39	0.521
	0.8348	67	0.46	0.469
Srivastava et al.	0.8448	61	0	1.000
	0.8448	61	0.22	0.853
	0.8448	61	0.39	0.552
	0.8448	61	0.47	0.476
	0.8448	61	0.56	0.413
	0.8448	61	0.6	0.364
Srivastava et al.	0.8708	63	0	1.000
	0.8708	63	0.26	0.750
	0.8708	63	0.39	0.585
	0.8708	63	0.48	0.494
	0.8708	63	0.56	0.398
	0.8708	63	0.65	0.301
	0.8708	63	0.68	0.256
Srivastava et al.	0.8816	59	0	1.000
	0.8816	59	0.16	0.804
	0.8816	59	0.44	0.482
	0.8816	59	0.47	0.392
	0.8816	59	0.54	0.339
	0.8816	59	0.63	0.249
	0.8816	59	0.67	0.216
Srivastava et al.	0.8927	42	0	1.000
	0.8927	42	0.47	0.344
	0.8927	42	0.56	0.195
	0.8927	42	0.62	0.188

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