



New correlations for CO₂-Oil solubility and viscosity reduction for light oils

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Abstract This paper presents the development of new empirical correlations for (1) CO₂ solubility in dead oil and (2) oil viscosity reduction ratio due to CO₂ 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 CO₂ injection into depleted oil fields and/or CO₂ sequestration.

Keywords CO₂ · 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_{oCO_2}	Viscosity of CO ₂ saturated oil (mPa-s)
μ_{oi}	Initial oil viscosity (mPa-s)
μ_{oCO_2}/μ_{oi}	Oil viscosity reduction ratio

Introduction

There is growing interest in the use of CO₂ for enhanced oil recovery, with the added benefit of co-sequestration of CO₂ 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–CO₂ systems are required for modeling the effects of CO₂ injection and predicting the amount of oil recovered and sequestered CO₂. Two key variables in this context are CO₂ solubility in oil and the corresponding reduction in oil viscosity due to the added CO₂. 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) CO₂-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 CO₂ 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 CO₂ enhanced oil recovery and co-sequestration are depleted and under-pressured. 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 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 CO₂-oil solubility for dead oil

Existing correlations

Some prevailing existing correlations for CO₂ 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 CO₂ 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.

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

Table 1 CO₂-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 CO₂-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_{oCO_2}/μ_{oi})	0.188–1.0

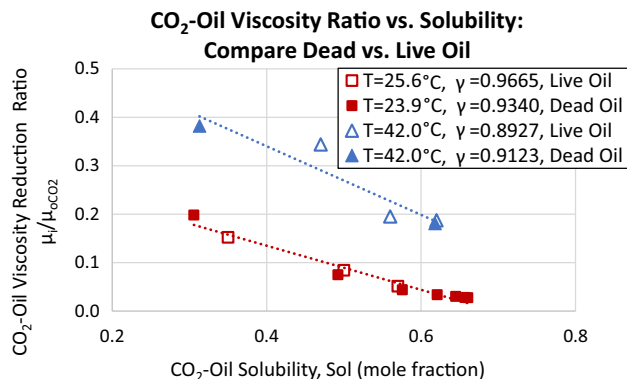


Fig. 1 Experiment data for CO₂-oil viscosity reduction ratio as a function of CO₂ solubility in oil with best fit lines for two pairs of data sets, each pair with one live oil and one dead oil data set. The first pair have temperatures of ~25 °C and oil gravities of ~0.95. The second pair have temperatures of ~42 °C and oil gravities of ~0.90

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 CO₂ 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 CO₂-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, R², 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 R² 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 C₁ + C₂ × 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

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

(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 R² 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 R² 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 CO₂-Dead Oil solubility as a function of pressure with data points colored by temperature

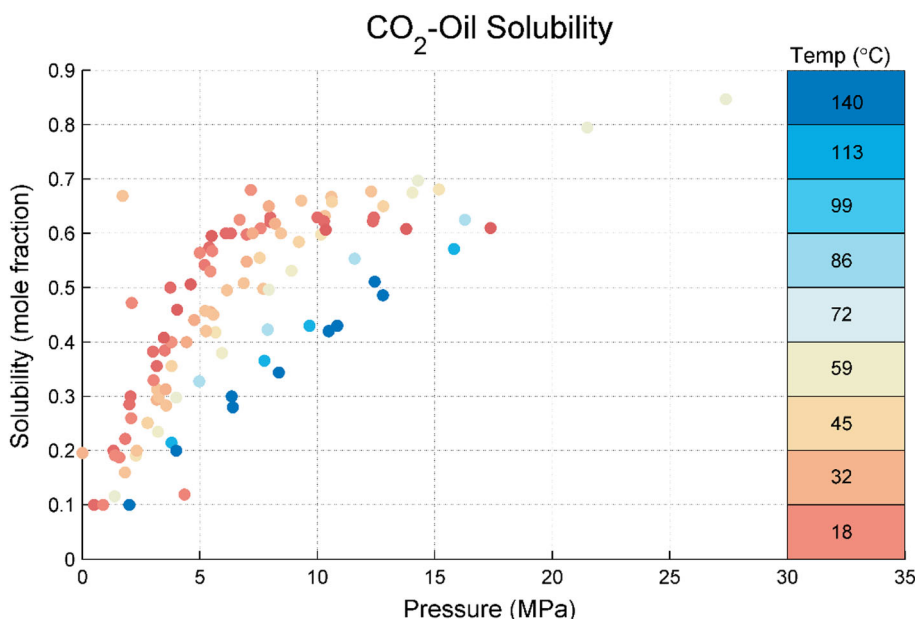
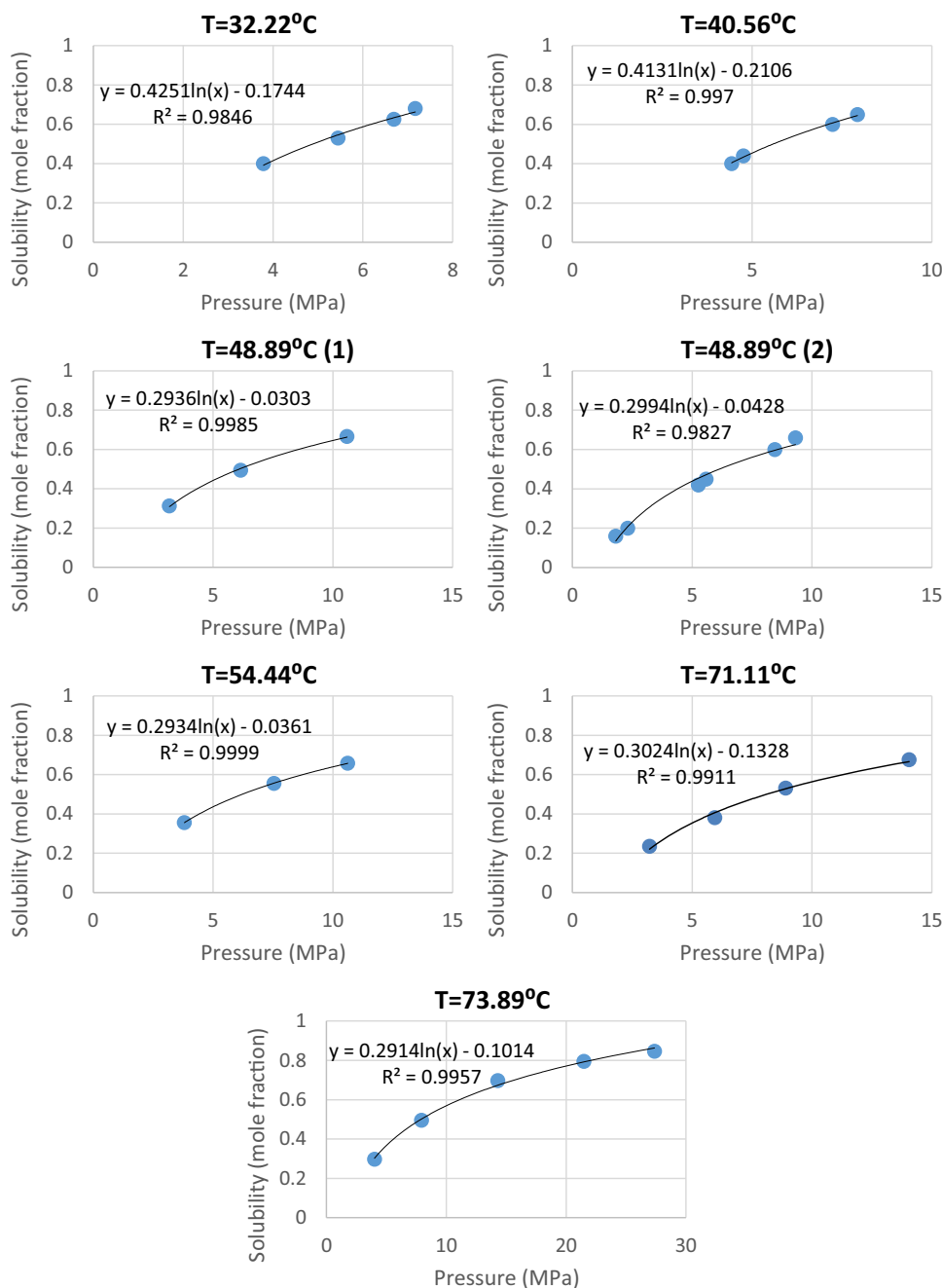


Fig. 3 Experimental CO₂-Dead Oil solubility as function of pressure with logarithmic best fit line for each data set



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 CO₂-oil solubility values. These five points are plotted in Fig. 5. The five points give an R² value of 0.9981 suggesting that the correlation is valid.

CO₂-oil viscosity ratio correlation development for live oil

Existing correlations

Some prevailing existing correlations for CO₂-Oil viscosity include:

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

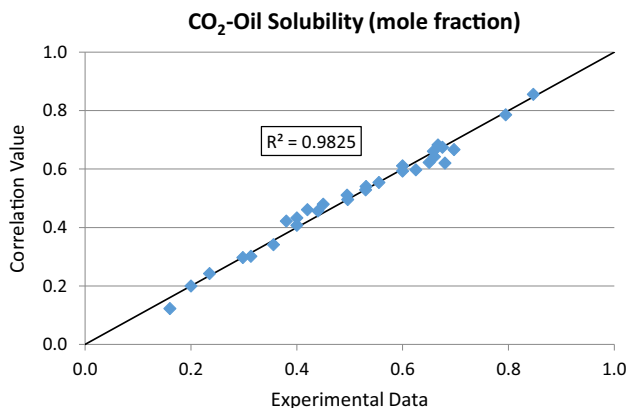


Fig. 4 CO₂-Dead Oil solubility correlation values versus experimental data for oil with gravities less than 0.9

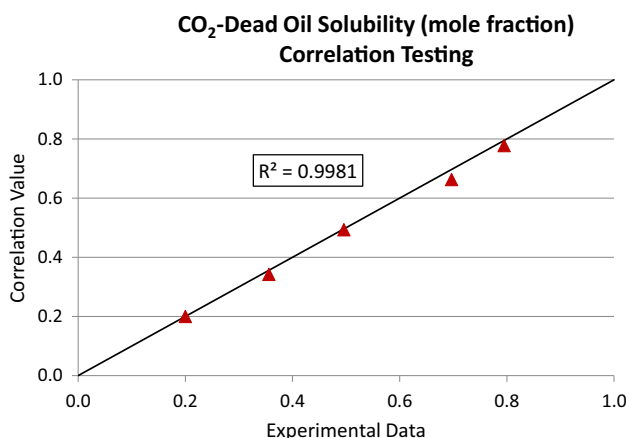


Fig. 5 CO₂-Dead Oil solubility correlation testing

- 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 CO₂ solubility
- Beggs and Robinson, function of temperature, dead oil viscosity, and oil gravity
- Emera, function of CO₂ 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 CO₂-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 CO₂-oil viscosity ratio is a ratio of the viscosity of the oil with CO₂ dissolved at a given pressure and temperature compared to the initial oil viscosity prior to increasing the pressure and dissolving CO₂. A plot of the viscosity ratio versus CO₂-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

$$\mu_{oCO_2} / \mu_{oi} = 1 + (0.01113T - 1.78210)\text{Sol} \tag{2}$$

(*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 R² 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 R² 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 CO₂-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 CO₂-oil solubility values and data set temperatures. These four points are plotted in Fig. 9. The four

Fig. 6 Experiment data for CO₂-oil viscosity reduction ratio as a function of CO₂ solubility in oil with best fit lines for different temperatures. Experimental data sets include live oil with gravities less than 0.9

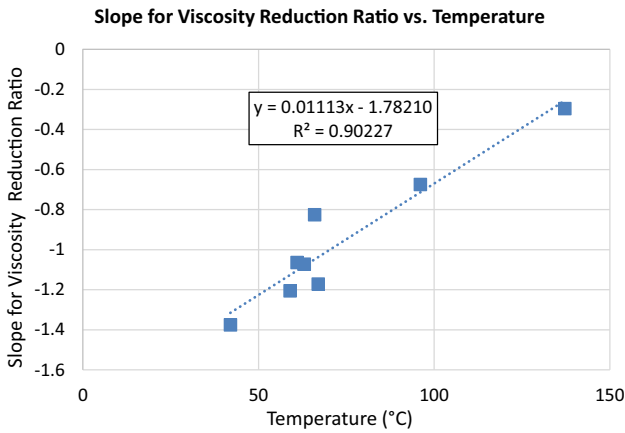
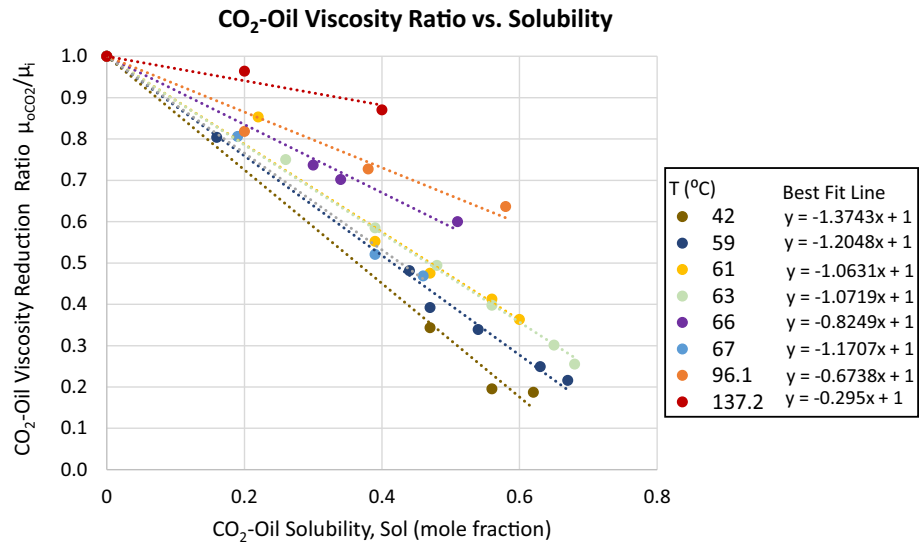


Fig. 7 Slopes of best linear fit lines determined for CO₂-Oil viscosity reduction ratio plotted against temperature

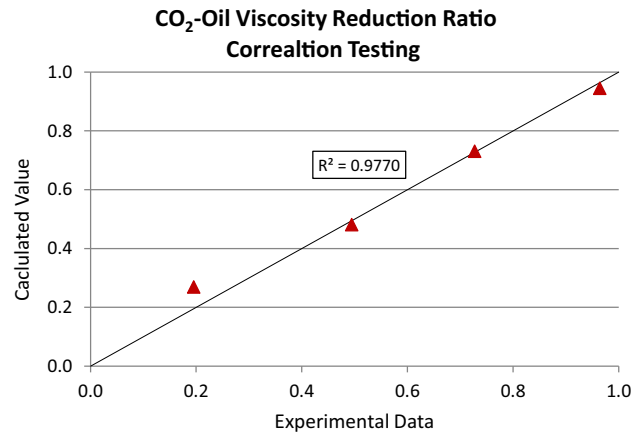


Fig. 9 CO₂-Oil viscosity ratio correlation testing

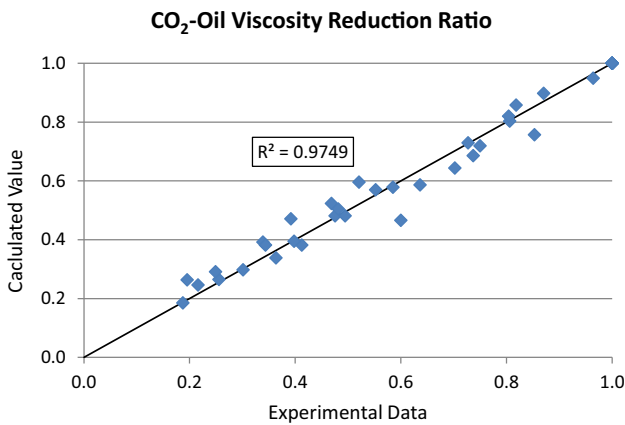


Fig. 8 CO₂-Oil viscosity ratio correlation calculation versus experimental values for live oil with oil gravities less than 0.9

points give an R² value of 0.9770 suggesting that the correlation is valid.

Concluding remarks

We have presented the development of new correlations for CO₂-oil solubility and the corresponding viscosity reduction of CO₂ 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 CO₂ 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 CO₂-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 CO₂ 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 CO₂-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_{oCO_2}/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
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
Srivastava et al.	0.8816	59	0.67	0.216
	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

References

- Beggs H, Robinson J (1975) Estimating the Viscosity of Crude Oil Systems. JPT 27(9):659–662
- Bon J, Sarma H (2004) A technical evaluation of a CO₂ flood for EOR benefits in the cooper basin, South Australia. SPE 88451 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, October, Perth, Australia pp 18–20
- Bou-Mikael S (2002) Post Waterflood CO₂ Miscible Flood in Light Oil Fluvial Dominated Deltaic Reservoir-Pre-Work and Project Appendix. DOE Final Report, Under Contract No. DE-FC22-93BC14960, February
- Chung F, Jones R, Nguyen H (1986). Measurements and correlations of the physical properties of CO₂-heavy crude oil mixtures. SPE paper 15080 presented at the 56th California Regional Meeting of the SPE, April 2–4, Oakland, CA

- Delaney R, Fish R (1980) Judy Creek CO₂ Flood performance prediction. Paper no. 80-31-23 presented at the 31st Annual Technical Meeting of the Petroleum Society of CIM. May 25–28, Calgary
- Dong M, Huang S, Srivastava R (2001) A laboratory study on near-miscible CO₂ injection in Steelman reservoir. JCPT 40-2(February):53–61
- Emera M (2006) Modeling of CO₂ and Green-House Gases (GHG) Miscibility and Interactions with Oil to Enhance the Oil Recovery in Gas Flooding Processes. Ph.D. Thesis, The University of Adelaide, Australian School of Petroleum, Adelaide, Australia
- Huang E, Tracht J (1974) The displacement of residual oil by carbon dioxide. SPE paper 4735 presented at the Improved Oil Recovery Symposium of Society of Petroleum Engineers of AIME. April 22–24, Tulsa, OK
- Lohrenz J, Bray B, Clark C (1964) Calculating viscosities of reservoir fluids from their composition. JPT 16(10):1171–1176
- Mehrotra A, Svrcek W (1982) Correlations for Properties of Bitumen Saturated With CO₂, CH₄ and N₂, and Experiments With Combustion Gas Mixtures. JCPT 21:95–104
- Simon R, Graue D (1965) Generalized Correlations For Predicting Solubility, Swelling, and Viscosity behaviour of CO₂-Crude Oil Systems. JPT 17(1):102–106
- Srivastava R, Huang S, Dong M (2000) laboratory investigation of weyburn CO₂ miscible flooding. JCPT 39-2:41–51
- Taylor M (1984) Effects of 10% N₂ contamination in CO₂ on the phase behaviour of wasson crude oil-CO₂ mixtures. PRRC report, New Mexico, pp 84–86
- Welker J, Dunlop D (1963) Physical properties of carbonated oils. JPT 15(8):873–875