New correlations predict aqueous solubility and density of carbon dioxide
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Alireza Bahadori, Hari B. Vuthaluru, Saeid Mokhatab

1. Introduction

The sequestration of anthropogenic carbon dioxide (CO2) into geological formations has been considered as a potential method to mitigate climate change. Accurate evaluation of the capacity of saline aquifers for CO2 sequestration and the fate of the injected fluids in sedimentary basins needs precise representation of brine and CO2 PVT data (Hassanzadeh et al., 2008). In the petroleum industry, compositional reservoir simulators use equation of state (EOS) thermodynamic models to calculate the phase equilibrium properties of fluid mixtures (Chang et al., 1998). Although these kinds of thermodynamic models are well suited for compositional modeling of enhanced oil recovery (EOR) processes, the disadvantage of such models for the specific case of large-scale flow simulation of geological CO2 storage in aquifers is that they represent computational “overkill” and are inappropriately expensive (Hassanzadeh et al., 2008).

Indeed, there are a large number of experimental equilibrium data on the CO2–brine system that have been used to tune the equations of state for CO2 and water under subsurface conditions. Accurate prediction of CO2 solubility over a wide range of temperature, pressure and ionic strength (T–P–m) is important to the studies of the carbonate precipitation and to the tracing of the global carbon cycle (Butcher et al., 1992). Although several models on CO2 solubility have been published, few can predict CO2 solubility in wide T–P–m range with accuracy close to experiment. For many temperature–pressure–composition conditions, CO2 solubilities are still unknown.

Based on the Peng–Robinson EOS, Henry’s law and the scaled-particle theory, Li and Ngheim (1986) presented a model (L–N model) to predict phase equilibrium of oil, gas and water/brine mixtures. This model is also intended to calculate the solubility of CO2 in pure water up to 473 K and in sodium chloride (NaCl) solutions with NaCl up to 4 molar. However, it is in general not accurate to predict the solubility of CO2 in aqueous NaCl solutions. Harvey and Prausnitz (1989) developed an EOS (H–P model) to predict CO2 solubility in pure water and in aqueous NaCl solutions at elevated pressures. However, it overestimates CO2 solubility by more than 10–20% in NaCl solutions. Zuo and Guo (1991) extended the Patel–Teja EOS to phase equilibrium calculations for electrolyte solutions (Z–G model). The Z–G model is no more accurate than the H–P model for CO2 solubility. For example, it underestimates CO2 solubility by more than 12% in 20 wt.% NaCl solutions at high pressures (>1000 bar) and overestimates CO2 solubility by more than 10% in 6 wt.% NaCl solution at moderate pressures. The precise knowledge of CO2 solubility in water is essential prior to any modelling activity. Several thermodynamic models are available to analyse the solubility of CO2 in aqueous solutions of alkanolamines and to correlate the equilibrium CO2 loading. These models involve a large number of parameters and require more complicated and longer computations.

Largely for environmental reasons, a great amount of work has been performed in order to determine the solubility of carbon
dioxide in water at various temperatures. These solubility data have been compiled and correlated. In most cases, however, the thermodynamics models may not be sufficient if accurate predictions are needed. Therefore, there is an essential need to develop a simple-to-use correlation for accurate predicting aqueous solubility of carbon dioxide. Since accurate predicting carbon dioxide density is a key parameter in carbon dioxide sequestration. In this study, a new correlation is also developed to predict density of CO2 as a function of pressure and temperature. This correlation is helpful to realize the variation of carbon dioxide density in CO2 recovery process and also for enhanced oil recovery process.

2. Proposed methodology for predicting aqueous solubility of carbon dioxide

The objective of the existing study is to identify a polynomial equation able to correlate the aqueous solubility of carbon dioxide in mole fraction with the most influential inlet properties including reduced temperature and reduced pressure. Even though all control parameters (temperature and pressure) remain constant, the resultant outcomes (aqueous solubility of carbon dioxide in mole fraction) vary. Therefore, a process of quantitatively estimating the trend of the outcomes becomes necessary. This method assumes that the best-fit polynomial equation of a given type is the one that has the minimal sum of the deviations squared (least square error) from a given set of data including temperature and pressure

\[ T_r = \frac{T}{T_c} \]

\[ P_r = \frac{P}{P_c} \]

\[ \Pi = \sum_{i=1}^{n} \left( x_i - \left( a + bP_{ri} + cP_{ri}^2 + dP_{ri}^3 \right) \right)^2 = \text{min} \]  

(3)

In order to calculate the coefficients \( a, b, c \) and \( d \) for Eq. (1), the best correlated data, \( x_i \), should have the least square error from the carbon dioxide reduced pressure.

Note that for this calculation, coefficients \( a, b, c \) and \( d \) are unknown while all \( x_i \) and \( P_{ri} \) are from Duan and Sun (2003). To obtain the least square error, the unknown coefficients, \( a, b, c \) and \( d \) must yield zero first derivatives:

\[ \frac{\partial \Pi}{\partial a} = 2 \sum_{i=1}^{n} \left[ x_i - \left( a + bP_{ri} + cP_{ri}^2 + dP_{ri}^3 \right) \right] = 0 \]  

(4)

\[ \frac{\partial \Pi}{\partial b} = 2 \sum_{i=1}^{n} \left[ x_i - \left( a + bP_{ri} + cP_{ri}^2 + dP_{ri}^3 \right) \right] = 0 \]  

(5)

\[ \frac{\partial \Pi}{\partial c} = 2 \sum_{i=1}^{n} \left[ x_i - \left( a + bP_{ri} + cP_{ri}^2 + dP_{ri}^3 \right) \right] = 0 \]  

(6)

\[ \frac{\partial \Pi}{\partial d} = 2 \sum_{i=1}^{n} \left[ x_i - \left( a + bP_{ri} + cP_{ri}^2 + dP_{ri}^3 \right) \right] = 0 \]  

(7)

Expanding the above equations, and revise them to linear equations form, yields the following:

\[ \sum_{i=1}^{n} x_i P_{ri} + \sum_{i=1}^{n} a P_{ri} + \sum_{i=1}^{n} b P_{ri}^2 + \sum_{i=1}^{n} c P_{ri}^3 + \sum_{i=1}^{n} d P_{ri}^4 = \text{min} \]

(8)

\[ \sum_{i=1}^{n} x_i P_{ri}^2 + \sum_{i=1}^{n} a P_{ri}^2 + \sum_{i=1}^{n} b P_{ri}^4 + \sum_{i=1}^{n} c P_{ri}^6 + \sum_{i=1}^{n} d P_{ri}^8 = \text{min} \]

(9)

\[ \sum_{i=1}^{n} x_i P_{ri}^3 + \sum_{i=1}^{n} a P_{ri}^3 + \sum_{i=1}^{n} b P_{ri}^6 + \sum_{i=1}^{n} c P_{ri}^9 + \sum_{i=1}^{n} d P_{ri}^{12} = \text{min} \]

(10)

\[ \sum_{i=1}^{n} x_i P_{ri}^4 + \sum_{i=1}^{n} a P_{ri}^4 + \sum_{i=1}^{n} b P_{ri}^8 + \sum_{i=1}^{n} c P_{ri}^{12} + \sum_{i=1}^{n} d P_{ri}^{16} = \text{min} \]

(11)

We know \( a, b, c \) and \( d \) are a function of carbon dioxide reduced temperature \( T_r \), so we need to generalize the previously tuned coefficients as a function of reduced temperature \( T_r \). So we have

\[ \Pi_a = \sum_{i=1}^{n} \left[ a - \left( A_1 + B_1 T_{ri} + C_1 T_{ri}^2 + D_1 T_{ri}^3 \right) \right]^2 = \text{min} \]

(12)

\[ \Pi_b = \sum_{i=1}^{n} \left[ b - \left( A_2 + B_2 T_{ri} + C_2 T_{ri}^2 + D_2 T_{ri}^3 \right) \right]^2 = \text{min} \]

(13)

\[ \Pi_c = \sum_{i=1}^{n} \left[ c - \left( A_3 + B_3 T_{ri} + C_3 T_{ri}^2 + D_3 T_{ri}^3 \right) \right]^2 = \text{min} \]

(14)

\[ \Pi_d = \sum_{i=1}^{n} \left[ d - \left( A_4 + B_4 T_{ri} + C_4 T_{ri}^2 + D_4 T_{ri}^3 \right) \right]^2 = \text{min} \]

(15)

We can derive all tuned coefficients for Eqs. (12)-(15) with repeating the procedure form Eqs. (3)-(11), where the required coefficients are given in Table 1.

In brief, Eq. (16) presents the new developed correlation for predicting CO2 solubility in aqueous solutions as a function of reduced pressure \( P_r \) and reduced temperature \( T_r \) of CO2

\[ x = a + bP_r + cP_r^2 + dP_r^3 \]

(16)

where

\[ a = A_1 + B_1 T_r + C_1 T_r^2 + D_1 T_r^3 \]

(17)

\[ b = A_2 + B_2 T_r + C_2 T_r^2 + D_2 T_r^3 \]

(18)

\[ c = A_3 + B_3 T_r + C_3 T_r^2 + D_3 T_r^3 \]

(19)

\[ d = A_4 + B_4 T_r + C_4 T_r^2 + D_4 T_r^3 \]

(20)

The units of \( x \) are ‘CO2 mole fraction’ for pure water and ‘CO2 moles per kg water’ for aqueous NaCl solutions.

Table 1 presents the tuned coefficients used in Eqs. (17)-(20) for determining the CO2 solubilities for pure water as well as different sodium chloride (NaCl) solutions. Eq. (21) is an interpolation formula to extend the calculated CO2 solubilities in other aqueous
In Eq. (21), \( X_j \) is the CO2 solubilities in aqueous NaCl solutions; \( M_j \) is the NaCl solution in “\( M \)” molarity. In fact, \( X_j \) is the interpolated mole fraction of the aqueous NaCl solutions between 1 and 4 molar solutions, and extrapolated mole fraction of the CO2 for concentrations less than 1 molar or more than 4 molar NaCl solutions.

### 3. New correlation for predicting carbon dioxide density

We use the above-mentioned methodology to develop the correlation for predicting carbon dioxide density. Eq. (22) presents the new developed correlation for predicting carbon dioxide density as a function of temperature (\( T \)) and CO2 pressure (\( P \)). The units of density is kg per cubic meter, \( T \) is in Kelvin and \( P \) is in bar

\[
\rho = \alpha + \beta T + \gamma T^2 + \delta T^3
\]

(22)

where

\[
\alpha = A_1 + B_1 P + C_1 P^2 + D_1 P^3
\]

(23)

\[
\beta = A_2 + B_2 P + C_2 P^2 + D_2 P^3
\]

(24)

\[
\gamma = A_3 + B_3 P + C_3 P^2 + D_3 P^3
\]

(25)

\[
\theta = A_4 + B_4 P + C_4 P^2 + D_4 P^3
\]

(26)

Table 2 presents the tuned coefficients used in Eqs. (23)–(26) for determining CO2 density.
Fig. 2. Predicting CO₂ solubility in one molar aqueous NaCl solution based on the proposed correlation.

Fig. 3. Predicting CO₂ solubility in two molar aqueous NaCl solution based on the proposed correlation.

Fig. 4. Predicting CO₂ solubility in four molar aqueous NaCl solution based on the proposed correlation.
4. Results

Fig. 1 compares results of the proposed correlation for predicting the solubility of CO₂ in pure water with the reported experimental data (Wiebe, 1941). Figs. 2–4 also compare the results of the proposed correlation for predicting the solubility of CO₂ in 1, 2 and 4 molar solutions of sodium chloride with the reported data (Duan and Sun, 2003). As can be seen, there is a good agreement between the observed data and the model predictions. Fig. 5 shows the results of new proposed correlation to predict density of carbon dioxide for pressure range between 25 and 700 bar and temperature range between 293 and 433 K.

The results illustrate that the new developed correlation has a good agreement with the reported data (Ahmed, 2007). Fig. 6 compares the results of proposed correlation for predicting the solubility of CO₂ in pure water and aqueous NaCl solutions. This study shows the solubility of CO₂ in aqueous NaCl solutions is more than pure water. Tables 3–5 compare the proposed correlation results in compare with (Duan and Sun, 2003) and these tables show good agreement between the proposed simple correlation and current models results. Fig. 7 shows the uniform performance of the proposed simple correlation to predict the density of carbon dioxide.

### Table 3
New correlation results in comparison with experimental data for pure water.

<table>
<thead>
<tr>
<th>Pressure, kPa</th>
<th>Temperature, K</th>
<th>Calculated pure water (mole fraction)</th>
<th>Pure water mole fraction (data, Diamond and Akinfiev, 2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>313.15</td>
<td>0.0175</td>
<td>0.016</td>
</tr>
<tr>
<td>700</td>
<td>313.15</td>
<td>0.0338</td>
<td>0.034</td>
</tr>
<tr>
<td>40,000</td>
<td>323.15</td>
<td>0.02509</td>
<td>0.028</td>
</tr>
<tr>
<td>10,000</td>
<td>348.15</td>
<td>0.01553</td>
<td>0.016</td>
</tr>
<tr>
<td>40,000</td>
<td>373.15</td>
<td>0.02518</td>
<td>0.026</td>
</tr>
<tr>
<td>70,000</td>
<td>373.15</td>
<td>0.0299</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Table 4
New correlation results in comparison with (Duan and Sun, 2003).

<table>
<thead>
<tr>
<th>Pressure, kPa</th>
<th>Temperature, K</th>
<th>One molar aqueous NaCl solutions (mol CO₂/kg water)</th>
<th>One molar aqueous NaCl solutions (Duan et al.) (mol CO₂/kg water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>303.15</td>
<td>0.9155</td>
<td>0.8729</td>
</tr>
<tr>
<td>70,000</td>
<td>333.15</td>
<td>1.4109</td>
<td>1.3952</td>
</tr>
<tr>
<td>10,000</td>
<td>333.15</td>
<td>1.201</td>
<td>1.1827</td>
</tr>
<tr>
<td>10,000</td>
<td>363.15</td>
<td>0.6354</td>
<td>0.6767</td>
</tr>
<tr>
<td>40,000</td>
<td>393.15</td>
<td>1.2043</td>
<td>1.1881</td>
</tr>
<tr>
<td>70,000</td>
<td>393.15</td>
<td>1.4639</td>
<td>1.4535</td>
</tr>
</tbody>
</table>

### Table 5
New correlation results in compare with (Duan and Sun, 2003).

<table>
<thead>
<tr>
<th>Pressure, kPa</th>
<th>Temperature, K</th>
<th>Calculated 2 molar aqueous NaCl solutions (mol CO₂/kg water)</th>
<th>2 molar aqueous NaCl solutions (Duan and Sun, 2003) (mol CO₂/kg water)</th>
<th>Calculated 4 molar aqueous NaCl solutions (mol CO₂/kg water) (Duan and Sun, 2003)</th>
<th>4 molar aqueous NaCl solutions (Duan and Sun, 2003) (mol CO₂/kg water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>333.15</td>
<td>0.5</td>
<td>0.4583</td>
<td>0.361</td>
<td>0.3314</td>
</tr>
<tr>
<td>20,000</td>
<td>303.15</td>
<td>0.0983</td>
<td>0.0981</td>
<td>0.6874</td>
<td>0.6849</td>
</tr>
<tr>
<td>60,000</td>
<td>363.15</td>
<td>1.066</td>
<td>1.0859</td>
<td>0.825</td>
<td>0.8395</td>
</tr>
<tr>
<td>10,000</td>
<td>423.15</td>
<td>0.4518</td>
<td>0.4798</td>
<td>0.3394</td>
<td>0.3538</td>
</tr>
<tr>
<td>60,000</td>
<td>423.15</td>
<td>1.2232</td>
<td>1.2771</td>
<td>0.9337</td>
<td>0.9671</td>
</tr>
<tr>
<td>70,000</td>
<td>393.15</td>
<td>1.219</td>
<td>1.2108</td>
<td>0.9492</td>
<td>0.9428</td>
</tr>
<tr>
<td>50,000</td>
<td>363.15</td>
<td>1.014</td>
<td>1.0216</td>
<td>0.7736</td>
<td>0.7793</td>
</tr>
</tbody>
</table>
5. Conclusion

Easy-to-use correlations, which are simpler than current available models involving a large number of parameters and requiring more complicated and longer computations, have been developed to accurately predict the CO₂ density as well as the solubility of carbon dioxide in pure water and in aqueous NaCl solutions. The density correlation predicts density of carbon dioxide for pressure between 25 and 700 bar and temperature between 293 and 433 K. The solubility correlation is recommended for prediction of CO₂ solubility in the pure water and different aqueous solutions of NaCl for CO₂ pressures up to 700 bar and temperatures less than 373 and 393 K, respectively.

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References

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