Solubility prediction of carbon dioxide in water by an iterative equation of state/excess Gibbs energy model

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Abstract. The solubility of carbon dioxide in water has been predicted extensively by various models, owing to their vast applications in process industry. Henry’s law has been widely utilized for solubility prediction with good results at low pressure. However, the law shows large deviations at high pressure, even when adjusted to pressure correction and improved conditions. Contrarily, equations of state/excess Gibbs energy models are a promising addition to thermodynamic models for prediction at high pressure non-ideal equilibria. These models can efficiently predict solubilities at high pressures, even when the experimental solubilities are not corroborated. Hence, these models work iteratively, utilizing the mathematical redundancy of local composition excess Gibbs energy models. In this study, an iterative form of Linear Combination of Vidal and Michelsen (LCVM) mixing rule has been used for prediction of carbon dioxide solubility in water, in conjunction with UNIFAC and translated modified Peng-Robinson equation of state. The proposed model, termed iterative LCVM (i-LCVM), predicts carbon dioxide solubility in water for a wide range of temperature (273 to 453 K) and pressure (101.3 to 7380 kPa). The i-LCVM shows good agreement with experimental values and predicts better than Henry’s law (53% improvement).

1. Introduction
The solubility of carbon dioxide in water is of immense importance because of their extensive applications in chemical process industries such as beverages, enhanced oil recovery, carboxylic acids manufacture, etc [1]. Furthermore, the recent carbon capture systems for greenhouse gas control employ water based solvents, which demands better knowledge of vapour-liquid equilibrium (VLE) of the CO₂ – H₂O system [2]. Carbon dioxide is a gas at ambient conditions and weakly soluble in water. The concentration of carbon dioxide in liquid phase [CO₂] is usually measured by Henry’s law [3], using the relationship given in equation (1). A number of relationships relate the Henry’s constant given in equation (2) to temperature, both at low pressures [4] and high pressures [5].

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\[ [\text{CO}_2] = \frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \]  
\[ H_{\text{CO}_2} = \exp\left(\frac{A}{T} + B \ln T + C T + D\right) \]  

where \( T \) is the temperature and \( A-D \) are the regressed constants.

Carbon dioxide shows positive non-ideal behaviour upon reactive dissolution in water and correlates well with Henry’s law at low pressures [4]. However, it deviates significantly from Henry’s law at high pressures. The root cause of this deviation is the weak definition of constant of proportionality present in Henry’s law, known as Henry’s constant. Interestingly, the term ‘constant’ is quite misleading, as Henry’s constant is a function of temperature [6].

\[ H_{\text{CO}_2} = \lim_{x\to 0} \frac{f_{\text{CO}_2}}{x_{\text{CO}_2}} \]  

Equation (3) can be theoretically applied to any temperature and pressure in \( \text{CO}_2 - \text{H}_2\text{O} \) system with limit of infinite dilution. However, real systems do not reach the limit of infinite dilution. Thus, for real systems, the infinite dilution limit has to be ignored and further assumed that \( f_{\text{CO}_2}/x_{\text{CO}_2} \) remains constant for non-zero values of \( x_{\text{CO}_2} \). This assumption is valid for very small values of \( x_{\text{CO}_2} \). This forms the main reason behind the large deviation of carbon dioxide from Henry’s law at high pressures. The accuracy of fitting to experimental data for determination of Henry’s constant also affects the end result [4] and the arbitrariness of units used in Henry’s constant creates confusion over the use of Henry’s law [7]. A number of previous works were evaluated for correlation of \( \text{CO}_2-\text{H}_2\text{O} \) system, using different Henry’s Constant equations [4,5,8,9] similar to equation (2). The performance of these equations was either weak in correlation or limited in application terms. Therefore, a recently developed EoS/G model for determination of liquid phase equilibria in carbon dioxide-water system [10] has been modified for iterative calculations. The model uses an iterative procedure to determine the excess Gibbs energy values (by initial guess values of mole fraction of components), which are correspondingly used to determine new mole fraction of carbon dioxide in the binary system, by equalization of individual fugacities. The model has been compared to Henry’s law prediction for carbon dioxide-water system.

2. Thermodynamic Framework

The translated modified Peng Robinson (tmPR) [11] was used as equation of state and given in equation (4).

\[ P = \frac{RT}{V + t - b} - \frac{a}{(V + t)(V + t + b) + b(V + t - b)} \]  

where \( P \) is the pressure, \( T \) is the temperature, \( R \) is the universal gas constant, \( V \) is the volume of the system, \( a \) and \( b \) are the co-volume parameters and \( t \) is the translated volume. The values of translation term and pure component values for water and carbon dioxide were taken from original work of Magoulas and Tassios [11].

Linear Combination of Vidal and Michelsen (LCVM) mixing rule [12] was used with the Universal Functional Activity Coefficients (UNIFAC) [13] to determine excess Gibbs energy and combined it with aforementioned EoS.

\[ \alpha = \left( \lambda A_V \frac{1 - \lambda}{A_M} \right) \frac{G_E}{RT A_M} + \lambda \sum_i x_i \ln \left( \frac{b_i}{b} \right) + \sum_i x_i \alpha_i \]  

where \( \alpha \) defined as \( a/bRT \) for all components in the system, \( \lambda \) is the LCVM constant, \( G_E \) is the excess Gibbs energy, \( x_i \) is the mole fraction of each component. Constants \( A_V \) and \( A_M \) represent individual Vidal and Michelsen mixing rules constants.
The input values to i-LCVM were vapour pressure of gas and equilibrium temperature (as in the original case of Henry’s law). Initial guess values were zero and one for carbon dioxide mole fraction in liquid and vapour phase, respectively. These values were used in determination of excess Gibbs energy, which resultantly calculated the new mole fractions in the model. The new values were then used again for the determination of new excess Gibbs energy values and vice versa. The loop continued until the condition of equalization of individual fugacities was satisfied in both vapour and liquid phase. Thus, the excess Gibbs energy formed an iterative function of liquid mole fraction, hence the reason for the name. The work mode of i-LCVM is given in Figure 1. The fugacity correlation for i-LCVM was taken from Boukouvalas et al. [12].

2.1. Optimization of UNIFAC Binary Interaction Parameters
The binary interaction parameters of UNIFAC (BIP) were fitted to experimental data given in Table 1. The selected experimental data was refined by using a recently developed statistical analysis technique [14]. Unconstrained minimization of the objective function, OF was carried out in MATLAB environment.

Table 1. Experimental data sources for carbon dioxide-water system

| Data Source                  | No. of Data Points | Temp. (K)     | Pressure (MPa) |
|------------------------------|--------------------|---------------|----------------|
| Bamberger, et al. [15]       | 12                 | 323 – 353     | 4.05 – 7.08    |
| Campos, et al. [16]          | 17                 | 303 – 323     | 0.10 – 0.54    |
| Dalmolin, et al. [17]        | 33                 | 288 – 308     | 0.11 – 0.47    |
| Han, et al. [18]             | 16                 | 313 – 333     | 0.37 – 2.00    |
| Houghton, et al. [19]        | 103                | 273 – 373     | 0.10 – 3.65    |
| Lucile, et al. [20]          | 29                 | 298 – 373     | 0.54 – 5.14    |
| Müller, et al. [21]          | 48                 | 373 – 453     | 0.60 – 7.21    |
| Steward and Munjal [22]      | 10                 | 273 – 285     | 1.01 – 4.56    |
| Valtz, et al. [23]           | 32                 | 298 – 318     | 0.51 – 7.03    |
| Zawisza and Malesinska [24]  | 27                 | 323 – 453     | 0.15 – 4.62    |

\[
OF = \frac{1}{N} \sum_{N=1}^{N} (x_{pr} - x_{ex})^2^{0.5}
\]  

where, \(x_{pr}\) and \(x_{ex}\) are predicted and experimental carbon dioxide solubilities. \(N\) represents the number of data points. The optimized UNIFAC BIP, \(A_{nm}\) and \(B_{nm}\) for carbon dioxide and water system are given in Table 2. The root mean square error for liquid phase calculations was 7.84x10^{-4}. The schematic for optimization of BIP of UNIFAC is given in Figure 2. The same schematic can be utilized for optimization of BIP for solubility of other gases in water/other solvents. Binary interaction parameters of UNIFAC for carbon dioxide and water system were optimized, taking zero and one as initial guess values of carbon dioxide mole fraction in liquid and vapour phase, respectively. These
were based on the qualitative assumption (later quantitatively proven) that initially liquid phase completely consists of water (zero carbon dioxide) and vapour phase completely consists of carbon dioxide (no water), which is valid theoretically.

### Table 2. Optimized UNIFAC BIP for carbon dioxide-water system

| Component (nm) | Binary Interaction Parameters | Initial Guess Value |
|----------------|------------------------------|---------------------|
|                | $A_{nm}$                     | $B_{nm}$            | $\text{Liquid}_{(nm)}$ | $\text{Vapor}_{(nm)}$ |
| Water – CO$_2$ | 283.121                      | 2.717               | 1                       | 0                     |
| CO$_2$ – Water | 610.493                      | -2.929              | 0                       | 1                     |

3. **Results and Discussion**

Figure 3 shows the prediction of Henry’s law, basic LCVM and i-LCVM against experimental data.

![Figure 3](image-url)

**Figure 3.** Comparison of i-LCVM (used predicted liquid mole fraction for excess Gibbs energy determination) with basic LCVM model (used experimental liquid mole fraction for excess Gibbs energy determination). Experimental data from Table 1.
The difference in absolute average relative percentage error (AARE) due to this iteration was found to be very small (0.23%) and deemed negligible. This proves that the effect of iteration on the prediction was insignificant and the assumption of initial conditions (liquid and vapour phase consist of water and carbon dioxide initially) was quantitatively valid. On the contrary, i-LCVM is better in prediction when compared to Henry’s law for a wide range of temperature and pressure (53% improvement). However, all three models over predict at higher solubilities. This behaviour is attributed to near-critical fluid like behaviour of carbon dioxide in high pressure ($\approx 7000$ kPa) and low temperature region ($<313.15$K). However, the deviation of i-LCVM is controlled as compared to Henry’s law.

The presence of temperature independent UNIFAC BIP provides streamlined prediction behaviour for the i-LCVM model. Although, the prediction of Henry’s law enhances with increase in temperature, the improvement is limited when compared to i-LCVM model. Similarly, the prediction of Henry’s law weakens heavily beyond carbon dioxide pressures of 1000 kPa [25], the i-LCVM predictions are unaffected by increase the pressure, up to 6500 kPa at all temperatures.

4. Conclusions

An iterative EoS/GEE based model, termed as i-LCVM has been developed for prediction of carbon dioxide solubility in water. The model uses an iterative procedure to determine the activity coefficient values for both carbon dioxide and water by initial guess values of mole fraction of components. These determined values are correspondingly used to determine new mole fraction of carbon dioxide in the binary system, by equalization of individual fugacities. The algorithm is bound by the UNIFAC binary interaction parameters that results in termination of iterative procedure. The model shows good correlation for prediction of carbon dioxide solubility and results are heavily improved as compared to Henry’s law. The proposed model can be used as an improved alternate to Henry’s law in prediction of carbon dioxide solubilities. The solubility of other gases in different solvents can be predicted by using the proposed methodology.

5. References

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