Calculation Method for Determining Phenanthrene

Solubility in Supercritical CO₂ Employing

Redlich-Kwong Modified Equation

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Abstract

Phenanthrene is a compound insoluble in water derived from petroleum which can be accumulated in organic matter. Phenanthrene is found in hydrocarbons mixtures. However, it requires efficient extraction methods. The relevance of calculating Phenanthrene solubility through modified state equation lies in the reduction of experimentation to predict the Phenanthrene concentration at different pressures during supercritical extraction. This research proposes a new method to determine the solubility of solids in supercritical fluids using a correlation based on Redlich-Kwong modified equation. In this method, the solubility of solids on equilibrium systems with solvents in a supercritical state was correlated with the Redlich-Kwong modified equation. Initially, the parameters a and b pertaining to modified equation were expressed by the Van der Waals rule; then two adjustable parameters (α and β) are defined and introduced into the equation for the calculation of solubility. α is related to the molecular interactions between the solute and solvent, and β with the molecular size. In order to find optimal values of adjustable parameters, the non-linear simplex method was employed. The proposed method is easy to use analytically and does not require the critical properties of the solid, which is important for thermolabile compounds. The average error ranged between 3% and 15%, acceptable for theoretical work.
Keywords: Phenanthrene, Solubility; Supercritical fluid

1 Introduction

Polycyclic aromatic hydrocarbon (PAH’s) are organic compounds with two or more aromatic rings, besides are petroleum-derived contaminants that are insoluble in water. Its origins in the urban environment, come from two sources: A) The anthropogenic that is the product of incomplete combustion of fossil fuels used and emissions generated by industries, domestic activities, oil refining, among others. B) From natural sources as the burning of biomass and volcanic emissions. Phenanthrene is used for drugs synthesis, clinical research, explosives production and colorants manufacture. To determine the phenanthrene presence in a different environment is necessary to extract it since it usually is mixed with other contaminating agents and its extraction is not easy to perform, for this reason, various extraction methods have been tested for their identification. Supercritical extraction is a separation process and mass transfer that takes place under conditions of pressure and temperature higher than those of the critical point of the solvent.

Supercritical fluids (SF) can extract certain chemical compounds with the use of specific solvents under adequate temperature and pressure conditions [13]. The extraction is based on the high power solvent that has SF. Therefore, supercritical extraction is an alternative to conventional methods such as distillation and solvent extraction. Currently, supercritical extraction is used in the pharmaceutical and food industry, in the production of energy and other areas [1, 4, 10]. It has been possible to predict the solubility of solid compounds in supercritical fluids [6]. Different researchers have used state equations to predict the solubility of solid compounds [8]. Solubility is the most important thermophysical property in the supercritical extraction process of a solute and must be determined to design a reliable model [11, 14, 15].

In general term, the models for calculating solubilities are classified into two groups: theoretical models and those based on states equations and empirical correlations. Among the state equations, cubic is widely used for solubilities calculation in supercritical fluids [1, 2, 7, 12]. The Redlich Kwong equation has shown good approximation, for this reason, it is the most used for this type of calculations. This equation involves two interaction parameters for a binary mixture, which are important for predicting solubility [1, 7]. In this research, a method of calculating the solubility of phenanthrene was developed using the Redlich Kwong modified equation to avoid the use of solid critical properties and facilitate the prediction of phenanthrene solubility in supercritical carbon dioxide.

2 Materials y Methods

The basic equation used to calculate the solubility of solids with low vapor pressure in supercritical fluids can be expressed as:
Calculation method for determining phenanthrene solubility

\[ y_2 = \left[ \frac{P_{sat}}{P_0} \right] \exp \left( \frac{V_{mol} (P - P_{sat})}{RT} \right) \]  

(1)

Where \( y_2 \) is the solubility of solids with low vapor pressure in supercritical fluids, \( \phi \) the fugacity coefficient, \( P_{sat} \) the saturation pressure, \( V_{mol} \) is the solid molar volume of the solute, \( R \) the universal constant of the gases, \( T \) the temperature and \( P \) the system pressure. Subscript 2 refers to the solid component. All terms can be obtained experimentally except \( \phi_2 \).

The Redlich-Kwong equation is used to calculate the fugacity coefficient, the expression for the calculation is as follows:

\[
\ln \hat{\phi}_2 = (Z - 1) \frac{b_2}{b_1} - \ln(Z - B) + \frac{a}{bRT^{1.5}} \left[ \frac{2(y_1a_{12} + y_2a_2)}{a} - \frac{b_2}{b} \right] \ln \frac{Z + B}{Z}
\]

(2)

Where \( A \) and \( B \) are the adjustable parameters, \( a_1 \) and \( b_1 \) are the solute Van der Waals parameters of solute, \( a_2 \) and \( b_2 \) are the solvent Van der Waals parameters, \( a \) and \( b \) are the mixture parameters and \( z \) is the compressibility factor, which depend on the solubility. For the fluid phase, \( a \) and \( b \) were calculated employing Van der Waals mixing rule, it can be observed that solubility is a \( Z \) function.

\[
a = \sum_i \sum_j y_i y_j a_{ij} = y_1^2 a_1 + 2y_1y_2 a_{12} + y_2^2 a_2
\]

(3)

\[
b = \sum_i y_i b_i = y_1 b_1 + y_2 b_2
\]

(4)

The subscripts \( i \) and \( j \) correspond to the solid and the solvent, which take values from 1 to 2 for binary systems.

To infinite dilution:

\[
y_2 = 0 \quad y_1 = 1 \quad b = b_1 \quad a = a_1
\]

(5)

The standard combination rule for \( a_{12} \) is:

\[
a_{12} = \sqrt{a_1 a_2}
\]

(6)

Equation 2 can be written as follows:

\[
\ln \hat{\phi}_2^\infty = (Z - 1) \frac{b_2}{b_1} - \ln(Z - B) + A \left( \frac{a_{12}}{a_1} - \frac{b_2}{b_1} \right) \ln \frac{Z + B}{Z}
\]

(7)

Defining:
The final equation for the fugacity coefficient at infinite dilution is:

\[ \ln \hat{\phi}_x^\infty = \beta (Z - 1) - \ln (Z - B) + \frac{A}{B} (\beta - 2\alpha) \ln \frac{Z + B}{Z} \]  

(10)

Where \( \alpha \) is the adjustment parameter with respect to the molecular interactions between the solute and the solvent, \( \beta \) the adjustment parameter in relation to the molecular size between the solute and the solvent. A and B in all the equations are defined as:

\[ A = \left( \frac{a_1}{T_1^3} \right) \frac{P}{(RT)^2}, \quad a_1 = \Omega_a \frac{R^2T_1^{2.5}}{P_{c1}}, \quad A = \Omega_a \frac{P_r}{T_r^{2.5}} \]  

(11)

\[ B = \frac{b_1 P}{RT}, \quad b_1 = \Omega_b \frac{RT_{c1}}{P_{c1}}, \quad B = \Omega_b \frac{P_r}{T_r} \]  

(12)

\[ \Omega_a = \frac{1}{9 \left( \frac{3}{2} \right)} = 0.427480, \quad \Omega_b = \frac{\sqrt{3} - 1}{3} = 0.086640 \]  

(13)

Where, \( P_r \) is the reduced pressure, \( T_r \) the reduced temperature and the symbol \( \infty \) denotes infinite dilution.

The reduced properties are normalized with respect to the critical properties of the solvent. To obtain the optimal values of \( \alpha \) and \( \beta \), the nonlinear simplex method was used. The model was compared with other models proposed based on absolute error, relative error and mean square error, which were defined as follows:

Average relative error:

\[ E_{r1} = \frac{100}{N_p} \sum_{i=1}^{N_p} \frac{|y_{i,\text{exp}} - y_{i,\text{calc}}|}{y_{i,\text{exp}}} \]  

(14)

Average error:
Calculation method for determining phenanthrene solubility

\[
Err_P = 100 \sqrt{\frac{\sum_{i=1}^{N_p} (y_{i,cal} - y_{i,exp})^2}{N_p}}
\]  

(15)

Mean square error:

\[
ECM = 100 \sqrt{\frac{\sum_{i=1}^{N_p} (y_{i,cal} - y_{i,exp})^2}{N_p}}
\]  

(16)

Where \( y_{i,cal} \) is the solubility calculated from component \( i \), \( y_{i,exp} \) the experimental solubility of component \( i \) and \( N_p \) is the data number.

The search for the optimal values of \( \alpha \) and \( \beta \) is based on the minimization of the objective function.

3 Results and Discussion

The solubility curve for the systems shows two characteristic. The first corresponds to the region of low pressure, where the solubility is inversely proportional to the pressure and the behavior is close to the ideal gas, thus:

\[
P_i = y_i p_i
\]

(17)

Accordingly,

\[
P_2 = P_2^{sat} = y_2 P
\]

(18)

Then,

\[
y_2 = \frac{P_2^{sat}}{P}
\]

(19)

At this point the mixture is ideal and the partial volume is greater than molar volume in the solid phase. Then the change in concentration concerning the pressure will present a minimum and the concentration will decrease when the pressure increases. This will occur when the partial volume becomes equal to the volume of the solid. The second phase belongs to the high-pressure region where it is observed that the solubility increases as the pressure increase [9].

This characteristic makes important the processes of supercritical extraction. The critical conditions of the solvent cause a solubility increase due to increase in the molecular interactions between the solute and the solvent. As a result of the increase
in density, the mass-volume ratio increases. The most of \( \alpha \) and \( \beta \) values ranging from 3 to 7. The above is observed in Figure 2 where the behavior of \( \alpha \) remains constant with temperature, while \( \beta \) presents variations with temperature for some systems \( \beta \) increases with temperature while in other systems \( \beta \) decreases with temperature.

It has been calculated solubilities using different target functions, which means that the selection of the target function is not important. The results obtained for the errors were the following: for the mean square error 15.14\%, for the average error 8.80\% and the relative error 11.95\%. These results are comparable with errors values determined by Caballero and Hernandez [3], which shows an average error of 8.07. The data obtained are plotted to visualize the errors for each of the target functions. It is important to know that the parameters \( \alpha \) and \( \beta \) involve all the effects of the binary interaction parameters. Also, to know optimal values of its parameters, it is not necessary to know the critical conditions of the solute, an interesting reason for the importance of this work.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( M ) g/mol</th>
<th>( P_c ) MPa</th>
<th>( T_c ) K</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>44.01</td>
<td>7.38</td>
<td>304.25</td>
<td>0.225</td>
</tr>
</tbody>
</table>

Table 1. Properties of the solvents used.

<table>
<thead>
<tr>
<th>Solute</th>
<th>( M ) g/mol</th>
<th>( A_a )</th>
<th>( B_a ) K</th>
<th>( V^{mol} ) M(^3)/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>178.24</td>
<td>14.631</td>
<td>4873.4</td>
<td>0.1512</td>
</tr>
</tbody>
</table>

Table 2. Properties of the solutes used.

<table>
<thead>
<tr>
<th>Model</th>
<th>( ErrP )</th>
<th>( ERlp )</th>
<th>( ECM )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redlich-Kwong Mod..</td>
<td>8.8</td>
<td>12.72</td>
<td>16.02</td>
</tr>
<tr>
<td>Redlich-Kwong conventional.</td>
<td>8.07</td>
<td>no calc</td>
<td>no calc</td>
</tr>
<tr>
<td>Redlich-kwong</td>
<td>9.02</td>
<td>11.84</td>
<td>15.72</td>
</tr>
</tbody>
</table>

Table 3. Comparison of the errors of the proposed model with the errors of other models.
Table 4 shows the comparison of the errors obtained using different objective functions for calculate optimal $\alpha$ and $\beta$ values.

Tabla 4. Comparison of errors for different objective functions

<table>
<thead>
<tr>
<th>Target function used to obtain $\alpha$ and $\beta$</th>
<th>$Fo_1$</th>
<th>$Fo_2$</th>
<th>$Fo_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.14</td>
<td>16.02</td>
<td>12.72</td>
</tr>
<tr>
<td></td>
<td>13.59</td>
<td>15.75</td>
<td>11.95</td>
</tr>
<tr>
<td></td>
<td>8.8</td>
<td>54.88</td>
<td>26.65</td>
</tr>
</tbody>
</table>

Figures 1a, 1b and 1c show the solubilities calculated by the conventional equations of Kwong Redlich, modified Kwong Redlich and experimental solubility. The modified Redlich Kwong model shows a reliable behavior since the values of the experimental solubility is on the solubility curve calculated with this model. The solubility calculated with the conventional Redlich Kwong model is far from the experimental solubility data. This behavior shows the difference between the calculations of these models [5]. It should be noted that the proposed model does not need knowledge of the critical conditions of the solute. In most cases, the values of $\alpha$ and $\beta$ for the same isotherm are quite similar.

Table 5. Values of $\alpha$, $\beta$ and Average Error for each system, using the Peng Robinson equation

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>$T$</th>
<th>$A$</th>
<th>$B$</th>
<th>ECM</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>30</td>
<td>5,536</td>
<td>6,849</td>
<td>6.78</td>
<td>178</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>45</td>
<td>5,813</td>
<td>7,423</td>
<td>6.66</td>
<td>178</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>50</td>
<td>5,643</td>
<td>6,974</td>
<td>6.87</td>
<td>178</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>55</td>
<td>5,856</td>
<td>7,421</td>
<td>3.57</td>
<td>178</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>65</td>
<td>5,892</td>
<td>7,456</td>
<td>2.23</td>
<td>178</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>CO$_2$</td>
<td>70</td>
<td>5,710</td>
<td>7,163</td>
<td>9.57</td>
<td>178</td>
</tr>
</tbody>
</table>
Figure 1. Behavior of the solubility in the supercritical CO$_2$ system and phenanthrene a) 338.15 K, b) 328.15 K and c) 323.15 K. Experimental data.

Figure 2. Variation of $\alpha$ and $\beta$ with respect to temperature.

The proposed model does not need knowledge of the critical conditions of the solute only needs to correlate the parameters $\alpha$ and $\beta$, which allow a simplified calculation of the solubility.
4 Conclusions

The modified Redlich-Kwong model presents characteristics of an easy-to-use algebraic equation since it has only two parameters, which is important for use in equilibrium solubility calculations of a solid in a supercritical solvent. Likewise, it has independence concerning the critical properties of the solid which it is important in the cases where is not possible to know the critical thermolabile properties of substances. The $\alpha$ and $\beta$ parameters not dependent on temperature. It was not found a relationship between $\alpha$ and $\beta$ with the solids nature or solvents studied. A non-linear simplex method is an excellent tool for calculating the values of the adjustable parameters $\alpha$ and $\beta$. The model found is efficient and easy to use for the calculation of solubilities of high molecular weight solids with thermolabile characteristics in supercritical fluids.

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References


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