Solubility Prediction of Supercritical Fluids Extraction By Equations of State

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Abstract
The main purpose of this work is to study the influence of the equations of state on the prediction of the performance of supercritical fluid extraction of herbal essential oils. The applied equations are van der Waals, Redlich-Kwong and the Peng-Robinson equations of state with their related mixing rules. To study of the performance of these equations on the solubility prediction, Mint (Spearmint) essential oil was chosen as the solute and supercritical carbon dioxide as the solvent. An experimental apparatus was used for extraction of Mint essence and the best operating conditions were reached after many experiments. Thermodynamic properties of Carvone, as the specific compound of Mint essential oil, including critical pressure; critical temperature and eccentric factor have been estimated. According to the experimental results, Peng-Robinson equation of state with its mixing rules was the best selected equation of state to assess the solubility of essential oils in supercritical carbon dioxide and showed the best results.

Keywords: Solubility, Equations of state, Mixing rules, Supercritical fluid extraction.

Introduction
The continued research for rapid, efficient and cost-effective technology to produce natural products and herbal essential oils has introduced supercritical fluids (SCFs) to produce these materials industrially [1]. Supercritical fluid extraction (SCFE) showed a promising separation and purification technology in many fields. In this respect, carbon dioxide (CO\textsubscript{2}) has been the most commonly used supercritical fluid since it is non-toxic, safe and inexpensive [2]. However, its solvent power is limited for many solutes, and thus investigations to enhance its solvent power by addition of a small amount of suitable co-solvent are receiving increasing attention [3]. The well known processes using supercritical (SC) gases especially CO\textsubscript{2} are decaffeination...
of coffee beans and tea and extraction of herbal essential oils. These processes have been established at industrial scale [1]. There has been raising concern in recent years over SCFs for organic waste treatment and other applications such as fine powders generation and recycling of polyethylene terephthalate [4].

The discovery of the existence of critical point dates back to 1822 [5]. Generally, the temperature and pressure beyond the critical point are the SC state [6]. In 1869, Thomas Andrews first recognized the presence of critical point, which gave birth to a new world of critical phenomena and SCFs science [7].

Supercritical fluid solvents (SCFS) make ideal conditions to be used in the development of new chemical and food processes, because thermodynamic conditions can be used to control the solvating properties of these fluids. This thermodynamic control arises because the density of SCF can be varied continuously from gas-like to liquid-like values by invoking modest changes in the pressure and/or temperature [8]. In 1999, Chemical Reviews edited comprehensive reviews on the state of the art on fundamentals and new fields of applications of SCFs [9].

Since SCFE deals with high pressure phase equilibria, the equations of state (EOS) method is the most suitable approach for modeling such kind of systems. Although; many investigations have been carried out for modeling solubility of natural compounds and solids in the SCFSs, but in modeling of SC processes and supercritical extraction (SCE) systems some major methods are used, including thermodynamic modeling and mathematical modeling.

In thermodynamic modeling, EsOS are using with mixing rules. However, another thermodynamic models or EsOS have been used in some studies. It is common to use, the set of Peng-Robinson (PR) equation of state with van der Waals (vdW) mixing rules in order to thermodynamic modeling for better performance and the results of this set will compare with other sets. In mathematical modeling various effective parameters on extraction process are studied. Some parameters like temperature and pressure of extraction process, solvent flow rate, co-solvent existing, solvent flow direction, size and geometry of extraction column are effective on the extraction rate and the yield of extraction. An overview of published papers for various method of SCFE modeling is given below.

In 1985, Mansoori et al. [10] published the results of thermodynamic modeling of SCFE by use of density expansion (DEX) mixing rules. In this work, conformal solution theory and the DEX expression of the radial distribution function of fluids are used to drive a set of mixing rules. The new mixing rules were composition, density and temperature dependent. To test the new mixing rules, they are used for thermodynamic modeling of SCFE. Comparison of the result of
calculation by the mixing rules with the vdW mixing rules indicates a profound improvement over the later in prediction of properties of mixtures consisting of species with large molecular size and shape differences. In another work, new concept for the developing of mixing rules for cubic equations of state consistent with statistical-mechanical theory of the vdW mixing rules have been published by Kawak and Mansoori in 1986 [11]. Application of this concept is illustrated by its application to Redlich-Kwong (RK) and Peng-Robinson (PR) EsOS. According to the results, when the unlike-interaction adjustable parameters of the mixing rules are fitted to the experimental data, the PR EOS with the corrected vdW mixing rules can predict solubility of heavy solids in SCF more accurately than with the original mixing rules over different ranges of temperature and pressure and for different solutes and SC solvents. Also another excellent work has been published by Mansoori and his research team on thermodynamic modeling of SCF systems [12-14].

For prediction of solubility of fatty acids in SC-CO$_2$, Madras et al., [15] have used a developed thermodynamic model. The model combines the PR EOS with the two parameters vdW mixing rules. The model is applied to predict the solubilities of various fatty acids. The two adjustable interaction parameters in the model are found to vary linearly with the chain length of the fatty acids. The results showed that this model can be used to predict the solubility of various fatty acids in SC-CO$_2$. Another method for modeling of SCFE is mathematical modeling. In this concept, models are based on effective operating parameters of SCFE. For more information about mathematical modeling of SCFE and its results, we recommend the readers to refer to references 16 to 22. Also the information of another modeling method of SCFE can be reached in references 23 to 25.

Herbal essential oils or in general, plant materials have many applications in different industries such as; medicines, food additives and natural pesticides [1]. But most of modeling studies in this field are on the modeling of oil seeds extraction and limited papers are published on essential oils. It is probably due to complexity of plants structure or lack of experimental data. One of the most important and most useful medical plants is Mint. Mint essential oil has many applications in medicine and food industries.

In this work a new concept for the development of van der Waals mixing rules for cubic equations of state (CEOS) for modeling of SCFE has been studied. Also results of an experimental study and determination of thermophysical, critical and solubility parameters of Carvone (specified compound of spearmint) in SC-CO$_2$ have been mentioned.
Thermodynamic Models Description

van der Waals Mixing Rules for Equations of State

Since SCFE deals with high-pressure phase equilibria, the equations of state (EOS) method is the most suitable approach for modeling such kind of systems. There has been extensive research progress made in recent years towards the development of analytical statistical-mechanical EOS applicable for process design calculations.

Since thermophysical modeling of many compounds in plants are not estimate in experimental form, in present work, critical temperature ($T_c$), critical pressure ($P_c$) and eccentric factor ($\omega$) for Mint's essence have been calculated by means of experimental expressions. This is a general method for calculation of supercritical solubility of natural compounds. Therefore for equilibrium calculations, van der Waals, Peng-Robinson and Redlich-Kwong EsOS and van der Waals mixing rules have been used.

The first cubic EOS that represented both vapor and liquid phase was proposed by van der Waals (vdW) almost a century ago [11].

\[
P = \frac{RT}{v-b} - \frac{a}{v^2}
\]

(1)

\[
a = \frac{27R^2T_c^2}{64P_c}
\]

(2)

\[
b = \frac{RT_c}{8P_c}
\]

(3)

According to vdW, the extension of this EOS to mixtures requires replacement of $a$ and $b$ by the following composition-depended expressions:

\[
d = \sum_i^n \sum_j^n X_iX_j d_{ij}
\]

(4)

\[
d = \sum_i^n \sum_j^n X_iX_j d_{ij}
\]

(5)

Equations (4) and (5) are called the vdW mixing rules. In these equations, $a_{ij}$ and $b_{ij}$ ($i=j$) are parameters corresponding to pure component $(i)$ while $a_{ij}$ and $b_{ij}$ ($i \neq j$) are called the unlike-interaction parameters. It is customary to relate the unlike-interaction parameters to the pure component parameters by the following expression:
In equation (6), $K_{ij}$ is a fitting parameter which is known as the coupling parameter. By substitution of equation (7) into (5), the expression for $b$ will reduce to the following summation form:

$$b = \sum_{i}^{n} X_i b_{ij}$$  (8)

Extensive research on EsOS has indicated that the vdW EOS is not accurate enough for the prediction of properties of compressed gases and liquids [11]. This deficiency of the vdW EOS has initiated a great deal of research on the development of other EsOS, through the use of principles of statistical mechanics or by empirical or semi-empirical means. The majority of EsOS used in chemical engineering calculations are of the second category and are mostly cubic in the volume, like the vdW EOS itself, but contain other forms of the temperature and volume dependencies. One such EsOS with a simple form is the Redlich-Kwong (RK) EOS [25]:

$$P = \frac{RT}{v-b} - \frac{a}{T^{\frac{1}{2}}v(v-b)}$$  (9)

$$a = \frac{0.42748R^2T_c^{\frac{3}{2}}}{P_c}$$  (10)

$$b = \frac{0.08664RT_c}{P_c}$$  (11)

This EOS has found widespread applications in chemical engineering calculations. Another EOS which is the modification of vdW EOS was proposed by Peng-Robinson (PR) [26] which is slightly different from equation (9) in the volume function:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$  (12)

$$a(T) = a(T_c)\left[1 + k(1-T_c^{\frac{1}{2}})\right]^2$$  (13)
20.45724 20.37464 1.54226 0.26992

\[
k = 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\]

\[
b = \frac{0.0778RT_c}{P_c}
\]

PR EOS is widely used for thermodynamic property calculations.

The vdW mixing rules for the RK EOS will be in the following form:

\[
a = \left( \sum_{i} \sum_{j} X_i X_j a_i^{2/3} b_j^{2/3} \right)^{1.5} / \left( \sum_{i} \sum_{j} X_i X_j b_i \right)^{1/2}
\]

\[
d = \sum_{i} \sum_{j} X_i X_j d_{ij}
\]

These mixing rules, when combined with the RK EOS; will constitute the RK EOS for mixtures, consistent with the statistical-mechanical basis of the vdW mixing rules.

In order to separate thermodynamic variables from the constant of the PR EOS; we will insert equations (13) and (15) into equation (12) and will rewrite it in the following form:

\[
Z = \frac{v}{v-b} - \frac{a}{RT} + d - 2 \frac{\sqrt{ad}}{(v+b) + \frac{b}{v}(v-b)}
\]

Where \( a = a(T_c)(1+K)^2 \) and \( d = \frac{a(T_c)K^2}{RT_c} \). This form of the PR EOS suggests that there exist three independent constants in this EOS: a, b and d. Now, following the prescribed guidelines for the vdW mixing rules; the mixing rules for a, b and d of the PR EOS will be:

\[
d = \sum_{i} \sum_{j} X_i X_j d_{ij}
\]

\[
d = \sum_{i} \sum_{j} X_i X_j d_{ij}
\]

\[
d = \sum_{i} \sum_{j} X_i X_j d_{ij}
\]
With the following interaction parameters:

\[ a_{ij} = (1 - K_{ij}) (a_i a_j)^{\frac{1}{2}} \]  

(23)

\[ d_{ij} = (1 - M_{ij}) \left[ \frac{d_i^{\frac{1}{2}} + d_j^{\frac{1}{2}}}{2} \right]^3 \]  

(24)

\[ d_{ij} = (1 - M_{ij}) \left[ \frac{d_i^{\frac{1}{3}} + d_j^{\frac{1}{3}}}{2} \right]^3 \]  

(25)

The mixing rules, when combined with the PR EOS; equation (12) will constitute the PR EOS of a mixture, consistent with the statistical-mechanical basis of the vdW mixing rules.

**Application of Modeling of Supercritical Fluid Extraction on Herbal Essential Oils**

Serious tests of mixture EsOS are shown to be the application for the prediction of solubility of natural essence [16, 22, 27-30] and heavy solutes [10, 11] in SCFs.

In the present article; we apply the vdW, RK and PR EsOS for SCFE of essential oils and study the effect of selecting different mixing rules to predict the solubility of natural products in SCFs.

For the calculation of solubility of spearmint essential oil (Carvone) in SCF, expression of solubility of solids in SCF has been used. The solubility of a condensed phase \( y_{2s} \) in a vapor phase at SC conditions can be defined as:

\[ y_2 = \left( \frac{P_{2s}}{P} \right) \left( \frac{1}{\Phi_2} \right) \Phi_{2s} \exp \left\{ \int_{P_{2s}}^P \left( \frac{v_{2s}}{RT} \right) dp \right\}. \]  

(26)

Where \( \Phi_{2s} \) is the fugacity coefficient of the condensed phase at the saturation pressure \( P_{2s} \); and the \( \Phi_2 \) is the vapor phase fugacity at pressure \( P \), provided that \( v_{2s} \) is independent of pressure.

Then above expression is converted to the following form:

\[ y_2 = \left( \frac{P_{2s}}{P} \right) \left( \frac{1}{\Phi_2} \right) \exp \left\{ \left( v_{2s} \right) \left( \frac{P - P_{2s}}{RT} \right) \right\}. \]  

(27)

In the case of vdW EOS, equation (1), with equations (4) and (5) as the mixing rules, the following expression for the fugacity coefficient of a solute in a SC gas will be derived:
\[ \Phi_i = \left( \frac{RT}{v-b} \right) \left( \frac{1}{P} \right) \exp \left[ \left( \frac{-b + 2 \sum X_i b_i}{v-b} \right) - \left( \frac{2 \sum X_i a_i}{vRT} \right) \right]. \] (28)

For RK EOS, with equations (4) and (5) as its mixing rules, the following expression for the fugacity coefficient is obtained:

\[
\ln \Phi_i = \ln \left( \frac{v}{v-b} \right) + \left( 2 \sum X_i b_i - b \right) / (v-b) - \ln z \\
+ a \left( 2 \sum X_i b_i - b \right) / (b^2 RT^{1.5}) \left( \ln \left( \frac{v+b}{v}\right) - b / (v+b) \right) - \left( 2 \sum X_i a_i / (bRT^{1.5}) \right) \times \ln \left( \frac{v+b}{v}\right). \] (29)

Now with the use of the correct version of the vdW mixing rules, equations (5) and (17), in the RK EOS, the fugacity coefficient will assume the following form:

\[
\ln \Phi_i = \ln \left( \frac{v}{v-b} \right) + \left( 2 \sum X_i b_i - b \right) / (v-b) - \ln z \\
+ a \left( 2 \sum X_i b_i - b \right) / (b^2 RT^{1.5}) \left( \ln \left( \frac{v+b}{v}\right) - b / (v+b) \right) \\
- \left( 3 \alpha \left( \frac{1}{(2 \sum X_i a_i)^{2/3} b_i^{1/3}} \right) / b^{1/2} - \alpha^2 \left( \frac{1}{(2 \sum X_i b_i)^{1/2}} / b^{1/2} \right) / (bRT^{1.5}) \right) \times \ln \left( \frac{v+b}{v}\right). \] (30)

Where

\[
\alpha = \sum_{i} \sum_{j} X_i X_j a_i^{2/3} b_j^{1/3} \] (31)

The fugacity coefficient based on the PR EOS with equations (4) and (5) as the mixing rules (as usually derived) have the following form:

\[
\ln \Phi_i = \left( \frac{2 \sum X_i b_i - b}{b} \right) (Z-1) - \ln (Z-B) - \ln \left( \frac{2 \sqrt{2} \sqrt{b}}{2 \sqrt{2} \sqrt{b}} \right) \times \ln \left( \frac{Z+2 \sqrt{2} \sqrt{b}}{Z-2 \sqrt{2} \sqrt{b}} \right) \] (32)

\[
A = \left( \frac{aP}{R^2 T^2} \right) \] (33)

\[
B = \left( \frac{bP}{RT} \right) \] (34)

**Experimental**

**Materials**

Mint (Mentha piperita, spearmint type) leaves grown in Bihbahan, Khuzestan, south-western province in Iran, was used as raw material for extraction of spearmint essential oil. Carbon dioxide (99.9%, Khorram-Noosh factory, Khorram-Shahr, Khuzestan) was used as SC solvent. The chemical
The chemical structure of Carvone (specified compound in spearmint essential oil) is shown in Figure 1.

**Figure 1.** Chemical structure of Carvone [15].

**Apparatus**

The separation experiments were carried out on Lab-Scale apparatus. Figure 2 shows a simplified process flow sheet of the experimental apparatus.

**Figure 2.** Schematic diagram of the experimental apparatus; (A gas cylinder with pressure capacity of 24 MPa was used for carbon dioxide storage (1), Gage pressure (2), A heat exchanger for increase gas pressure (3), Extraction column (6). Hot water bath for control of temperature in the extraction column (7). High pressure expansion valve (8). Two glass separators for separation of extracted essential oil and condensed solvent (9). Rotameter for calculation of the volumetric flow rate of gas (10)).
Procedure

After Mint leaves were dried in shadow under ambient conditions; they are grinded mechanically. Carbon dioxide, purity of 99.9% was used as solvent. The extraction process was done under semi-batch conditions (grinded leaves were the solid motionless phase and CO$_2$ was the SC movement phase).

A known amount of raw material (120 g grinded leaves for each run) was placed into the extraction column. The pressure of gas was controlled by heat exchanger and the temperature of extraction was controlled by hot water bath in specific temperature. The extraction vessel was closed and the SC solvent started to load. After few seconds pressure reached the specified value. After this point, when SC solvent and essential oil were completely mixed and solvent (mixture of SC solvent and extracted essential oil) was moved to the glass separator vessels. To prevent freezing the equipments, the pressure of the mixture was reduced in two stages. In this part, the extracted essential oil and condensed gas was separated in glass separator vessels. At the end of the process, extracted essential oil was stored in the glass vessels and CO$_2$ was moved to the rotary meter for calculation of the volumetric flow rate and then vented atmospher.

Result and Discussion

For calculation of critical parameters for Carvone (as specified compound in Mint essential oil) the suggested methods [31] have been used.

To estimate the critical temperature and critical pressure ($T_c$ (K) and $P_c$ (atm)), the following expression has been suggested by Leaderson:

$$T_c = \frac{T_b}{0.567 + \sum \Delta T - (\sum \Delta T)^2}$$

(35)

And

$$P_c = \frac{M}{(0.34 + \sum \Delta P)^2}$$

(36)

Where $M$ is molecular weight and $\sum \Delta P$ and $\sum \Delta P$ are auxiliary parameters for temperature and pressure respectively.

For calculation of eccentric factor ($\omega$), Lee-Kesler suggested the following expression:

$$\omega = \frac{-\ln P_c - 5.92714 + 6.09648 \theta^{-1} + 1.28864 \ln \theta + 0.169347 \theta^6}{15.2518 - 15.6875 \theta^{-1} - 13.7421 \ln \theta + 0.43577 \theta^6}$$

(37)
Where $\theta = \frac{T_e}{T_c}$ and $P_c$ is in atm.

Bhirad method has been used for calculation of saturation molar volume ($v^{sat}$) which is suggested for non-polar compounds at absolute temperature (K).

$$\ln\left(\frac{v^{sat} \times P_c}{RT_c}\right) = (\ln U)^0 + \omega(\ln U)^1$$  \hspace{1cm} (38)

Where $(\ln U)^1$ and $(\ln U)^1$ are functions of reduced temperature for carvone.

Riedel equation (RE) [31, 32] has been used for calculation of saturation vapor pressure. In this method, calculation of $P^{sat}$ critical temperature and critical pressure as well as another extra vapor pressure (for example normal vapor pressure) are needed.

In RE by following expression:

$$\ln P^{sat} = A^0 - \frac{B^0}{T_r} + C^0 \ln T_r + D^0 T_r^6$$  \hspace{1cm} (39)

$Y_2$ and $P^{sat}_r$ are reduced temperature and saturation reduced pressure respectively. Also $A^0, B^0, C^0$ and $Y_2$ are constant parameters of RE. When $P^{sat}_r$ will be estimate, vapor pressure for Carvone can calculate by the following expression:

$$P^{sat} = P^{sat}_r \times P_c$$  \hspace{1cm} (40)

Tables 1 shows thermodynamic properties, Table 2 shows numerical values of saturation vapor pressure and saturation molar volume and in Table 3 constant parameters of RE are shown.

**Table 1.** Thermodynamic properties for Carvone as specified compound of Mint essential oil.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carvone</th>
<th>Critical temperature (K)</th>
<th>Critical pressure (atm)</th>
<th>Eccentric factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>724.9</td>
<td></td>
<td>35.67</td>
<td>0.502</td>
</tr>
</tbody>
</table>

**Table 2.** Numerical values of saturation vapor pressure and saturation molar volume for Carvone at three references temperatures.

<table>
<thead>
<tr>
<th>Saturation molar volume $(cm^3/mole)$</th>
<th>Saturation vapor pressure $(bar)$</th>
<th>Reference temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>126.74</td>
<td>0.000296</td>
<td>313</td>
</tr>
<tr>
<td>127.4</td>
<td>0.000429</td>
<td>318</td>
</tr>
<tr>
<td>128.6</td>
<td>0.000746</td>
<td>323</td>
</tr>
</tbody>
</table>
Table 3. Constant parameters in Riedel equation for calculation of saturation vapor pressure of Carvone.

<table>
<thead>
<tr>
<th>$D^\circ$</th>
<th>$C^\circ$</th>
<th>$B^\circ$</th>
<th>$A^\circ$</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3796</td>
<td>-7.673</td>
<td>13.665</td>
<td>13.252</td>
<td>Carvone</td>
</tr>
</tbody>
</table>

For calculation of solubility of Carvone in SC-CO$_2$ by means of EsOS and comparing the results with experimental data, a computer program with QBasic has been written to solve the cubic EsOS.

By considering index 1 for solvent (SC-CO$_2$) and index 2 for solute (Carvone) and the use of aforementioned expressions, the solubility of Carvone in SC-CO$_2$ can be estimate at specified temperature that are 313, 318 and 323K, for each EOS.

The results of calculations for each EOS are shown Figures 3 to 10. According to the results, more essential oil can be produced by increasing the temperature. However at high temperatures, thermal sensitive compound may face chemical deformation. Furthermore, the amount of produced essential oil decreases. Experimental results show that the optimum temperature is in the range of 308K to 313K ranges.

As shown in Figures 3 to 10, each curve has a maximum and minimum point with meaning definitions. At maximum point, the amount of produced essential oil is maximum, quantity. This point is in the packed extraction column. At this point an equilibrium condition between fugacity in solid phase and fugacity in SCF phase will exist. Whereas, the density gradient is the main factor for mass transfer (compound transfer) from solid phase (grinded leaves of Mint) to solvent phase (SC solvent), and also the density of solid phase is more than SC solvent phase. Therefore, as the diversity of densities is higher, the higher amount of essential oil can be produced. In other word at maximum point we have maximum diversity of densities and therefore maximum amount of essential oil. However it can change with changing of thermodynamics conditions, temperature and/or pressure. In fact, maximum point shows the best thermodynamics conditions for extraction unit (packed extraction column). At minimum point, the lower solubility of solute (Carvone) in SC solvent exists. Therefore, this is the best thermodynamics conditions for solute-solvent (SS) separation unit.

Thereby; based on experimental results, the best pressure conditions (at specified temperature conditions) for extraction unit (packed column) and SS separation unit in supercritical fluid extraction plant, are 98 to 102 bar and 18 to 25 bar respectively. These values are derived from Figures 3 to 10.
Conclusion

The solubility of Carvone as the specified compound of spearmint essential oil in supercritical carbon dioxide has been studied. The applied equations of state (van der Waals, Peng-Robinson and Redlich-Kwong) showed identical characteristic for solubility up to pressure of 105 bar. But at above 105 bar, the characteristic for solubility was altered.

In Figures 3 and 4, the solubility of Carvone in SC-CO2 is plotted vs. pressure at 313, 318 and 323K as well as the predictions obtained from the vdW EOS. As is shown, solubility of Carvone in SC-CO$_2$ was reduced at pressures above 105 bar by use the vdW EOS.

![Figure 3](image.png)

**Figure 3.** Solubility of carvone in supercritical carbon dioxide at 313 and 318K vs. pressure, the results of van der Waals mixing rules.

![Figure 4](image.png)

**Figure 4.** Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323K vs. pressure by fitting parameter of ($K_i$) of -0.158. The solid dots are experimental data and solid lines are the results of van der Waals equation of state and its mixing rules (equations 1, 4 and 5).
In Figures 5 and 6, the experimental solubility data as in Figures 3 and 4 are compared with predictions using the RK EOS. Accordingly solubility of Carvone in SC-CO$_2$ had ascension increase at pressures above 105 bar.

**Figure 5.** Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323 K vs. pressure by fitting parameter of $(K_{ij})$ of -0.2251. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 9, 17 and 18).

**Figure 6.** Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323 K vs. pressure by fitting parameter of $(K_{ij})$ of -0.205. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 9, 17 and 18).
In Figures 7 to 10, the solubility of Carvone in SC solvent (CO$_2$) is plotted vs. pressure at 313, 318 and 323K as well as predictions obtained from the PR EOS. As is shown in these figures, the solubility of Carvone had good conditions (equilibrium conditions) up to pressure of 250 (bar).

**Figure 7.** Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323K vs. pressure by fitting parameters of $K_{ij}$= 0.14 and $L_{ij}$=-0.118. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 12, 20, 21 and 22).

**Figure 8.** Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323K vs. pressure by fitting parameters of $K_{ij}$= 0.124 and $L_{ij}$=0.8. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 12, 20, 21 and 22).
Figure 9. Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323 K vs. pressure by fitting parameter of $K_{ij} = 0.149$. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 12, 20, 21 and 22).

Figure 10. Solubility of Carvone in supercritical carbon dioxide at 313, 318 and 323 K vs. pressure by fitting parameter of $K_{ij} = 0.1788$. The solid dots are experimental data and solid lines are the results of Redlich-Kwong equation of state and its mixing rules (equations 12, 20, 21 and 22).

Therefore; based on the comparison of experimental results with modeling results, Peng-Robinson equation of state with its mixing rules (equations 12, 20 and 21) is the best choice to select equation of state to assess the solubility of essential oils in supercritical carbon dioxide.
Notation

- A, B: variables in the Peng-Robinson equation of state
- a, b: parameter in the equation of state
- d: parameter in the Peng-Robinson equation of state
- $L_{ij}$: Binary fitting parameter
- $L_{ij}$: Binary fitting parameters in the Peng-Robinson equation of state
- P: pressure (bar)
- R: universal gas constant
- T: temperature (K)
- $\nu$: molar volume
- Y: gas phase mole fraction
- Z: compressibility factor
- $Y_2$: Mass fraction of solid phase (solute)
- $Y_2$: Mass fraction of solvent
- $Y_2$: Mass fraction of solute in supercritical phase

Greek letters

- $\Phi$: fugacity coefficient
- $\omega$: eccentric factor
- $\varepsilon$: interaction energy parameter

Subscripts

- i, j: component identifiers
- 1: solvent
- 2: solute
- C: critical properties

Abbreviation

- SC: supercritical
- SCFs: supercritical fluids
- SCFE: supercritical fluid extraction
- SCS: supercritical solvent
EsOS  equations of state
CEOS  cubic equation of state
CO2   carbon dioxide
SC-CO2 supercritical carbon dioxide
SCW   supercritical water
vdW   van der Waals
RK    Redlich-Kwong
PR    Peng-Robinson
RE    Riedel Equation

References