Vegetable oils are an important source of polyunsaturated fatty acids known as essential fatty acids (EFAs). The main EFA in human diet is linoleic acid which is metabolized within the body. In the absence of EFAs in the diet, virtually all systems of the body became abnormal. This is because EFAs are required for the structural maintenance of all the membranes in the body and because they are precursors of short - acting substances important in regulation [1].

Soybean [2], sunflower [1] and evening primrose (Oenothera biennis) [13] seed oils have a similar polyunsaturated fatty acid content (Table 1).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Soybean</th>
<th>Sunflower</th>
<th>Evening Primrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic</td>
<td>43 - 56</td>
<td>44 - 75</td>
<td>65 - 80</td>
</tr>
<tr>
<td>Alpha-linolenic</td>
<td>5 - 11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gamma-linolenic</td>
<td>-</td>
<td>3 - 15</td>
<td>-</td>
</tr>
<tr>
<td>Oleic</td>
<td>15 - 33</td>
<td>14 - 43</td>
<td>4 - 12</td>
</tr>
<tr>
<td>Palmitic</td>
<td>7 - 11</td>
<td>3 - 6</td>
<td>4 - 12</td>
</tr>
<tr>
<td>Stearic</td>
<td>2 - 6</td>
<td>1 - 3</td>
<td>1 - 6</td>
</tr>
</tbody>
</table>

The literature experimental data on the solubility (S) and mole fractions (y) of soybean [4], sunflower [4] and evening primrose seed oil [5], respectively, in supercritical carbon dioxide at 313 K are shown in Tables 2, 3 and 4.

Experimental data on the solubility of vegetable oil in supercritical carbon dioxide are limited by the experimental temperature and pressure conditions. If there is a possibility to find a suitable mathematical model for the estimation of the solubility of vegetable oil in the range of existing experimental data the number of necessary experiments could be reduced. In the last twenty years there have been many investigations on the correlation of the solubilities of solids and liquids in supercritical fluids. Many of them applied cubic equations of state [6-12]. If the mixture parameters of the EOS are determined using a simple van der Waals type mixing model, binary interaction parameters must be obtained by fitting the experimental solubility [6,13] or vapor pressure [7] data. The binary interaction parameters are very sensitive to solubility calculations, and no reliable correlation can be found for these empirical parameters.

The aim of this work was to find a mathematical model for predicting the solubility of vegetable oils with a high content of polyunsaturated fatty acids in their triglycerides in supercritical carbon dioxide based on Cubic EOS.

Table 2. Solubility and mole fraction of soybean seed oil in supercritical carbon dioxide at 313 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (mg/dm³)</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>y \times 10^3</td>
<td>0.523</td>
<td>0.697</td>
<td>0.872</td>
<td>1.13</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Table 3. Solubility and mole fraction of sunflower seed oil in supercritical carbon dioxide at 313 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (mg/dm³)</td>
<td>5.33</td>
<td>10.7</td>
<td>13.3</td>
<td>17.3</td>
<td>20</td>
</tr>
<tr>
<td>y \times 10^3</td>
<td>0.464</td>
<td>0.933</td>
<td>1.16</td>
<td>1.51</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table 4. Solubility and mole fraction of primrose seed oil in supercritical carbon dioxide at 313 K

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (mg/dm³)</td>
<td>5.94</td>
<td>10.1</td>
<td>16.7</td>
<td>27.2</td>
<td>5.67</td>
</tr>
<tr>
<td>y \times 10^3</td>
<td>0.457</td>
<td>0.804</td>
<td>1.33</td>
<td>2.17</td>
<td></td>
</tr>
</tbody>
</table>
FORMULATION OF THE MODEL

A binary system at temperature T and total pressure P consisting of a liquid component 1 and a supercritical component 2 was considered. The equilibrium condition for solute 1 is given by the equation:

$$ f_1^f = f_1^L $$

(1)

where $f_1^L$ is the fugacity of the solute in the liquid phase, and $f_1^f$ is the fugacity of the solute in the supercritical phase.

The fugacity of the solute in the supercritical phase is related to the mole fraction by:

$$ f_1^f = y_1 \phi_1^f P $$

(2)

where $\phi_1^f$ is the fugacity coefficient of the solute in the supercritical phase, $y_1$ is the mole fraction of the solute in the supercritical phase and P is the pressure.

An analytical expression for the fugacity coefficient in the supercritical phase can be derived applying Cubic EOS on the thermodynamic formulation of the fugacity coefficient:

$$ \ln \phi_1^f = \frac{\alpha}{\kappa T} \rho \left( \frac{\partial P}{\partial \rho} \right)_{T,V,n} - \ln z $$

(3)

where $\alpha$ is the temperature, $n$ is the number of moles, $V$ is the total volume and $z$ is the compressibility factor.

For the fugacity of the liquid phase, the expanded liquid model [14] is adopted:

$$ f_1^L = f_1^L \gamma_1 x_1 \exp \left( \frac{y_1}{\frac{RT}{M}} \right) P $$

(4)

where $y_1$ is the partial molar volume of the solute, $\gamma_1$ is the activity coefficient of the solute, $x_1$ is the mole fraction of the solute in the liquid phase and superscript 0 denotes the reference state. When the mole fraction of the supercritical solvent in the liquid phase $x_2$ is small, the liquid phase is ideal with respect to the solvent and $y_1^L = 1$. If $x_2$ exceeds 0.2 a small correction for liquid phase nonideality may be required [14]. The partial molar volume is calculated from the Cubic EOS and it has a constant value in the range of pressures of interest. The critical pressure of a liquid component is adopted as the reference pressure, as is the approximation $f_1^L = P \gamma_1 = \text{const.}$

When equations (2) and (4) are substituted into equation (1), the vapor phase solubility is:

$$ y_1 = \frac{\gamma_1 \phi_1^f f_1^L}{\phi_1^f P} \exp \left( \frac{y_1}{\frac{RT}{M}} \right) (P - P_1^L) $$

(5)

Vegetable oil was treated as a pseudo component – represented by linoleic acid, the acid with the highest content in the triglycerides of the oil.

The Soave–Redlich–Kwong (SRK) EOS is defined by the expression [15]:

$$ P = \frac{RT}{u-b} - \frac{a}{u(u-b)} $$

where $a$ and $b$ are the parameters for the pure substance, or as a function of the compressibility factor $z$:

$$ z^2 - 2z + (A - B - B^2)z - AB = 0 $$

and:

$$ z = \frac{P}{RT} \quad A = \frac{aP}{RT^2} \quad B = \frac{bP}{RT} $$

For the pure substance:

$$ a = a_a \quad a_a = 0.4274 \quad \frac{RT^2}{P_c} \quad \alpha = \left[ 1 + \kappa \left( 1 - \frac{T_f}{T} \right) \right]^2 $$

$$ \kappa = 0.480 + 1.574 \omega - 0.176 \omega^2 $$

where $\omega$ is the acentric factor.

The expression for the fugacity coefficient in the supercritical phase can be derived by applying the SRK EOS on equation (3):

$$ \ln \phi_1^f = \frac{b_i}{b_m} (z_m - 1) - \ln(z_m - B_m) - $$

$$ \frac{A_m}{B_m} \left( \frac{2 \gamma_i a_i}{i} \right) \ln \left( 1 + \frac{B_m}{z_m} \right) $$

where index m denotes the mixture parameters.

The Peng–Robinson (PR) EOS is defined by expression [16]:

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

or as a function of the compressibility factor $z$:

$$ z^2 - (1 - B)z^2 + (A - 3B^2 - 2B)z - (AB - B^2 - B^3) = 0 $$

where the expressions for $A$ and $B$ are the same as for the SRK EOS.

For the pure substance:

$$ a = a_a \quad a_a = 0.45724 \quad \frac{RT^2}{P_c} \quad \alpha = \left[ 1 + \kappa \left( 1 - \frac{T_f}{T} \right) \right]^2 $$

$$ \kappa = 0.37464 + 1.54226 \omega - 0.26692 \omega^2 $$

The expression for the fugacity coefficient in the supercritical phase can be derived by applying the PR EOS on equation (3):

$$ \ln \phi_1^f = \frac{b_i}{b_m} (z_m - 1) - \ln(z_m - B_m) - $$

$$ + \frac{A_m}{2 \gamma_i a_i} \left( \frac{2 \gamma_i a_i}{i} \right) \ln \left( \frac{z_m + 2.414B_m}{z_m - 0.414B_m} \right) $$

The calculation of the parameter $a_m$ is based on:

- the Square mixing rule (SMR):
\[ a_m = \sum_{i} (1 - k_i) \prod_{j} (a_i a_j)^{0.5} \]

where \( k_i \) is the binary interaction parameter, and

- the Modified square interaction mixing rule (MSMR):

\[ a_m = (1 - k) \sum_{i} \prod_{j} (a_i a_j)^{0.5} \]

where \( k \) is the modified binary interaction parameter.

Parameter \( b_m \) was calculated using the linear mixing rule:

\[ b_m = \sum_{i} y_i b_i \]

RESULTS AND DISCUSSION

Optimization of the binary interaction parameter of the Model \( k_{12} \) or the modified binary interaction parameter of the Model \( k \) (depending on the applied mixing rule) was performed for each experimental point and each EOS. These values for each EOS and applied mixing rule are shown in Figure 1. The optimization gave the dependence of these parameters on pressure, at constant temperature, which was approximated by a polynomial function of the second order:

- binary interaction parameter (square mixing rule):

\[ k_{12} = A_0 + A_1 P + A_2 P^2 \]

- modified binary interaction parameter (modified square mixing rule):

\[ k = A_0 + A_1 P + A_2 P^2 \]

for each EOS.

The parameters of these functions for soybean, sunflower and evening primrose seed oil are shown in Table 5.

A calculation based on the optimized functions was performed. The experimental and calculated values of the oil mole fraction in supercritical carbon dioxide at 313 K for soybean, sunflower and evening primrose seed oil, respectively, are shown in Figures 2, 3 and 4 for each EOS and applied mixing rule.

The SRK and PR EOS gave almost the same values of the oil mole fraction in supercritical carbon dioxide. The average deviation from the experimental data at 313 K for SRK-SMR, SRK-MSMR, PR-SMR and PR-MSMR was 2.96, 5.61, 3.03 and 5.58%, respectively, for soybean oil, 6.23, 6.06, 6.24 and 6.07%, respectively.

### Table 5. Optimization results for soybean, sunflower and primrose seed oil at 313 K

<table>
<thead>
<tr>
<th>Model</th>
<th>Function parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_0 )</td>
</tr>
<tr>
<td>SRK-SMR</td>
<td>0.6733</td>
</tr>
<tr>
<td>SRK-MSMR</td>
<td>0.9849</td>
</tr>
<tr>
<td>PR-SMR</td>
<td>0.6363</td>
</tr>
<tr>
<td>PR-MSMR</td>
<td>0.9911</td>
</tr>
</tbody>
</table>

Figure 1. Determination of \( k_{12} \) – binary interaction parameter and \( k \) – modified binary interaction parameter applying SRK and PR EOS. Symbol used: □ – soybean; ◀ – sunflower and △ – primrose seed oil.
for sunflower oil, and 2.39, 7.26, 2.59 and 7.26%, respectively, for evening primrose seed oil.

**CONCLUSION**

By applying the suggested mathematical model on the solubility estimation of vegetable oils in supercritical carbon dioxide, it is possible to calculate the solubilities of soybean, sunflower and evening primrose seed oil with an average deviation from the experimental data of less than 7.26%. The SRK and PR EOS gave almost the same values. The SMR gave better results than the MSMR. The influence of the adopted approximations of the Model was compensated by the empirical dependence of the binary interaction parameter and modified binary interaction parameter of the Model on pressure.

**NOTATION**

- \( a, b, A, B \) — variables in the Cubic Equation of State
- \( f \) — fugacity
- \( k_i \) — binary interaction parameter of the Model
- \( n \) — number of moles
- \( P \) — pressure
- \( R \) — gas constant
- \( T \) — temperature
- \( v \) — molar volume
- \( V \) — total volume
- \( x \) — mole fraction in the liquid phase
- \( y \) — mole fraction in the supercritical phase
- \( Z \) — compressibility factor

**GREEK LETTERS**

- \( \alpha, \kappa, \omega \) — constants in the Cubic Equation of State
- \( \phi \) — fugacity coefficient
- \( \gamma \) — activity coefficient
- \( \omega \) — acentric factor

**SUPERSCRIPTS**

- \( L \) — liquid phase
- \( s \) — reference state
- \( sf \) — supercritical phase

**SUBSCRIPTS**

- \( c \) — critical parameter
- \( m \) — mixture
- \( l \) — liquid component
- \( 2 \) — supercritical component

**REFERENCES**

IZVOD

IZRAČUNAVANJE RASTVORIVOSTI BILJNIH ULJA U NATKRITIČNOM UGLJEN DIOKSIDU PRIMENOM KLIJNIH JEDNAČINA STANJA

(Naučni rad)

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Tehničko-metalurški fakultet, Beograd, Jugoslavija

Za izračunavanje rastvorljivosti ulja biljnog porekla u ugljen dioksidu pod natkritičnim uslovima primenjena je Soave-Redlich-Kwong i Peng-Robinson jednačina stanja uz pretpostavku važenja modela ekspandovane tečne faze. U radu se analizira rastvorljivost ulja iz semena noćurke (ulje sa velikim sadržajem polinezasićenih masnih kiselina u svom sastavu), kao i ulja soje i sunčeketa. Za primenu odgovarajućeg modela procesen je binarni interakcioni parametar na osnovu eksperimentalnih podataka rastvorljivosti navedenih sировina (ulja) u natkritičnom ugljen dioksidu. Predložen model ekspandovane tečnosti omogućava izračunavanje rastvorljivosti ulja sa relativnom greškom u odnosu na eksperimentalne podatke koja je manja od 7,2%.

Key words: Supercritical extraction • Equations of State • Solubility • Seed oil • Essential fatty acids • Ključne reči: Natkritična ekstrakcija • Jednačine stanja • Rastvorljivost • Uljane semenke • Esencijalne masne kiseline •
\[ y \cdot 10^3 \]

\[ y \cdot 10^3 \]

\[ y \cdot 10^3 \]

\[ y \cdot 10^3 \]