IRENA ŽIŽOVIĆ
DEJAN SKALA

Faculty of Technology and
Metallurgy, Belgrade, Yugoslavia

SCIENTIFIC PAPER

665.33+541.8:66.061+665.12:536.71

CALCULATION OF THE SOLUBILITY OF VEGETABLE OILS IN SUPERCRITICAL CARBON DIOXIDE BASED ON CUBIC EQUATIONS OF STATE AND THE EXPANDED LIQUID MODEL

The Soave–Redlich–Kwong equation of state, the Peng–Robinson equation of state, and the expanded liquid model were applied in this study to calculate the solubilities of vegetable oils with a high content of polyunsaturated fatty acids in their triglycerides in supercritical carbon dioxide. Binary interaction parameters were calculated using the experimental data on the solubility of soybean, sunflower and evening primrose seed oil in supercritical carbon dioxide. This model yields satisfactory solubility results with an average deviation from the experimental data less than 7.26%.

Vegetable oils are an important source of polyunsaturated fatty acids known as ssential 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*) [1,3] seed oils have a similar polyunsaturated fatty acid content (Table 1).

Table 1. Seed oil fatty acid content (%)

Fatty acid	Soybean	Sunflower	Primrose
Linoleic	43 – 56	44 – 75	65 – 80
Alpha–linolenic	5 – 11	–	–
Gamma–linolenic	–	–	3 – 15
Oleic	15 – 33	14 – 43	4 – 12
Palmitic	7 – 11	3 – 6	4 – 12
Stearic	2 – 6	1 – 3	1 – 6

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

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

P (MPa)	20	23.5	25.5	29	30	34
S (mg/dm$_N^3$)	6	8	10	13	14	18
y · 10^3	0.523	0.697	0.872	1.13	1.22	1.57

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

P (MPa)	20	24	28	32	35	40
S (mg/dm$_N^3$)	5.33	10.7	13.3	17.3	20	25.3
y · 10^3	0.464	0.933	1.16	1.51	1.74	2.21

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

P (MPa)	20	25	30	35
S (mg/dm$_N^3$)	5.94	10.1	16.7	27.2
y · 10^3	0.457	0.804	1.33	2.17

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.

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:

$$f_1^L = f_1^{sf} \tag{1}$$

where f_1^L is the fugacity of the solute in the liquid phase, and f_1^{sf} 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:

$$f_1^{sf} = y_1 \, \phi_1^{sf} \, P \tag{2}$$

where ϕ_1^{sf} 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:

$$\ln \phi_1^{sf} = \int_V^\infty \left[\frac{1}{RT} \left(\frac{\partial P}{\partial n_1} \right)_{T,V,n_2} - \frac{1}{V} \right] dV - \ln z \tag{3}$$

where T 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:

$$f_1^L = f_1^{OL} \, \gamma_1 \, x_1 \, \exp \int_{p^0}^P \left(\frac{v_1}{RT} \right) dP \tag{4}$$

where v_1 is the partial molar volume of the solute, γ_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 $\gamma_1^L = 1$. 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 aproximation

$$f_1^{OL} = P_1^{OL} \, \phi_1^0 = const.$$

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

$$y_1 = \frac{\gamma_1 x_1 P_1^0 \phi_1^0}{\phi_1^{sf} P} \exp \left[\frac{v_1^{OL} (P - P_1^0)}{RT} \right] \tag{5}$$

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–Rewdlich–Kwong (SRK) EOS is defined by the expression [15]:

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

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

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

and:

$$z = \frac{P\upsilon}{RT} \qquad A = \frac{aP}{R^2 T^2} \qquad B = \frac{bP}{RT}$$

For the pure substance:

$$a = \alpha a_c \quad a_c = 0.42747 \frac{R^2 T_c^2}{P_c} \quad \alpha = \left[1 + \kappa(1 - T_r^{0.5}) \right]^2$$

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

where ω 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):

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

$$- \frac{A_m}{B_m} \left(\frac{2\Sigma_j y_j a_{ij}}{a_m} - \frac{b_i}{b_m} \right) \ln \left(1 + \frac{B_m}{z_m} \right)$$

where index m denotes the mixture parameters.

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

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

or as a function of the compressibility factor z:

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

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

For the pure substance:

$$a = \alpha a_c \quad a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad \alpha = \left[1 + \kappa (1 - T_r^{0.5}) \right]^2$$

$$\kappa = 0.37464 + 1.54226 \, \omega - 0.26992 \, \omega^2$$

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

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

$$- \frac{A_m}{2\sqrt{2} B_m} \left(\frac{2\Sigma_j y_j a_{ij}}{a_m} - \frac{b_i}{b_m} \right) \ln \left(\frac{z_m + 2.414 B_m}{z_m - 0.414 B_m} \right)$$

The calculation of the parameter a_m is based on:
– the Square mixing rule (SMR):

$$a_m = \Sigma\Sigma \, (1 - k_{ij}) \, y_i \, y_j \, (a_i \, a_j)^{0.5}$$
$$\quad\quad i \; j$$

where k_{ij} is the binary interaction parameter, and
   – the Modified square mixing rule (MSMR):

$$a_m = (1 - k) \, \Sigma \, \Sigma \, y_i \, y_j \, (a_i \, a_j)^{0.5}$$
$$\quad\quad i \; j$$

where k is the modified binary interaction parameter.

Parameter b_m was calculated using the linear mixing rule:

$$b_m = \Sigma \, y_i b_i.$$
$$\quad\; i$$

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):

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

Model	Function parameters		
	A_0	A_1	A_2
SRK–SMR	0.6733	–0.0110	$1.2648 \cdot 10^{-4}$
SRK–MSMR	0.9849	–0.0104	$1.2925 \cdot 10^{-4}$
PR–SMR	0.6363	–0.0108	$1.2386 \cdot 10^{-4}$
PR–MSMR	0.9911	–0.0115	$1.4100 \cdot 10^{-4}$

$$k = A_0 + A_1 P + A_2 P^2$$

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,
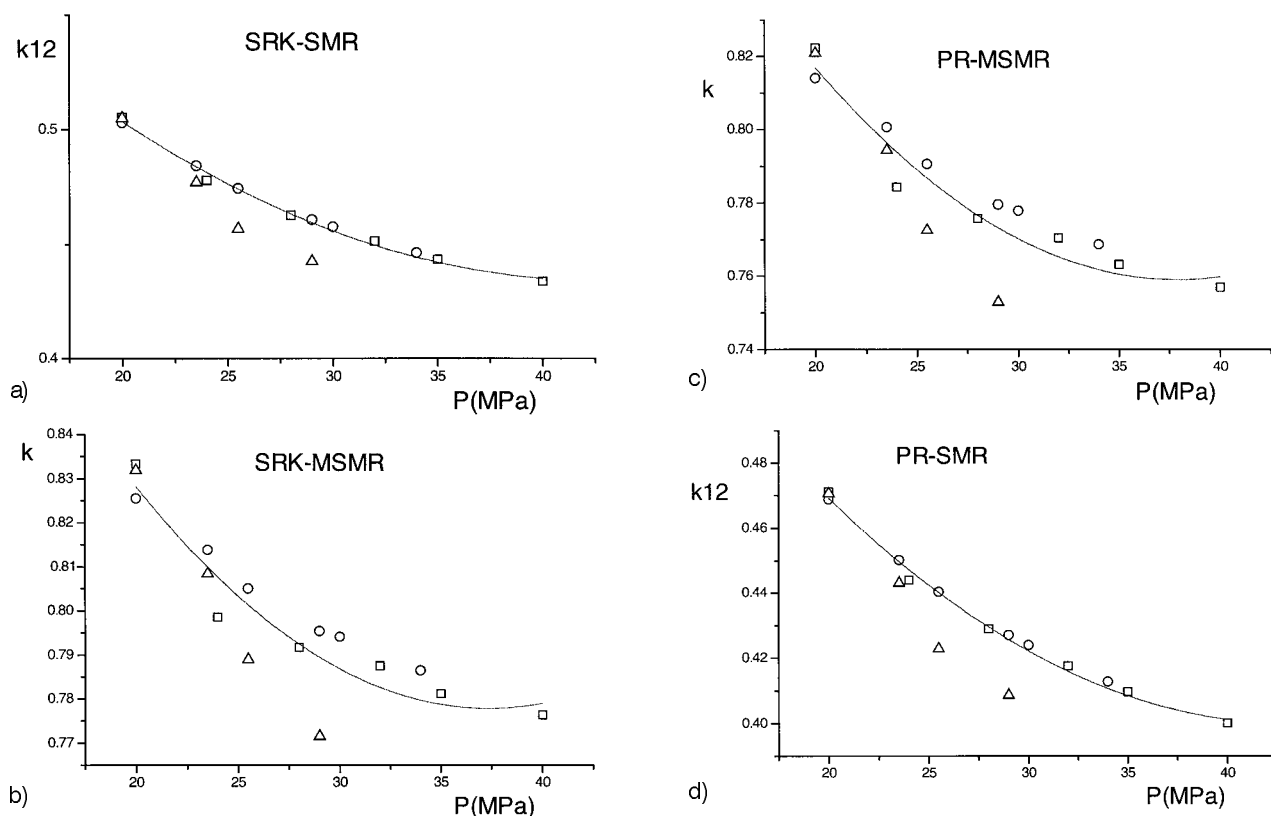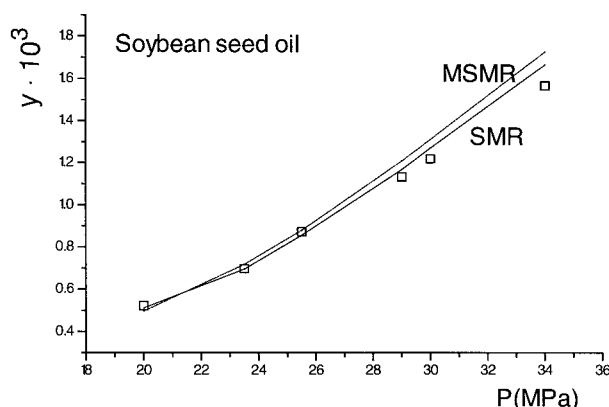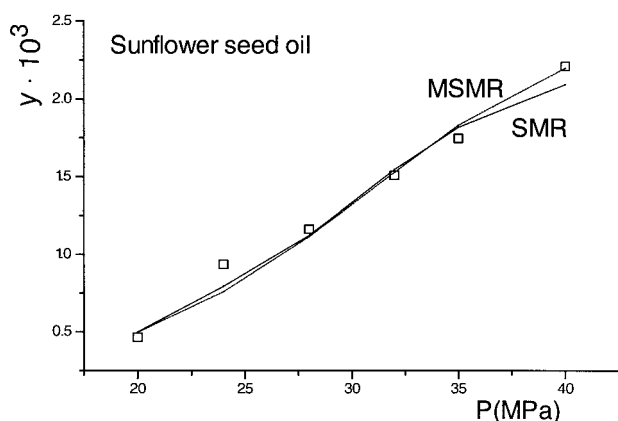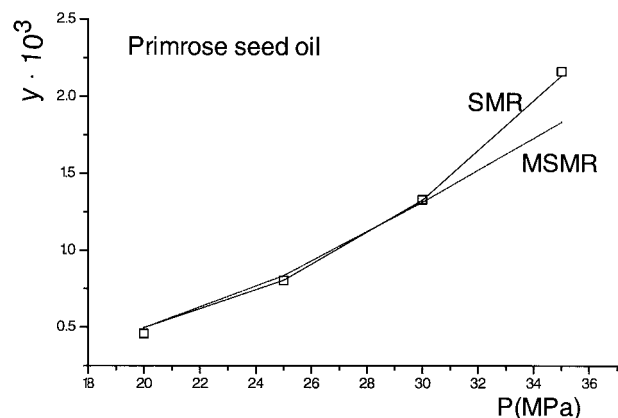

Figure 1. Determination of k_{12} – binary interaction parameter and k – modified binary interaction parameter applying SRK and PR EOS. Symbol used: □– soybean; o – sunflower and Δ – primrose seed oil.

Figure 2. *Calculated mole fraction in supercritical CO_2*

Figure 3. *Calculated mole fraction in supercritical CO_2*

Figure 4. *Calculated mole fraction in supercritical CO_2*

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 snd 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_{ij} —   binary interaction parameter of the Model
k   —   modified 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

α, κ, Ω_a, Ω_b —   constants in the Cubic Equation of State
ϕ —   fugacity coefficient
γ —   activity coefficient
ω —   acentric factor

SUPERSCRIPTS

L   —   liquid phase
0   —   reference state
sf   —   supercritical phase

SUBSCRIPTS

c   —   critical parameter
m   —   mixture
1   —   liquid component
2   —   supercritical component

REFERENCES

[1]   P. J. Carter, Gamma–Linolenic Acid as a Nutrient, Food Technology, **42** (6) (1988) 72.

[2]   F. I. Collins and R. W. Howell, Variability of Linolenic and Linoleic Acids in Soybean Oil, J. Am. Oil Chemists' Soc., **34** (1957) 491.

[3]   I. Žižović, D. Skala and M. Ristić, Extraction of Oenothera biennis Seed Oil with Supercritical carbon Dioxide – Determination of the content of Gamma linolenic acid in Seed Oil, J. Serb. Chem. Soc., **63** (1998) 883.

[4]   E. Stahl, E. Shutz and H.K. Mangold, Extraction of Seed Oils with Liquid and Supercritical Carbon Dioxide, J. Agric. Food Chem., **28** (1980) 1153.

[5]   I. Žižović, Solubility of polyunsaturated fatty acids in supercritical carbon dioxide, Master Thesis, Faculty of Technology and Metallurgy, Belgrade University, Belgrade, Yugoslavia, 1996.

[6]   P. Alessi, A. Cortesi, I. Kikic and N. R. Foster, Determination and Correlation of Solubility of Pharmaceutical Products in Supercritical Carbon Dioxide, Chem. Biochem. Eng. Q., **11** (1) (1997) 19.

[7] W. L. Weng, J. T. Chen and M. J. Lee, High–Pressure Vapor–Liquid Equilibria for Mixtures Containing a Supercritical Fluid, Ind. Eng. Chem. Res., **33** (1994) 1955.

[8] T. Y. Kwak and G. A. Mansoori, van der Waals Mixing Rules for Cubic Equations of State, Applications for Supercritical Extraction Modelling, Chem. Eng. Sci., **41** (5) (1986) 1303.

[9] L. Coniglio, K. Knudsen and R. Gani, Model prediction of Supercritical Fluid – Liquid Equilibria for Carbon Dioxide and Fish Oil Related Compounds, Ind. Eng. Chem. Res., **34** (1995) 2473.

[10] P.C. Chen, M. Tang and Y. P. Chen, Calculations of the Solubilities of Solids in Supercritical Fluids Using the Peng–Robinson Equation of State and a Modified Mixing Model, Ind. Eng. Chem. Res., **34** (1995) 332.

[11] E.Yu, M. Richter, P. Chen, X. Wang, Z. Zhang and L. L. Tavlarides, Solubilities of Polychlorinated Biphenyls in Supercritical Carbon Dioxide, Ind. Eng. Chem. Res., **34** (1995) 340.

[12] X. Nanping, W. Zhaohui, D. Junhang and S. Jun, Estimation of Solubility of Solids in Supercritical Carbon Dioxide, Chinese J. of Chem. Eng., **5** (1) (1997) 29.

[13] I. Žižović and D. Skala, Calculations of the solubility of vegetable oils based on cubic equations of state, CHISA'96, Praha, paper P3.158, 1996.

[14] J. M. Prausnitz and P. R. Benson, Solubility of Liquids in Compressed Hydrogen, Nitrogen, and Carbon Dioxide, A.I.Ch.E. Journal, **5** (2) (1959) 161.

[15] G. Soave, Chem. Eng. Sci., **27** (1972) 1197.

[16] D.Y. Peng and D.B. Robinson, A New Two–Constant Equation of State, Ind. Eng. Chem. Fundam., **15** (1) (1976) 59.

IZVOD

IZRAČUNAVANJE RASTVORLJIVOSTI BILJNIH ULJA U NATKRITIČNOM UGLJEN DIOKSIDU PRIMENOM KUBNIH JEDNAČINA STANJA

(Naučni rad)

Irena Žižović, Dejan Skala
Tehnološko–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 noćurka (ulje sa velikim sadržajem polinezasićenih masnih kiselina u svom sastavu), kao i ulja soje i suncokreta. Za primenu odgovarajućeg modela procenjen je binarni interakcioni parametar na osnovu eksperimentalnih podataka rastvorljivosti navedenih sirovina (ulja) u natkritičnom ugljendioksidu. Predložen model ekspandovane tečnosti omogućava izračunavanje rastvorljivosti ulja sa relativnom greškom u odnosu na eksperimentalne podatke koja je manja od 7,2%.

$y \cdot 10^3$

$y \cdot 10^3$

$y \cdot 10^3$

$y \cdot 10^3$