



J. Serb. Chem. Soc. 87 (6) 735–747 (2022)
JSCS–5554

Correlation of the solubility of solid hydrocarbons in supercritical CO₂ using different equations of state and mixing rules

NARJES SETOODEH and ABOLHASAN AMERI*

Department of Chemical Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran

(Received 17 August 2021, revised 3 December 2021, accepted 15 January 2022)

Abstract: The supercritical extraction process is a technique that has increasingly been applied in various industries in recent years. Solubility determination in the supercritical region is the key feature for this process. However, high expenses and time consuming experiments for this task obligates the need for process modeling. In this study, a thermodynamic model is proposed to correlate the solubility of solid hydrocarbons, namely, 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid in supercritical conditions, using Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations of state with one-parameter van der Waals (vdW1) and two-parameters (vdW2) and covolume dependent (CVD) mixing rules. For the above combination of equations of state and mixing rules, binary interaction parameters were determined, utilizing the differential evolution optimization strategy. The validity of the model was assessed by comparing the experimental solubility data with the results obtained from thermodynamic model based on average absolute relative deviation (*AARD*). An empirical correlation was proposed for the correlation of the solid solubilities in supercritical CO₂. For each compound, the constants of this equation were obtained in such a manner to correlate the solubility at different temperatures and pressures.

Keywords: supercritical extraction; solid compounds; thermodynamic modeling; PR; SRK.

INTRODUCTION

Application of new technologies in different industrial processes has led to increase in the yield of processes. The supercritical fluid extraction (SFE) process is a technology of growing interest in recent years covering various industries, such as food, pharmaceutical, chemical, perfume and essence.

* Corresponding author. E-mail: ameri@iaushiraz.ac.ir
<https://doi.org/10.2298/JSC210817002S>



Application of SFE in separation processes results in reducing energy consumption, extraction at ambient temperature, improving product quality and being healthy, full extraction of solute from solvent by the change of pressure or temperature and reducing environmental pollution.¹

The relatively high density of supercritical fluids leads to high solubility of heavy hydrocarbons in supercritical fluid (SCF), while their solubility in fluids in the gaseous state is low. Despite this, the solubility of compounds in SCF depends on the solute and solvent properties. A supercritical fluid such as CO₂ plays the role of solvent and dissolves a solid compound in itself. The solubility of these solid compounds in CO₂ depends on temperature and pressure. This solubility can be calculated using phase equilibrium relations by equations of state and mixing rules for a mixture of solid and SCF.

One of the most important applications of the SFE process is the extraction of heavy hydrocarbons from the solid phase using supercritical CO₂. In order to correlate the solubility of heavy components in supercritical CO₂, the use of an appropriate equation of state (EoS) and mixing rule are required. As a result, it is important to verify which EoS and mixing rule could better correlate the solubility and are in better agreement with the experimental data.

Chafer *et al.* proposed a thermodynamic model for the solubility of quercetin in supercritical CO₂ using the group contribution equation of state (GC-EoS), and the Soave–Redlich–Kwong (SRK) EoS. They used ethanol as a co-solvent.² Yang and Zhong used the statistical associating fluid theory (SAFT) equation of state with a one-parameter mixing rule.³ They modeled the solubility of aromatic compounds in supercritical fluids. Schultz *et al.* predicted the solubility of hexane in supercritical carbon dioxide with the virial equation of state (V EoS) and calculated its coefficients up to fourth-order using Mayer-sampling Monte Carlo.⁴ Two sparse Bayesian methods were applied by Tarasova *et al.* to derive predictive models of the solubility of organic dyes and polycyclic aromatic compounds in supercritical carbon dioxide.⁵ Zeinolabedini *et al.* correlated the solubility of mefenamic acid in supercritical carbon dioxide with four empirical correlations, namely Chrastil, Mendez–Santiago–Teja (MST), Bartle and Kumar and Johnston (K-J).⁶ A model was proposed for the solubility of fifteen pharmaceutical compounds in supercritical carbon dioxide with the regular solution model and the Flory–Huggins equation by Huang *et al.*⁷ Chie-Shaan Su fitted the experimental data for the solubility of some fatty acids in supercritical carbon dioxide by using a two-parameter solution model developed from the regular solution model coupled with the Flory–Huggins equation.⁸ Shojaee *et al.* correlated the solubility data of carvedilol in supercritical carbon dioxide. Their model was fitted using density-based semi-empirical models, namely Bartle *et al.*, Mendez–Santiago–Teja, Chrastil and Kumar and Johnston.⁹ Cheng *et al.* correlated the solubility data of ergosterol in supercritical carbon dioxide at high pressures

by the Schmitt–Reid and Giddings models.¹⁰ A model was developed for drug solubility in supercritical carbon dioxide using equation of state based on the hole theory with molecular surface charge density by Sakabe *et al.*¹¹ Asgarpour Khansary *et al.* developed a new model for the empirical prediction of solute solubility in supercritical carbon dioxide.¹² Li *et al.* investigated the solubilities of organic compounds in supercritical CO₂ using a modified solution model and expanded liquid model.¹³

Due to the time-consuming and high expense of experimental measurements, modeling of the solubility behavior of solid compounds is needed. In this study, a thermodynamic modeling was performed to correlate the solubility of thirteen solid compounds, namely, 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid under supercritical conditions, in the range of 303.1–343.1 K and 52.1–574.8 bar for various solid compounds,^{10,14–21} using the PR and SRK equations of state with vdW1, vdW2 and CVD mixing rules. For the above combinations of equations of state and mixing rules, binary interaction parameters were determined, utilizing the differential evolution optimization strategy. As a result, which EoS and mixing rule could better correlate the solubility behavior of compounds in supercritical CO₂ could be chosen. In addition, an empirical correlation is proposed for the correlation of the solid solubilities in supercritical CO₂. For each compound, the constants of this equation were determined in such a manner to correlate the solubility at different temperatures and pressures.

THERMODYNAMIC MODEL

One of the important issues in order to correlate the solubility of heavy hydrocarbons from the solid or liquid phase in SCF is the proper selection of the EoS and mixing rule. Authors have used different equations of state, such as Peng–Robinson (PR), Redlich–Kwong (RK), perturbed-hard-chain, Carnahan–Starling–van der Waals (CS–vdW); and different mixing rules such as van der Waals 1 (vdW1), van der Waals 2 (vdW2), Huron–Vidal, modified Huron and Viddal of order 1 (MHV1), modified Huron and Viddal of order 1 (MHV2), group contribution of the Vidal and Michelsen (GCVM), linear combination of the Vidal and Michelsen (LCVM), Wong–Sandler (WS), Orbey–Sandler (OS) and covolume dependent (CVD). In this study, the PR and SRK equation of states along with vdW1, vdW2 and CVD mixing rules were used and a comparison was made with experimental data for thirteen heavy compounds, namely, 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid.^{22,23}

Using phase equilibrium relations for a mixture of a solid and a supercritical fluid, Eq. (1) was obtained:

$$f_2^s = f_2^{scf} \quad (1)$$

Subscript 2 represents the heavy component and f^s and f^{scf} are fugacities of the solid compound and supercritical fluid, respectively. The solid phase is pure and nonideal behavior

is for the supercritical fluid. Thus, the fugacity of the pure solid component, f_2^s , at a specific pressure P and temperature T is calculated by Eq. (2):

$$f_2^s = P_2^{\text{sat}} \phi_2^{\text{sat,s}} \exp \left[\frac{v_2^s (P - P_2^{\text{sat}})}{RT} \right] \quad (2)$$

where, P_2^{sat} and $\phi_2^{\text{sat,s}}$ are representative of the saturation vapor pressure and saturation fugacity coefficient of solid compound, v_2^s is molar volume of solid solute and P , T and R are pressure, temperature and universal gas constant, respectively. Due to low vapor pressure of a solid compound, $\phi_2^{\text{sat,s}}$ is assumed to equal 1. On the other hand, the fugacity of a solid compound in SCF, f_2^{scf} is obtained by Eq. (3):

$$f_2^{\text{scf}} = y_2 \phi_2^{\text{scf}} P \quad (3)$$

where, y_2 and ϕ_2^{scf} represent solubility and fugacity coefficient of solid compound in SCF. Now, with assumption of equilibrium between the two phases, by equating Eqs. (2) and (3), the solubility relation for solid compound in the SCF is given by Eq. (4):

$$y_2 = \left(\frac{P_2^{\text{sat}}}{P} \right) \left(\frac{1}{\phi_2^{\text{scf}}} \right) \exp \left[\frac{v_2^s (P - P_2^{\text{sat}})}{RT} \right] \quad (4)$$

P_2^{sat} , the vapor pressure of the heavy component, is calculated from the Antoine Equation.

The accuracy of the solubility calculation depends on the proper selection of the equation of state and mixing rule for the calculation of ϕ_2^{scf} . The two parameters PR and SRK equations of state can be written as in Eq. (5):

$$P = \frac{RT}{v - b} - \frac{a}{(v + c_1 b)(v + c_2 b)} \quad (5)$$

where, a and b are constants of the equation of state and v represents the molar volume. The constants of Eq. (5) for the PR and SRK equations of state and vdW1, vdW2 and CVD mixing rules are given in the Supplementary material to this paper.

The optimal values of these model adjustable parameters were obtained using the robust population-based differential evolution (DE) method for experimental data points. The most accurate combination of equations of states with the mixing rules, which leads to the least "absolute average relative deviation" (AARD, Eq. (6)) of the results from experimental values are reported.

$$AARD = \sum_i^N \left(\left| \frac{y_{\text{exp}}^i - y_{\text{calc}}^i}{y_{\text{exp}}^i} \right| \frac{1}{n} \right) 100 \quad (6)$$

where y_{exp}^i and y_{calc}^i are experimental and calculated solubilities, respectively and n is the number of data points. The value of ϕ_2^{scf} is identified with ϕ_1 in Eq. (7).²⁴ Considering a mixture of solid compound and SCF for PR and SRK equations of states we have:

$$\ln \hat{\phi}_1 = -\ln(Z - B) + \frac{\hat{b}_1}{b} (Z - 1) + \frac{a}{bRT(c_1 - c_2)} \left[-\frac{\hat{a}_1}{a} + \frac{\hat{b}_1}{b} \right] \ln \frac{Z + c_1 B}{Z + c_2 B} \quad (7)$$

\hat{a}_1 and \hat{b}_1 in Eq. (7) are derivatives related to the attractive and repulsive parameters of EoS and can be calculated according to equations in the Supplementary material to this paper.

The compressibility factor value, Z , needed for calculation of $\hat{\phi}_1$ is obtained from the EoS using Eqs. (8) or (9):

For PR EoS:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (8)$$

For SRK EoS:

$$Z^3 - Z^2 + (AB - B^2)Z - AB = 0 \quad (9)$$

Parameters A and B are defined by Eqs. (10) and (11):

$$A = \frac{aP}{R^2T^2} \quad (10)$$

$$B = \frac{bP}{RT} \quad (11)$$

The adjustable parameters in the mixing rules (k_{ij} , l_{ij} and M_{ij} , see Supplementary material) were fitted to the experimental data by the following objective function:

$$OF = \sum_i^N \left(\frac{y_{\text{exp}}^i - y_{\text{calc}}^i}{y_{\text{exp}}^i} \right)^2 \quad (12)$$

The physical properties of 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid are given in Table I. Joback group contribution methods were applied for the calculation of the critical temperature and pressure.²⁵ The values of the acentric factor were estimated using the Ambrose–Walton corresponding-state method.²⁵ The Molbase chemical E-commerce platform site was referenced for the introduction of the molar volume of the solid compounds.

TABLE I. Physical properties of the studied compounds

Component	T_c / K	P_c / bar	ω	$v^{\#}_2$ / m ³ kmol ⁻¹
Carbon dioxide (solvent)	304.2	73.7	0.225	–
1-Hexadecanol	761	14.9	0.748	0.2965
1-Octadecanol	777	13.4	0.863	0.3330
Anthracene	869.15	30.8	0.353	0.1426
Benzoin	853.52	26.6	0.599	0.1620
Fluorene	826.4	29.5	0.406	0.1393
Hexamethylbenzene	758	24.4	0.515	0.1527
Mandelic acid	903.79	34.73	34.73	0.1170
Naphthalene	748.4	40.51	0.302	0.111
Palmitic acid	776	14.9	1.083	0.2857
Phenanthrene	882.65	31.715	0.437	0.182
Propyl 4-hydroxybenzoate	815.92	31.30	0.722	0.1316
Pyrene	936	25.7	0.509	0.1585
Stearic acid	779	13.4	1.084	0.3024

RESULTS AND DISCUSSION

The fitted binary parameters for modeling results and $AARD$ for the combination of PR or SRK EoS and three mixing rules are given for 1-hexadecanol, 1-octadecanol, anthracene, benzoin, fluorene, hexamethylbenzene, mandelic acid, naphthalene, palmitic acid, phenanthrene, propyl 4-hydroxybenzoate, pyrene and stearic acid at different pressures and temperatures in Table S-I (Supplementary material) for the calculation of the solubility of heavy compounds in supercritical CO₂.

At higher temperatures and pressures for some compounds, the *AARD* becomes greater. 1-Hexadecanol shows high errors at 318.1 and 338.15 K for vdW1 and all temperatures of the CVD mixing rule. 1-Octadecanol does not match well with the experimental data at 328.1 and 338.1 K for vdW1 and CVD mixing rules. Anthracene shows acceptable *AARD* values at almost all temperatures and mixing rules. Benzoin compound depicts *AARD* less than 10 % at all its data points. CVD mixing rule at 343.1 K for fluorene does not show tolerable *AARD*. Although, other conditions are in an appropriate circumstances. Hexamethylbenzene is another solid compound with low values of *AARD* for all temperature and pressure ranges and mixing rules. Only the vdW2 mixing rule resulted in low *AARD* for mandelic acid, and vdW1 and CVD mixing rules did not respond well for this substance. All temperatures of the vdW2 mixing rule illustrate a low *AARD* for naphthalene.

However, the vdW1 and CVD mixing rules show good results only for temperatures of 308.1 and 328.1 K. This model did not responded well for palmitic acid and high *AARD* values were obtained at all temperatures and for all mixing rules. On the other hand, the results of phenanthrene were in good agreement with the experimental data and all *AARD* values were acceptable enough over wide temperature and pressure ranges. Propyl 4-hydroxybenzoate was also a compound with low *AARD* values, except at 328.1 K, which showed a little higher *AARD*. Pyrene and stearic acid did not show low *AARD* values for any mixing rules at 343.15 and 338.1 K, respectively. Moreover, some compounds, such as 1-hexadecanol, 1-octadecanol, mandelic acid and palmitic acid, showed greater deviation from the experimental data due to their chemical structure and intermolecular forces and bonds and irregular trend of experimental data according to pressure. As they are alcohols and carboxylic acids and their –OH and –COOH functional groups caused inappropriate *AARD* values. For instance, at higher pressures, the cubic EoS could not well predict the solubilities of solids in SCF and this causes higher error values at high pressures. As the values of T_c , P_c and ω are not from experimental data and have been calculated from correlations, this also could be considered as another source of uncertainty of data correlated by the proposed model. The results show that the PR EoS has more accuracy than the SRK EoS at most data points. In addition, the vdW2 mixing rule is more accurate than vdW1, as was to be expected. Finally, the CVD mixing rule revealed less accuracy compared with the other mixing rules. Comparison of the *AARD* values for different compounds revealed that the applied thermodynamic model was not satisfactory for four compounds, namely, 1-hexadecanol, 1-octadecanol, mandelic acid and palmitic acid and the calculated and experimental solubilities deviate greatly. This could be due to their linear structure unlike the other compounds that contain an aromatic ring in their chemical structure. This shows that the proposed model could not well correlate the solubilities of hydrocarbons

containing only a linear chain no aromatic ring. In almost most compounds, the modeling results indicated less accuracy at higher temperatures. This fact could be related to the non-ideality of the system due to the effect of factors such as molecular weight and molecular interaction of solid compound and Brownian motion at higher temperatures. The intermolecular forces are more dominant at higher pressures and lower temperatures due to the reduced kinetic energy. As a result, the non-ideality of the gas becomes more prominent. As the gas molecules would be close to each other at low temperatures and reach conditions for converting into the liquid phase. As a result, the physical and thermodynamic properties of the compounds could alter the accuracy of the proposed model the base of which is theoretical.

A comparison of the calculated solubility results with the experimental data^{10,17,18,26} for some solid compounds in supercritical carbon dioxide is shown in Fig. 1 for the PR EoS and vdW2 mixing rule at 308.15 K, for example. The solubility of a solid compound in SCF increases with increasing pressure due to a reduction of the intermolecular distance. This leads to increasing density of the supercritical CO₂. As a result, the solubility of a solid compound in SCF increases due to the higher solvating strength at higher pressures.

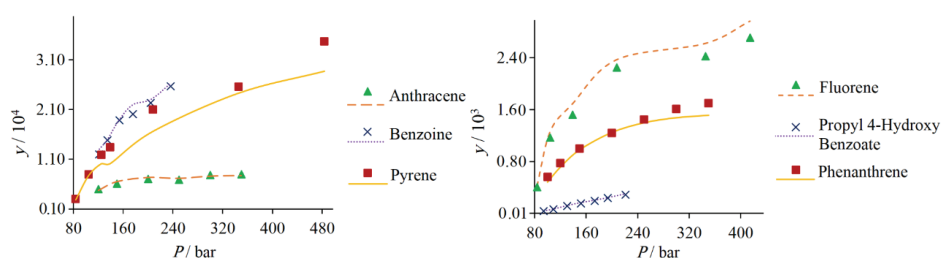


Fig. 1. Comparison of solubility of solid components in supercritical CO₂ using the PR EoS and vdW2 mixing rule at $T = 308.15$ K with experimental data^{10,17,18,26} (symbols: experimental data, lines: calculated data).

Temperature has the same effect on the solubility of hydrocarbons in SCF as pressure. The solubility increases with temperature at a constant pressure. Unfortunately, the solvating strength decreased as the temperature increases due to increasing density. On the other hand, increasing the temperature favors the solubility of a solid in SCF due to enhanced solid vapor pressure. The net effect of these two factors is in favor of solubility improvement.

For compounds shown in Fig. 1, anthracene, benzoine, pyrene, fluorene, propyl 4-hydroxy benzoate and phenanthrene, it could be seen that the correlated model results are in close agreement with the experimental data at most points.

A comparison of the results for different mixing rules with PR and SRK EoS with the experimental data for phenanthrene at 308.15 K is shown in Fig. 2. It

could be observed that the vdW2 mixing rule is better than the vdW1 rule and then the CVD, and PR results are more exact than the SRK EoS results. This trend holds for most of the data obtained from modeling.

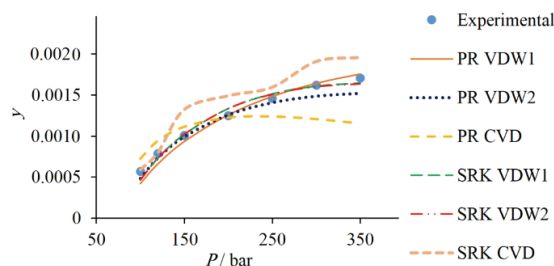


Fig. 2. Comparison of solubility of phenanthrene in supercritical CO₂ at 308.15 K for PR and SRK EoS and three different mixing rules with the experimental data.¹⁸

In this study, an empirical correlation was evaluated by Eq. (13), by fitting experimental data for thirteen solid compounds at various temperature and pressure conditions:

$$y = a + \frac{b}{T} + c \ln P + \frac{d}{T^2} + e(\ln P)^2 + f \frac{\ln P}{T} + \frac{g}{T^3} + h(\ln P)^3 + i \frac{(\ln P)^2}{T} + j \frac{\ln P}{T^2} \quad (13)$$

where, a , b , c , d , e , f , g , h , i and j are the constants of the equation and T is in K and P is in bar. This kind of equation with ten constants was chosen in order to contain all compounds investigated in this study. The constants of the proposed equation are given in Table II along with $AARD$ and the R -squared values (r^2) for

TABLE II. Constants of the correlated Eq. (13) from solubility data of different solid components in supercritical CO₂

Component	a	b	c	d
1-Hexadecanol	11.54705	-1106.09888	-6.11915	-1684300.000
1-Octadecanol	58.09549	-47365.50854	-6.04540	12968094.14
Anthracene	-0.08523	70.96200	0.00544	-17060.97261
Fluorene	0.02995	20.50137	-0.05487	25370.86890
Hexamethylbenzene	-0.20310	383.07771	-0.14506	-98450.62687
Mandelic acid	0.43494	222.04041	-0.40145	-115354.7488
Naphthalene	-778.75029	716040.4887	23.55648	-217758344.2
Palmitic acid	29.98129	-19851.83296	-5.71884	5389525.856
Phenanthrene	-1.04090	938.09129	-0.00131	-286301.88
Propyl 4-hydroxybenzoate	0.17340	-1.833323	-0.10634	-30732.90725
Pyrene	0.18200	-117.85981	-0.03993	28506.07751
Stearic acid	26.55206	-18856.81082	-4.39775	4924193.745
Component	e	f	g	h
1-Hexadecanol	0.44706	2474.25705	295954000	-0.00422
1-Octadecanol	0.24566	3162.35737	-1212649300	0.00127

TABLE II. Continued

Component	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	
Fluorene	0.02569	-36.37337	-9020275.86	-0.00059	
Hexamethylbenzene	0.04026	-24.61846	5557533.278	-0.00171	
Mandelic acid	0.06161	57.53582	-1639495.818	0.00109	
Naphthalene	0.64636	-16838.10238	21924540172	-0.01076	
Palmitic acid	0.67430	1397.120595	-716773367.1	0.00626	
Phenanthrene	0.00416	-2.44702	30967674	-0.00044	
Propyl 4-hydroxybenzoate	0.00868	40.690182	3269272.063	0.00037	
Pyrene	0.00426	13.02016	-2736351.611	0.000070	
Stearic acid	0.38118	1573.72658	295954000	-0.00422	
Component	<i>i</i>	<i>j</i>	No. of points	<i>AARD</i> / %	<i>r</i> ²
1-Hexadecanol	-120.32106	-204469.418	43	4.95	0.999
1-Octadecanol	-85.97946	-378429.2624	41	3.71	0.999
Anthracene	-0.17868	1288.87653	140	9.78	0.997
Fluorene	-5.31945	12796.2177	157	8.73	0.998
Hexamethylbenzene	-4.64411	9827.18519	23	9.70	0.997
Mandelic acid	-23.67834	27243.98579	21	8.84	0.998
Naphthalene	-153.59875	2889216.912	66	9.41	0.997
Palmitic acid	-251.28354	205916.2349	19	9.50	0.997
Phenanthrene	0.72572	-2029.6518	151	7.50	0.999
Propyl 4-hydroxybenzoate	-4.34060	101.23586	21	7.35	0.999
Pyrene	-1.01282	-632.60526	142	5.38	0.999

each equation obtained from comparing experimental data and results of this equation for several sets of data. As could be seen, the results are in good agreement with the experimental data and the *AARD* is given for each set of data for each component. Hence, in the absence of experimental data at different temperatures and pressures and due to high expense and time-consuming experiments, the proposed equation could be used to obtain the solubility of the herein studied solid compounds in supercritical CO₂ at different temperatures and pressures with good accuracy and reliability.

As an example, the solubility data obtained from Eq. (13) for some of these solid compounds namely, pyrene, anthracene, Mandelic acid and propyl 4-hydroxybenzoate, are compared with experimental data in Fig. 3, which shows that the correlated results with proposed equation match well with experimental data.

CONCLUSIONS

In this work, a thermodynamic approach was applied for the calculation of the solubility of heavy hydrocarbons in supercritical CO₂ using PR and SRK EoS's and three vdW1, vdW2 and CVD mixing rules. The results were in good agreement with the experimental data reported for the specified temperature and pressure ranges. The results showed that the points correlated using the PR EoS were more precise than those using the SRK EoS for most points. Additionally, the vdW2 mixing rule revealed the maximum accuracy followed by the vdW1 and

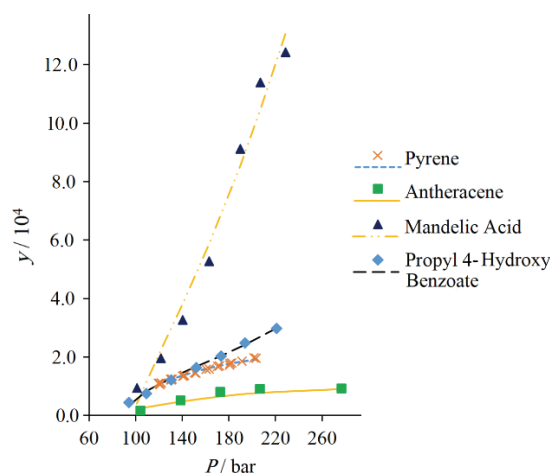


Fig. 3. Comparison of solubility of some compounds in supercritical CO₂ from Eq. (13) with experimental data^{10,17,20,26} (symbols: experimental data, lines: calculated data).

CVD mixing rules. Furthermore, the solubility values increased with increasing temperature and pressure. For each combination of equation of state and mixing rule, the optimized binary interaction parameters were reported for different cases by fitting. In order to correlate the solubility of heavy compounds in supercritical CO₂, an empirical equation with 10 constants was evaluated and proposed by fitting several experimental sets of data according to temperature and pressure. The constants of this equation were given for the compounds investigated in this study in order to predict the solubilities of these thirteen solid compounds in SCF at other temperatures and pressures without need to perform experiments. In the same manner, a separate empirical equation could be obtained for other solid compounds for the prediction of their solubility in SCF.

NOMENCLATURE

<i>AARD</i>	Absolute average relative deviations
k_{ij}	Binary interaction parameter
<i>OF</i>	Objective function
l_{ij}	Binary interaction parameter
P_c	Critical pressure
<i>n</i>	Number of points
P^{sat}	Saturation vapor pressure
vdW1	One-parameter van der Waals
PR	Peng-Robinson
vdW2	Two-parameter van der Waals
SCFs	Supercritical fluids
<i>y</i>	Solubility of solid solute
SRK	Soave-Redlich-Kwong
y_{calc}^i	Calculated mole fraction of component <i>i</i>
T_c	Critical temperature
y_{exp}^i	Experimental mole fraction of component <i>i</i>
T_r	Reduced temperature

ϕ^{scf}	Fugacity coefficient of supercritical fluid
Z	Compressibility factor
ϕ^{sat}	Saturation fugacity coefficient
a	Indicative of intermolecular attractive energy
ϕ_i	Fugacity coefficient
b	Indicative of size of the molecule
v	Molar volume
f^s	Fugacity of solid
v^s	Molar volume of the solid solute
f^{scf}	Fugacity of supercritical fluid
ω	Acentric factor

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11074>, or from the corresponding author on request.

ИЗВОД

КОРЕЛИСАЊЕ РАСТВОРЉИВОСТИ ЧВРСТИХ УГЉОВОДНИКА У НАДКРИТИЧНОМ CO₂ КОРИШЋЕЊЕМ РАЗЛИЧИТИХ ЈЕДНАЧИНА СТАЊА И ПРАВИЛА МЕШАЊА

NARJES SETOODEH и ABOLHASAN AMERI

Department of Chemical Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran

Надкритична екстракција се последњих година све више примењује у разним индустријским процесима. Један од најважнијих параметара који је потребно одредити за ове процесе је растворљивост једињења у надкритичној области. Међутим, услед високих трошкова и дуготрајних експеримената јавља се потреба за одређивањем растворљивости моделовањем. У овом раду предложен је термодинамички модел за корелисање растворљивости чврстих угљоводоника (1-хексадеканол, 1-октадеканол, антрацена, бензоина, флуорена, хексаметилбензена, бадемове киселине, нафталена, палмитинске киселине, фенантрена, пропила 4-хидробензобензола, пирена и стеаринске киселине) у надкритичним условима, коришћењем Peng–Robinson (PR) и Soave–Redlich–Kwong (SRK) једначине стања, и њиховим комбиновањем са једнопараметарским (vdW1), двопараметарским (vdW2) van der Waals и (CVD) правилима мешања. За наведене комбинације једначина стања и правила мешања, бинарни интеракциони параметри су одређени оптимизацијом, применом алгоритма диференцијалне еволуције. Валидност модела је утврђена на основу апсолутне вредности средњег процентуалног релативног одступања (AARD), односно, поређењем експерименталних података растворљивости са резултатима добијеним применом термодинамичког модела. Такође, на основу резултата, предложена је емпиријска корелација растворљивости чврстих угљоводоника у надкритичном CO₂. Добијене константе предложене корелације се могу користити за одређивање растворљивост на различитим температурама и притисцима.

(Примљено 17. августа 2021, ревидирано 3 децембра 2021, прихваћено 15. јануара 2022)

REFERENCES

1. R. D. Smith, J. P. Blitz, J. L. Fulton, in *Supercritical Fluid Science, Technology*, Vol. 406, K. P. Johnston, J. M. L. Penninger, Eds., ACS Publications, Washington DC, 1989, pp. 165

2. A. Chafer, T. Fornari, A. Berna, R. P. Stateva, *J. Supercrit. Fluids* **32** (2004) 89 (<https://doi.org/10.1016/j.supflu.2004.02.005>)
3. H. Yang, C. Zhong, *J. Supercrit. Fluids* **33** (2005) 99 (<https://doi.org/10.1016/j.supflu.2004.05.008>)
4. A. J. Schultz, K. R. S. Shaul, S. Yang, D. A. Kofke, *J. Supercrit. Fluids* **55** (2010) 479 (<https://doi.org/10.1016/j.supflu.2010.10.042>)
5. A. Tarasova, F. Burden, J. Gasteiger, D. A. Winkler, *J. Mol. Graphics Modell.* **28** (2010) 593 (<https://doi.org/10.1016/j.jmgm.2009.12.004>)
6. A. Z. Hezave, M. H. Khademi, F. Esmailzadeh, *Fluid Phase Equilib.* **313** (2012) 140 (<https://doi.org/10.1016/j.fluid.2011.09.031>)
7. C.-Y. Huang, L.-S. Lee, C.-S. Su, *J. Taiwan Inst. Chem. Eng.* **44** (2013) 349 (<https://doi.org/10.1016/j.jtice.2012.12.004>)
8. C.-S. Su, *J. Supercrit. Fluids* **81** (2013) 79 (<https://doi.org/10.1016/j.supflu.2013.05.001>)
9. S. A. Shojaee, H. Rajaei, A. Z. Hezave, M. Lashkarbolooki, F. Esmailzadeh, *J. Supercrit. Fluids* **81** (2013) 42 (<https://doi.org/10.1016/j.supflu.2013.04.013>)
10. S.-H. Cheng, F.-C. Yang, Y.-H. Yang, C.-C. Hu, W.-T. Chang, *J. Taiwan Inst. Chem. Eng.* **44** (2013) 19 (<https://doi.org/10.1016/j.jtice.2012.09.001>)
11. J. Sakabe, H. Uchida, Y. Shimoyama, *Chem. Eng. Res. Des.* **92** (2014) 2970 (<https://doi.org/10.1016/j.cherd.2014.08.003>)
12. M. A. Khansary, F. Amiri, A. Hosseini, A. H. Sani, H. Shahbeig, *Chem. Eng. Res. Des.* **93** (2015) 355 (<https://doi.org/10.1016/j.cherd.2014.05.004>)
13. H. Li, D. Jia, R. Liu, B. Shen, *Fluid Phase Equilib.* **385** (2015) 10 (<https://doi.org/10.1016/j.fluid.2014.10.036>)
14. K. P. Johnston, C. A. Eckert, *AIChE J.* **27** (1981) 773 (<https://doi.org/10.1002/aic.690270511>)
15. A. Kramer, G. Thodos, *J. Chem. Eng. Data* **33** (1988) 230 (<https://doi.org/10.1021/je00053a002>)
16. A. Kramer, G. Thodos, *J. Chem. Eng. Data* **34** (1989) 184 (<https://doi.org/10.1021/je00056a011>)
17. E. Kosal, G. D. Holder, *J. Chem. Eng. Data* **32** (1987) 148 (<https://doi.org/10.1021/je00048a005>)
18. J. M. Dobbs, K. P. Johnston, *Ind. Eng. Chem. Res.* **26** (1987) 1476 (<https://doi.org/10.1021/ie00067a035>)
19. J. Kwiatkowski, Z. Lisicki, W. Majewski, *Ber. Bunsen. Phys. Chem.* **88** (1984) 865 (<https://doi.org/10.1002/bbpc.19840880919>)
20. K. D. Bartle, A. A. Clifford, S. A. Jafar, *J. Chem. Eng. Data* **35** (1990) 355 (<https://doi.org/10.1021/je00061a037>)
21. M. McHugh, M. E. Paulaitis, *J. Chem. Eng. Data* **25** (1980) 326 (<https://doi.org/10.1021/je60087a018>)
22. M. Mukhopadhyay, *Natural extracts using supercritical carbon dioxide*, CRC press, Cleveland, OH, 2000
23. G. M. Kontogeorgis, G. K. Folas, *Thermodynamic models for industrial applications: from classical, advanced mixing rules to association theories*, John Wiley & Sons, Hoboken, NJ, 2009
24. I. Polishuk, I. Kapry, M. Madar, *Chem. Eng. Commun.* **196** (2008) 448 (<https://doi.org/10.1080/00986440802483970>)

25. R. C. Reid, J. M. Prausnitz, B. E. Poling, *The properties of gases, liquids*, McGraw Hill Book Co., New York, 1987
26. K. P. Johnston, D. H. Ziger, C. A. Eckert, *Ind. Eng. Chem. Fundam.* **21** (1982) 191 (<https://doi.org/10.1021/i100007a001>).