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RESEARCH ARTICLE

A New Simple Equation of State for Calculating Solubility of Solids in Supercritical Carbon Dioxide

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Abstract
In this work, a modified Redlich–Kwong (βRK) equation of state has been proposed to calculate the solubilities of twenty solids including Ascorbic acid, Fluoranthene, Propyl gallate, Acenaphthene, Asprin, Climbazole, Cinnamic acid, Triclocarban, 4-methoxyphenylacetic acid, Phenoxyacetic acid, Cholesterol,Cholesteryl butyrate, Cholestrol acetat,Triphenylene, Ibuprofen, Acetanilide, Propanamide, Butanamide, Chrysene and Dodecyl gallate in supercritical carbon dioxide (440 data points). The proposed equation of state has been coupled with the van der Waals zero (vdW0) mixing rule. To distinguish the accuracy of the proposed model, the results of the model have been compared with the results of Peng–Robinson (PR) equation of state in combination with the van der Waals one (vdW1) and the Wong-Sandler (WS) mixing rules. The calculation results showed that the proposed model performed well for reproducing the solubility of these twenty solids in supercritical carbon dioxide with absolute average relative deviation (AARD) = 5.7 %.

Keywords
solid solubility, supercritical fluid, carbon dioxide, βRK-EoS

1 Introduction

In recent years, attentions have been focused on supercritical fluid extraction because this method is potentially applicable in many processes such as food processing, mixture separation, caffeine removal from coffee, extraction of lipids, making fine particles by Rapid Expansion of Supercritical Solutions (RESS), etc. In comparison with the conventional extraction methods, supercritical fluid extraction leads to higher speed of extraction, easier separation of solvent and better recovery, and less solvent usage and waste generation. Among supercritical fluids, carbon dioxide is the most commonly used supercritical fluid because of nontoxic, nonflammable nature of carbon dioxide. Furthermore, carbon dioxide is relatively inexpensive and it has reasonable critical properties (Tc=304.2 K and Pc=73.8 bar) [1-4]. The most important thermo-physical property in the supercritical extraction process is the solubility of solutes in supercritical fluid. To design optimized operating conditions, this property must be determined and modeled so that developing a reliable model for determining the solubility of solids in supercritical fluids is of importance. In general, the models for solubility calculation are classified into two different groups including theoretical models such as models based on the equations of state and empirical correlations such as density based equations. In the first group, different equations of state (EoS) along with various mixing rules are used. Among various types of EoSs, the cubic EoSs are widely used for calculation of solid solubility in supercritical fluid due to their flexibility and reliability and their proper speed of calculations [5-11]. However, cubic EOSs have a limited predictive capability. In addition, they are not accurate for complex systems such as the systems with associating or very heavy compounds [12]. In order to improve the accuracy of the results, an option is applying more complex equations of state based on the molecular theory of statistical mechanics (such as SAFT equation of state) or using more powerful mixing rules (such as Wong-Sandler mixing rule). In spite of considerable developments of theoretical equations of state (e.g. SAFT EOSs), their application is still limited because of their complexity and time consuming for calculation. Another way to overcome the above mentioned limitation is applying empirical

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models such as density-based models of Chrastil [13], Méndez-Santiago-Teja [14], Jafari Nejad et al. [15] for phase equilibrium calculation of the supercritical-solid systems. The parameters of these models are obtained based on the error minimization for proposed equations that are versus density of pure supercritical carbon dioxide, temperature and pressure. Although density-based models does not have any theoretical bases, but they are applied in different applications because of their simplicity in the correlation of experimental data. The main disadvantages of this approach are its requirement to large amount of solubility data and its unconfident for extrapolation.

Many investigators were modeled the solubility of solids in supercritical carbon dioxide. Cheng et al. [1] used the Schmitt–Reid and Giddings models to correlate the high-pressure solubility of phytosterol in supercritical carbon dioxide. They also used Me´ndez-Santiago and Teja density based models to fit the experimental data. Huang et al. [4] applied a correlation and a semi-empirical model to reproduce the solubility of 15 pharmaceutical compounds in supercritical carbon dioxide at various thermodynamic conditions. Housaindokht et al. [5] applied modified Peng-Robinson equation of state to correlate the solubility of solids in supercritical carbon dioxide. They also determined interaction parameters for these systems. Yazdizadeh et al. [6] applied the Peng–Robinson (PR) and the Esmaeilzadeh–Roshanfekr (ER) equations of state (EoSs) in combination with the van der Waals one (vdW1) and two (vdW2), Wong–Sandler (WS) and the co-volume dependent (CVD) fluid mixing rules to calculate the solubilities of 52 solids in supercritical carbon dioxide. Wang and Lin [7] presented a predictive model to determine the solubility of drugs in supercritical carbon dioxide. They used melting temperature and heat of fusion to calculate the fugacity of solid phase. They also used Peng–Robinson (PR) EoS to calculate the fugacity in fluid phases. Su [8] modeled the solubilities of solid solutes in carbon dioxide by using the predictive Soave–Redlich–Kwong (PSRK) equation of state. The results of this investigation showed that the PSRK EoS was a simple but a reliable model for solubility evaluation in supercritical fluid technology containing CO2-expanded organic solvents. Asgarpour et al. [8] developed a new equation of state based on Pitzer correlation for the virial equation of state to determine the solubility of drugs in supercritical carbon dioxide. Baseri et al. [10] used the Peng-Robinson EOS to model the solubilities of different solid components in supercritical CO2. They also tested the effects of three different mixing rules containing van der Waals, Panagiotopoulos and Reid, and modified Kwak and Mansoori mixing rules. The modified Kwak and Mansoori mixing rule had the best performance. Aghamiri and Nickmand [16] calculated the solubility of cholesterol in (supercritical fluid+co-solvents) containing carbon dioxide+ethane, carbon dioxide+methanol, ethane+acetone, ethane+hexane and ethane+propane mixed solvents. They used SRK, PR, and SAFT equations of state.

In this work, a modified Redlich-Kwong (βRK) EOS was proposed and combined with the van der Waals zero (vdW0) mixing rule for reproducing the solubilities of 20 solid compounds in supercritical carbon dioxide. In addition, the Peng-Robinson (PR) equation of state was coupled with the van der Waals one (vdW1) and Wong-Sandler (WS) mixing rules for the same purpose. In order to show the performance of the new proposed EoS in reproducing solubilities of solids in supercritical CO2, the results obtained by proposed model were compared with the results of the PR-EoS.

2 Thermodynamic model description

2.1 Phase equilibrium of solid–supercritical fluid

It is known that the solubility of solid in supercritical phase can be obtained by the equality of the fugacity of solid solute in supercritical and solid phases.

$$f_i^{Solid}\left(T,P\right)=f_i^{Supercritical}\left(T,P,\left\{x_i\right\}\right) \tag{1}$$

In Eq. (1), f_i is the fugacity, T is the temperature, P is the pressure and x_i is the mole fraction in supercritical phase. When the temperature and the pressure of the system are known, the solubility of solid in supercritical phase is calculated by solving Eq. (1).

2.2 Fugacity in solid phase

By neglecting the supercritical fluid solubility in solid phase, assuming the constant solid molar volume and considering the saturation fugacity coefficient of solid to be unity, the fugacity in solid phase can be written as follows:

$$f_i^{solid}=P_i^{Sat}\exp\left[\frac{v_i^S\left(P-P_i^{Sat}\right)}{RT}\right] \tag{2}$$

In Eq. (2), P_i^{Sat} denotes the vapor pressure of solid at temperature T, v_i^S is the molar volume of solid and R is the universal gas constant.

2.3 Fugacity of components in the fluid phase

As it is shown in Eqs. (3) and (4), in order to obtain the fugacity of components in the supercritical phase, an appropriate equation of sate should be considered.

$$RT\ln\phi_i^{\sup ercritical}=\int_V^{\infty}\left(\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}}-\frac{RT}{V}\right)dV-\ln Z \tag{3}$$

$$f_i^{Supercritical}=P\phi_i^{\sup ercritical}x_i \tag{4}$$

In Eqs. (3) and (4), ϕ shows the fugacity coefficient of the solute in supercritical phase and Z is the compressibility factor of supercritical phase.

Table 1 Critical properties of the solid components used in this work.

Compound	T_C (K)	P_C (bar)	ω	V_m (cm^3/mol)	Ref.
Dodecyl gallate	905.9	18.46	1.2	267.9	[21]
Ascorbic acid	790.91	44.19	1.57	106.7	[21]
Propyl gallate	862.87	47.72	0.86	155	[21]
Triclocarban	935.8	34.9	0.760	206.3	[24]
Climbazole	872	23.7	0.819	223.8	[24]
Cholesterol	1168.23	41.55	0.95	371.56	[27]
cholesteryl butyrate	1234.20	34.09	0.955	433	[27]
cholestrol acetat	1185.65	36.87	0.883	403.2	[27]
Ibuprofen	754.6	21.8	0.749	182.1	[11]
Acetanilide	735.85	40.1	0.5774	118.93	[28]
Propanamide	707.31	51.2	0.5986	69.21	[28]
Butanamide	706.28	47	0.6061	84.55	[28]
Aspirin	762.9	32.8	0.82	128.7	[22]
Fluoranthene	905	26.1	0.59	161.6	[6]
Triphenylene	1013.6	29.28	0.49	175	[6]
Chrysene	1027.8	29.28	0.49	179	[6]
Acenaphthene	803.15	31	0.38	126.2	[6]
Cinnamic acid	803.94	38.58	0.688	118.8	[20]
phenoxyacetic acid	802.61	39.91	0.760	113	[20]
4-methoxyphenylacetic acid	827.3	34.85	0.808	127.9	[20]

The RK-EoS [17] is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a}{T_r^{0.5} v\left(v+b\right)} \tag{5}$$

The energy and volume parameters of RK EOS are calculated in terms of the critical properties. The critical properties for pure components are given in Table 1.

$$a = 0.42747\frac{(RT_c)^2}{P_c} \tag{6}$$

$$b = 0.0778\frac{RT_c}{P_c} \tag{7}$$

For calculating the molar volume of supercritical CO_2, Heidaryan and Jarrahian [18] proposed a correction for energy parameter of RK equation of state as a function of reduced pressure and temperature. In this work, for better calculation of solid solubility in supercritical phase, a new correction for energy parameter of RK EOS is proposed as a function of reduced temperature:

$$P = \frac{RT}{v-b} - \frac{\beta a}{v\left(v+b\right)} \tag{8}$$

In Eq. (8), β is a correction that is written as follows:

$$\beta_i = \frac{1+\beta_{i1}T_r}{1-\beta_{i2}T_r} \tag{9}$$

In Eq. (9), i belongs to CO_2 or solid solute. Therefore, β_{11}-β_{12} and β_{21}-β_{22} are the parameters belonging to solute and CO_2, respectively. In this investigation, two differences exist in comparison with the work of Heidaryan and Jarrahian [18]. First, the β function includes two parameters for each compound in this work, but the β function includes six parameters for each compound in the work of Heidaryan and Jarrahian [18]. The second difference is that they applied β function in terms of reduced temperature and reduced pressure while in this work β is only expressed in terms of reduced temperature. Therefore, not only our β function is a new function but also our application is different and the proposed model is used for solubility calculation while Heidaryan and Jarrahian calculated the molar volume of supercritical CO_2. β_{11}-β_{12} and β_{21}-β_{22} are determined based on the minimization of average absolute relative deviation percent (AARD%), expressed by the following equation:

$$AARD = \frac{100}{N}\sum_i \frac{\left|y_i^{\exp} - y_i^{cal}\right|}{y_i^{\exp}} \tag{10}$$

In order to optimize the model parameters, a non-linear optimization technique based on the Nelder–Mead simplex algorithm was applied.

The Peng-Robinson equation of state (PR EoS) [19] was also considered to determine the fugacity of components in the fluid (supercritical) phase. The PR EoS is written as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \tag{11}$$

In Eq. (11), a and b show the energy and volume parameters, respectively. The parameters of the PR EoS are as follows:

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \alpha(T) \tag{12}$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{13}$$

In Eqs. (12) and (13), v shows the molar volume and subscripts c and r indicate the critical and reduced properties, respectively.

The $\alpha(T)$ parameter of PR EOS, is expressed as follows:

$$\alpha(T) = (1 + m(1 - T_r^{0.5}))^2 \tag{14}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{15}$$

In Eqs. (14) and (15), ω is the acentric factor that represented the acentricity or nonsphericity of a molecule with respect to both the geometry and polarity [29].

In this investigation, the PR-EOS is combined with van der Waals one (vdW1) and Wong-Sandler (WS) mixing rules.

The van der Waals mixing rule can be written as follows:

$$a_m = \sum_i \sum_j a_{ij} x_i x_j \tag{16}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{17}$$

$$b_m = \sum_i b_i y_i \tag{18}$$

In Eq. (17), if k_{ij} is set equal to zero, the mixing rule is named vdW0 instead of vdW1 mixing rule.

The Wong Sandler mixing rule can be expressed as follows:

$$b_m = \frac{Q}{1-D} \tag{19}$$

$$a_m = RTDb_m \tag{20}$$

In Eqs. (19) and (20):

$$Q = \sum_i \sum_j x_i x_j \left(a - \frac{b}{RT}\right)_{ij} \tag{21}$$

$$D = \sum_i \frac{y_i a_i}{b_i RT} + \frac{G^E}{\Omega RT} \tag{22}$$

In Eq. (21):

$$\left(a - \frac{b}{RT}\right)_{ij} = \left[b_i - \frac{a_i}{RT} + b_j - \frac{a_j}{RT}\right]\left(\frac{1-k_{ij}}{2}\right) \tag{23}$$

In this paper, the van-Laar activity model is chosen to calculate the excess Gibbs energy in Eq. (22).

3 Results and discussion

In this modeling investigation, the solubilities of tweny solid components containing Ascorbic acid, Fluoranthene, Propyl gallate, Acenaphthene, Asprin, Climbazole, Cinnamic acid, Triclocarban, 4-methoxyphenylacetic acid, Phenoxyacetic acid, Cholesterol, Cholesteryl butyrate, Cholestrol acetat,Triphenylene, Ibuprofen, Acetanilide, Propanamide, Butanamide, Chrysene and Dodecyl gallate in supercritical carbon dioxide have been calculated. The experimental solubilities were obtained from the literature [10,20-28]. To reproduce the solid solubility in supercritical carbon dioxide, the Peng Robinson equation of state (PR EOS) has been applied in combination with the van der Waals (vdW1) and Wong Sandler (WS) mixing rules. In order to determine the parameters of van der Waals (vdW1) and Wong Sandler (WS) mixing rules (i.e. binary interaction parameter), the parameters have been determined by a minimization program. The average absolute relative deviations (AARD%) and the determined parameters for the applied models including PR-vdW1, PR-WS and βRK-vdW0 models have been reported in Table 2. Figs. 1 and 2 compare the results of PR-vdW1, PR-WS and βRK-vdW0 models with the experimental solubilities of acenaphthene and chrysene in supercritical CO_2, respectively. It can be concluded that the WS mixing rule is much more accurate than vdW1 mixing rule so that the PR EOS in combination with the WS mixing rule performs more accurately for modeling the solubilities of these solids in supercritical carbon dioxide.

In order to reveal the precision of the proposed EoS (βRK-EoS) combining with the simple vdW0 mixing rule, the proposed model has been used to reproduce the solubilities of these twenty solid components in supercritical carbon dioxide. The accuracy of the proposed model and the parameters of the proposed model have been presented in Table 2. One can see in Table 2 that the proposed model performs much more accurately than the Peng-Robinson EoS and vdW1 mixing rule, even it is better than the couple of PR-EoS and WS mixing rule. By considering the results of the applied models, it can be concluded that the βRK is able to reproduce the solubilities of these twenty solid components in supercritical carbon dioxide. This model does not need any complicated mixing rule so that combination of βRK and the simple mixing rule of vdW0 is a reliable approach of computing the phase equilibrium of (solid + supercritical carbon dioxide) systems.

Table 2 The parameters and AARD (%) of applied models in this work

Compound	T(k)	P(MPa)	ND[a]	Ref[b]	Models	Model parameter				AARD[c] (%)
						Kij	Aij	Aji		
						β_{11}	β_{12}	β_{21}	β_{22}	
1. Ascorbic acid	313	13-20	4	[21]	PR-vdW1[D]	0.4692	-	-	-	11.16
					PR-WS[E]	0.8831	-0.0888	21.3486	-	2.3
					βRK-vdW0[F]	0.1907	2.4727	-1.0096	-9.5896	0.217
2. fluoranthene	308.15	8.9-24.7	12	[23]	PR-vdW1	0.12	-	-	-	5.5
					PR-WS	0.7893	1.5690	7.2349	-	4.47
					βRK-vdW0	1.89	0.7272	-0.0041	0.25	3.84
	318.15	9-24.9	9	[23]	PR-vdW1	0.1148	-	-	-	16.3
					PR-WS	0.7785	0.0953	8.8956	-	8.5
					βRK-vdW0	2.3550	0.0105	-0.0357	-0.3184	7.1
	328.15	12.1-20.9	5	[23]	PR-vdW1	0.1060	-	-	-	5.6
					PR-WS	0.7940	1.6033	5.3485	-	5.3
					βRK-vdW0	2.3021	0.1149	-0.0741	-0.1923	5.43
3. Propyl gallate	313.15	15-25	4	[21]	PR-vdW1	0.2430	-	-	-	5.41
					PR-WS	0.7546	-4.5518	11.9579		0.62
					βRK-vdW0	15.0493	-0.1158	-2.2806	2.4304	0.14
	333.15	15-25	4	[21]	PR-vdW1	0.22787	-	-	-	13.03
					PR-WS	0.7407	-3.1512	11.3529	-	2.47
					βRK-vdW0	8.4990	-0.3624	0.3298	2.7554	0.68
4. acenaphthene	308.15	12.1-35.5	9	[25]	PR-vdW1	-0.2284	-	-	-	27
	308.15	12.1-35.5	9	[25]	PR-WS	0.5351	-2.5321	-6.6329	-	9.5
					βRK-vdW0	5.0797	-0.3487	0.1060	0.1404	3.73
	318.15	12.1-35.5	9	[25]	PR-vdW1	-0.2421	-	-	-	32
					PR-WS	0.5445	-0.2320	-9.2907	-	10.9
					βRK-vdW0	3.8617	0.2699	0.1103	-0.1714	2.9
	328.15	12.1-35.5	9	[25]	PR-vdW1	-0.2488	-	-	-	39
					PR-WS	0.4827	-0.1273	-7.0662	-	12.4
					βRK-vdW0	2.8263	0.7004	0.0850	0.1849	3.7
	338.15	12.1-35.5	9	[25]	PR-vdW1	-0.2798	-	-	-	43
					PR-WS	0.4530	-0.1915	-6.4648	-	15.1
					βRK-vdW0	3.6189	0.1976	0.1055	-0.5609	0.9
	348.15	12.1-35.5	9	[25]	PR-vdW1	-0.3047	-	-	-	48
					PR-WS	0.4185	-0.1681	-5.2579	-	16.7
					βRK-vdW0	3.0085	0.4589	0.0503	0.1117	4.4

[a] number of data , [b] reference, [c] the average absolute relative deviation between experimental data and calculation results, [D] Peng Robinson equation of state with van der Waals one mixing rules, [E] Robinson equation of state with Wong-Sandler mixing rules, [F] modified Redlich–Kwong with van der Waals zero mixing rules (proposed model)

Table 2 (Continued)

Compound	T(k)	P(MPa)	ND[a]	Ref[b]	Models	Model parameter				AARD[c] (%)
						Kij	Aij	Aji		
						β$_{11}$	β$_{12}$	β$_{21}$	β$_{22}$	
5.Asprin	308.15	12-25	8	[22]	PR-vdW1	0.216	-	-	-	2.32
					PR-WS	0.7676	0.7179	8.8559		1.21
					βRK-vdW0	-16.043	0.2868	-2.2806	-0.1732	2.47
	318.15	12-25	8	[22]	PR-vdW1	0.2112	-	-	-	7.39
					PR-WS	0.7769	1.2229	7.5078	-	2.38
					βRK-vdW0	-16.112	0.2009	-2.1150	-0.1367	1.31
	328.15	12-25	8	[22]	PR-vdW1	0.209	-	-	-	8.7
					PR-WS	0.7692	0.1453	7.9679	-	4.35
					βRK-vdW0	-13.119	0.4986	-1.1072	0.3496	5.75
6. Climbazole	313.2	10.5-40	8	[24]	PR-vdW1	0.1480	-	-	-	10.49
					PR-WS	0.8137	2.0944	8.6670	-	5.3
					βRK-vdW0	2.5621	0.2623	-0.0277	0.0736	7.6
	323.2	13-36.5	8	[24]	PR-vdW1	0.1542	-	-	-	5.17
					PR-WS	0.7769	1.2229	7.5078	-	2.38
					βRK-vdW0	2.2565	0.3343	-0.0521	0.0657	6.4
	333.2	14.5-35.5	8	[24]	PR-vdW1	0.1594	-	-	-	5.87
					PR-WS	0.8196	1.0461	8.6648	-	1.4
					βRK-vdW0	2.0541	0.3902	-0.0760	0.1135	3.89
7. Cinnamic acid	308.2	15-23	4	[20]	PR-vdW1	0.0274	-	-	-	4.9
					PR-WS	0.6467	0.0051	4.5907	-	4.95
					βRK-vdW0	2.6560	0.6394	-0.0255	0.0348	4.1
	318.2	12-23	7	[20]	PR-vdW1	0.0288	-	-	-	10.8
					PR-WS	0.7013	0.7778	0.1893	-	8.96
					βRK-vdW0	2.9771	0.3035	-0.0728	-0.2576	3.2
	3282	14.5-23.5	6	[20]	PR-vdW1	0.0296	-	-	-	3
					PR-WS	0.6840	0.5619	1.3847	-	2
					βRK-vdW0	3.2057	-0.1603	-0.0989	-0.6008	1.7
8. triclocarban	313.2	10.9-39	8	[24]	PR-vdW1	0.1955	-	-	-	15.16
					PR-WS	0.7962	-0.5928	10.2380	-	2.037
					βRK-vdW0	3.1083	2.4722	-0.0105	0.0325	3.1
	323.2	12-33.3	8	[24]	PR-vdW1	0.1944	-	-	-	16.44
					PR-WS	0.7953	7.9431	10.4874	-	5.22
					βRK-vdW0	3.1225	2.3595	-0.0307	0.0309	5.01
	333.2	13.7-30.5	8	[24]	PR-vdW1	0.2047	-	-	-	11.93
	333.2	13.7-30.5	8	[24]	PR-WS	0.7987	-10.927	10.3580	-	1.01
					βRK-vdW0	3.0913	2.2582	-0.0545	0.0316	1.47

Table 2 (Continued)

Compound	T(k)	P(MPa)	ND[a]	Ref[b]	Models	Model parameter Kij	Aij	Aji		AARD[c] (%)
						β_{11}	β_{12}	β_{21}	β_{22}	
9. 4-methoxyphenylacetic acid	308.2	11.5-24	7	[20]	PR-vdW1	-0.1298	-	-	-	16.4
					PR-WS	0.6363	1.8589	-3.3767	-	3.8
					βRK-vdW0	52.0292	-1.6455	0.0161	0.4433	4.1
	318.2	12.5-23	8	[20]	PR-vdW1	-0.1351	-	-	-	13.8
					PR-WS	0.6394	2.3698	-3.2314		3
					βRK-vdW0	112.7861	-6.8023	0.0296	3.9067	3.2
	328.2	14-23.5	7	[20]	PR-vdW1	-0.1375	-	-	-	8.8
					PR-WS	0.6547	0.2993	-3.9677	-	4.1
					βRK-vdW0	109.9834	-6.8570	0.0244	1.5701	3.9
10. phenoxyacetic acid	308.2	12-22	7	[20]	PR-vdW1	-0.1298	-	-	-	16.4
					PR-WS	0.7503	0.7516	4.5344	-	3.8
					βRK-vdW0	41.7481	-3.6182	-0.2508	-4.3556	2.7
	318.2	12-22	7	[20]	PR-vdW1	-0.1351	-	-	-	13.8
					PR-WS	0.7502	0.7288	4.5434	-	3.37
					βRK-vdW0	40.5517	-3.6971	-0.3499	-3.9642	2.9
	328.2	12-22	8	[20]	PR-vdW1	0.1489	-	-	-	9.7
					PR-WS	0.7474	0.8288	4.4401	-	4.1
					βRK-vdW0	40.7857	-4.0229	-0.3899	-3.5015	3.4
11. Cholesterol	313.15	10-25	6	[26]	PR-vdW1	0.4911	-	-	-	8.5
					PR-WS	0.9026	0.5515	35.8405	-	9
					βRK-vdW0	-0.2195	1.6612	0.0001	0.9736	3
	323.15	10-25	6	[26]	PR-vdW1	0.5032	-	-	-	44
					PR-WS	0.9322	-7.5416	30.2097	-	24
					βRK-vdW0	-7.8E-6	3.6151	1.969E-5	0.94153	17.7
	333.15	13-25	5	[26]	PR-vdW1	0.5093	-	-	-	35.4
					PR-WS	0.9340	5.0424	28.9155	-	17.2
					βRK-vdW0	-0.4956	0.0407	-0.4350	-1.6693	12.5
12. cholesteryl butyrate	308.15	10-24	7	[27]	PR-vdW1	0.4353	-	-	-	21
					PR-WS	0.9067	58.1398	37.0256	-	12.35
					βRK-vdW0	0.6280	-0.2244	-0.0252	-0.2409	12.6
	318.15	10-24	7	[27]	PR-vdW1	0.4439	-	-	-	18.6
					PR-WS	0.9114	579.2555	35.1620	-	14
					βRK-vdW0	0.4311	0.2463	-0.0585	-0.0605	7.5
	328.15	12-24	6	[27]	PR-vdW1	0.4553	-	-	-	17.6
					PR-WS	0.9185	79.1976	33.3959	-	11.6
					βRK-vdW0	0.2306	0.1524	-0.1070	-0.2988	6.9

Table 2 (Continued)

Compound	T(k)	P(MPa)	ND[a]	Ref[b]	Models	Model parameter				AARD[c] (%)
						Kij	Aij	Aji		
						β_{11}	β_{12}	β_{21}	β_{22}	
13. cholestrol acetat	308.15	9-24	8	[27]	PR-vdW1	0.412824	-	-	-	20.27
					PR-WS	0.8876	-495.129	32.5868	-	5.9
					βRK-vdW0	0.6013	-0.2888	-0.0014	-0.3520	6.8
	318.15	9-24	9	[27]	PR-vdW1	0.42260	-	-	-	17.66
					PR-WS	0.9	1542.2	29.4	-	14.5
					βRK-vdW0	0.4778	-0.2843	-0.0488	-0.0859	10.8
	328.15	9-21	7	[27]	PR-vdW1	0.4312	-	-	-	37.66
					PR-WS	0.9177	-117.823	24.0926	-	13.3
					βRK-vdW0	0.2960	1.8023	-0.0946	0.0662	9.2
14. Triphenylene	308.15	8.5-24.7	10	[23]	PR-vdW1	0.0874	-	-	-	22
					PR-WS	0.7766	0.1093	7.0432	-	10.4
					βRK-vdW0	3.0380	-0.0567	0.0126	-0.0829	3.8
	318.15	9.6-25.2	10	[23]	PR-vdW1	0.0797	-	-	-	29
					PR-WS	0.7681	-57.3892	7.8926		8.9
					βRK-vdW0	2.6831	0.1899	-0.0186	-0.4474	7.5
	328.15	10.7-25.1	8	[23]	PR-vdW1	0.0776	-	-	-	24
					PR-WS	0.7751	-60.7706	6.6758	-	8.7
					βRK-vdW0	78.0323	-86.8448	-0.00001	0.9267	3.5
15. Ibuprofen	308.15	8-13	11	[11]	PR-vdW1	0.0873	-	-	-	23
					PR-WS	0.7847	0.8483	2.4358	-	15.6
					βRK-vdW0	-18.9573	0.3299	-2.2443	-0.1455	9.1
	313.15	9-13	9	[11]	PR-vdW1	0.0757	-	-	-	14.8
					PR-WS	0.7824	0.7263	1.7011	-	6.5
					βRK-vdW0	-19.0053	0.2821	-2.2414	-0.1660	8.5
	318.15	8-13	11	[11]	PR-vdW1	0.0875	-	-	-	28
					PR-WS	0.7893	0.5901	0.3562	-	8.7
					βRK-vdW0	-18.7651	0.2793	-2.1858	-0.1650	7.9
16. Acetanilide	308.2	9-40	10	[28]	PR-vdW1	0.3136	-	-	-	70
					PR-WS	0.8198	-6.3799	4.6974	-	34
					βRK-vdW0	0.8266	0.4058	-0.1172	0.0030	5.7
	313.2	9-40	10	[28]	PR-vdW1	0.3260	-	-	-	68
					PR-WS	0.8013	-1.6914	4.2210	-	19.2
					βRK-vdW0	0.9953	0.2535	-0.1491	-0.0214	7.4
	323.2	10-40	9	[28]	PR-vdW1	0.2155	-	-	-	48.1
					PR-WS	0.7689	-3.8279	4.9670	-	26
					βRK-vdW0	1.0401	-0.4126	-0.1369	-0.1348	18.8

Table 2 (Continued)

Compound	T(k)	P(MPa)	ND[a]	Ref[b]	Models	Model parameter				AARD[c] (%)
						Kij	Aij	Aji		
						β_{11}	β_{12}	β_{21}	β_{22}	
17. Propanamide	308.2	9-40	10	[28]	PR-vdW1	0.1392	-	-	-	6.7
					PR-WS	0.6288	0.3821	4.3651	-	4.2
					βRK-vdW0	1.6992	-0.5152	-0.0305	-0.2956	5.6
	313.2	9-40	10	[28]	PR-vdW1	0.1404	-	-	-	5.8
					PR-WS	0.6129	0.8504	4.4979		5.1
					βRK-vdW0	1.4258	-0.6370	-0.0257	-0.2734	4.9
	323.2	10-40	10	[28]	PR-vdW1	0.1376	-	-	-	21.4
					PR-WS	0.5929	64.5507	4.7321	-	14.4
					βRK-vdW0	1.5906	-0.5278	-0.0284	-0.2891	13.3
18. Butanamide	308.2	9-40	10	[28]	PR-vdW1	0.1487				7.4
					PR-WS	0.6408	2.2683	4.5660		7.2
					βRK-vdW0	1.6144	-0.5244	-0.0290	-0.2902	6.1
	313.2	9-40	10	[28]	PR-vdW1	0.1398				10.5
					PR-WS	0.6475	-2.5151	4.0516		10.4
					βRK-vdW0	1.5155	-0.6062	-0.0213	-0.2840	9.5
	323.2	10-40	10	[28]	PR-vdW1	0.1402				10.2
					PR-WS	0.6270	-1.6628	4.1685		74
					βRK-vdW0	1.5625	-0.6371	-0.0537	-0.2405	7.9
19. Chrysene	308.15	8.4-25.1	11	[23]	PR-vdW1	0.1020	-	-	-	16.2
					PR-WS	0.7878	7.3497	7.3190		8.1
					βRK-vdW0	2.8767	0.0484	0.0008	-0.2020	4.2
20. Dodecyl gallate	313.1	15-25	4	[21]	PR-vdW1	0.0253	-	-	-	14.1
					PR-WS	0.7561	4.2943	4.0208	-	4
					βRK-vdW0	3.8443	-0.0718	0.0320	-0.4279	2.7
Total AARD(%)	308-348	8-40	440				PR-vdW1			19.4
							PR-WS			9.6
							βRK-vdW0			5.7

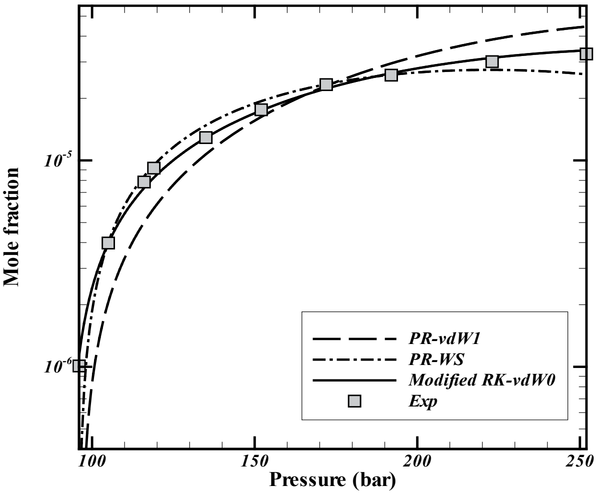

Fig. 1 Experimental and calculated solubilities of acenaphthene in supercritical CO_2 at T=318.15 K

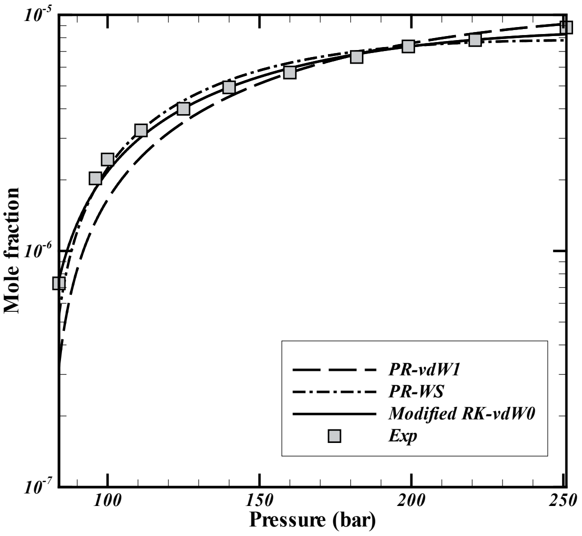

Fig. 2 Experimental and calculated solubilities of Chrysene in supercritical CO_2 at T=308.15 K

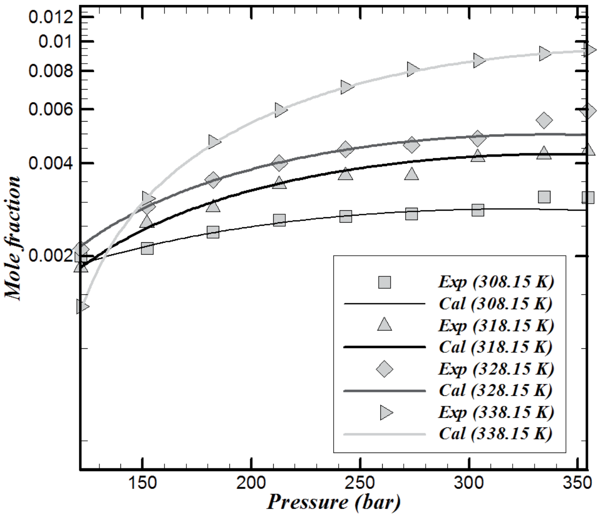

Fig. 3 Experimental and calculated solubilities of Acenaphthene in supercritical CO_2 at different isotherms.

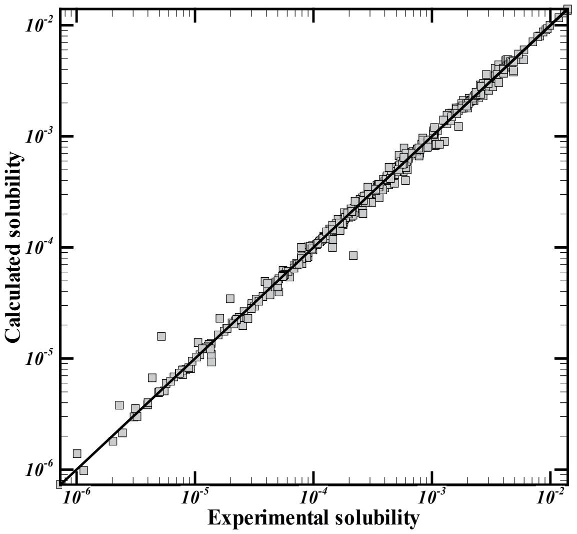

Fig. 4 The calculated solubilities versus experimental solubilities for all of 440 points

Figure 3 demonstrates the solubilities for Acenaphthene at different isotherms using the proposed model. Also Fig. 4 shows the calculated solubilities versus experimental solubilities for all of 440 points. The close points to solid line show the accurate performance of the applied model so that it is found that the proposed model is able to reproduce the solubility of solids in the SC-CO2 with an acceptable deviation.

4 Conclusion

A new modified RK equation of state (βRK-EoS) combined with the vdW0 mixing rule proposed to reproduce the solubilities of twenty solids in supercritical carbon dioxide. The parameters of the model have been determined and reported. Additionally, the results of this proposed model have been compared with the PR EoS-VdW1 and PR EoS-WS models. It is found that the relative error (AARD%) between the calculation results and the experimental data for the proposed model is 5.7%. The results showed that the proposed model performs more accurate than PR EOS-VdW1 and PR EOS-WS models.

Nomenclature

A_{ij},A_{ji}	parameters used in WS mixing rules
a	attraction parameter
a_m	attraction parameter of the supercritical solution
AARD%	average absolute relative deviation (%)
b	co-volume parameter
b_m	co-volume parameter of the supercritical solution
EoSs	equation of states
f_i	fugacity of component i
k_{ij}	binary intraction parameter

P	ressure
PR	Peng–Robinson
R	universal gas constant
RK	Redlich–Kwong
T	temperature
V	volume
vdW	van der Waals
y_i	mole fraction of component i

Greek symbols

α	temperature-dependent parameter for calculation of a(T)
β	coefficients of proposed EoS
βRK	modified Redlich–Kwong EoS
φ	fugacity coefficient

Subscripts

c	critical point
i	belongs to CO2 or solid solute

Superscripts

s	solid phase
sat	saturation
cal	calculated
exp	experimental

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