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Modified Redlich-Kwong and Peng-Robinson Equations of State for Solubility Calculation of Solid Compounds in Supercritical Carbon dioxide

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Abstract

The modified Redlich-Kwong (βRK) and modified Peng-Robinson (βPR) Equations of State (EoSs) combined with the van der Waals mixing rule (vdW0) have been proposed to evaluate the solubilities of ten solid compounds in supercritical CO_2. These ten solid compounds are including Methimazole, Ascorbic acid, Ascorbyl palmitate, Propyl gallate, Aspirin, Fluoranthene, Triclocarban, Hinokitiol, Phenol, and Climbazole. In order to recognize the accuracy of the proposed EoSs, the results of these models have been compared with the calculation results of SRK and PR equations of state in combination with the vdW1 and the Wong-Sandler (WS) mixing rules and other models reported in the literature. The results showed that the proposed models are well for solubility calculation of these ten solid compounds in supercritical CO_2 and the βRK EoS in combination with the vdW0 mixing rule led to better correlation (AARD = 5.1%) compared with other ones.

Keywords: βPR-EoS, βRK-EoS, Equation of State, Solid Solubility, Supercritical CO_2, WS Mixing Rule

1. Introduction

Supercritical fluids can be used as the promising solvents in many applications such as separation, purification and particle sizing of pharmaceuticals, cosmetics, food supplements, natural products, etc. In the supercritical processes, the solubility of the solutes in supercritical fluid is a key parameter for designing optimized operating conditions. The experimental solubilities of the solid compounds and their mixtures in supercritical fluids are limited due to the difficulties of experimental measurements and also time-consuming and costly nature of these measurements. Therefore, it is desirable to develop the predictive and reliable methods for estimating the solubility of solid compounds in supercritical fluids. One way to achieve this aim is using Equation of the State (EoSs). The cubic EoSs are flexible and reliable according to their accuracy. Although considerable progresses in the development of equations of state were reported in the literature, the application of the EoSs is still limited because of their complexity. Additionally, the semi-empirical models do not have theoretical basis, but they are widely used in industrial and engineering applications due to their simplicity[1–4]..

In recent years, some of researchers have worked on the prediction of solid solubility in supercritical fluids by using cubic Equations of the State (EOSs). Khamda et al.[1] investigated the cefixime trihydrate and oxymetholone solubilities in supercritical carbon dioxide. They also used semi-empirical correlation and the Peng-Robinson Equation of State (PR EOS) for modeling of these solubilities. Park et al.[2] investigated the equilibrium solubilities of two biocides, climbazole, and triclocarban in supercritical carbon dioxide. Subsequently, they applied PR EOS and quasi-chemical nonrandom lattice fluid model for these systems. Chen et al.[5] reported the experimental solubilities of cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid in supercritical carbon dioxide. In order to model these solubilities, they also used Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. De Zordi et al.[6] studied the solubility behavior of pharmaceutical compounds

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containing antioxidants, antibiotics, steroids and anti-inflammatory in supercritical fluids. They used a model based on activity coefficients and they determined the parameters of the model as a function of the pharmaceutical compound properties. Housaindokht et al.[3] applied various modified Peng-Robinson equations of state to model the solubility of solid compounds in supercritical carbon dioxide. They also determined interaction parameters for these systems. Cheng et al.[7] investigated the solubility of ergosterol in supercritical carbon dioxide. They used the Peng-Robinson Equation of State (EOS) in combination with the one-parameter and two-parameter van der Waals mixing rules to fit the experimental solubility data. Spiliotis et al.[8] studied the prediction of the liquid and solid aromatic hydrocarbons solubility in supercritical CO_2 with the Linear Combination of the Vidal and Michelsen (LCVM) and Modified Huron-Vidal Two (MHV2) models. Yazdizadeh et al. [4] applied the Peng-Robinson (PR) and the Esmaeilzadeh-Roshanfekr (ER) (EoSs) in combination with Wong-Sandler (WS), the Covolume Dependent (CVD) and the van der Waals one (vdW1) and two (vdW2) fluid mixing rules and the Van-Laar excess Gibbs energy (G^{ex}) model to model the solubilities of solid compounds in supercritical carbon dioxide.

In this work, the modified RK (bRK) and modified PR (bPR) equations of state in combination with the van der Waals zero (vdW0) mixing rule were proposed for calculation of solid solubilities in supercritical carbon dioxide. The Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) (EoSs) in combination with the van der Waals one (vdW1) and Wong-Sandler (WS) mixing rules were also applied for modeling the solubilities of solid compounds in supercritical carbon dioxide. To identify the advantages of the new proposed models in predicting solubilities of solid compounds in supercritical carbon dioxide, the results of proposed models were compared with the results of the conventional SRK and PR Equations of State (EoSs).

2. Thermodynamic model

2.1 Calculation of Solubility

To determine the solid solubility in supercritical fluid, the thermodynamic equilibrium is used as follows:

$$f_i^{PureSolid} = f_i^{Supercritical} \tag{1}$$

where $f_i^{PureSolid}$ is the fugacity of each pure solute and $f_i^{Supercritical}$ is the fugacity of the solute in supercritical fluid. In this study, the following assumptions were considered to obtain the required expression for performing the phase equilibrium calculations:

1. The solubility of supercritical fluid in the solid phase is neglected.
2. The pure solid fugacity is considered to be equal to the fugacity of the solute i in the mixture.
3. The molar volume of the solid phase is constant.
4. The solid phase fugacity coefficient in saturation condition is considered to be unity.

Considering these assumptions, Equation (1) can be expressed as follows:

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

where P and T are pressure and temperature, v denotes the molar volume, R is the universal gas constant. Sat stands for saturation. y and φ are mole fraction and fugacity coefficient of the solid solute in supercritical phase, respectively. The saturation vapor pressures at different temperatures were given in Table 1.

2.1.1 The Modified Redlich-Kwong Equation of State (βRK)

The RK EOS[14] can be written as follows:

$$P = \frac{RT}{v-b} - \frac{a}{T_r^{0.5} v(v+b)} \tag{3}$$

The energy parameter (a) and volume parameter (b) are obtained from the critical properties. The critical properties of pure fluids were listed in Table 2.

$$a = \text{ˇˇˇ}\;\frac{(RT_c)^2}{P_c} \tag{4}$$

$$b = 0.0778\frac{RT_c}{P_c} \tag{5}$$

In this investigation, a new functionality for energy parameter of Redlich-Kwong EoS as a function of temperature and pressure similar to the work of Heidaryan and Jarrahian[15] and similar to our previous work[20] was proposed to evaluate the solubilities of ten solid compounds in supercritical CO^2.

$$P = \frac{RT}{v-b} - \frac{\beta a}{v(v+b)} \tag{6}$$

Table 1. Vapor pressures of the solids used in this study at different temperatures

Compound	Sublimation Vapor (Pa)			Unit	References
	A	B	C		
1. Triclocarban	10.533	5588.4	-	bar	[2]
2. Hinokitiol	9.797	4644.7	-	bar	[19]
3. Phenols	13.7	3580	-	Pa	[18]
4. Climbazole	10.382	5479.6	-	bar	[2]
	Temperature (K)				
5. Methimazole	T = 308.15 K 7.9	T = 318.15 K 18	T = 328.15 K 39	Pa	[17]
6. Ascorbic acid	T=313.15 0.62	-	-	Pa	[10]
7. Ascorbyl palmitate	T=313.15 1.4×10^{-9}	-	-	Pa	[10]
8.Propyl gallate	T = 313.15 K 0.0025	T = 313.15 K (adjustable parameter)	-	Pa	[10]
9. Aspirin	T = 308.15 K 0.09021	T = 318.15 K 0.2803	T = 328.15 K 0.8011	Pa	[11]
10. Fluoranthene	T = 308.15 K 0.00257	T = 318.15 K 0.00905	T = 328.15 K 0.0295	Pa	[12]

In which β is a temperature dependant parameter that can be expressed in terms of reduced temperature as follows:

$$\beta_i = \frac{\beta_{i1} + \beta_{i2} T_r}{1 - \beta_{i3} T_r} \tag{7}$$

In which *i* refer to CO_2 or solute. Thus, β_{11}-β_{13} and β_{21}-β_{23} are related parameters to solute and CO_2, respectively. It worth noting that the b function (including three parameters for each compound) used in this work is different with the β function (including six parameters for each compound) used in the work of Heidaryan and Jarrahian[15]. Therefore, not only our β function is a new function but also our application is different and the proposed models were used for solubility calculation.

2.1.2 The Modified Peng-Robinson Equation of State (βPR)

The PR EOS[14] is expressed as:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \tag{8}$$

where *a* shows the energy parameter and *b* denotes the volume parameter. The PR EOS parameters are defined in terms of critical properties as follows:

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \alpha(T) \tag{9}$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{10}$$

The other parameters of PR EOS are expressed as follows:

$$\alpha(T) = (1 + m(1 - T_r^{0.5}))^2 \tag{11}$$

$$m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2 & \omega \le 0.49 \\ 0.379642 + 1.485030\omega - 0.164423\omega^2 + 0.016666\omega^3 & \omega > 0.49 \end{cases} \tag{12}$$

where ω shows the acentric factor.The subscripts *c* and *r* are related to the critical and reduced properties, respectively.

In this work, the modified version of PR EoS is also suggested for determining the phase equilibrium.

$$P = \frac{RT}{v-b} - \frac{\beta a}{v(v+b) + b(v-b)} \tag{13}$$

Similar to Equation (7), a temperature dependant expression in terms of reduced temperature is considered for b function.

In this work, the van der Waals and Wong Sandler mixing rules were used for the solid-supercritical equilibrium calculations.

Table 2. Critical properties of the chemicals used in this study

Compound	Molecular weight (*g/mol*)	T_C (K)	P_C (bar)	ω	V_m (cm³/mol)	References
1. Methimazole	114.17	731.7	60.75	0.44	162.1	[17]
2. Ascorbic acid	176.12	790.91	44.19	1.57	106.7	[10]
3. Ascorbyl palmitate	414.53	870.81	11.56	1.85	340.5	[10]
4. Propyl gallate	212.2	862.87	47.72	0.86	155	[10]
5. Aspirin	180.157	762.9	32.8	0.82	128.7	[11]
6. Fluoranthene	202.26	905	26.1	0.59	161.6	[12]
7. Triclocarban	315.58	935.8	34.9	0.760	206.3	[2]
8. Hinokitiol	164.2	803.1	37.8	0.760	180.1	[19]
9. Phenols	94.11	692.2	60.5	0.45	89	[18]
10. Climbazole	292.76	872	23.7	0.819	223.8	[2]

The van der Waals mixing rule is expressed as follows

$$a_m = \sum_i \sum_j a_{ij} y_i y_j \tag{14}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{15}$$

$$b_m = \sum_i b_i y_i \tag{16}$$

where y_i denotes the mole fraction of component *i* in supercritical phase. If the parameter k_{ij} was taken as zero, the mixing rule was denoted as the vdW0 instead of vdW1 mixing rules.

The Wong Sandler mixing rule is written as follows,

$$b_m = \frac{Q}{1 - D} \tag{17}$$

$$a_m = RTDb_m \tag{18}$$

in which, $$Q = \sum_i \sum_j y_i y_j \left(a - \frac{b}{RT}\right)_{ij} \tag{19}$$

$$D = \sum_i \frac{y_i a_i}{b_i RT} + \frac{G^E}{\Omega RT} \tag{20}$$

in which,

$$\left(a - \frac{b}{RT}\right)_{ij} = \left[b_i - \frac{a_i}{RT} + b_j - \frac{a_j}{RT}\right]\left(\frac{1 - k_{ij}}{2}\right) \tag{21}$$

In this study, the van-Laar activity model[4] was applied for calculating the excess Gibbs energy.

3. Results and Discussion

In this work, the solubilities of ten solid compounds including Methimazole, Ascorbic acid, Ascorbyl palmitate, Propyl gallate, Aspirin, Fluoranthene, Triclocarban, Hinokitiol, Phenol and Climbazole in supercritical CO_2 were modeled. The experimental solubilities of solids were obtained from the literature[2,9–13,19]. In order to model the solubilities of these solids in supercritical CO_2, the Peng Robinson and the SRK equations of state (EOSs) combined with the van der Waals (vdW1) and Wong Sandler (WS) mixing rules were used. To obtain the binary interaction parameters and the parameters of the model for van der Waals (vdW1) and Wong Sandler (WS) mixing rules, the parameters were obtained via regression with the experimental data through the minimization of an objective function. The average absolute relative deviation percent (AARD%), defined by the following expression:

$$AARD = \frac{100}{N} \sum_i \frac{\left|y_{i,\exp} - y_{i,calc}\right|}{y_{i,\exp}} \tag{22}$$

in which *N* represents the number of experimental points, $y_{i,exp}$ is the experimental solubility data and $y_{i,exp}$ represents the calculated solubility. The average absolute relative deviations percent (AARD%), optimized model and binary interaction parameters were represented in Table 3. Figs. 1-2 compare the calculated solubility results by the sets of PR-vdW1, SRK-vdW1, PR-WS and SRK-WS with the experimental data for Phenol and Triclocarban compounds, respectively. One can see that the performance of WS mixing rule is much better than vdW1 mixing rule. Therefore, the combination of the SRK and the PR EOSs with the WS mixing rule is more suitable for modeling the solubilities of these ten solids in supercritical CO_2.

Table 3. The results of PR and SRK EOSs in combination with the vdW1 and WS mixing rules

Compound	T(K)	P(bar)	ND	References	Mixing rule	Model parameters			AARD%
						A_{ji}	A_{ij}	k_{ij}	
1. Triclocarban	313.2	109.3-389.6	8	[2]	PR-vdW1	0.1955 - -			14.4
					SRK-vdW1	0.1966 - -			9.4
					PR-WS	0.7962	-0.5988	10.3180	3.4
					SRK-WS	0.8100	-13.9666	10.4969	3.4
	323.2	120-333.4	8	[2]	PR-vdW1	0.1944 - -			15.5
					SRK-vdW1	0.1982 - -			12.2
					PR-WS	0.7953	7.9441	10.4984	5.3
					SRK-WS	0.8111	-48.1986	10.2291	5.4
	333.2	137.5-305.8	8	[2]	PR-vdW1	0.2047 - -			11.4
					SRK-vdW1	0.2049 - -			9.3
					PR-WS	0.7987	-10.9396	10.4580	3.9
					SRK-WS	0.8147	-2.1419	10.1348	3.8
	313.2-333.2	109.3-389.6	24	[2]	PR-vdW1	0.1985 - -			16.4
					SRK-vdW1	0.1554 - -			10.5
					PR-	0.7977	-0.3676	10.0060	5.3
					WSSRK-WS	0.8105	-16.6153	10.3834	5.4
2. Hinokitiol	313.2	101.4-378.3	9	[19]	PR-vdW1	0.2328 - -			26
					SRK-vdW1	0.2355 - -			22.1
					PR-WS	0.7313	0.5115	11.5295	2.8
					SRK-WS	0.7567	1.4562	10.3387	2.9
	323.2	122.1-331.7	10	[19]	PR-vdW1	0.2291 - -			19.7
					SRK-vdW1	0.2329 - -			16.5
					PR-WS	0.7409	1.6999	10.5892	6.1
					SRK-WS	0.7606	0.7495	10.5702	5.6
	333.2	142.3-358.4	11	[19]	PR-vdW1	0.2457 - -			13.1
					SRK-vdW1	0.2487 - -			10.7
					PR-WS	0.7532	2.2150	10.3167	8.7
					SRK-WS	0.7680	0.5519	10.8610	7.9
	313.2-323.2	101.4-378.3	30	[19]	PR-vdW1	0.2405 - -			25
					SRK-vdW1	0.2410 - -			22.4
					PR-WS	0.7479	0.7783	10.6279	15.4
					SRK-WS	0.7682	1.9292	9.9060	13.2
3. Aspirin	308.15	120-250	8	[11]	PR-vdW1	0.2175 - -			3
					SRK-vdW1	0.2225 - -			4.2
					PR-WS	0.7676	0.7179	8.8559	1.2
					SRK-WS	0.7843	0.6111	8.6266	1.5
	318.15	120-250	8	[11]	PR-vdW1	0.2112 - -			7.5
					SRK-vdW1	0.2112 - -			9.2
					PR-WS	0.7769	1.2229	7.5078	2.4
					SRK-WS	0.7914	0.6020	7.3850	2.2
	328.15	120-250	8	[11]	PR-vdW1	0.209 - -			10
					SRK-vdW1	0.1785 - -			10.9
					PR-WS	0.7692	0.1453	7.9679	6.4
					SRK-WS	0.7836	0.2864	5.1352	6.1
	308-328	120-250	24	[11]	PR-vdW1	0.2131 - -			8.2
					SRK-vdW1	0.1804 - -			10.3
					PR-WS	0.7593	0.0285	10.2572	5.5
					SRK-WS	0.7703	0.0171	7.9728	4.9

4. Methimazole	308.15	122-355	8	[9]	PR-vdW1	0.3860 - -			15.8
					SRK-vdW1	0.3939 - -			18.4
					PR-WS	0.7636	0.3900	9.7963	7.5
					SRK-WS	0.7895	-0.0262	9.4004	7.2
	318.15	122-355	8	[9]	PR-vdW1	0.4247 - -			31
					SRK-vdW1	0.4322 - -			32.9
					PR-WS	0.8715	-0.0070	7.0825	7.8
					SRK-WS	0.8464	-0.0376	8.6183	8.4
	328.15	122-355	8	[9]	PR-vdW1	0.4754 - -			46.3
					SRK-vdW1	0.4841 - -			47.2
					PR-WS	0.8834	-0.0279	7.6304	7.4
					SRK-WS	0.9046	-0.0131	7.2419	7.2
	308-328	122-355	24	[9]	PR-vdW1	0.4297 - -			44.8
					SRK-vdW1	0.4225 - -			46.5
					PR-WS	0.8870	-0.0064	6.7516	13.5
					SRK-WS	0.8791	-0.0046	5.3369	14.8
5. Phenol	309.2	80-246	24	[13]	PR-vdW1	0.1132 - -			20.8
					SRK-vdW1	0.1147 - -			19.9
					PR-WS	0.4666	3.1288	4.365	5.5
					SRK-WS	0.5000	3.4982	4.1872	6.4
	318.15	80-198.4	15	[13]	PR-vdW1	0.0877 - -			40.9
					SRK-vdW1	0.0894 - -			40.5
					PR-WS	0.4773	2.1281	2.8590	4.3
					SRK-WS	0.5014	1.5996	3.0470	4.8
	333.15	112-350	21	[13]	PR-vdW1	0.1381305			34.8
					SRK-vdW1	- -			32.3
					PR-WS	0.135541 - -			8.4
					SRK-WS	0.4855	1.0221	4.5394	7.5
						0.5639	2.2661	2.9096	
	309-333	80-350	60	[13]	PR-vdW1	0.1381 - -			50.4
					SRK-vdW1	0.13564 - -			47.7
					PR-WS	0.4580	0.9290	5.1744	18.9
					SRK-WS	0.4970	0.8701	4.9394	20.4
6. Ascorbic acid	313.15	130-200	4	[10]	PR-vdW1	0.4692 - -			11.3
					SRK-vdW1	0.4707 - -			12.2
					PR-WS	0.8834	922.065	21.4489	2.72
					SRK-WS	0.8811	71.4240	21.9458	2.4
7. Ascorbyl palmitate	313.15	130-200	4	[10]	PR-vdW1	0.1873 - -			24.3
					SRK-vdW1	0.1842 - -			26.4
					PR-WS	0.9146	-1.0746	16.8344	2.5
					SRK-WS	0.9186	0.3142	14.8145	2.2
	313.15	150-250	4	[10]	PR-vdW1	0.2430 - -			5.4
					SRK-vdW1	0.2459 - -			4.1
					PR-WS	0.7546	-4.5518	11.9579	0.7
					SRK-WS	0.7594	-1.3870	9.9372	0.60
8. Propyl gallate	333.15	150-250	4	[10]	PR-vdW1	0.22787 - -			13
					SRK-vdW1	0.2291 - -			12.2
					PR-WS	0.6628	-16.7837	9.0533	4.8
					SRK-WS	0.7058	-4.4478	9.1827	4.7
	313-333	120-250	8	[10]	PR-vdW1	0.2414 - -			15.9
					SRK-vdW1	0.1960 - -			14.3
					PR-WS	0.7548	-0.8756	11.9585	1.4
					SRK-WS	0.7725	-4.1846	11.8902	1.6

9. Climbazole	313.2	105-398.9	8	[2]	PR-vdW1	0.1480 - -			10.5
					SRK-vdW1	0.1530 - -			7.2
					PR-WS	0.8137	2.0944	8.6670	5.3
					SRK-WS	0.8293	2.7648	7.9110	6.4
	323.2	128.4-365.5	8	[2]	PR-vdW1	0.1542 - -			5.8
					SRK-vdW1	0.1598 - -			4.2
					PR-WS	0.8206	86.0095	7.9460	3
					SRK-WS	0.8340	1.8375	7.8356	3.9
	333.2	146.1-357.2	8	[2]	PR-vdW1	0.1594 - -			5.7
					SRK-vdW1	0.1648 - -			3.9
					PR-WS	0.8196	1.0461	8.6648	1.5
					SRK-WS	0.8378	183.917	7.3174	2.5
	308-328	120-250	24	[2]	PR-vdW1	0.1556 - -			17.3
					SRK-vdW1	0.1597 - -			13.8
					PR-WS	0.8189	2.7510	8.2799	8.6
					SRK-WS	0.9984	8.1118	0.8331	8.6
10. Fluoran-thene	308.15	89-247	12	[12]	PR-vdW1	0.1200 - -			5.5
					SRK-vdW1	0.1275 - -			5.7
					PR-WS	0.7893	1.5690	7.2349	4.5
					SRK-WS	0.8048	0.5901	7.0887	5.4
	318.15	90-249	9	[12]	PR-vdW1	0.1148 - -			16.3
					SRK-vdW1	0.1202 - -			15.2
					PR-WS	0.7878	-0.0523	6.1854	8.5
					SRK-WS	0.7976	0.1119	8.1144	9.4
	328.15	121-209	5	[12]	PR-vdW1	0.1046 - -			8.5
					SRK-vdW1	0.1103 - -			7.9
					PR-WS	0.8006	-0.0208	3.3987	6.2
					SRK-WS	0.8074	0.3835	5.7097	6.1
	308-328	89-247	26	[12]	PR-vdW1	0.1153 - -			15.3
					SRK-vdW1	0.1233 - -			16.5
					PR-WS	0.7816	-0.0492	9.4473	9.8
					SRK-WS	0.7997	0.0669	8.3321	11.6
Total	308-333	80-398.9	273		PR-vdW1				18.5
					SRK-vdW1				17.5
					PR-WS				6.04
					SRK-WS				6.2

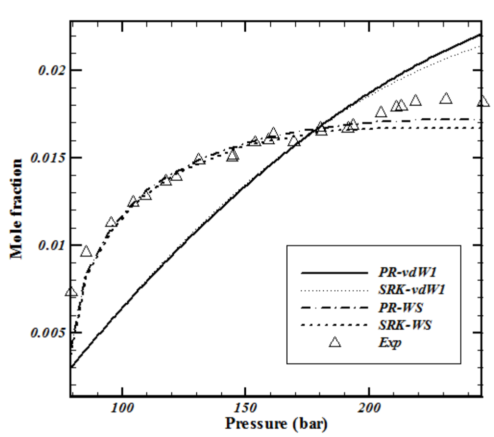

Figure 1. The experimental and calculated solubilities of Phenol in supercritical CO2 at T = 309 K.

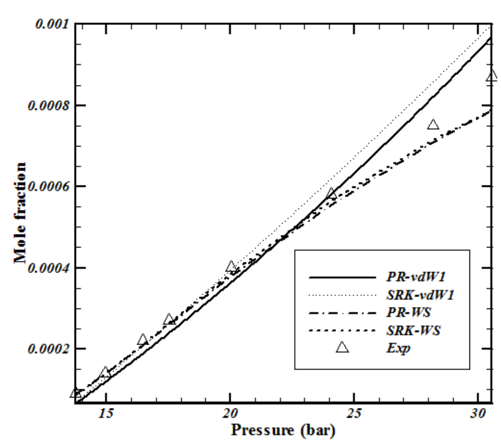

Figure 2. The experimental and calculated solubilities of Triclocarban in supercritical CO2 at T = 333 K.

Subsequently, to investigate the performance of the proposed EOSs (bRK and bPR EOSs) in combination with the simple mixing rule of vdW0, these proposed equations were applied to model the solubilities of these ten solids in supercritical CO_2. The results of Average Absolute Relative Deviations Percent (AARD%) and the model parameters were reported in Table 4. Figures 3–4 show the calculated solubility results by the sets of PR-vdW1, SRK-vdW1, βPR-vdW0 and βRK-vdW0 for Phenol and Triclocarban compounds, respectively.

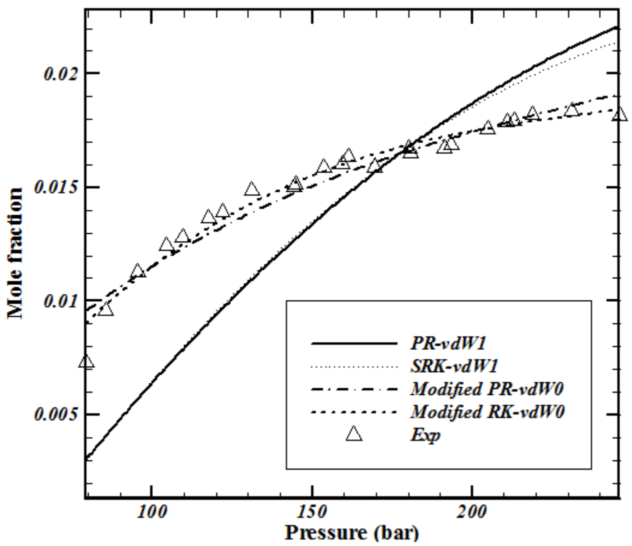

Figure 3. The experimental and calculated solubilities of Phenol in supercritical CO2 by usingthe proposed and other models at T = 309 K.

As it is shown in Table 4, the accuracy of the proposed models is much better than the combination of SRK and PR EOSs with vdW1 mixing rule, even better than combination of SRK and PR EOSs with WS mixing rule. The calculation results of the models demonstrated that the bRK and bPR EoSs are capable of modeling the solubilities of these ten solid in supercritical CO_2 without using the complicated mixing rule. Therefore, bRK and bPR EOSs in combination with the simple mixing rule (vdW0) are reliable methods for determining the phase equilibrium of (solid + supercritical CO_2) systems.

In order to investigate the validity of the proposed EOSs, these proposed models were compared with the models reported in literature. First, the results of the proposed models for seven compounds including Methimazole, Ascorbic acid, Ascorbyl palmitate, Propyl gallate, Aspirin, Fluoranthene and Phenol were compared with the results of Esmaeilzadeh-Roshanfekr (ER) equation of state in combination with vdW1, vdW2, CVD and WS mixing rules [4]. The results of AARD% are presented in Table 5. It can be concluded that the proposed models performed better than the results of Esmaeilzadeh-Roshanfekr (ER) equation of state in combination with vdW1, vdW2, CVD and WS mixing rules.

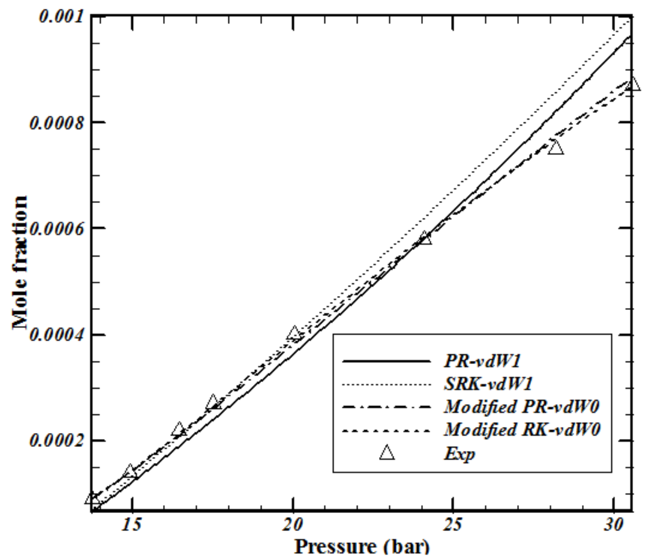

Figure 4. The experimental and calculated solubilities of Triclocarban in supercritical CO2 by using the proposed and other models at T = 333 K.

The results of the proposed models (βPR-vdW0 and βRK-vdW0) for three compounds including Propyl gallate, Methimazole and Aspirin were also compared with the results of regular solution model (One-parameter and Two-parameter) and Two commonly used semi-empirical equations (Chrastil and Mendes-Santiago and Teja equations) in Table 6. In comparison with the results of these models[16], the present models (βPR-vdW0 and βRK-vdW0) perform better than regular solution and semi-empirical models. It is found that the present model is reliable for solubility calculations of these ten solids in supercritical carbon dioxide.

Table 4. The results of βRK and βPR EOSs in combination with the vdW0 mixing rule

Compound	T	EOS	β Parameters						AARD
			β_{11}	β_{12}	β_{13}	β_{21}	β_{22}	β_{23}	%
1.Climbazole	313.2	βPR	0.7350	0.0873	-242.1818	1.8275	-262.984	-317.619	4.1
		βRK	1.9163	0.0173	-0.2018	1.1097	-0.1761	0.0528	3.8
	323.2	βPR	0.7273	0.0889	-241.6297	1.8256	-263.151	-316.231	3.4
		βRK	1.9286	0.0683	0.0781	1.1459	-0.2274	-0.1659	6.3
	333.2	βPR	0.7209	0.0861	-240.5956	1.8307	-265.094	-315.850	2.1
		βRK	1.9346	-0.0304	0.1238	0.9320	-0.0237	0.0394	3.8
	313-332	βPR	0.8163	-0.0648	1.9679	2.0093	-107.650	-105.529	4.2
		βRK	2.4308	-0.3998	1.8291	1.8338	-0.7165	0.1422	6.5
2. Triclocarban	313.2	βPR	0.6434	0.0879	-238.8405	1.8264	-244.556	-300.691	6
		βRK	1.7726	-0.0252	0.1345	1.0018	-0.0128	0.0246	3
	323.15	βPR	0.6288	0.9363	-270.0828	1.8894	-276.678	-318.834	5.3
		βRK	1.7313	-0.0416	0.1379	0.9887	-0.0221	0.0051	5
	333.2	βPR	0.6250	0.0883	-242.1100	1.8139	-244.594	-305.931	2.4
		βRK	1.6806	-0.0381	0.1698	1.0224	-0.0681	0.1210	1.4
	313-333	βPR	0.9737	-0.9935	-0.0171	0.9199	0.0983	-0.0359	5.2
		βRK	2.1172	-0.2876	2.1742	1.2678	-0.1049	0.5958	3.2
3. Hinokitiol	313.2	βPR	0.5077	0.0047	-0.0634	1.1040	-0.0263	-0.0506	9.7
		βRK	5.8754	0.0085	0.1955	1.0092	-0.0001	0.1436	7.1
	323.2	βPR	0.5074	0.0050	-0.0589	1.1146	-0.0246	-0.0520	10.4
		βRK	5.7148	0.0084	0.1991	0.9645	0.0001	0.1449	8.9
	333.2	βPR	0.4960	0.0050	-0.0622	1.1418	-0.0215	-0.0560	9.2
		βRK	5.4729	0.0085	0.1995	0.9306	0.00001	0.1447	8.4
	313-333	βPR	0.4978	0.0268	-0.1390	1.0189	0.0710	-0.0347	10.2
		βRK	9.4541	-3.8955	1.4585	1.8398	-0.8975	-0.0998	8.6
4. Phenol	309	βPR	-1.4785	18.9055	-6.9507	-0.0612	-0.8335	1.7649	3.6
		βRK	0.2044	10.4581	-6.9687	0.0664	-1.8403	2.9699	2.5
	318	βPR	-0.1683	31.5896	-30.322	2.8984	3.5702	2.8389	5.8
		βRK	-2.1186	24.0466	-4.1138	-0.0747	-0.7489	1.6805	4.2
	333	βPR	-1.4112	14.1039	-3.7537	0.1355	-1.0597	2.0398	4.6
		βRK	-1.5583	29.5005	-5.9344	0.1122	-1.1123	2.1733	4.6
	309-332	βPR	-1.4927	11.1705	-2.7640	0.0068	-1.1191	2.0832	8.5
		βRK	-1.9397	27.6133	-5.4517	-0.4014	-0.9976	1.6901	6.7
5. Aspirin	308	βPR	0.618531	0.08827	-245.0303	1.81659	-248.532	-299.354	1.6
		βRK	-4.35446	40.2392	-13.01034	-0.8435	1.48448	13.9888	2.6
	318	βPR	0.635285	0.08194	-2340.259	1.75290	-207.677	-266.2329	0.8
		βRK	-4.3678	40.2387	-13.0235	-0.8172	1.4573	13.9802	1.5
	328	βPR	0.6262	0.0868	-240.595	1.8164	-246.885	-298.6693	5
		βRK	1.7211	0.0796	-246.115	1.5764	-192.281	-286.8362	5.7
	308-328	βPR	0.6185	0.0972	-233.484	1.8064	-244.310	-299.3311	7.2
		βRK	1.7507	-0.1433	-49.3746	150.173	-20107.7	-133.7767	4.1
6. Propyl gallate	313	βPR	0.2784	1.1966	-1.5487	0.8079	2.5087	12.0657	0.3

		βRK	0.6553	2.3662	0.6351	1.0716	0.6614	9.6333	0.2
	333	βPR	0.5533	0.0181	-0.9059	-0.1212	0.6567	0.3551	0.4
		βRK	1.7131	0.0003	-0.5841	-0.1856	1.3017	-0.2183	0.5
	313-333	βPR	0.2765	1.1767	-1.5840	0.8207	-2.5452	11.7604	1.6
		βRK	1.8596	-0.0077	2.5455	0.5651	1.0845	-1.7338	3
7. Ascorbic acid	313	βPR	0.0273	0.6957	-0.0183	0.9293	0.0408	7.3613	0.2
		βRK	1.2983	-0.1050	0.2411	0.7850	0.0818	0.2421	0.3
8. Ascorbyl palmitate	313	βPR	0.6362	0.1252	0.0159	0.0541	0.6389	0.2690	2.4
		βRK	3.0641	0.0967	-0.0003	0.0759	0.3248	0.5933	3.6
9. Fluoranthene	308	βPR	0.7531	-0.2079	13.4416	0.0454	0.8413	0.1114	2.7
		βRK	1.8580	0.1555	23.1246	0.0236	0.8478	0.1138	3.8
	318	βPR	0.7520	-0.2309	12.9059	0.0461	0.8122	0.1150	6.2
		βRK	1.8349	0.1986	53.2446	0.0523	0.9105	-0.0339	7
	328	βPR	0.7581	-0.4640	13.4484	0.0437	0.7692	0.1218	4.9
		βRK	2.1011	-5.6143	-21.6413	0.0182	0.7329	0.1266	5.4
		βPR							7.8
		βRK	0.7730	-0.7447	271.027	0.1922	4.0050	-3.9408	7.5
	308-328	βPR	1.23861	-857.1282	1091.387	2.68619	-3.0389	-0.80599	7.1
		BRK	0.3650	-0.2300	15.9464	0.0520	0.7318	0.1200	7
10. Methimazole	308	βPR	1.0310	0.6322	5.3944	-0.2978	-0.1661	1.1303	7.2
		βRK	0.3953	-0.1483	15.5585	0.0717	0.5063	0.1223	7.1
	318	βPR	1.8763	1.6651	4.0485	-0.4001	-0.1913	1.1471	14.7
		βRK	0.7011	-0.3496	5.7744	0.1878	0.0485	0.3671	15.4
	328	βPR	-0.0384	3.1011	0.1546	0.3739	0.0789	2.4486	10.1
		βRK	0.2931	0.9407	1.8051	-0.2052	-0.1070	1.0843	10.7
	308-328		1.6653	0.4349	2.9157	-0.2063	-0.1236	1.1138	
		βPR							5.3
Total		BRK							5.1

Table 5. The comparison of different models4 with the present model

Model	βPR	βRK	ER-WS	PR-WS	ER-CVD	PR-CVD	ER-vdW2	PR-vdW2	ER-vdW1
AARD%	4.318	4.6	10.36	15.34	28.6	31.6	12.58	16.06	19.1

Table 6. The comparison of different models16 with the present model

Compound	AARD%					
	Regular Solution Models		Semi-Empirical Models		Present Model	
	One-Parameter	Two-Parameter	Chrastil	Mendez-Santiago and Teja	βRK	βPR
Propyl gallate	21.6	6.6	3.4	4.8	3.0211	1.59
Methimazole	21.1	12	12.7	10.7	10.7	10.1
Aspirin	19.1	10.7	5.2	4.7	4.15	7.27

4. Conclusions

In this investigation, the modified RK (bRK) and the modified PR (bPR) equations of state in combination with the vdW0 mixing rule were used to determine the solubilities of ten solid compounds in supercritical CO_2. The optimized parameters of the proposed models were determined and reported. Subsequently, the results of these models were compared with the SRK and PR EOSs in combination with VdW1 and WS mixing rules and the other applied models in the literature. It is demonstrated that the relative error (AARD%) between experimental data and the calculated results by the proposed model is less than 5.1% indicating that the proposed models in this work has higher precision than the models in the literature.

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