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Research Article

A Simplified Cubic Equation of State Approach to Model the Solubility of Solids in Supercritical Carbon Dioxide

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Abstract: The modelling of the solubility of a solute in a supercritical solvent system using the cubic equation of state (cEoS) requires the critical properties (Critical temperature (Tc) & Critical pressure (Pc)), vapour pressure, acentric factor, and molar volume of the solute and the solvent. Generally, experimental critical properties of solvents are readily available, but, the critical properties of solutes are barely available. However, group contribution methods can be used to overcome this limitation. Often, there is a lack of availability of group contribution methods for several typical solutes, which hinders the use of cEOS modelling. Thus, this study focuses on the development of new correlations for solid solute's solubility in supercritical fluids using the equation of state in its limiting form, $y_2 = \frac{p_2^s}{P\hat{\phi}_2^\infty}\exp\left[\frac{\left(P-p_2^s\right)g\left(\rho_1\right)}{RT}\right]$, where y_2 is the mole fraction of solubility of the solute in the $scCO_2$, P is pressure, and T is temperature; molar volume (v_2) is expressed as a function of solvent density as $g(\rho_1) = \exp(\beta_1 \times \ln(\rho_1) + \beta_2)$, where β_1 and β_2 are the model constants and $\hat{\phi}_2^\infty$ is the solute's fugacity at infinite dilution which is a function of the solute's equation of state parameters a_2 and b_2. The proposed approach was evaluated with the solubility of parabens (Methylparaben, Ethylparaben, and Propylparaben), Aspirin, Griseofulvin, Ibuprofen, and Salicylic acid in supercritical carbon dioxide ($scCO_2$). Further, the accuracy of the proposed cEoS approach was compared with existing EoS model correlations. Finally, the proposed approach was observed to give satisfactory results in terms of the relative deviation and Akaike's information criteria.

***Keywords*:** cubic equation of state (cEoS), simple model, solubility, $scCO_2$

Symbols

a	[J m^3 mol^{-1}]	Pure component property in PR EoS
$a(T)$	[J m^3 mol^{-1}]	PR EoS Energy parameter
b	[m^3]	PR EoS volume correction parameter
k_{ij}	[-]	Binary interaction parameter in EoS

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l_{ij}	[-]	Binary interaction parameter in PR EoS
N_i	[-]	Number of data points
P	[MPa]	Pressure
Q	[-]	Number of data points
R	[J/mol K]	Universal gas constant
T	[K]	Temperature
v	[m^3/mol]	Molar volume in PR EoS
v_2	[m^3/mol]	Molar volume of the solute
y_2	[-]	Mole fraction paraben compound

Greek letters

ρ	[kg m^{-3}]	Density
α	[-]	PR EoS parameter
β_1	[-]	v_2 expression parameter
β_2	[-]	v_2 expression parameter
ω	[-]	Acentric factor
$\hat{\phi}$	[-]	Fugacity coefficient of component in mixture

Superscript and subscript

1	Solvent
2	Solute
cal	Calculated mole fraction
exp	Experimental mole fraction
S	Pure solid
SCF	Supercritical Fluid

Abbreviations

AARD	Average Absolute relative deviation
AIC	Akaike's information criterion
AICc	Corrected Akaike's information criterion
EOS	Equation of state
PR	Peng-Robinson
R^2	Square of correlation coefficient
$scCO_2$	Supercritical carbon dioxide
SSE	Sum of squares due to error

1. Introduction

Supercritical fluid technologies (SFT) are finding use in petrochemicals, chromatography, biotechnology, pharmaceuticals, dyeing, and several industries [1]-[4]. Usually, in all these applications, targeted solute compounds are extracted or dissolved using a supercritical fluid (SCF). Substances include colourants and pigments, nutraceuticals, active pharmaceutical ingredients, and food additives. These solutes are frequently solid at room temperature as a result of their high molar masses. Furthermore, they only dissolve in the SCF. In principle, any substance can be used in its supercritical form, but carbon dioxide and water are the most frequently utilised supercritical fluids [1]-[4] due to their chemical and physical properties.

In recent years, the use of supercritical carbon dioxide ($scCO_2$) in the dyeing, food processing, and pharmaceutical

industries has grown in importance. Supercritical fluid technology, especially via a green solvent such as supercritical carbon dioxide ($scCO_2$) has many applications in various topics [5]-[8]. The solubility data determines the utility of $scCO_2$, and it can also act as a substitute for organic solvents that are usually used in regular unit operations [9]-[12]. As $scCO_2$ has distinctive qualities, including non-toxicity, non-flammability, and adjustable density, it can be a substitute for many solvents. It has a moderate critical pressure of 7.39 MPa and a critical temperature of 304.12 K. A precise understanding of the compound's solubility is required for the effective implementation of $scCO_2$-based technology in industry. However, acquiring solubility data under the necessary pressure and temperature circumstances is a difficult process. Thus, modelling is important for solubility data interpolation [13], [14].

In recent years, a variety of methods have been used to model solubility data. These methods can be grouped broadly into five categories, of which the three most user-friendly are equation of state (EoS) models, density models, and mathematical models. The first model needs the compounds' physical characteristics, such as vapour pressure, molar volume, critical properties, and acentric factor. The equation of state modelling would be quite beneficial if it had all the required physical characteristics [13]-[15]. Unfortunately, many compounds lack the necessary property data. On the other hand, the remaining methods that do not require these data have drawn more interest and succeeded. Density and mathematical models are quite effective at modelling solubility because of their ease of use [14]-[16]. The main feature of these models is that solubility is treated as a function of temperature, solvent density, and pressure. Since there won't be a single model that accounts for all compounds, research is always being done, and many new models are being developed [14]. The cEoS method has a more sound theoretical basis than the density and mathematical models. Thus, there is a need to address EoS models appropriately. Solubility is highly nonlinear, which poses challenges in developing solubility models.

The work is presented in two stages. In the first stage, the strategy for the model development is done, and in the second stage, the proposed cEoS strategy is validated with the help of literature-reported solubility data of parabens (Methylparaben, Ethylparaben, and Propylparaben), Aspirin, Griseofulvin, Ibuprofen, and Salicylic acid in $scCO_2$.

2. Modelling

Although there are many cEoS models in the literature, the Peng-Robinson equation of state (PR EoS) is frequently used to correlate the solubilities of solids in $scCO_2$ due to its better correlating ability [17], [18]. Thus, PR EoS [19] is used for model development.

2.1 *Thermodynamic modelling*

The solubility of a solute in a solvent is denoted as [17]-[19]:

$$y_2 = \frac{p_2^S \hat{\phi}_2^S}{P\hat{\phi}_2^{SCF}} \exp\left[\frac{\left(P - p_2^S\right)V_S}{RT}\right] \tag{1}$$

where all parameters have their usual meaning. The pure solid solute saturation fugacity coefficient is assumed to be unity. The fugacity of the solute $\hat{\phi}_2^{SCF}$ in the supercritical phase is calculated using the cubic equation and the mixing rules. $\hat{\phi}_2^{SCF}$ is obtained using pressure explicit form of EoS by eq. (18).

$$\ln(\hat{\phi}_2^{SCF}) = \frac{1}{RT}\int_v^\infty \left[\left(\frac{\partial P}{\partial n_2}\right)_{T,v,N_1} - \frac{RT}{v}\right] dv - \ln\left(Z\right) \tag{2}$$

2.2 *PR EoS [19]*

The pressure explicit form is

$$P = \frac{RT}{v-b} - \frac{a\,(T)}{v\,(v+b)+b\,(v-b)} \tag{3}$$

where

$$a\,(T) = 0.45724\frac{RT_c^2}{P_c}\alpha\left(T_r,\,\omega\right) \tag{4}$$

$$\alpha\left(T_r,\,\omega\right) = \left[1+(0.37464+1.5422\omega-0.26992\omega^2\left(1-\sqrt{T_r}\right)\right]^2 \tag{5}$$

$$b = 0.0778\frac{R\,T_c}{P_c} \tag{6}$$

Mixing rules Type 1 by van der Waals,

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{7}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{8}$$

$$a_{ij} = \left(1-k_{ij}\right)\sqrt{a_{ii}a_{jj}} \tag{9}$$

$$b_{ij} = \frac{\left(b_{ii}+b_{jj}\right)}{2} \tag{10}$$

Mixing rules Type 2 by van der Waals,

$$a_{ij} = \left(1-k_{ij}\right)\sqrt{a_{ii}a_{jj}} \tag{11}$$

$$b_{ij} = \left(1-l_{ij}\right)\frac{\left(b_{ii}+b_{jj}\right)}{2} \tag{12}$$

The expression for the fugacity coefficient is

$$\ln\left(\hat{\phi}_2^{SCF}\right) = \frac{\hat{b}}{b}(Z-1) - \ln\left[Z\left(1-\frac{b}{v}\right)\right] + \frac{a}{\left(2\sqrt{2}\right)bRT}\left[\frac{\hat{a}}{a}-\frac{\hat{b}}{b}\right]\ln\left(\frac{Z-0.414b}{Z+2.414b}\right) \tag{13}$$

where $\hat{a} = \frac{1}{n}\frac{\partial n^2 a}{\partial n_i} = 2\sum x_i a_{ij}$; $\hat{b} = \frac{\partial nb}{\partial n_i} = 2\sum x_i b_{ij} - b$

Combining equations (1) to (13), we get the solubility expression as a function of

$$a_1, b_1, a_2, b_2, T, P, p_2^s, \hat{\phi}_2^{SCF}, k_{12}, l_{12}$$

Thus,

$$y_2 = f\left(a_1, b_1, a_2, b_2, T, P, p_2^s, \hat{\phi}_2^{SCF}, k_{12}, l_{12}\right) \tag{14}$$

If all the physical properties of the solute and the solvent are available, the left-out adjustable parameters would be k_{12}, l_{12}, depending on the mixing rules.

To implement the above method, the critical properties (Tc & Pc), vapour pressure, acentric factor, and molar volume of the solute and solvent are required. Quite often, it is difficult to get the solute properties. Thus, a new approach is proposed in the following section that does not require the critical properties of the solute (i.e., Tc, Pc, vapour pressure, acentric factor, and molar volume), but the critical properties of the solvent are necessary. Mode details are presented in the following section.

3. Simplified cubic equation of state approach

The basic equations relevant to the solubility model mentioned in the previous section are applicable. In the proposed approach, the following assumptions are applied to the modelling.

Assumption 1: The solute's solubility in the solvent is not high; therefore the solute is infinitely diluted. This results in the following expression for the Fugacity coefficient, in which solute parameters are treated as adjustable parameters [20], [21]. Thus, the following expression is obtained.

$$\ln\left(\hat{\phi}_2^{scCO_2}\right) \approx b_2/b_1\left(Z_1 - 1\right) - \ln\left(P\left(V_1 - b_1\right)/RT\right) - a_1/\left(2\sqrt{2}\,RTb_1\right)\left\{\left[2(a_2)/a_1\right] - b_2/b_1\right\}\ln\left[\frac{V_1 + 2.414b_1}{V_1 - 0.414b_1}\right] \tag{15}$$

Assumption 2: Solute molar volume (v_2) is a function of $scCO_2$ (solvent) density (ρ_1) [22]. The following expression is used:

$$v_2 = g(\rho_1) = \exp\left(\beta_1 \ln(\rho_1) + \beta_2\right) \tag{16}$$

Applying assumptions 1 and 2 results in the solubility expression as a function of

$$y_2 = f\left(a_1, b_1, a_2, b_2, \rho_1, \beta_1, \beta_2, T, P, p_2^s\right) \tag{17}$$

If p_2^s pdata is available, then the adjustable constants are a_2, b_2, β_1, β_2.

It is important to note that the present study is exemplified only with PR EoS and vdW mixing rules, but the same idea can be extended to any EoS along with mixing rules. This study is important when the molar volume, critical properties, and acentric factor of the solute are unavailable. In case of the non-availability of the solute's sublimation pressure, an appropriate temperature function can be used [15] in place of sublimation pressure but it has not been

addressed in this work.

4. Results and discussion

The proposed strategy for the correlating solubility of solids in supercritical fluids is tested with a solubility of parabens (Methylparaben, Ethylparaben, and Propylparaben), aspirin, griseofulvin, ibuprofen, and salicylic acid in supercritical carbon dioxide ($scCO_2$). [12], [23]-[26]. Parabens are the derivatives of para-hydroxybenzioc acid (PBHA), and they have been widely used in the personal care, cosmetics, drug, and food industries as preservatives for almost a century. Thus, validating the proposed model with them is useful. In literature, the solubilities of Methylparaben (at 308, 318, 328, and 338 K), Ethylparaben (at 308, 318, and 328 K), Propylparaben (at 308, 318, and 328 K), Aspirin (at 308.15, 318.15, and 328.15 K), Griseofulvin (at 313.15 and 333.15 K), Ibuprofen (at 308.15, 313.15, and 318.15 K), and Salicylic acid (at 313.15 and 333.15 K) are available. The data ranges of compounds considered in this work and other properties [12], [23]-[28] obtained from literature are reported in Tables 1, 2, and 3. For the case of aspirin, griseofulvin, ibuprofen, and salicylic acid compounds, the required saturation pressures are obtained from their critical properties data using the lee-Kessler expression [29]. Table 4 shows the simplified cubic equation of state approach results and Tables 5 and 6 show PR EoS model (Single and two binary interaction parameters) results.

Table 1. Summary of compounds solubility data in $scCO_2$ considered in the study [8], [22].

System	Formula	Temperature range (K)	Pressure range (MPa)	Mole fraction range
Methylparaben-$scCO_2$	$C_8H_8O_3$	308-348	12.2-35.5	0.000113-0.001213
Ethylparaben-$scCO_2$	$C_9H_{10}O_3$	308-328	8.0-21	0.0000164-0.0001755
Propylparaben-$scCO_2$	$C_{10}H_{12}O_3$	308.15-328.15	9.41-22.02	0.000044-0.000612
Aspirin-$scCO_2$	$C_9H_8O_4$	308.15-328.15	12.0-25.0	0.000063-0.000347
Griseofulvin-$scCO_2$	$C_{17}H_{17}ClO_6$	313.15-333.15	12.0-33.0	0.0000090232-0.00028045
Ibuprofen-$scCO_2$	$C_{13}H_{18}O_2$	308.15-318.15	8.0-22.0	0.000018492-0.0074932
Salicylic acid-$scCO_2$	$C_7H_6O_3$	313.15-333.15	10.0-35.0	0.000082994-0.00070923

Table 2. Paraben sublimation pressures [23], [24]

Compound	Sublimation pressure of Paraben (Where P^*/Pa and T/K)
Methylparaben	$\ln(P^*) = (34.3 \pm 0.3) - (11{,}889 \pm 92)/T$
Ethylparaben	$\ln(P^*) = (34.7 \pm 0.2) - (12{,}132 \pm 80)/T$
Propylparaben	$\ln(P^*) = (42.6 \pm 0.2) - (14{,}883 \pm 77)/T$

Table 3. Summary of Critical Properties, Acentric Factor, and Molar Volume considered in the study [12], [26]

Compound name	Tc/K	Pc/MPa	ω	$V_s/m^3 \cdot mol^{-1}$
Methylparaben	776.93	3.93307	0.660718	1.1295×10^{-4}
Ethylparaben	820.05	3.64208	0.54280	1.278×10^{-4}
Propylparaben	787.73	3.35372	0.711154	1.4283×10^{-4}
Aspirin	763.54	3.312	0.82202	1.2855×10^{-4}
Griseofulvin	1,082.74	1.848	1.2110	2.2386×10^{-4}
Ibuprofen	749.52	2.315	0.820	1.8214×10^{-4}
Salicylic acid	861.17	5.087	0.7844	0.9575×10^{-4}

Table 4. New PR EoS correlation results (Present study)

System	New PR EoS correlation (present study) a_2; b_2, β_1; β_2	R^2	AARD (%)
Methylparaben-$scCO_2$	7.9839; 1.9257×10^{-4}; 0.79703; -12.758	0.947	20.63
Ethylparaben-$scCO_2$	32.133; 4.5476×10^{-4}; 1.0011; -13.863	0.910	33.48
Propylparaben-$scCO_2$	40.685; 5.2235×10^{-4}; 1.4423; -16.659	0.978	18.11
Aspirin-$scCO_2$	9.2623; 2.3429×10^{-4}; 2.4101; -23.786	0.897	11.031
Griseofulvin-$scCO_2$	11.890; 1.7056×10^{-4}; -0.38578; -4.0819	0.811	39.475
Ibuprofen-$scCO_2$	11.878; 2.5626×10^{-4}; 1.5202; -17.301	0.834	19.468
Salicylic acid-$scCO_2$	50.259; 6.2300×10^{-4}; 2.4127; -23.724	0.751	16.926

Table 5. PR EoS correlation results with single interaction parameter

System	Correlation constant k_{ij}	R^2	AARD (%)
Methylparaben-$scCO_2$	0.067500	0.882	23.117
Ethylparaben-$scCO_2$	0.098402	0.898	35.375
Propylparaben-$scCO_2$	0.056916	0.985	13.601
Aspirin-$scCO_2$	0.20845	0.979	6.975
Griseofulvin-$scCO_2$	-0.29534	0.873	48.60
Ibuprofen-$scCO_2$	0.0838	0.931	16.841
Salicylic acid-$scCO_2$	0.0064606	0.465	41.312

Table 6. PR EoS correlation results with two interaction parameters

System	PR EoS Correlation constants k_{ij}; l_{ij}	R^2	AARD (%)
Methylparaben-$scCO_2$	-0.023926; -0.22141	0.923	16.955
Ethylparaben-$scCO_2$	-0.10283; -0.51347	0.965	18.526
Propylparaben-$scCO_2$	0.063332; 0.016814	0.987	13.340
Aspirin-$scCO_2$	0.21722; 0.021462	0.982	6.811
Griseofulvin-$scCO_2$	-0.61094; -0.64618	0.906	24.343
Ibuprofen-$scCO_2$	0.096687; 0.027346	0.932	16.418
Salicylic acid-$scCO_2$	-0.092425; -0.20036	0.538	27.532

For data correlation, the following objective function, eq. (18), is used [30].

$$OF = \sum_{i=1}^{N} \frac{\left| y_{2i}^{\exp} - y_{2i}^{cal} \right|}{y_{2i}^{\exp}} \tag{18}$$

where N is the number of solubility data points. With the help of MATLAB's (fminsearch) built-in functions, the correlation exercise with and without the solute's critical properties has been carried out, and the results are reported in Tables 4, 5, and 6. Figures (1) to (7) indicate the correlating ability of the proposed cEoS approach for the compounds considered in the study.

The accuracy of the simplified cubic equation of state approach model correlations is compared with the existing PR EoS model correlations, which are based on the critical properties of the solute. Tables 4, 5, and 6 show present study correlations and PR EoS model correlations respectively along with the coefficient of determination (R^2) values and absolute average relative deviation percentage (AARD%). Figures (4), (5), (6), and (7) clearly indicate the relative performance of the present study and the existing model correlation. Further, the relative performance of the two approaches with and without critical properties of the solute is quantified with Akaike's information criteria (AIC) and corrected AIC (AICc) [31]-[34].

AIC and AICc [8], [9] are related as follows

$$AICc = AIC + \frac{2Q(Q+1)}{N-Q-1} \tag{19}$$

Where

$$AIC = N \ln(\sigma^2) + 2Q \tag{20}$$

In eqs. (19) and (20), σ, N, and Q represent the variance of deviations, number of data points, and model parameters, respectively. The calculated AIC and AICc values are shown in Table 7. The best model will have the least AIC and AICc values. From Table 7, the present study is observed to provide satisfactory correlations for the Methylparaben, Propylparaben, and Aspirin compounds compared to other compounds. AICc values are the least for the

proposed study for those compounds; hence, the new approach is acceptable.

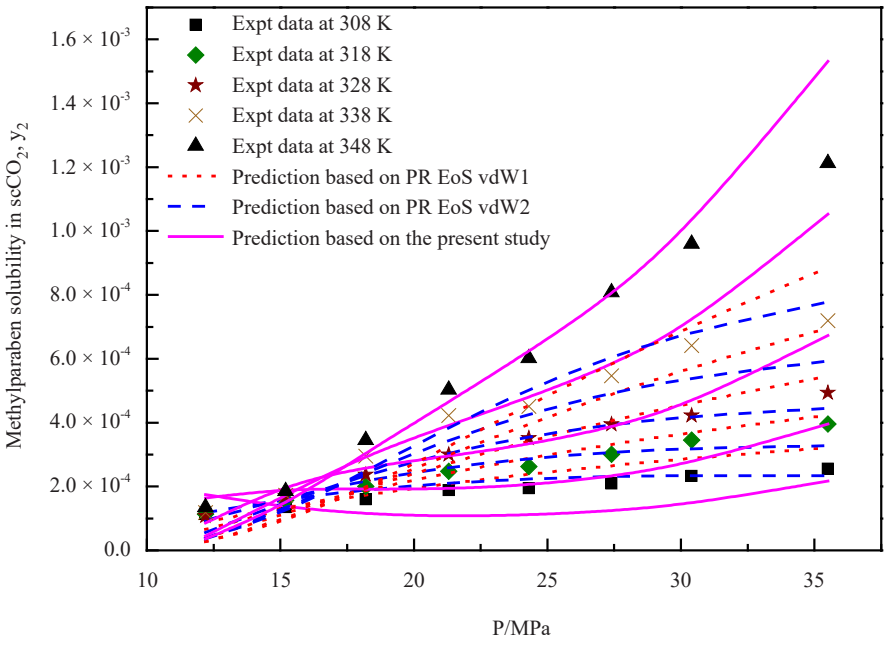

Figure 1. Methylparaben solubility in $scCO_2$ vs. P

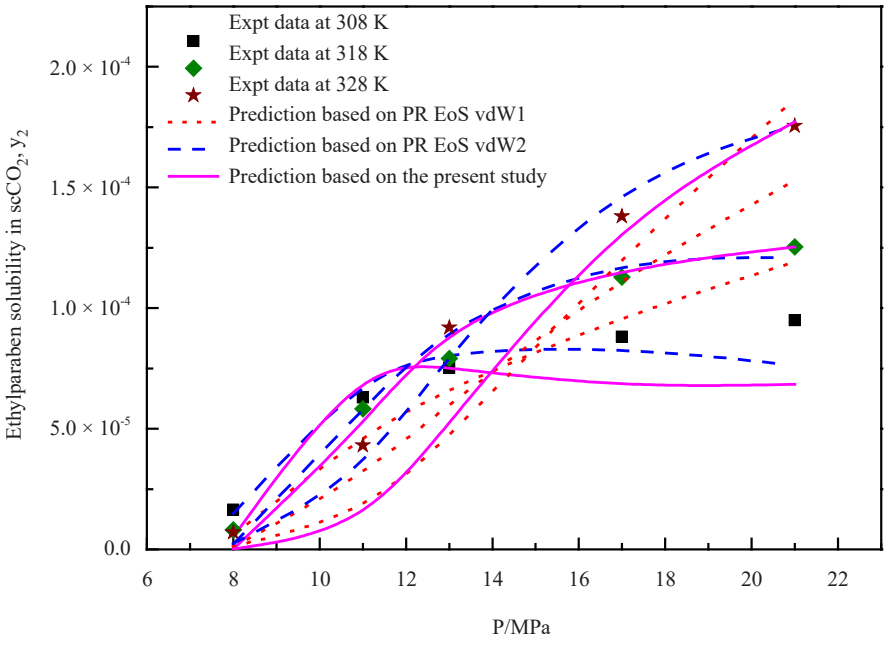

Figure 2. Ethylparaben solubility in $scCO_2$ vs. P

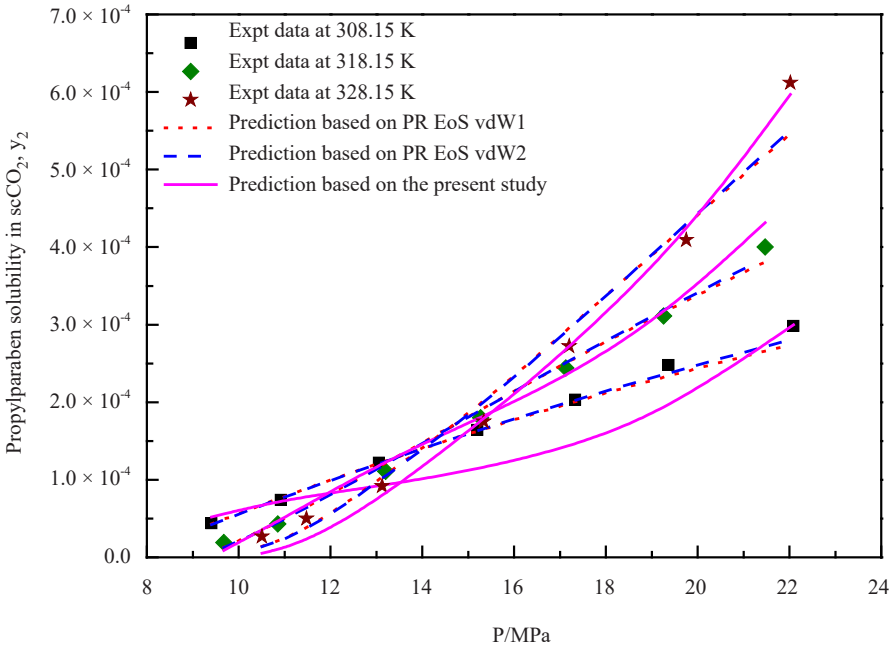

Figure 3. Propylparaben solubility in $scCO_2$ vs. *P*

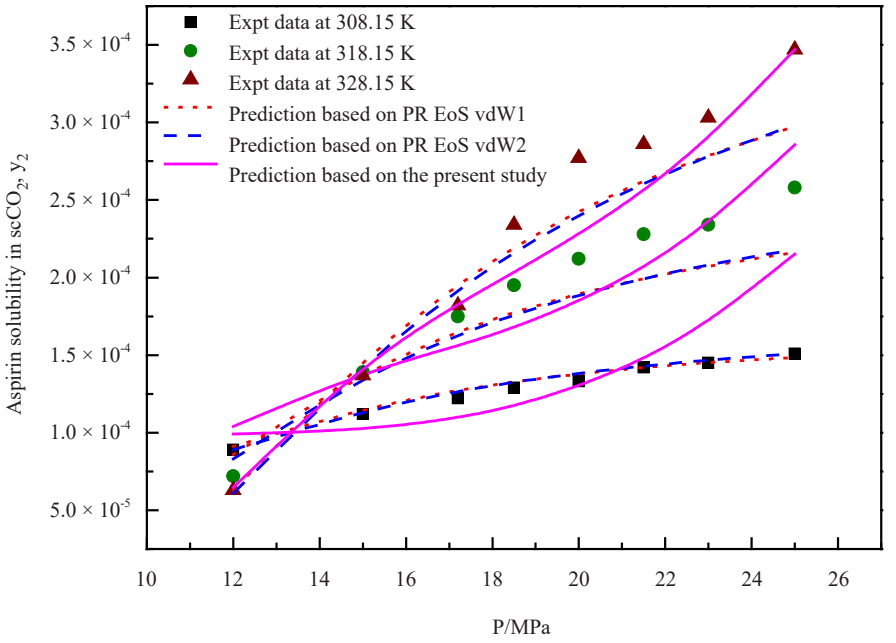

Figure 4. Aspirin solubility in $scCO_2$ vs. P

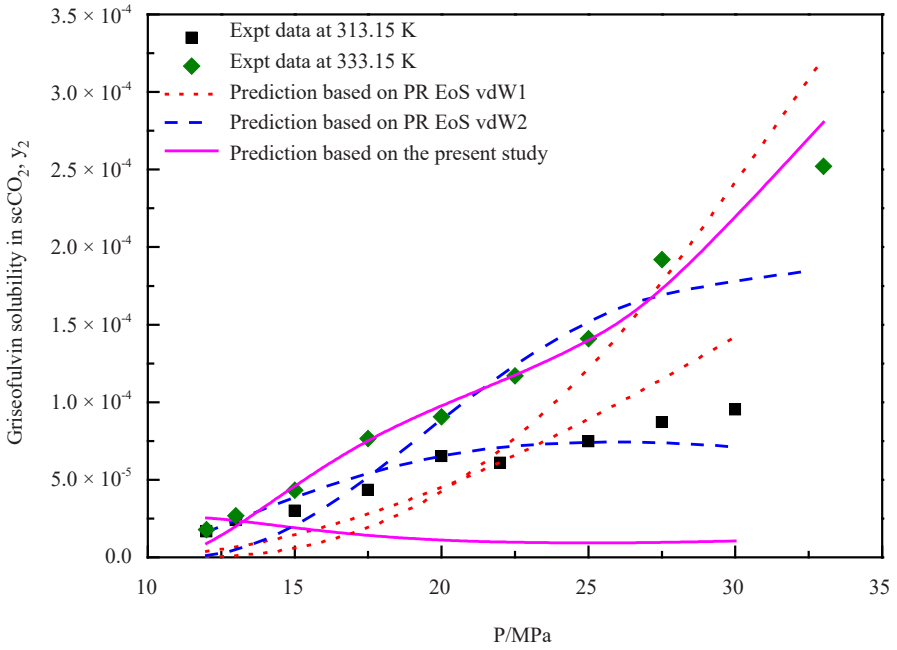

Figure 5. Griseofulvin solubility in $scCO_2$ vs. P

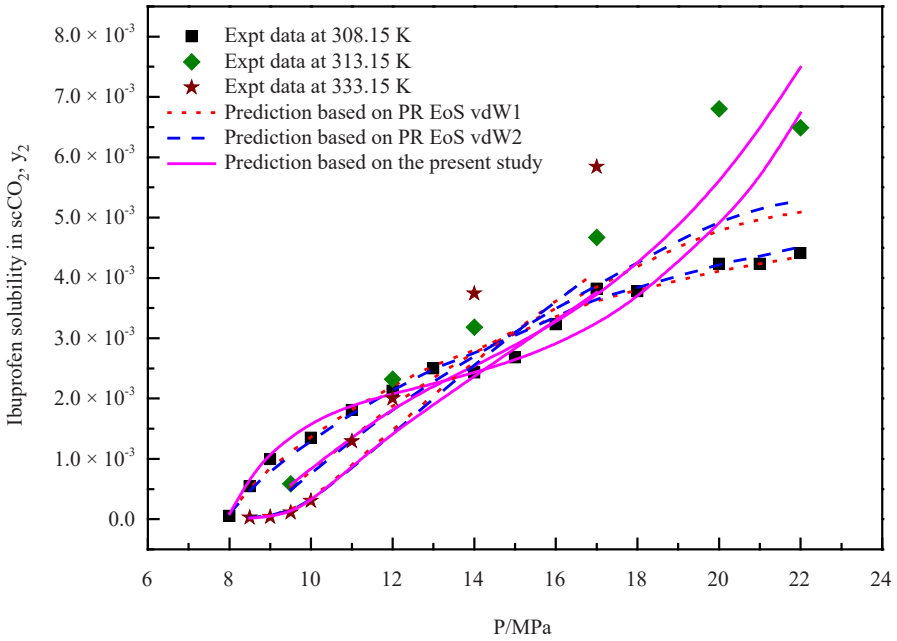

Figure 6. Ibuprofen solubility in $scCO_2$ vs. P

Table 7. Summary of SSE, AIC, and AICc of the systems

Model system	Number of parameters	Number of data points	SSE	AIC	AICc
	New PR EoS correlation (present study)				
Methylparaben-$scCO_2$	4	40	3.374×10^{-7}	-735.63	-734.49
Ethylparaben-$scCO_2$	4	15	4.692×10^{-9}	-320.28	-316.28
Propylparaben-$scCO_2$	4	21	1.378×10^{-8}	-436.03	-433.53
Aspirin-$scCO_2$	4	24	1.4014×10^{-8}	-502.27	-500.16
Griseofulvin-$scCO_2$	4	18	2.574×10^{-8}	-358.58	-355.50
Ibuprofen-$scCO_2$	4	29	1.978×10^{-5}	-403.74	-402.07
Salicylic acid-$scCO_2$	4	23	2.488×10^{-7}	-413.86	-411.64
	PR EoS with vdW1				
Methylparaben-scCO2	1	40	4.02×10^{-7}	-734.60	-734.49
Ethylparaben-scCO2	1	15	6.342×10^{-9}	-321.76	-321.45
Propylparaben-scCO2	1	21	7.847×10^{-9}	-453.86	-453.65
Aspirin-$scCO_2$	1	24	9.656×10^{-9}	-517.21	-517.03
Griseofulvin-$scCO_2$	1	18	2.031×10^{-8}	-368.84	-368.58
Ibuprofen-$scCO_2$	1	29	1.169×10^{-5}	-424.98	-424.83
Salicylic acid-$scCO_2$	1	23	9.055×10^{-7}	-390.15	-389.96
	PR EoS with vdW2				
Methylparaben-scCO2	2	40	4.14×10^{-7}	-731.48	-731.16
Ethylparaben-scCO2	2	15	1.411×10^{-9}	-342.30	-341.30
Propylparaben-scCO2	2	21	6.594×10^{-9}	-455.51	-454.85
Aspirin-$scCO_2$	2	24	9.668×10^{-9}	-515.18	-514.61
Griseofulvin-$scCO_2$	2	18	8.127×10^{-9}	-383.33	-382.53
Ibuprofen-$scCO_2$	2	29	1.089×10^{-5}	-425.05	-424.58
Salicylic acid-$scCO_2$	2	23	6.133×10^{-7}	-397.11	-396.51

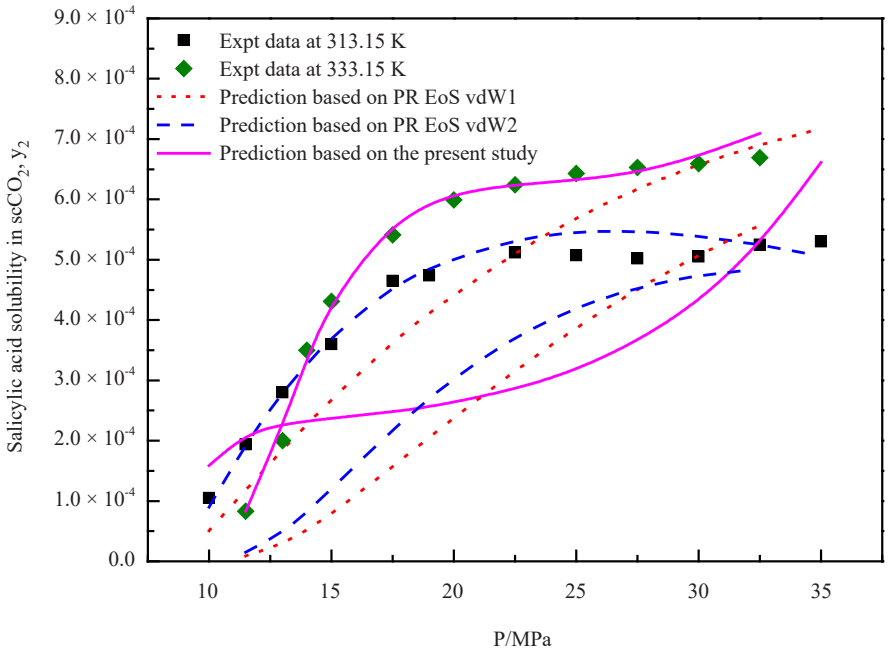

Figure 7. Salicylic acid solubility in $scCO_2$ vs. P

5. Conclusions

Correlating the solubilities of solid solutes in supercritical solvents is essential for the effective deployment of supercritical fluid technology. This study successfully deals with the solubility modelling of solids in $scCO_2$ without the solute's properties. The model results clearly show that, in the case of Methylparaben, Propylparaben, and Aspirin, the present study is performing on par with the existing PR EoS models (with two binary interaction parameters). AARD, AIC, and AICc analyses also indicate that the suggested new approach is yielding acceptable correlation results. Finally, the suggested simplified approach can be extended to any solute-supercritical fluid solvent system with appropriate EoS and mixing rules.

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Conflict of interest

The authors declare no competing financial interest.

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