A modified cubic equation of state model and parameter optimization in modeling supercritical fluid solubility

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Abstract: Cubic equation of state (EOS) is one of most attracting models in modeling solute solubility in supercritical fluid. The traditional implementation in EOS models requires critical parameters and acentric factor of the solute, however, estimating these physical parameters is not a trivia. As a modification of the traditional EOS method, in this paper, we do not estimate critical properties and acentric factor, but consider the energy parameter of solute and the binary interaction parameter in the co-volume term as adjustable parameters. These adjustable parameters are optimized using pattern search (PS) method by minimizing average absolute relative deviation (AARD) between calculated and experimental solubility data. To illustrate the efficiency of our modified model, a comparison with traditional EOS model is presented. The result shows that our modified model gives better performance reflected by lower AARD. Moreover, the optimization method, PS, is compared with the genetic algorithm(GA), and it is found that the former gives better optimizations and more significant reduction of computing times than the latter. Finally, the rationality of the modified model is further discussed.

Key–Words: Supercritical fluid, Solubility, Equation of state, Critical property, Parameter optimization, Pattern search method

1 Introduction

A supercritical fluid (SCF) is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Supercritical fluid extraction (SFE) is the process of separating one component (the extractant) from another using supercritical fluids as the extracting solvent. SFE has a great potential in chemical, food, pharmaceutical, waste treatment, polymers and monomers processing, and biochemical industries because of using non-toxic and environmentally safe solvents, e.g., CO_2 instead of traditional organic solvents [1].

In order to facilitate the development of efficient SCF extraction technology, it is requisite to accurately obtain the solid solubility data in SCFs. However, the accurate measurement of the solid solubility in a supercritical fluid is difficult and time-consuming [2]. Thus, many mathematics models have been used to describe the solid-supercritical fluid equilibria behavior from limited solubility data. One of the most extensively applied methods is the equation of state (EOS) model. This method associates an EOS with a mixing rule based on the thermodynamic equilibrium conditions. Undoubtedly, the most used EOS is cubic EOS [3–5], like Peng-Robinson(PR), Soave-Redlich-Kwong (SRK), together with several mixing and combining rules, like classical van der Waals mixing rules (vdW). In the work described here, SRK and PR equations of state are also used to model the solid solubility in SCF .

In the traditional cubic EOS models, two types of computations are essential for accurate simulation results. One hand, in order to calculate the energy parameter and volume parameter in the cubic EOS, critical properties (critical temperature and critical pressure) and acentric factor of the solute and supercritical fluid have to be estimated. It is not difficult to estimate these parameters of supercritical fluid, such as CO_2, and the main difficulty is to estimate those physical properties of solutes. The other hand is that one or more temperature dependent interaction parameters which characterize the interaction between supercritical fluid and the solute must be determined by fitting experimental solubility data.

Some estimation methods [6–8] have been developed and proposed for prediction of critical properties and acentric factor. These methods used for pre-

diction of critical properties may be purely empirical with only a weak theoretical basis. Moreover, all of the widely used estimation for acentric factor require that the critical temperature and pressure are known, then the estimation error of the acentric factor may be magnified since those errors of critical properties are inevitable.

As above discussed, we can see that the critical properties and acentric factor obtained by estimation are sometimes not very reliable, and this would affect the accuracy of solubility computation. Just because of the deficiencies of estimation methods for the critical properties and acentric factor, in this paper, we try to modify the traditional cubic EOS model. For us, the ultimate aim of estimating these parameters is to calculate the energy parameter and volume parameter in EOS. We note that the energy parameter is not only related to critical properties but also a function with respect to the temperature, and the volume parameter is only a constant which is proportional to the ratio of critical temperature to critical pressure. As an alternative, we do not estimate the critical properties and acentric factor of the solute but perform the following changes. First, we consider the energy parameter of the solute as adjustable parameter which is temperature dependent. Second, because the volume parameter of the solute is a constant, a fixed value for it is given by artificially, and the adjustability of the co-volume between solute and SCF is reflected by the binary interaction parameter. To sum up, in our modified model, the energy parameter of the solute and binary interaction parameter in co-volume term are handled as adjustable parameters which are determined by fitting the experimental data. Comparing with the traditional EOS model, our modified model, due to not estimating critical properties and acentric factor of the solute, reduces the workload. The performance of our model will be investigated and compared with the traditional model in the following section .

The optimization of two adjustable parameters involved in modified model is performed by minimizing the objective function, average absolute relative deviation (AARD) between experimental and calculated solubility. Since it is difficult to obtain explicit expressions for gradient of the objective function AARD, those optimization methods based on gradients are ill-suited, and naturally derivative-free optimization methods would be preferred where only the values of the objective function are used instead. Up to now, derivative-free optimization methods mainly include direct search methods and evolutionary algorithms. Direct search methods [9, 10], like pattern search algorithm, simplex method, and so on, are deterministic methods. Evolutionary algorithms [11–14], such as cuckoo search algorithm (CA), particle swarm optimization (PSO) and the most widely used genetic algorithm (GA), are stochastic method arising from the simulation of natural evolution. To date, some literatures about parameter determination in supercritical fluid solubility model are available and the parameter optimization methods used are mainly genetic algorithm [15, 16], particle swarm optimization [17, 18], and in addition, in our previous work [20], pattern search (PS) method has firstly been successfully used to optimize two interaction parameters of traditional EOS model. This paper, PS method is still used to determinate adjustable parameters of modified EOS model. Moreover, the performance comparison between PS and GA is also involved in this paper.

The rest of this paper is organized as follows. The solubility model of traditional cubic EOS and the modified model were firstly introduced in detail. After formulation of the model, in section 3, the numerical algorithms of parameters optimization and solubility calculation are proposed . Next, numerical results of adjustable parameters determination and AARD are given and the performance comparisons between our modified model and the traditional model as well as different optimization methods are both displayed. In section 5, some further discussions are made, mainly including the rationality of the modified model and the effect of the solute co-volume parameter given artificially on the computation performance. Finally, section 6 concludes this paper with some comments.

2 Problem formulation

2.1 Traditional solubility model of cubic equations of state

The EOS approach is often used in modeling SCF phase equilibria. The molar solubility of the solid solute in the supercritical fluid, y_2, is given by the following expression [21]:

$$y_2 = \frac{P_2^{sub}\Phi_2^{sub}}{P\Phi_2^{SCF}} \exp\left(\frac{v_2^s(P - P_2^{sub})}{RT}\right) \qquad (1)$$

where P_2^{sub} is the sublimation vapor pressure of the pure solid solute at system temperature T, P is the system pressure and R is the universal gas constant. Φ_2^{sub} is the fugacity coefficient of the solute at saturation and is assumed to be unity because the solute is assumed to be nonvolatile. The molar volume of the solute, v_2^s, is a constant. The quantity Φ_2^{SCF} refers to the fugacity coefficient of the solute in supercritical fluid phase at the prevailing temperature T and pressure P which can be evaluated via an equation of state.

The cubic Peng-Robinson equation of state (PR EOS) and Soave-Redlich-Kwong equation of state (S-RK EOS) have been found success in modeling high-pressure phase equilibria, and will be used in this work. These two EOSs are as the following expression:
PR EOS:

$$\begin{aligned} P &= \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \\ a &= 0.45724\frac{R^2T_c^2}{P_c}\left[1+k(1-\sqrt{\frac{T}{T_c}})\right]^2 \\ k &= 0.37464 + 1.5422\omega - 0.26992\omega^2 \\ b &= 0.0778\frac{RT_c}{P_c} \end{aligned} \quad (2)$$

and SRK EOS:

$$\begin{aligned} P &= \frac{RT}{v-b} - \frac{a}{v(v+b)} \\ a &= 0.42747\frac{R^2T_c^2}{P_c}\left[1+k(1-\sqrt{\frac{T}{T_c}})\right]^2 \\ k &= 0.48 + 1.574\omega - 0.176\omega^2 \\ b &= 0.08664\frac{RT_c}{P_c} \end{aligned} \quad (3)$$

where a and b are energy and volume parameters respectively, T_c is the critical temperature, P_c is the critical pressure, ω is called as acentric factor.

In order to extend the use of a pure-fluid EOS to mixtures, mixing and combining rules are necessary. The most commonly used mixing rule is the so-called van der Waals mixing rules:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}, \quad b_m = \sum_i \sum_j y_i y_j b_{ij} \quad (4)$$

Where y_i is the molefraction of the ith molecule in the mixture, obviously, $\sum_i y_i = 1$. The cross terms a_{ij} (energy) and b_{ij} (co-volume) are given in the following classical combining rules:

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1-k_{ij}), \;\; b_{ij} = \frac{b_{ii}+b_{jj}}{2}(1-l_{ij}) \quad (5)$$

where for a binary solid+CO_2 system $(i,j = 1,2)$, k_{12} and l_{12} are adjustable interaction parameters dependent temperature, a_{11}, b_{11} and a_{22}, b_{22} are those characteristic parameters of pure supercritical CO_2 and solute respectively , which can be evaluated by the cubic EOS (2) or(3) .

Based on the EOS, it is easy chemically to obtain the fugacity coefficient Φ_2^{SCF}, which can be calculated as the following (6) and (7)for PR and SRK EOS respectively:

$$\begin{aligned} \ln\Phi_2^{SCF} &= \frac{b_{22}}{b_m}\left(\frac{Pv}{RT}-1\right) - \ln\frac{P(v-b_m)}{RT} \\ &- \frac{a_m}{2\sqrt{2}b_m RT}\left(\frac{2y_1a_{12}+2y_2a_{22}}{a_m} - \frac{b_{22}}{b_m}\right)\ln\frac{v+(1+\sqrt{2})b_m}{v+(1-\sqrt{2})b_m} \end{aligned} \quad (6)$$

and

$$\begin{aligned} \ln\Phi_2^{SCF} &= \frac{b_{22}}{b_m}\left(\frac{Pv}{RT}-1\right) - \ln\frac{P(v-b_m)}{RT} \\ &- \frac{a_m}{b_m RT}\left(\frac{2y_1a_{12}+2y_2a_{22}}{a_m} - \frac{b_{22}}{b_m}\right)\ln\frac{v+b_m}{v} \end{aligned} \quad (7)$$

In order to correlate the solubility of the solute in SCF using the traditional EOS models, there are two types work to be done. One hand, critical temperature, critical pressure and acentric factor must be estimated for the computation of energy and volume parameters in EOS. On the other hand, adjustable interaction parameters for binary system, k_{12}, l_{12}, need to be fitted with experimental data by minimizing the objective function, average absolute relative deviation (AARD) between experimental and calculated solubility, given as:

$$\mathrm{AARD}(\%) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{y_{2,i}^{cal}-y_{2,i}^{exp}}{y_{2,i}^{exp}}\right| \quad (8)$$

where n is the number of experimental data points at each temperature, and $y_{2,i}^{cal}$ and $y_{2,i}^{exp}$ are ith calculated and experimental values of the solid solubility respectively.

2.2 Modified solubility model of cubic equations of state

From the cubic EOS (2) and (3), it is easily found that the energy parameter a and volume parameter b of pure component are associated with critical temperature T_c , critical pressure P_c , acentric factor ω , and then, in order to calculate a and b of pure component, two critical parameters and acentric factor are necessary data. For CO_2, these parameters are easy to get, however, there are some difficulties more or less for the solute involved in this study. Then, changing a train of thought is may be a feasible way.

Note that the energy parameter a is a function with respect to the temperature T, and volume parameter b is only a constant, which is proportional to the ratio of critical temperature T_c to critical pressure P_c. Different from the traditional EOS model, we perform the following modifications. We do not estimate the critical properties and acentric factor of the solute but consider the energy parameter of the solute a_{22} along with the binary interaction adjustable parameter l_{12} in the co-volume term as two adjustable parameters. As for the b_{22}, since it is a constant, we artificially give

a fixed value, and the adjustability of the co-volume term is reflected by l_{12}. In addition, the binary interaction parameter in the energy term k_{12} is set to be zero since the adjustability of the energy term can be reflected by a_{22}. To sum up, the interaction term a_{12}, b_{12} for binary system is given :

$$a_{12} = \sqrt{a_{11}a_{22}}, \qquad b_{12} = \frac{b_{11} + b_{22}}{2}(1 - l_{12}) \quad (9)$$

Two adjustable parameters, a_{22} and l_{12} , are optimized by minimizing AARD in (8).

In what follows, for the simplicity, symbols, TM and MM, are used to denote the traditional EOS model and modified one respectively. To illustrate the differences betweens these two models, the comparison about them is displayed in Table 1. We can see that MM avoids to estimate the difficult-to-obtain critical properties and acentric factor. Moreover, the number of optimized parameters in MM is same as that in TM. So the MM needs fewer computations.

Table 1: Comparison between the traditional EOS model (TM) and the modified EOS model (MM).

Characteristic	TM	MM
Estimate T_c P_c, ω or not	need to	not need to
Optimized parameters	k_{12}, l_{12}	a_{22}, l_{12}
a_{22}	computed by T_c, P_c, ω	as an optimized parameter
b_{22}	computed by T_c, P_c, ω	given as a fixed value
a_{12}	$\sqrt{a_{11}a_{22}}(1 - k_{12})$	$\sqrt{a_{11}a_{22}}$
b_{12}	$\frac{b_{11}+b_{22}}{2}(1 - l_{12})$	$\frac{b_{11}+b_{22}}{2}(1 - l_{12})$

3 Estimation of unknown parameters and numerical computation of solubility

3.1 The pattern search method

The optimization method used to determinate adjustable parameters a_{22}, l_{12} in modified EOS model is pattern search method (PS). The PS method was firstly proposed by R. Hooke and T.A. Jeeves in 1961 [22] and it has survived until now because it is conceptually simple, easy to implement and computationally efficient in solving many optimization problems [20,23,24]. It do not need the derivatives of objective functions. Alternatively, only the function values are compared to choose the new iterate. It thus belongs to the so-called derivative-free, direct search method, and is superior to other direct search methods such as Powell method and Simplex method in both robustness and number of function evaluations [10].

In brief, the PS method consists of a series of exploratory moves and pattern moves. The iteration process is as following, and auxiliary illustration can be achieved by Figure 1. For the sake of clarity, $F(\mathbf{x})$is utilized to denote the objective function, $\mathbf{x} \in \mathbb{R}^2$ is an 2-dimensional real vector that needs to be optimized. For the problem on hand, $\mathbf{x} = (a_{22}, l_{12})$, $F(\mathbf{x})$ denote AARD in expression (8). The optimization starts from the exploration move at initial point $\mathbf{x}_0$ given by the user. At kth iteration, the exploration move, from $\mathbf{x}_k$ point to new points represented by $\mathbf{x}_+ = \mathbf{x}_k \pm \Delta_k^i \mathbf{e}^i$, is successively tested along the coordinate direction, where Δ_k^i is the step size of ith direction and $\mathbf{e}^i$ is standard 2-dimensional unit basis vectors ($i = 1, 2$). Let $\mathbf{\Delta_k} = (\Delta_k^1, \Delta_k^2)$ denote a step size vector. After the calculations for 2 directions are all done, if there is no such point $\mathbf{x}_+$ that satisfy $F(\mathbf{x}_+) < F(\mathbf{x}_k)$, the first exploration move is then unsuccessful and a second exploratory move is repeated at $\mathbf{x}_k$ but with reduced step size $\mathbf{\Delta_{k+1}} = \theta \mathbf{\Delta_k}$, $\theta < 1$ is a contraction factor, and let $\mathbf{x}_{k+1} = \mathbf{x}_k$. On the other hand, when the point $\mathbf{x}_+$ that of $F(\mathbf{x}_+) < F(\mathbf{x}_k)$ is found, the exploratory move is successful, and then let $\mathbf{x}_{k+1} = \mathbf{x}_+$ and $\mathbf{\Delta_{k+1}} = \mathbf{\Delta_k}$, meanwhile the pattern move starts for the sake of speeding up the search.

A pattern move consists of a move step from $\mathbf{x}_{k+1}$ to $\mathbf{x}_{k+1} + \delta(\mathbf{x}_{k+1} - \mathbf{x}_k)$, where δ is the pattern step size and $0 < \delta < 2$, namely, the direction of move is along the direction of vector $\mathbf{x}_{k+1} - \mathbf{x}_k$, as shown in Figure 1. Then the PS method continues to perform a new exploratory move at the point $\mathbf{x}_{k+1} + \delta(\mathbf{x}_{k+1} - \mathbf{x}_k)$. If the exploratory move is successful, and then the point $\mathbf{x}_{k+1} + \delta(\mathbf{x}_{k+1} - \mathbf{x}_k)$ is accepted as the new iteration point $\mathbf{x}_{k+2}$. On the contrary, if exploratory move fails, the pattern move is omitted and return to $\mathbf{x}_{k+1}$ for proceeding exploratory move to find the $\mathbf{x}_{k+2}$.

When $\Delta_k^i < \varepsilon (i = 1, 2)$, the PS stops, meanwhile $\mathbf{x}_k$ is accepted as the optimization result of parameters, where ε is the given step tolerance. In this paper, a generalization of original PS method has been used, the generalization mainly includes two aspects. One hand is that the step size $\mathbf{\Delta_k}$, the steps Δ_k^1, Δ_k^2 are not necessarily equal to each other as original PS. On the other hand, the pattern step size, δ, varies from 0 to 2, however, it is set to be 1 in original PS.

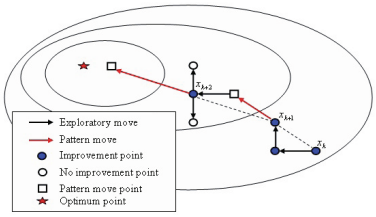

Figure 1: Diagram of exploratory and pattern moves in the pattern search method.

3.2 Solubility computation

From the equation (1) and (6) or (7), it is easy to find that the equation of solubility is nonlinear. In order to illustrate simply, the solubility equation of the solute for the modified EOS model can be rewritten as:

$$y_2 = f(y_2, v, a_{22}, l_{12}, b_{22}) \tag{10}$$

The overall computation flow of the modified EOS model is given in the following:

Step 1. For each temperature T, input n experimental datas of $(P_i, y_{2,i}^{exp})$,$(i = 1, 2, \cdots, n)$, and some physical parameters: v_2^s, P_2^{sub}, and give the value of b_{22} artificially.

Step 2. Give T_c, P_c, ω of CO_2 and then the characteristic parameters of pure CO_2, a_{11}, b_{11}, can be computed by the expression a, b respectively in(2) or (3).

Step 3. Give the initial values of optimization parameters a_{22}, l_{12}, the initial step size vector $\mathbf{\Delta_0}$, contraction factor θ, tolerance ε.

Step 4. Compute a_{12}, b_{12} using (9), and then a_m, b_m is valuated through mixing rules (4).

Step 5. Substitute a_m, b_m into the EOS (2) or (3) and thus v can be solved out.

Step 6. Compute numerically the solubility $y_{2,i}^{cal}, (i = 1, 2, \cdots, n)$ in equation (10) by means of iterative algorithm.

Step 7. The objective function AARD is given out by (8).

Step 8. Check whether step size of PS is less than the tolerance ε or not. If it is true, the program is stopped, and output AARD, a_{11}, l_{12}. Otherwise, turn to the next step.

Step 9. Renew a_{22}, l_{12} and step size using the PS method discussed in section 3.1, and return to Step 4.

From above, we can see the computational solubility, $y_{2,i}^{cal}$, should be evaluated. The equation (10) is nonlinear , and iterative algorithms are suitable to compute the solubility . Here, for the simplicity, we omit the subscripts, and y^{cal} is used to represent the computational solubility of the solute. The iteration process is performed as follows.

Step 1. Give the initial value of solubility $y^{(0)}$, for example, the experimental solubility date can be used as $y^{(0)}$, the tolerance $\epsilon = 1 \times 10^{-7}$, and the iteration steps is limited to 200.

Step 2. Let $y_2 = y^{(0)}$, and substitute y_2 into the right hand of (10), then we yield the value of $f(y_2, v, a_{22}, l_{12}, b_{22})$.

Step 3. Calculate the difference $|y_2 - f(y_2, v, a_{22}, l_{12}, b_{22})|$. If the difference is less than ϵ or the iterations exceeds the limit, the process is stopped and let y^{cal}= $f(y_2, v, a_{22}, l_{12}, b_{22})$. Otherwise, turn to Step 4.

Step 4. Renew y_2 by $f(y_2, v, a_{22}, l_{12}, b_{22})$, substitute renewed y_2 into the right side of (10), and renewed $f(y_2, v, a_{22}, l_{12}, b_{22})$ is thus obtained, then switch to Step 3.

4 Numerical results

4.1 Numerical results of modified model

In this study, 50 different solubility data sets of 10 binary systems at five temperatures have been used to the solubility model. Original 438 experimental data points of 10 binary systems are collected from literatures [25–27]. The temperature range of these experimental data are 308-348K under pressure of 121.6-355 bar, where for each temperature, several experimental solubility data are provided for different pressures. The physical properties required in the computation of studied ten systems, sublimation pressure P_2^{sub} and molar volume of the solute v_2^s are shown in Table 2, the estimate methods for these two physical properties can be referred to [28,29], this is not our focus and is omitted. Moreover, critical properties and acentric factor of supercritical solvent CO_2 are respectively: T_c=304.2K, P_c=73.82bar, ω=0.225.

For the volume parameter of the solute, b_{22}, a fixed value is given artificially in the beginning of computation. According to the expression of b in the EOS (2) or (3) and the empirical value of critical property, we can calculate that the magnitude order of b_{22} is about 10^{-4}. So, in the following calculations, for the simplicity, we set b_{22} to be 5×10^{-4} for all systems, and in what follows the affections of different b_{22} will be discussed. The adjustability of co-volume term is reflected by the interaction parameter l_{12}.

In Table 3, adjusted parameters, a_{22}, l_{12}, and AARD values obtained by using the modified EOS models for 10 supercritical CO_2-drug systems are provided. The calculation results are in satisfactory agreement with experimental data, reflected by AARD values. In the ten compounds, the best performance is of Lovastatin, the average AARD for five temper-

Table 2: Physical properties of all compounds used.

Compound	$v_2^s(cm^3/mol)$	$P_2^{sub}(Pa)$				
		308K	318K	328K	338K	348K
Atorvastatin	426.54	1.863×10^{-4}	7.574×10^{-4}	2.803×10^{-3}	9.526×10^{-3}	2.995×10^{-3}
Atropine	233.89	1.344×10^{-1}	4.231×10^{-1}	1.232	3.339	8.485
Bisacodyl	282.79	1.443×10^{-2}	4.960×10^{-2}	1.569×10^{-1}	4.598×10^{-1}	1.258
Carbamazepine	180.48	9.262×10^{-2}	2.896×10^{-1}	8.377×10^{-1}	2.258	5.707
Codeine	224.68	4.257×10^{-2}	1.393×10^{-1}	4.207×10^{-1}	1.181	3.099
Diazepam	210.53	1.197×10^{-1}	3.777×10^{-1}	1.102	2.993	7.619
Fluvastatin	317.90	1.044×10^{-3}	3.938×10^{-3}	1.358×10^{-2}	4.320×10^{-2}	1.276×10^{-1}
Lovastatin	346.38	2.743×10^{-3}	1.002×10^{-2}	3.356×10^{-2}	1.038×10^{-1}	2.986×10^{-1}
Rosuvastatin	360.90	9.982×10^{-4}	3.812×10^{-3}	1.330×10^{-2}	4.277×10^{-2}	1.277×10^{-1}
Simvastatin	361.32	4.920×10^{-3}	1.769×10^{-2}	5.837×10^{-2}	1.780×10^{-1}	5.053×10^{-1}

atures is 2.67% and 2.56%, from PR EOS and S-RK EOS, respectively. Overall, for the 50 solubility isotherms of ten compounds, except that AARD values of atorvastatin and simvastatin at 328, 338 and 348 K isotherms are above 20%, the others are mostly less than 10.0%, these results are perfectly acceptable for SCF extraction process. In additon, in other literatures [19, 20], similar results that AARD value was high at higher temperatures are also found. M. R. Housaindokht and M. R. Bozorgmehr [19] used semi empirical Mendez-Santiago-Teja equation to model solubility in SCF , they found that AARD value was high at higher temperatures, and concluded that the deviation of calculated results at higher temperature may be related to the inaccuracy of experimental data, we agree with this point of view.

To further illustrate the efficiency of our model, the calculated solubilities corresponding to all 438 experimental data are achieved. The perfect fit, i.e., calculated solubility values equal to experimental data, is also shown in Figure 2 by the dashed line. Obviously, the calculated solubility values are agreeing with the experimental data rather well for most of data points, indicating the satisfactory performance of the modified EOS model and PS optimization method.

A main purpose of modelling the solubility by mathematical model is to predict the solubility under other temperatures or pressures where there are not experimental data. Given a isotherm and the corresponding set of optimized parameters, a_{22} and l_{12}, the solubilities for different pressures can be obtained following the computation process of y^{cal} in section 3.2. Lovastatin as an example, Figure 3 gives the experimental solubility data (denoted by discrete points) at five temperatures and fitted curve (represented by full line) for different pressures range of 115-360 bar using the modified PR EOS model. From the figure, it is obvious the fitting is very well and we would think the prediction is also accurate.

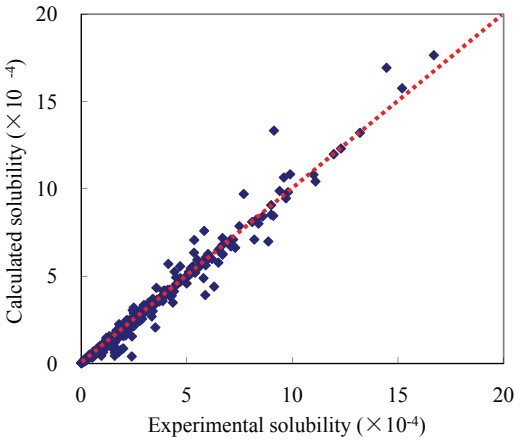

Figure 2: The fitting between experimental solubility data and calculations by modified PR EOS.

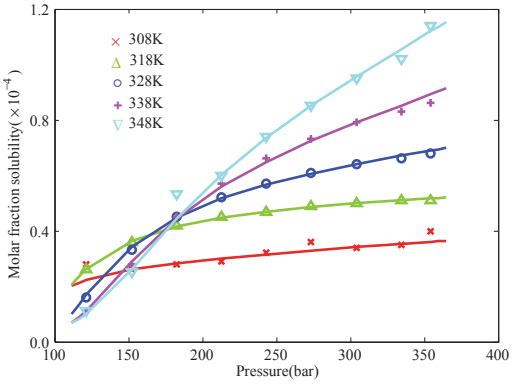

Figure 3: Experimental solubility data (denoted by discrete points) at five temperatures of lovastatin and fitted curves (represented by full line) using the modified PR EOS model.

Table 3: Optimized parameters and AARD results of our modified solubility model.

Compound	EOS	Parameters	Temperature T(K)				
			308	318	328	338	348
Atorvastatin	PR	a_{22}	17.1892	14.9282	11.8267	8.8070	7.8028
		l_{12}	-1.2113	-0.9810	-0.5998	-0.1735	-0.0373
		AARD%	4.47	10.23	21.77	36.93	35.35
	SRK	a_{22}	16.0529	14.1983	11.2383	9.1228	8.0000
		l_{12}	-1.2833	-1.0649	-0.6477	-0.3130	-0.1424
		AARD%	3.74	9.24	20.97	34.51	33.43
Atropine	PR	a_{22}	7.4890	7.3076	6.6641	6.2649	6.0176
		l_{12}	-0.4871	-0.3985	-0.3484	-0.2889	-0.2475
		AARD%	9.95	8.84	9.45	8.23	7.57
	SRK	a_{22}	6.9593	6.9271	6.3499	6.0937	6.0000
		l_{12}	-0.5333	-0.4552	-0.4073	-0.3654	-0.3497
		AARD%	9.64	9.01	10.72	8.55	7.88
Bisacodyl	PR	a_{22}	9.6291	8.0494	6.3438	4.3583	3.2320
		l_{12}	-0.6164	-0.4408	-0.1980	0.1613	0.4064
		AARD%	4.15	3.42	8.49	8.85	14.41
	SRK	a_{22}	9.0722	7.7692	6.0931	4.4349	3.2475
		l_{12}	-0.6791	-0.5241	-0.2508	0.0794	0.3649
		AARD%	3.52	2.79	8.48	8.69	13.96
Carbamazepine	PR	a_{22}	7.1700	6.2407	4.8969	3.1302	2.0000
		l_{12}	-0.3174	-0.1844	0.0269	0.4354	0.7448
		AARD%	1.18	4.65	3.15	7.35	17.57
	SRK	a_{22}	6.2166	5.8979	4.7729	3.1168	2.4993
		l_{12}	-0.2655	-0.2200	-0.0253	0.4038	0.5698
		AARD%	1.44	4.70	3.40	7.21	17.45
Codeine	PR	a_{22}	8.9089	8.0000	8.4799	6.2417	5.8344
		l_{12}	-0.4602	-0.3843	-0.4917	-0.2244	-0.0936
		AARD%	5.71	8.34	4.36	11.32	7.08
	SRK	a_{22}	8.5174	7.5498	8.1608	6.1694	5.6967
		l_{12}	-0.5275	-0.4282	-0.5685	-0.3187	-0.1498
		AARD%	5.85	7.68	4.74	11.49	7.22
Diazepam	PR	a_{22}	8.6104	7.5210	6.9807	6.0574	5.7370
		l_{12}	-0.4976	-0.3762	-0.3422	-0.2204	-0.2162
		AARD%	4.40	5.92	9.41	10.29	11.92
	SRK	a_{22}	8.0702	7.1423	6.6885	5.8594	5.7757
		l_{12}	-0.5452	-0.4314	-0.4060	-0.2838	-0.3277
		AARD%	4.63	6.43	9.93	10.79	12.77
Fluvastatin	PR	a_{22}	13.8640	12.4021	10.2098	8.7292	7.7405
		l_{12}	-0.9599	-0.8079	-0.5394	-0.3442	-0.1988
		AARD%	1.79	2.22	3.16	3.83	5.83
	SRK	a_{22}	12.9081	11.8066	10.0076	8.7628	7.6113
		l_{12}	-1.0162	-0.8875	-0.6404	-0.4589	-0.2648
		AARD%	2.37	1.83	2.29	3.55	6.07
Lovastatin	PR	a_{22}	14.9813	14.9321	13.4086	11.8019	10.5066
		l_{12}	-1.2963	-1.3608	-1.2696	-1.1549	-1.0661
		AARD%	5.19	0.62	1.69	1.93	3.90
	SRK	a_{22}	13.7944	13.8174	12.5285	11.3282	10.1143
		l_{12}	-1.3696	-1.4451	-1.3649	-1.2883	-1.1964
		AARD%	5.49	0.77	0.56	1.36	4.61
Rosuvastatin	PR	a_{22}	16.0261	13.1454	10.8764	8.7843	7.1740
		l_{12}	-1.2646	-0.9933	-0.7633	-0.5189	-0.3035
		AARD%	2.08	6.58	13.73	14.62	15.80
	SRK	a_{22}	14.9392	12.4787	10.4126	8.6068	7.7461
		l_{12}	-1.3467	-1.0881	-0.8510	-0.6194	-0.5188
		AARD%	2.05	6.07	12.44	12.92	13.73
Simvastatin	PR	a_{22}	12.2398	10.3158	7.4305	4.0000	2.0000
		l_{12}	-0.9348	-0.7525	-0.3782	0.2430	0.7093
		AARD%	4.58	10.10	22.03	33.70	26.76
	SRK	a_{22}	11.4094	9.7213	7.1555	4.0000	1.9762
		l_{12}	-1.0023	-0.8224	-0.4489	0.1880	0.7131
		AARD%	3.94	9.25	20.91	32.56	26.42

4.2 Model comparison

In recent years, to promote the performance of EOS, some literatures have contributed to modify the traditional EOS or mixing rules [2, 30–32], to the best of our knowledge, both critical properties and acentric factor needed to be estimated in these studies. In our previous work [20], solid solubility in supercritical CO_2 for the same ten compounds as this paper were modelled using TM. Comparing the model of literature [20] with this paper, the difference is also that critical properties and acentric factor were estimated in our existing reference, however, this need not to be done in present modified model. To compare the performance of TM and MM, Table 4 provides the AARD results averaged over five temperatures for all ten solutes. It is obviously that the vast majority data of AARD of the MM are lower than that of TM for comparison, except for Diazepam in both EOS and Atropine, Carbamazepine in PR EOS. The total average AARD for all ten compounds of MM is 9.65 and that of TM is 10.09. The better performance of modified EOS model may be contributed the novel idea, i.e., not estimating critical properties and acentric factor, which eliminate the error of estimating them.

Table 4: Comparison of AARD (%) values averaged by five temperatures between modified model (MM) and traditional model (TM).

Compound	EOS	AARD(%)	
		MM	TM
Atorvastatin	PR	21.75	24.93
	SRK	20.38	23.35
Atropine	PR	8.84	8.96
	SRK	9.16	9.50
Bisacodyl	PR	7.86	8.53
	SRK	7.49	7.99
Carbamazepine	PR	6.78	6.88
	SRK	6.84	6.84
Codeine	PR	7.36	7.44
	SRK	7.40	7.49
Diazepam	PR	8.39	8.31
	SRK	8.91	8.85
Fluvastatin	PR	3.37	3.71
	SRK	3.22	3.42
Lovastatin	PR	2.67	2.73
	SRK	2.56	2.64
Rosuvastatin	PR	10.56	10.88
	SRK	9.44	9.73
Simvastatin	PR	19.43	20.18
	SRK	18.62	19.39

4.3 Optimization method comparison

Genetic algorithm (GA) is a stochastic optimization technique inspired by Darwins theory of hereditary evolution, this method has been widely applied to many engineering optimizations [34, 35]. At the beginning of the computation a number of individuals represented by chromosomes are randomly given, forming a set known as the initial population. In this study, the population size of 20 was taken. Following the evaluation of objective function, a new generation is generated by applying a set of genetic operators to the original population. The basic genetic operations are selection, crossover and mutation. The process of selection, crossover and mutation continues until either the generation exceeds a number limit or the objective function AARD does not improve in 50 generations. The maximum generation limit used is 200 for lower temperatures of 308 and $318K$, and 500 for other higher temperatures.

A comparison between PS and GA is shown in Table 5, the performance is reflected by the overall AARD and CPU time averaged by five temperatures. From the AARD, we can find that the PS method has performed marginally better than the GA one. Further, if comparing the run time, PS is outstandingly better in time-saving than the GA method. As we can see, the CPU time used for running the PS algorithm is much less than or close to 1s for all tested systems whereas for GA the CPU time used is ranging from 6 to 17s. The reason for it may be due to that the GA is run with a population of starting points rather than a single initial point like the PS, subsequently requiring more computing time.

Table 5: Comparison of AARD (%) values averaged by five temperatures and CPU time between pattern search method (PS) and genetic algorithm (GA) for modified PS EOS model

Compound	AARD(%)		CPU time(s)	
	PS	GA	PS	GA
Atorvastatin	21.75	23.36	0.52	15.87
Atropine	8.84	8.97	0.39	9.26
Bisacodyl	7.86	8.45	0.51	16.42
Carbamazepine	6.78	7.03	0.48	10.79
Codeine	7.36	7.56	0.61	13.76
Diazepam	8.39	8.78	0.43	9.88
Fluvastatin	3.37	3.59	0.57	10.64
Lovastatin	2.67	2.92	0.45	14.72
Rosuvastatin	10.56	11.17	0.67	11.23
Simvastatin	19.43	20.24	0.85	12.64

5 The discussion of modified model

5.1 The changing trend of a_{22}

In our present work, a_{22} is considered as an adjustable parameter, its value is obtained by fitting the experi-

mental and calculated solubility data. From the fitted data of a_{22} in the Table 3, we can find that the values of a_{22} decrease with increase of temperature T. Of course, there are a little bit of data that does not strictly follow above rule, including from 318K to 328K of Codeine for both EOS and from 308K to 318K of Lovastatin for SRK EOS only, which may be caused by the inaccuracy of experimental data or the error of numerical computation, after all, errors are inevitable for all numerical methods. In spite of this, we think it would not become the obstacle of a_{22} overall variation trend with temperature.

Whether the fitted trend of a_{22} by modified model is consistent with the traditional EOS theory or not is a problem in front of us. Theoretically speaking, a_{22} is a function of temperature T, which can be found easily from the equation of state. PR as example still, let us consider the expression of a in traditional EOS (2). Differenting the expression of a with respect to the temperature T, it yields,

$$\frac{\partial a}{\partial T} = 0.45724 \frac{R^2 T_c^{\frac{3}{2}}}{P_c} [\frac{k^2}{\sqrt{T_c}} - \frac{k(1+k)}{\sqrt{T}}] \qquad (11)$$

In fact, generally acentric factor, ω, is in the range of [0,1], thus, judging from the expression of k in (2) , $k > 0$ is concluded. In addition, for our compounds studied in this paper, the range of experimental temperature T is from 308K to 348K, it is far below the critical temperature T_c , whose estimated data can be referred to the literature [15]. Therefore, $\frac{k^2}{\sqrt{T_c}} < \frac{k(1+k)}{\sqrt{T}}$ is true, and then $\frac{\partial a}{\partial T} < 0$ is concluded. From above deduction, it is shown that the energy parameter of solute in EOS is decreasing with the increasing temperature T, thus the fitted result is consistent with theoretical variation tendency. In another words, the fitted results of a_{22} are logical.

5.2 Affection of solute volume parameter

In the previous correlation process of solubility, the value of b_{22} is given artificially, it was set to be 5×10^{-4} for all systems. What will happen if the value of b22 changes is in our concern. In order to verify this, we newly let $b_{22} = 1 \times 10^{-4}, 4 \times 10^{-4}, 8 \times 10^{-4}$, respectively. The parameters optimization results and AARD derived from different b_{22} are listed respectively in Table 6 for comparison. To simplify, only the results of PR EOS is provided. SPK EOS has similar correlated results and the details are omitted.

From Table 6, it shows that the values of l_{12} obtained from different b_{22} are significantly deviation. Through further analysis, we can find l_{12} is increasing following the increase of b_{22}. Because of the fact that $b_{12} = \frac{b_{11}+b_{22}}{2}(1 - l_{12})$ and the changes between b_{22} and $(1 - l_{12})$ are in the opposite directions, the variance of b_{12} is offset a bit, it is natural to guess that the optimization results of l_{12} would not significantly influence that of a_{22} and AARD. This is verified as shown Table 6, it is obvious that the variation of a_{22} and AARD are flat. Judged by the similar results of AARD obtained from different b_{22}, we can conclude that the performance is almost unaffected by different b_{22} as long as it varies in a relatively reasonable scope. To conclusion, it is not a very difficult thing to give out a reliable value of b_{22} in the beginning of computation.

6 Conclusions

In this paper, PR and SRK EOS are used to correlate solid solubility in supercritical CO_2. Different from traditional way, this paper, without estimating critical properties and acentric factor of the solute, correlated ten solid+SCF solubility data by considering the solute energy parameter and the binary interaction parameter in the co-volume term as adjustable parameters, which were optimized by minimizing the AARD. The correlation results show that this method has performed very well for ten materials examined as reflected by lower AARD values. Comparing with the traditional EOS model, this modified model avoids the use of difficult-to-obtain critical properties and acentric factor and achieves a better performance.

The solute energy parameter values optimized by PS method are decreasing with the increasing temperature, this trend is consistent with EOS theory. As for co-volume parameter of the solute, b_{22}, because of the absence of the critical property, a fixed value is given artificially in the beginning of correlation. The affection on correlation performance was discussed through different man-made fixed values. The results show that the variation of AARDs from different b_{22} is very flat, namely, the performance is almost unaffected when b_{22} varies in a relatively reasonable scope. In a word, it is not a difficult thing to give out artificially a reliable b_{22} value in the beginning of computation.

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Table 6: The effects of different b_{22} given artifically on optimation results with modified PR EOS model.

Item	Compound	$b_{22} \times 10^4$	Temperature T(K)				
			308	318	328	338	348
AARD	Atorvastatin	1	4.47	10.23	21.77	36.93	35.35
		4	4.44	10.14	21.50	36.34	34.83
		8	4.48	10.01	21.22	35.74	34.12
	Fluvastatin	1	1.79	2.22	3.16	3.83	5.83
		4	1.80	2.24	3.12	3.73	5.75
		8	1.82	2.19	3.03	3.58	5.72
	Lovastatin	1	5.19	0.62	1.69	1.93	3.90
		4	5.29	0.62	1.69	1.92	3.80
		8	5.22	0.63	1.72	1.87	3.88
	Rosuvastatin	1	2.08	6.58	13.73	14.62	15.80
		4	2.08	6.59	13.70	14.57	15.74
		8	2.17	6.85	13.68	14.51	15.66
	Simvastatin	1	4.58	10.10	22.03	33.70	26.76
		4	4.55	10.06	21.95	32.90	26.56
		8	4.58	10.00	21.88	32.68	26.45
a_{22}	Atorvastatin	1	17.1892	14.9282	11.8267	8.8070	7.8028
		4	17.1861	14.9019	11.7957	9.1391	7.7203
		8	17.2549	14.8647	11.7650	9.0862	7.6519
	Fluvastatin	1	13.8640	12.4021	10.2098	8.7292	8.7292
		4	13.8622	12.4146	10.4360	8.7286	7.6866
		8	13.8542	12.3586	10.4106	8.7139	7.6577
	Lovastatin	1	14.9813	14.9321	13.4086	11.8019	10.5066
		4	14.9054	14.9112	13.3904	11.8009	10.6543
		8	14.9603	14.9222	13.4334	11.8758	10.5302
	Rosuvastatin	1	16.0261	13.1454	10.8764	8.7843	7.1740
		4	16.0224	13.1390	10.8660	8.7779	7.2327
		8	16.0571	12.9105	10.8638	8.7607	7.2618
	Simvastatin	1	12.2398	10.3158	7.4305	4.0000	2.0000
		4	12.2785	10.2955	7.4236	4.5190	1.9401
		8	12.2982	10.2714	7.3177	4.4787	1.8994
l_{12}	Atorvastatin	1	-1.2113	-0.9810	-0.5998	-0.1735	-0.0373
		4	0.3438	0.4131	0.5268	0.6375	0.6980
		8	0.6602	0.6979	0.7566	0.8147	0.8466
	Fluvastatin	1	-0.9599	-0.8079	-0.5394	-0.3442	-0.1988
		4	0.4184	0.4630	0.5337	0.6012	0.6474
		8	0.7000	0.7240	0.7600	0.7947	0.8191
	Lovastatin	1	-1.2963	-1.3608	-1.2696	-1.1549	-1.0661
		4	0.3213	0.3000	0.3270	0.3605	0.3802
		8	0.6486	0.6386	0.6519	0.6685	0.6830
	Rosuvastatin	1	-1.2646	-0.9933	-0.7633	-0.5189	-0.3035
		4	0.3279	0.4086	0.4771	0.5496	0.6103
		8	0.6526	0.7000	0.7303	0.7681	0.7982
	Simvastatin	1	-0.9348	-0.7525	-0.3782	0.2430	0.7093
		4	0.4243	0.4808	0.5914	0.7415	0.9201
		8	0.7026	0.7327	0.7920	0.8683	0.9614

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