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Measurement and Modeling of Acridine Solubility in Supercritical Carbon Dioxide

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Abstract

Supercritical carbon dioxide has gained increasing attention in food and pharmaceutical processing owing to the fact that it is environmentally inexpensive, not flammable, essentially non-toxic, and it has a convenient critical point. Also, it has been attracting much attention in many fields, such as extraction of sensitive materials and pharmaceutical processing and polymerization processes. For designing these processes, solubility data of solute in $SCCO_2$ are needed as the fundamental knowledge. And the correlation and extension of existing equilibrium data is an important step in the application and development of such processes.

Acridine is a raw material used for the production of dyes and some valuable drugs and its derivatives have antiseptic properties like Proflavine. In this research, the solubility of Acridine in supercritical carbon dioxide was measured at temperatures of 313, 323 and 333 K and in the pressure range of 120 to 350 bar using static method. The crossover pressure of Acridine was observed at about 150 bar. The experimental data were correlated using Peng- Robinson (PR) and Soave- Redlich- Kwong (SRK) equations of state (EOS) and van der Waals mixing rule with one (vdW 1) and two adjustable parameters (vdW 2) and Huron-Vidal mixing rules. For applying the Huron-Vidal mixing rule, NRTL activity coefficient model was used. The binary interaction parameters of the studied models were reported. The results of average absolute relative deviations (AARD) illustrated good accuracy of the studied models. Furtheremore, the modeling has been done with and without considering the sublimation pressure of the solid (Acridine) as an additional adjustable parameter. It can be concluded when sublimation pressure is considered as adjustable parameter, the AARD results of the studied models significantly decrease. Also, the estimated values of sublimation pressure of Acridine were reported at different temperatures. The results also showed that, among the studied models, PR- HV model with adjusted P^{sub} has the minimum AARD (2.47 %).

Keywords: Acridine, Equation of state; Mixing rule; Solubility; Supercritical CO_2

Introduction

Recently, there has been an increasing level of interest in using supercritical fluids (SCFs) and supercritical fluid technology for processing pharmaceutical materials. This interest mainly arises from some advantages associated SCFs: a) the possibility of adjusting the solvation power of a SCF, simply by manipulating temperature and pressure, b) the possibility of using solvents with low toxicity or using processes that do not leave appreciable residues of toxic solvents and c) use of low cost supercritical carbon dioxide ($SCCO_2$) with the possibility of working at relatively low temperatures without thermally degrading labile substances (like most pharmaceuticals) [1]. The solubility data of solutes in supercritical fluids are important for effectively designing and building up any practical supercritical separation processes. In the past years, a lot of investigators have published equilibrium solubility data for various solids in supercritical fluids [2-7].

Acridine is a raw material used for the production of dyes and some valuable drugs. The motivation for this research stems from the fact that Acridine and its derivatives have antiseptic properties like Proflavine. Schmitt and Reid [8] measured the solubility of Acridine in different supercritical solvents at various temperatures and pressures. Also Dobbs et al. [9] reported the solubility of Acridine in pure CO_2 and CO_2 - cosolvent mixtures at T= 308 K. Generally, solubility data of

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solids in supercritical fluids are limited and more experimental measurements at different temperatures are required for essential thermodynamic modeling and design.

Several correlations have been developed in order to correlate and extrapolate solubility data at various pressures and temperatures. The supercritical solubility models generally use an equation of state (EOS) approach for modeling. To apply these EOSs for mixtures, different mixing rules have been developed. Among them van der Waals (vdW) one-fluid mixing rule is usually used for solubility calculations. The main shortcoming of the van der Waals mixing rule is that it is only applicable to mixtures that exhibit relatively moderate solution nonidealities [10,11].

Also, several mixing rules have been developed that make use of excess Gibbs energy (G^E) models. One of these models is Huron-Vidal mixing rule [12], which is derived for high pressure phase equilibria calculations.

Because of the necessity for having enough solubility data in supercritical fluids for designing and development of supercritical extraction processes, in this research, the solubility of Acridine in supercritical CO_2 was measured using a static method. The solubility was measured for at least three times and the percent relative standard deviations in the range of 2-6% were obtained.

In this study, the experimental solubility data of Acridine were correlated using Peng- Robinson [13] and Soave- Redlich-Kwong [14] EOSs. In mentioned EOSs, van der Waals as a classical, and Huron-Vidal as a G^E- EOS mixing rule were used.

1. Experimental

1.1. Materials

Carbon dioxide (Sabalan, Tehran, Iran, with the purity of 99.99%) was used in all experiments. HPLC grade methanol (Fluka) was used without any further purification and Acridine was obtained (with purities better than 99.5%) from the Merck.

1.2. Equipment and experimental procedure

A Suprex MPS/225 integrated SFE/SFC system equipped with a modified static system was employed for solubility determination in the $SCCO_2$. A schematic diagram of the modified static system is shown in figure 1. A detailed description of the apparatus and the operating procedure has been given previously [15].

Solubility measurements were accomplished with a 1-ml extraction vessel in the pressure range of 120-350 bar at T= (313, 323 and 333) K for 30 minutes. It is worth noting that by monitoring the solubility data versus time, 30 minutes was found to be adequate to ensure the attainment of equilibrium condition. The equilibrium temperature and pressure were measured to the accuracies of ±1 K and ±0.1 bar, respectively.

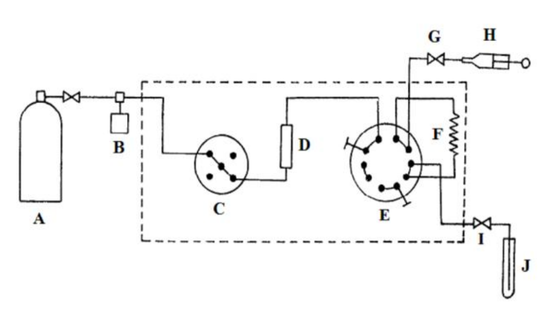

Figure 1: Schematic diagram of the experimental apparatus for measuring solubility: (A) CO_2 gas tank; (B) supercritical fluid pump; (C) 5-port 4-position valve; (D) 1 ml equilibrium cell; (E) 10-port, 2-postition valve; (F) injection loop; (G) on, off valve; (H) syringe; (I) micro adjust valve and (J) collection vial.

The solid solute (100-200 mg) was mixed well with some glass beads and packed into the extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the supercritical fluid, and consequently, reduces the equilibration time. Sintered stainless steel filters (5 ?m) were used to prevent any carryover of the solutes.

Supercritical CO_2 was pressurized and passed into the vessel D through the 5-port 4-position valve, C one time. After reaching equilibrium at the desired temperature and pressure (for about 30 minutes), 118 ?l portion of the saturated supercritical CO_2 was loaded into the injection loop, F, by means of a 10- port, 2-position valve, E. Then the loop was depressurized into the collection vial, J, containing a known volume of methanol by switching the injection valve, E. It should be noted that this is a static method and there is no circulation between C-D-E. In order to prevent solvent dispersal, the depressurizing rate of the sample loop was adjusted by the valve, I. Finally, the G and I valves were completely opened and the sample loop was washed with some methanol and collected into the collection vial, J. The solubilities were calculated by absorbance measurements at $\lambda_{\max}$ = 340 nm of each compound using a Shimadzu UV–Vis spectrophotometer Model 2100. The stock solutions of the compound were prepared by dissolving appropriate amounts of the solid samples in methanol. A set of standard solutions were then prepared by appropriate dilution of the stock solutions. The calibration curves obtained (with the regression coefficients better than 0.999) were used to establish the concentration of Acridine in the collection vial.

2. Models

The correlation of solubility in supercritical fluids requires a suitable EOS for the system under investigation. At present, hundreds of EOSs are available in the literature for this purpose. However, the applicability of each EOS is limited to certain groups of compounds and certain process conditions. Therefore, it is necessary to use different EOSs for different process conditions. The most extensively used EOSs are two-parametric cubic EOSs. However, the choice of the most suitable EOS for a certain solute/SCF system is empirical. In the other words, no single EOS will work for all systems [21]. In the EOS approach, the supercritical fluid is assumed as high-pressure gas, while in other approaches, the supercritical fluid is treated as a liquid. The solubility of a solid (component 2) in supercritical carbon dioxide (component 1) can be predicted as:

$$y_2 = \frac{P_2^{\mathrm{sub}}\,\varphi_2^{\mathrm{s}}\exp\left(\int_{P_2^{\mathrm{s}}}^{P} v_2^{\mathrm{s}}dP \big/ RT\right)}{\varphi_2 P} \qquad (1)$$

Where, P_2^{sub} is the sublimation pressure of the solid, φ_2^{s} is fugacity coefficient of the solid in the sublimation pressure usually equal to one, v_2^{s} is the solid molar volume and φ_2 is the fugacity coefficient of the solid in the supercritical phase, which can be derived from any EOS by following the well-known thermodynamic relationship:

$$RT\ \ln\varphi_2 = -RT\ \ln Z + \int_V^{\infty}\left\{\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j\neq n_i} - RT/V\right\}dV \qquad (2)$$

In this work, PR and SRK equations of state were used. PR equation is as follows:

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

Where *a* accounts for interactions between the species in the mixture and *b* accounts for the excluded volume of the species of the mixture. *a* and *b* are calculated from following correlations for each pure component:

$$a = 0.45724\,\frac{R^2T_{\mathrm{C}}^2}{P_{\mathrm{C}}}\alpha(T_{\mathrm{r}},\omega) \qquad (4)$$

$$\alpha(T,\omega) = [1+\mathrm{K}(1-\sqrt{T_{\mathrm{r}}})]^2 \qquad (5)$$

$$\mathrm{K} = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \qquad (6)$$

$$b = 0.07780\,\frac{RT_{\mathrm{C}}}{P_{\mathrm{C}}} \qquad (7)$$

SRK equation is as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \qquad (8)$$

$$a = 0.42747\,\frac{R^2T_{\mathrm{C}}^2}{P_{\mathrm{C}}}\alpha(T_{\mathrm{r}},\omega) \qquad (9)$$

$$\alpha(T,\omega) = [1+\mathrm{m}(1-\sqrt{T_{\mathrm{r}}})]^2 \qquad (10)$$

$$\mathrm{m} = 0.480 + 1.574\,\omega - 0.176\,\omega^2 \qquad (11)$$

$$b = 0.08664\,\frac{RT_{\mathrm{C}}}{P_{\mathrm{C}}} \qquad (12)$$

In these equations, ω is acentric factor; T_C and P_C are critical temperature and critical pressure of each component, respectively (table 1).
In order to use EOS for the correlation and prediction of the solubility data in supercritical fluids, the mixing and combining rules must be introduced for the EOS parameters. In this work classical van der Waals mixing rules were used for the solubility calculation of Acridine in supercritical CO_2. For a multicomponent mixture, the model parameters (a and b), using the mentioned mixing rules are written as below:

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{13}$$

$$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij}) \tag{14}$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \tag{15}$$

$$b_{ij} = \frac{(b_i + b_j)}{2}(1 - l_{ij}) \tag{16}$$

Where, a_{ij} and b_{ij} are the cross coefficient parameters and k_{ij} and l_{ij} are adjustable parameters, which are obtained by correlation of the experimental solubility data with the EOS.

Table 1: Molecular weight (*Mw*), acentric factor (ω), critical temperature (T_C), critical pressure (P_C) of used components and molar volume (v^s) and constants of sublimation pressure (P^{sub}) of Acridine (A and B).

Components	CO_2	Acridine
Mw/g.mol^{-1}	44 [22]	179.2 [18]
ω	0.225 [22]	0.428 [17,18]
T_C /K	304.2 [22]	890.10 [17,18]
P_C /bar	73 [22]	29.72 [17,18]
v^s /Cm^3.mol^{-1}	-	178 [8,18]
A[a]	-	13.721 [8]
B[a]	-	4740.1[8]

[a] $\log P^{(sub)}$ (Pa) =A-B/T (K) for use in the range of T= (308-343) K

When l_{ij} is set to zero, the co-volume parameter b is expressed by a linear mixing rule. Eq. (15) reduces to:

$$b = \sum_i y_i b_i \tag{17}$$

And van der Waals mixing rule will have only one adjustable parameter, k_{ij} (vdW 1 model).

The van der Waals mixing rules, especially with a single binary interaction parameter, (vdW 1) cannot describe highly non-ideal mixtures [20]. To solve this problem, some developed models use excess energy functions for calculating the mixture parameters of an EOS. The first successful one of these models that combines an EOS and excess Gibbs energy function was presented by Huron and Vidal. They suggested the mixing rule for high pressure phase equlibria calculations. The Huron and Vidal mixing rule correlation is:

$$a_m = b_m \left\{ \sum_i y_i \frac{a_i}{b_i} + \frac{g_\infty^E}{C^*} \right\} \tag{18}$$

Where, g_∞^E is the excess Gibbs energy of an appropriate activity coefficient model at infinite pressure and C^* is a constant that depends on the EOS and for the PR EOS, it is equal to:

$$C^* = -\frac{1}{2\sqrt{2}} \ln \left\{ \frac{2+\sqrt{2}}{2-\sqrt{2}} \right\} \tag{19}$$

While for the SRK EOS, it is equal to:

$$C^* = -\ln 2 \tag{20}$$

In this paper, NRTL activity coefficient model of Renon and Prausnitz [16] was used for calculation of the excess Gibbs energy at infinite pressure:

$$\frac{g_\infty^E}{RT} = \sum_{i=1}^{n} y_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} y_j}{\sum_{l=1}^{m} G_{li} y_l} \tag{21}$$

Where:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{22}$$

$$G_{ji} = \exp\,(-\alpha_{ji} \tau_{ji}) \tag{23}$$

$$\alpha_{ji} = \alpha_{ij} \tag{24}$$

τ_{ji} is adjustable interaction parameter of NRTL model, which is obtained from the correlation of experimental solubility data and α_{ji} is non-randomness parameter. The NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{ji} varies from about 0.2 to 0.47; when experimental data are scarce, the value of α_{ji} can often be set arbitrarily [21]. In this study α_{ji} is set equal to 0.3 in the calculations. As already mentioned, these models have one or two correlation interaction parameters, according to the mixing and combining rules employed.

3. Results and discussion

The solubility prediction of Acridine in supercritical CO_2 using cubic EOS requires the compounds critical properties. Table 1 summarizes the critical properties of the compounds along with the corresponding references [16,17,22] used in this study. The solubility of Acridine in supercritical CO_2 was measured at 313, 323 and 333 K in the pressure range of 120 - 350 bar and the obtained results are summarized in table 2.

The experimental data are plotted as a function of pressure in figure 2, along with experimental data reported by Schmitt et al. at T=318 K [8].

Table 2: Experimental solubility of Acridine (y_2) in SCCO$_2$ at T= (313, 323 and 333) K.

P /bar	y_2 at T/K		
	313	323	333
121.6	0.00033	0.00026	0.00013
152	0.00060	0.00068	0.00074
182.4	0.00085	0.00100	0.00131
212.8	0.00094	0.00124	0.00176
243.2	0.00101	0.00149	0.00220
273.6	0.00109	0.00170	0.00262
304	0.00115	0.00189	0.00308
334.4	0.00121	0.00210	0.00342
354.6	0.00126	0.00220	0.00365

Below the crossover pressure region, the effect of density is more dominant than the vapor pressure; indicated by the decrease of solubility as the temperature increases.

Figure 2 show that obtained experimental data are comparable with available experimental data in the literature at other temperature.

Above the crossover point, the solubility increases with the increase of temperature due to the dominant effect of vapor pressure. Also, at all temperatures, the solubility of Acridine increases by increasing of pressure.

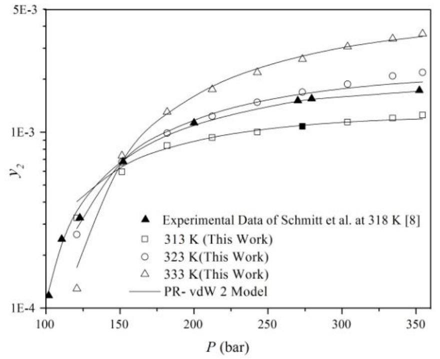

Figure 2: Experimental solubility of Acridine in SCCO$_2$ (y_2) against pressure (P) at different temperatures. Solid lines represent the calculated results from the PR EOS and vdW 2 mixing rule

Calculation of Acridine's solubility in supercritical CO_2 was accomplished using the Matlab software. The model parameters were obtained by minimizing the average absolute relative deviation function as follows:

$$\text{AARD}\ \% = \frac{100}{\text{N}} \sum_{1}^{\text{N}} \left| \frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}} \right| \qquad (25)$$

Where, y_{cal} and y_{exp} are the predicted and experimental mole fractions of the solute in the supercritical phase, respectively, and N is the number of experimental data. In these calculations, classical van der Waals mixing rule with one and two adjustable parameters and Huron-Vidal mixing rule with two adjustable parameters of NRTL equation for activity coefficient were used. The calculated solubilities of Acridine in SCCO$_2$ at 312, 323 and 333 K with PR EOS and vdW mixing rule with two adjustable parameters (vdW 2) are depicted in figure 2.

The sublimation pressure of high molecular weight compounds (like Acridine) is too small for accurate experimental measurement [19]. As suggested by other investigators the sublimation pressure can be considered as an adjustable parameter as well [19,20]. Thus, we considered this additional parameter in the calculation of solubility at the studied models. The comparison of PR and SRK EOSs with different mixing rules, used in this study for obtaining the correlation of Acridine's solubility in $SCCO_2$ at 333 K is shown in figure 3. It can be seen that the deviation of SRK EOS along with vdW 1 mixing rule from the solubility data is larger than that of other models.

The fitted parameters of vdW 1, vdW 2 and HV mixing rules for PR and SRK EOSs and the fitted sublimation pressures of Acridine as an additional adjustable parameter at different temperatures are summarized in table 3. Also the average absolute relative deviation (AARD %) of the models defined in equation (25) are presented in table 3.

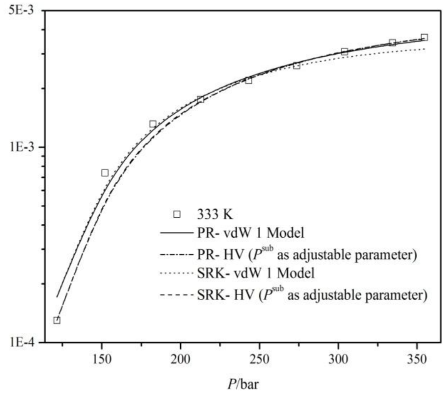

Figure 3: Comparison of the experimental solubility data of Acridine (y_2) at T= 333 K; with the calculated results of PR and SRK EOSs coupled with the different studied mixing rules.

As table 3 shows HV mixing rule with the AARD of 3.52% for PR EOS and 3.36% for SRK EOS at three temperatures, can correlate the experimental data better than vdW mixing rules. Also HV mixing rule is more effective in decreasing the AARDs of SRK model than those of PR model. When P^{sub} is considered as an additional adjustable parameter, it considerably decreases AARD result for both of the studied EOSs. As shown in table 3, considering of P^{sub} as an adjustable parameter can improve the capability of both PR and SRK EOS for correlating the solubility of Acridine in $SCCO_2$.

Using P^{sub} as an adjustable parameter along with HV mixing rule can reduce the AARD of both PR and SRK EOSs to 2.47% and 2.66%, respectively.

It can be seen that when the number of adjustable parameters are the same (in the case of vdW 2 and HV mixing rules) without considering P^{sub} as an adjustable parameter, HV mixing rule can correlate the experimental data completely better than van der Waals mixing rule. But considering P^{sub} as an adjustable parameter in the calculations decreases the differences in correlation results due to the intrinsic nature of employed EOSs and mixing rules.

4. Conclusions

The solubility of Acridine in supercritical CO2 was measured at 313, 323 and 333 K in the pressure range of 120 - 350 bar. The experimental data showed that the crossover pressure region for Acridine is observed at about 150 bar. The mole fraction of Acridine in SCCO2 at this pressure is in the range of $y_2 = 5\times10\wedge(-4) - 8\times10\wedge(-4)$. Modeling with different EOSs and mixing rules correlated the experimental solubility data very well.

HV mixing rule, which has been derived for high pressure phase equilibria calculations, reduced the deviation of solubility data calculations more than the classical vdW mixing model did. The average of AARD results by combining of PR EOS and HV mixing rule with NRTL activity coefficient model at three studied temperatures was about 3.52%, indicating that this model can correlate the solubility data of Acridine in $SCCO_2$ very well. This value for SRK EOS decreased to about 3.36%. This shows that applying of HV model on SRK EOS is more effective than the other models.

Also, it can be concluded that considering the sublimation pressure of solid (as additional adjustable parameter) can reduce deviation of PR and SRK EOSs to 2.47% and 2.66%, respectively.

Table 3: Fitted parameters and AARD % of the PR and SRK EOSs with different mixing rules at different temperatures

Model	Parameters at T/K	313	323	333	Average
PR– vdW 1	k_{12}	0.1041	0.1016	0.0893	
	AARD%	4.95	4.72	6.74	5.47
PR– vdW 2	k_{12}	0.0986	0.1024	0.1019	
	l_{12}	-3.1196	0.2231	2.1855	
	AARD%	4.70	4.71	5.82	5.08
PR– HV	τ_{12} of NRTL	10.442	8.893	7.775	
	τ_{21} of NRTL	-2.423	-2.125	-1.991	
	AARD%	2.92	1.97	5.67	3.52
PR – vdW1 (P^{sub} as parameter)	k_{12}	0.0775	0.0853	0.0605	
	P^{sub} fitted	1.580E-07	7.623E-07	1.544E-06	
	AARD%	3.05	2.81	4.62	3.49
PR – vdW2 (P^{sub} as parameter)	k_{12}	0.0740	0.0716	0.0859	
	l_{12}	5.2097	-1.7582	1.8029	
	P^{sub} fitted	1.082E-07	6.395E-07	2.160E-06	
	AARD%	1.91	2.35	4.51	2.93
PR– HV (P^{sub} as parameter)	τ_{12} of NRTL	16.600	10.472	1.697	
	τ_{21} of NRTL	3.331	-2.295	7.704	
	P^{sub} fitted	7.903E-05	1.678E-06	1.421E-06	
	AARD%	1.31	1.60	4.50	2.47
SRK– vdW 1	k_{12}	0.1071	0.1035	0.0907	
	AARD%	8.95	9.19	8.22	8.79
SRK– vdW 2	k_{12}	0.0959	0.1101	0.1060	
	l_{12}	-4.7705	1.8611	2.7269	
	AARD%	8.17	8.79	6.45	7.80
SRK– HV	τ_{12} of NRTL	12.247	10.164	8.757	
	τ_{21} of NRTL	-2.829	-2.503	-2.337	
	AARD%	2.42	2.43	5.22	3.36
SRK – vdW 1 (P^{sub} as parameter)	k_{12}	0.0486	0.0753	0.0546	
	P^{sub} fitted	6.976E-08	5.818E-07	1.404E-06	
	AARD%	2.76	4.45	4.77	3.99
SRK – vdW 2 (P^{sub} as parameter)	k_{12}	0.0594	0.0261	0.0594	
	l_{12}	2.5892	-4.0233	0.2555	
	P^{sub} fitted	7.824E-08	2.888E-07	1.495E-06	
	AARD%	2.36	4.01	4.76	3.71
SRK– HV (P^{sub} as parameter)	τ_{12} of NRTL	14.502	11.710	7.377	
	τ_{21} of NRTL	-2.353	-2.471	-2.311	
	P^{sub} fitted	2.156E-06	2.215E-06	1.676E-06	
	AARD%	1.92	1.73	4.33	2.66

But when sublimation pressure of solid is considered as an additional adjustable parameter the correlation results of different EOSs and mixing rules get closer together. Finally, PR-HV model with P^{sub} as adjustable parameter has the least deviation among the studied models.

Nomenclature

a	energy parameter of the cubic EOS ($Nm^4 .mol^{-2}$)
AARD	average absolute relative deviation
b	volume parameter for cubic EOS ($m^3 .mol^{-1}$)
C^*	constant of HV mixing rule
EOS	equation of state
HV	Huron - Vidal mixing rule
k_{ij}	adjustable parameter of vdW mixing rule
l_{ij}	adjustable parameter of vdW mixing rule
N	number of experimental points
M_w	molecular weight ($g.mol^{-1}$)
P	pressure (Pa)
P^{sub}	sublimation pressure (Pa)
PR	Peng-Robinson equation of state
R	ideal gas constant ($J. mol^{-1} .K^{-1}$)
$SCCO_2$	supercritical carbon dioxide
SCF	supercritical fluid
SRK	Soave-Redlich-Kwong equation of state
T	temperature (K)
v	molar volume ($m^3 .mol^{-1}$)
V	volume (m^3)
vdW 1	van der Waals mixing rule with one adjustable parameter
vdW 2	van der Waals mixing rule with two adjustable parameters
y	mole fraction solubility
y_2	mole fraction solubility of the solid in supercritical phase

Greek symbols

α_{ij}	non-randomness parameter of NRTL equation
$\alpha(T_r, \omega)$	temperature-dependent function in the attractive parameter of EOS
φ	fugacity coefficient
τ_{ji}	adjustable interaction parameter of NRTL equation
ω	Pitzer's acentric factor

Subscripts

1	solvent (SCF)
2	solute (solid)
C	critical property
cal	Calculated
exp	Experimental
i, j	component *i,j*

Superscripts

s	Solid
sub	Sublimation
SCF	supercritical fluid

References:

1- Coimbra, P., Duarte, C.M.M. and de Sousa, H.C. (2006). "Cubic equation-of-state correlation of the solubility of some anti-inflammatory drugs in supercritical carbon dioxide." *Fluid Phase Equilibria*, Vol. 239, PP. 188–199.

2- Garlapati, C. and Madras, G. (2010). "Solubilities of palmitic and stearic fatty acids in supercritical carbon dioxide." *Journal of Chemical Thermodynamics,* Vol. 42, PP. 193–197.

3- Park, C.I., Shin, M.S. and Kim, H. (2009). "Solubility of climbazole and triclocarban in supercritical carbon dioxide: Measurement and correlation." *Journal of Chemical Thermodynamics,* Vol. 41, PP. 30–34.

4- Huang, C. C., Tang, M., Tao, W.H. and Chen, Y.P. (2001). "Calculation of the solid solubilities in supercritical carbon dioxide using a modified mixing model." *Fluid Phase Equilibria,* Vol. 179, PP. 67–84.

5- Banchero, M., Ferri, A., Manna, L. and Sicardi, S. (2006). "Solubility of disperse dyes in supercritical carbon dioxide and ethanol." *Fluid Phase Equilibria,* Vol. 243, PP. 107–114.

6- Bahramifar, N., Yamini, Y. and Shamsipur, M. J. (2005). "Investigation on the supercritical carbon dioxide extraction of some polar drugs from spiked matrices and tablets." *Journal of Supercritical Fluids,* Vol. 35, PP. 205–211.

7- Hojjati, M., Yamini, Y., Khajeh, M. and Vatanara, A. (2007). "Solubility of some statin drugs in supercritical carbon dioxide and representing the solute solubility data with several density-based correlations." *Journal of Supercritical Fluids,* Vol. 41, No. 2, PP. 187–194.

8- Schmitt, W. J. and Reid, R. C., (1986). "Solubility of monofunctional organic solids in chemically diverse supercritical fluids." *Journal of Chemical and Engineering Data,* Vol. 31, PP. 204–212.

9- Dobbs, J. M., Wong, J. M., Lahiere, R. J. and Johnston, K. P. (1987). “Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents.” *Industrial & Engineering Chemistry Research,* Vol. 26, PP. 56–65.

10- Shibata, S. and Sandler, S. (1989). “Critical evaluation of equation of state mixing rules for the prediction of high-pressure phase equilibria.” *Industrial & Engineering Chemistry Research,* Vol. 28, PP. 1893–1898.

11- Sheng, Y.J., Chen, P.C., Chen, Y.P. and Wong, D.S.H. (1992). “Calculations of solubilities of aromatic compounds in supercritical carbon dioxide.” *Industrial & Engineering Chemistry Research,* Vol. 31, PP. 967–973.

12- Huron, M.J. and Vidal, J. (1979). “New Mixing Rules in Simple Equation of State for Representing Vapor-Liquid Equilibria of Strongly Non-ideal Mixtures.” *Fluid Phase Equilibria,* Vol. 3, PP. 255–271.

13- Peng, D.Y. and Robinson, D.B. (1976). “A new two constant equation of state.” *Industrial & Engineering Chemistry Fundamentals,* Vol. 15, PP. 59–64.

14- Soave, G. (1993). “Equilibrium constants from a modified Redlich–Kwong equation of state.” *Chemical Engineering Science,* Vol. 27, PP. 1197–1203.

15- Yamini, Y., Fathi, M. R., Alizadeh, N. and Shamsipur, M. (1998). “Solubility of Dihdroxybenzene Isomers in Supercritical Carbon Dioxide.” *Fluid Phase Equilibria,* Vol. 152, PP. 299–305.

16- Renon, H. and Prausnitz, J.M. (1965). “Local compositions in thermodynamic excess functions for liquid mixtures.” *AIChE Journal,* Vol. 14, PP. 135–144.

17- Bartle, K.D., Clifford, A.A. and Shilstone, G.F. (1992). “A model for dynamic extraction using a supercritical fluid.” *Journal of Supercritical Fluids,* Vol. 5, PP. 220–225.

18- Skerger, M., Novk-Pintaric, Z., Kenz, Z. and Kravanja, Z. (2002). “Estimation of solid solubilities in supercritical carbon dioxide: Peng–Robinson adjustable binary parameters in the near critical region.” *Fluid Phase Equilibria,* Vol. 203, PP. 111–132.

19- Gordillo, M.D., Blanco, M.A., Pereyra, C. and Mart´ınez de la Ossa, E.J. (2005). “Thermodynamic modeling of supercritical fluid–solid phase equilibrium data.” *Computers & Chemical Engineering,* Vol. 29, PP. 1885–1890.

20- Reverchon, E., Della Porta, G., Taddeo, R., Pallado, P. and Stassi, A. (1995). “Solubility and micronization of Griseofulvin in supercritical CHF3.” *Industrial & Engineering Chemistry Research* ,Vol. 34, PP. 4087–4091.

21- Prausnitz, J.M., Rüdiger, N.L. and Gomes de Azevedo, E. (1999). *Molecular Thermodynamics of Fluid-Phase Equilibria. 3*th. Ed., Prentice-Hall Pub. Co. New Jersey.

22- Reid, R.C. Prausnitz, J.M. and Poling, B.E. (1987). *The Properties of Gases and Liquids. 4th*. Ed., McGraw-Hill Book Co. New York.