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RESEARCH ARTICLE

A Novel Equation of State: Determination and Validation for Dyes and Drugs Solubility Calculations in Supercritical Carbon Dioxide

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Abstract

Based on Pitzer correlations for the compressibility factor and virial equation of state, a new equation of state has been developed in this study, which is a function of total number of atoms present in the solute molecule, normal boiling point temperature and reduced temperature. Thirty dyes and sixty drugs solubility data, 2417 data points, have been collected from literature and compared with the Peng-Robinson EOS plus the two adjustable parameters van der Waals mixing rules, and the new proposed EOS. As the results show, the proposed EOS presents more accurate predictions for solubility data in Supercritical Carbon Dioxide.

Keywords

Carbon dioxide · Phase Equilibria · State equation · Supercritical fluid · Thermodynamics Process · Solubility

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1 Introduction

Supercritical fluid processes have been attracted considerable attentions in recent years. This technology is increasingly applied in chemical and petroleum, pharmaceutical, food, biotechnology, biomedical, nuclear, material and polymer processing industries [1-18]. The need for automated, simpler, faster, non-destructive and selective methods for extraction preferably can be fulfilled by employing supercritical fluid technology using non-toxic extraction media, which are easily disposed of. Supercritical fluids have unique physical and chemical properties and usually low toxicity and this technology is an environment friendly one. By setting suitable operating condition (temperature, pressure and density) a desired selectivity can be obtained which leads to a variation in solvating power [19]. Supercritical fluids are categorized as rapid processes due to high diffusivity and lower viscosity. One of the most commonly used supercritical fluids is carbon dioxide. The critical temperature and pressure of carbon dioxide is relatively low, 304 K and 73.7 bar, respectively. Supercritical carbon dioxide is low in cost, nontoxic, and nonflammable, and the carbon dioxide can be recycled and has no environmental hazard [20, 21].

For the design of supercritical fluid process, there is a vital need to know about the solubility data and mathematical modeling of these solubility data [22-25]. In fact, mathematical modeling provides better understanding of the process and also can be used for the prediction of solubility at interested pressures and temperatures. Mathematical modeling leads to different equations of solubility data in supercritical carbon dioxide. Generally, these models are classified into two groups: theoretical or semi-empirical equations (such as models based on equations of state), and empirical equations (such as density based equations).

Some researchers tend to use empirical correlations such as density-based correlations [26-28] or the Ziger–Eckert semi-empirical correlations [29]. These models are based on the simple error minimization and they use only density of pure supercritical carbon dioxide and operational pressure and temperature. Several equations have been presented by different

authors, covering from three to six parameters, which are necessary to determine solutes solubility. But these empirical correlations require accurate experimental solubility data in order to obtain the best coefficients of the models.

On the other hand, using theoretical models such as cubic equation of state require the knowledge of the solute (dyes here) properties including critical properties, acentric factor, molar volumes and sublimation pressure. These properties should be calculated using some group contribution method if these data are unavailable in the literature [30].

Based on Pitzer correlations [31] for the compressibility factor and virial equation, a new equation of state has been developed in this study as the supercritical fluids are assumed like a gas in modeling. The new equation is a function of n, total number of atoms present in the solute molecule, and T_b, normal boiling point temperature and reduced temperature. Solubility data of thirty dyes and sixty drugs are collected from literature and correlated with the Peng-Robinson EOS [32] plus the two adjustable parameters van der Waals mixing rules, and the proposed EOS. Two types of components i.e. dyes and drugs are used to ensure the generality of the obtained EOS. As the results show, the proposed EOS presents more accurate predictions for solubility data in Supercritical Carbon Dioxide.

2 Theoretical

2.1 Peng-Robinson EOS (PR EOS)

The solubility of a solute at equilibrium with a supercritical fluid can be calculated using Eq. 1.

$$y_2 = \frac{P_2^{sat}}{P}\frac{1}{\varphi_2^{SCF}}\exp\left[\frac{v_2^l\left(P-P_2^{sat}\right)}{RT}\right] \tag{1}$$

In solubility calculation using Eq. 1, an equation of state is used to calculate the fugacity coefficient which representing the non-ideality of the fluid phase φ_2^{SCF}. Here P_2^{sat} is the saturation pressure of solute, which can be measured experimentally or calculated using some estimation methods from literature. v_2^l is the molar volume of the solute.

The Peng-Robinson equation of state (PR-EOS) which is commonly used in studies is defined as follows.

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{2}$$

$$a = 0.45724\left(\frac{R^2T_c^2}{P_c}\right)\left[1+m\left[1-T_r^{0.5}\right]\right]^2 \tag{3}$$

$$m = 0.37464 + 1.5422\omega - 0.2699\omega^2 \tag{4}$$

$$b = 0.7780\frac{RT_c}{P_c} \tag{5}$$

For a binary mixture the PR-EOS needs some mixing rules. In this study we employed the van der Waals (vdW) mixing rules, with two adjustable parameters, k_{ij} and l_{ij} (vdW2).

$$a = \sum_i\sum_j y_i y_j \left(a_i a_j\right)^{0.5}\left(1-k_{ij}\right) \tag{6}$$

$$b = \sum_i\sum_j y_i y_j \left(\frac{b_i+b_j}{2}\right)\left(1-l_{ij}\right) \tag{7}$$

k_{ij} and l_{ij} are the binary interaction parameters which are obtained by fitting experimental data and through minimization of an objective function. The fugacity coefficient for a component i in a mixture is given by Prausnitz using mixing rules as follows [33].

$$\ln\overline{\varphi_i} = \frac{b_i}{b}\left(\frac{Pv}{RT}-1\right) - \ln\frac{P(v-b)}{RT} - \frac{a}{2\sqrt{2}bRT}\left[\frac{2\sum_j y_j a_{ij}}{a} - \frac{b_i}{b}\right]\ln\frac{v+\left(1+\sqrt{2}\right)b}{v+\left(1-\sqrt{2}\right)b} \tag{8}$$

Here y_j is the mole fraction of component j.

2.2 Theory of Proposed Equation of State

For development of the new EOS, Berlin virial EOS which is power series in pressure has been used preferably.

$$Z = 1 + B'P + C'P^2 + \cdots \tag{9}$$

Where coefficients, B', C' and etc. are virial equivalent coefficients.

$$B' = \frac{B}{RT}, C' \approx \frac{C-B^2}{(RT)^2}, \cdots\cdots \tag{10}$$

Pitzer and Curl [34] proposed a correlation for $\overline{B}$ $\left(=\frac{BP_c}{RT_c}\right)$ as follows.

$$\frac{BP_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \tag{11}$$

Here the function $f^{(0)}$ represents the reduced second virial coefficient for simple fluid, i.e. ω = 0 and the function $f^{(1)}$ is a correlation represents the effect of eccentricity. These two functions were obtained from experimental data and modified by[35]. Pitzer et al. proposed a second correlation for $\overline{B}$ [31].

$$\overline{B} = B^{(0)} + \omega B^{(1)} \tag{12}$$

Where $B^{(0)}$ and $B^{(1)}$ are function of T_r only and given by following equations.

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{13a}$$

$$B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{13b}$$

Orbey and Vera [36] expressed the reduced temperature depended coefficients of a Pitzer type correlation for $\overline{C}$, which itself is related to third virial coefficient through $\frac{CP_c^2}{(RT_c)^2}$, as illustrated for B as follows.

$$C^{(0)} = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{10.5}} \tag{14a}$$

$$C^{(1)} = -0.02676 + \frac{0.05539}{T_r^{2.7}} - \frac{0.00242}{T_r^{10.5}} \tag{14b}$$

So following equations can be obtained for B' and C'.

$$B' = \frac{T_c}{P_c}\frac{1}{T}\left(B^{(0)} + \omega B^{(1)}\right) \tag{15}$$

$$C' = \left(\frac{T_c}{P_c}\right)^2 \frac{1}{T^2}\left[\left(C^{(0)} + \omega C^{(1)}\right) - \left(B^{(0)} + \omega B^{(1)}\right)^2\right] \tag{16}$$

As mentioned previously, $B^{(0)}$, $B^{(1)}$, $C^{(0)}$ and $C^{(1)}$ are functions of reduced temperature only. According to Lee and Kessler equation for acentric factor, it can be seen that ω is a function of critical temperature and pressure, and also normal boiling point temperature. As critical properties such as critical temperature and pressure for all materials always can't be measured experimentally or their values aren't available in literature, one has to use some group contribution methods like Joback and Reid method for calculation of their value. In fact, Group Contribution Methods relate these critical properties to chemical structure of materials [37]. Thus, From the work of Joback and Reid, it's can be shown that critical temperature and pressure, themselves, are a function of total number of atoms present in material, n, and normal boiling point temperature, T_b, in the form of following equation.

$$\theta = \alpha + \beta n + \gamma T_b \tag{17}$$

Here θ is the critical property of interest. α, β and γ are constants for each critical property of interest. So far, we qualitatively found that acentric factor and critical temperature and pressure, and consequently virial coefficients, can be expressed as functions of n and T_b. Finding these desired functions, new functions can be found for virial coefficients of Eq. 9 by introducing Eq. 15 and 16 into it and the new EOS is obtained. The experimental data of 30 dyes and 60 drugs were used to formulate the critical temperature in the form of Eq. 17 and finding its coefficients. Where there's an absent of experimental normal boiling point temperature data, one can use some group contribution method for estimation of T_b. Equation 18 shows this new obtained relation in this work for T_c (**R^2>0.99**). The reason for such replacement is that the need for complicated calculations of chemical structure and arrangement of bonds and groups could be resolved in this way. Then the applicability of obtained new equation for T_c calculation, Eq. 18, for other materials was validated using the available data of 60 drugs and it found that the Eq. 18 can be used for other materials also.

$$T_c = 55.7812 + 1.434T_b - 1.88n \tag{18}$$

In development of the new EOS, M is defined as the ratio of P and T (P/T), the operating parameter of new EOS. The definition is with regard to the appearance of the reciprocal of T in Eq. 15 and 16 and P in corresponding term in Eq. 9. So by this definition, T and P are merged as the new parameter M. This definition also makes the estimation of P_c possible as formulation of critical pressure in the form of Eq. 17 will never result in constant coefficients. The critical pressure appears in nominator of the critical M, M_c. So by finding the functionality of M_c to n and T_b, the critical pressure can be determined indirectly, in other words P_c can be calculated by multiplying T_c into the M_c. Equation 19 is derived and validated in the way described above for T_c in this work (**R^2>0.99**).

$$\begin{aligned} 1/M_c = {} & 0.0053 + 1.782\times10^{-10}\left(10^4 n + \left(T_b - 198.2\right)^3\right) \\ & + 3.019\times10^{-5}\left(T_b - 198.2\right) \\ & - 1.178\times10^{-7}\left(T_b - 198.2\right)^2 \end{aligned} \tag{19}$$

So the critical value of M, M_c, together with Eq. 18 can be used to estimate the critical pressure. Moreover ω can be calculated using following new proposed equation in this paper (**R^2>0.98**).

$$\omega = \frac{0.1861T_b}{55.8712 + 0.4343T_b - 1.884n}\left(\ln P_c - 0.0131\right) - 1 \tag{20}$$

Inserting Eq. 15 and 16 into Eq. 9, the general form of new EOS is formed as Eq. 21. Separating the new parameter M in each term, what remains is the general coefficient of new EOS, $A^{(1)}$ and $A^{(2)}$.

$$Z = 1 + A^{(1)}M + A^{(2)}M^{(2)} \tag{21}$$

The coefficients $A^{(1)}$ and $A^{(2)}$ are formulated in a Pitzer like form as shown Eq. 22 and 22.

$$A^{(1)} = k_0^{(1)}\left(k_1^{(1)} + \omega k_2^{(1)}\right) \tag{22}$$

$$A^{(2)} = k_0^{(2)}\left(k_1^{(2)} + \omega k_2^{(2)}\right) - \left(A^{(1)}\right)^2 \tag{23}$$

Here $A^{(1)}$ and $A^{(2)}$ are two different functions of new independent variables n and T_b, and as well as T_r, structural parameters. For development of these two coefficients of new EOS and their parameters, the obtained equations for critical properties, acentric factor, and the new parameter M are used and the coefficients of these parameters are found. Then the drugs data are used for evaluation of applicability and generality of coefficients and formulas for using for materials other than the dyes. The obtained functions of these parameters as a function of new independent variable T_b and n are (All with **R^2>0.99**).

$$k_0^{(1)} = -0.005341 + 6.185\times10^{-6} n + 3.056\times10^{-5}\left(T_b - 198.2\right) - 6.834\times10^{-8}\left(T_b - 198.2\right)n - 1.173\times10^{-7}\left(T_b - 198.2\right)^2 + 2.201\times10^{-10}\left(T_b - 198.2\right)^2 n + 1.709\times10^{-10}\left(T_b - 198.2\right)^3 \quad (24)$$

$$k_1^{(1)} = \frac{0.3608T_r - 0.8658}{T_r^2 + 0.6689T_r - 0.02824} \quad (25)$$

$$k_2^{(1)} = \frac{5.716T_r - 3.408}{T_r^2 + 0.1656T_r - 0.007622} \quad (26)$$

And for $A^{(2)}$ we have also

$$k_0^{(2)} = 2.748\times10^{-5} + 1.826\times10^{-7}\left(n + 1.5575T_b - 308.6965\right) + 1.177\times10^{-8} n^2 - 3.75\times10^{-9} n\left(T_b - 198.2\right) - 2.805\times10^{-10}\left(T_b - 198.2\right)^2 \quad (27)$$

$$k_1^{(2)} = -0.00313T_r^{-10.5} + 0.02008 \quad (28)$$

$$k_2^{(2)} = \alpha / \beta$$

$$\alpha = -2.566T_r^6 + 290.8T_r^5 - 12820T_r^4 + 2.694\times10^5 T_r^3 - 2.677\times10^6 T_r^2 + 1.066\times10^7 T_r - 1.01\times10^7 \quad (29)$$

$$\beta = 95.89T_r^6 - 10870T_r^5 + 479000T_r^4 - 1.007\times10^7 T_r^3 + 10^8 T_r^2 - 3.985\times10^8 T_r + 3.775\times10^8$$

Although that choosing coefficients $A^{(1)}$ and $A^{(2)}$ in a Pitzer like form leads to these complicated relationships (Eq. 24-29), but attentions would be given to the accuracy that can be achieved using this EOS with these parameters which will be shown in section 4.

In order to use this new EOS for a binary mixture, Pseudo parameters are defined for the normal boiling temperature and the total number of atoms. Pseudo n and T_b can be obtained by solving following system of two equations for a binary mixture (Eq. 30-31). Using experimental solubility data, the value of Pseudo n and T_b can be obtained through solving the system of two equations formed employing an objective function, **OF**,

$$OF = \sum\left(\frac{y^{cal} - y^{\exp}}{y^{\exp}}\right)^2$$

and finding the best optimal value of the adjustable parameter K_{ij}. Then the new EOS can be used for the binary mixture calculations with these calculated pseudo n and T_b.

$$T_{pc} = \sum_i y_i\left(1 - K_{ij}\right)T_{ci} \quad (30)$$

$$P_{pc} = \sum_i y_i\left(1 - K_{ij}\right)P_{ci} \quad (31)$$

Finally the fugacity coefficient of component i in the fluid mixture is expressed as.

$$\ln\overline{\varphi_i} = \int_0^P \frac{\left(Z_i - 1\right)}{P} dP \quad (32)$$

$$M = \frac{P}{T} \rightarrow dP = TdM \quad (33)$$

Inserting relations in Eq. 34 into Eq. 33, we get the fugacity coefficient as following function.

$$\ln\overline{\varphi_i} = A^{(1)}MT + \frac{A^{(2)}M^2T^2}{2} \quad (34)$$

3 Material and Methods

Solubility data of thirty dyes and sixty drugs, a large number of solubility data more than 2417 data points, have been collected from literature [10, 11, 38-91]. Table 1 shows the details of these solubility data, references, temperature and pressure ranges, and number of data points for each system. All estimated critical properties and molecular weight of these dyes are listed in Table 2. These critical properties are calculated using proposed equations in this paper. In order to compare the accuracy of the new EOS with PR-EOS as a reference, it is assumed that all the experimental data are correct. The objective function, **OF**,

$$OF = \sum\left(\frac{y^{cal} - y^{\exp}}{y^{\exp}}\right)^2$$

has been minimized using experimental solubility data of each system of study by the well-known optimization method of genetic algorithm in MATLAB (R2009a) environment [92]. The reported AARD in Figures is Average absolute relative deviation and defined as following function, for comparison of calculated solubility values and experimental ones.

$$AARD(\%) = \frac{100}{N}\sum\left(\frac{\left|y_2^{Cal} - y_2^{Exp}\right|}{y_2^{Exp}}\right) \quad (35)$$

Where y_2^{Cal} and y_2^{Exp} are calculated and experimental solubility of solute respectively. N is the number of experimental data points.

Tab. 1. The details of studied solute in supercritical carbon dioxide

No.	Solute	N_p [a]	Temperature(K)	Pressure(bar)	References
1	(Rac) Boc-piperazine	19	308–328	90–200	Uchida et al., 2004
2	(S) Boc-piperazine	21	308–328	90–200	Uchida et al., 2004
3	1,4-Naphthoquinone	18	318–343	100–360	Schmitt and Reid, 1986
4	1,5-NDA	27	313.15-333.15	110-200	Khimeche et al., 2007
5	1-methyl-aminonthraquinone	4	313.15-393.15	100-250	Joung and Yoo, 1998
6	2-methyl-N-phenylacetamide	24	308.2-328.2	121.6-225.0	Huang et al., 2007
7	3,3,4,5,7-Pentahydroxy flavone	8	308–318	100–250	Matsuyama et al., 2003
8	4-methyl-N-phenylacetamide	24	308.2-328.2	121.6-225.0	Huang et al., 2007
9	7,8-Dihydroxy flavone	9	308–318	90–250	Matsuyama et al., 2003
10	9,10-Anthraquinone	17	308–318	80–310	Joung et al., 1998
11	AC03	69	305-340	79-190	Wagner et al., 1999
12	Amical-48	18	318–338	100–300	Sahle-Demessie et al., 2003
13	APAN	15	283.15-383.15	200-350	Özcan et al., 1997
14	AQ2	45	308-348	122-355	Shamsipur et al., 2004
15	AQ3	45	308-348	122-355	Shamsipur et al., 2004
16	AQ4	45	308-348	122-355	Shamsipur et al., 2004
17	AQ5	45	308-348	122-355	Shamsipur et al., 2004
18	AQ6	45	308-348	122-355	Shamsipur et al., 2004
19	Artemisinin	36	310–338	100–270	Xing et al., 2003
20	Ascorbyl palmitate	8	308–313	130–200	Cortesi et al., 1999
21	Aspirin	24	308–328	120–250	Huang et al., 2004
22	Azobenzene	14	308.2-333.2	91-253	Maeda et al., 2001
23	Beclomethasoneipropionate	21	338–358	210–390	Elvassore et al., 2005
24	Benzocaine	40	308–348	120–360	Garmroodi et al., 2004
25	Bisacodyl	39	308–348	120–360	Asghari-Khiavi and Yamini, 2003
26	Blue 134	15	323.15-383.15	100-250	Tamura and Shinoda, 2004
27	Blue 14	12	313.15-393.15	100-250	Gordillo et al., 2003;Gordillo et al., 2005;Joung and Yoo, 1998
28	Blue 3	23	323.7-413.7	105.1-329.8	Cabral et al., 2007; Lee et al., 2001
29	Blue 60	45	313.15-423.15	150.8-342.0	Coimbra et al., 2005
30	Blue 79	12	353.2-393.2	150-300	Cabral et al., 2007;Lee et al., 2001; Lin et al., 2001; Banchero et al., 2006
31	Blue 79:1	12	353.2-393.2	150-300	Lin et al., 2004
32	Budesonide	21	338–358	210–390	Elvassore et al., 2005
33	Caffeine	56	313–368	80–350	Burgos-Solórzano et al., 2004; Li et al., 1991; Johannsen and Brunner, 1994
34	Carbamazepine	39	308–348	120–360	Yamini et al., 2001

35	Chlorothalonil	23	318–338	100–300	Sahle-Demessie et al., 2003
36	Cholesterol	24	313–333	100–250	Asghari-Khiavi et al., 2004; Yun et al., 1991
37	Cholesteryl acetate	24	308–328	90–240	Asghari-Khiavi et al., 2004
38	Cholesteryl benzoate	20	308–328	120–270	Asghari-Khiavi et al., 2004
39	Cholesteryl butyrate	20	308–328	100–240	Asghari-Khiavi et al., 2004
40	Codeine	45	308–348	120–360	Yamini et al., 2001
41	D1	45	308-348	122-355	Fasihi et al., 2004
42	D2	45	308-348	122-355	Fasihi et al., 2004
43	D3	45	328-358	122-355	Fasihi et al., 2004
44	DADPM	27	313.15-333.15	110-200	Khimeche et al., 2007
45	DDT	18	313–333	100–210	Macnaughton and Foster, 1994
46	Diazepam	45	308–348	120–360	Yamini et al., 2001
47	DY82	6	283.15-383.15	200-300	Özcan et al., 1997
48	Eflucimibe	20	308–318	80–300	Sauceau et al., 2004
49	Erythromycin	8	313–333	100–300	Burgos-Solórzano et al., 2004
50	Ferulic acid	18	313–333	120–280	Sovová, 2001
51	Flurbiprofen	27	303–323	80–250	Duarte et al., 2004
52	Ketoprofen	25	313–332	90–250	Stassi et al., 2000; Macnaughton et al., 1996
53	Medroxyprogesterone acetate	48	308–348	110–360	Mu et al., 2004
54	Methimazole	40	308–348	120–360	Asghari-Khiavi and Yamini, 2003
55	Methyl gallate	27	313–333	100–500	Murga et al., 2002
56	Methylparaben	40	308–348	120–360	Asghari-Khiavi and Yamini, 2003
57	Metronidazole benzoate	40	308–348	120–360	Garmroodi et al., 2004
58	Modified Yellow 119	12	353.2-393.2	200-300	Lin et al., 2004
59	Mordant Brown	8	333.15-353.15	132-195	Guzel and Akgerman, 1999
60	Mordant Red 11	8	333.15-353.15	132-189	Guzel and Akgerman, 1999
61	Naproxen	58	308–348	90–360	Garmroodi et al., 2004; Ting et al., 1993
62	Nifedipine	29	333–373	130–300	Knez et al., 1995
63	Nimesulide	8	313–332	130–220	Macnaughton et al., 1996
64	Nimodipine	21	313–333	100–250	Medina and Bueno, 2001
65	N-phenylacetamide	24	308.2-328.2	104.4-225.0	Huang et al., 2007
66	Orange 11	8	333.15-353.15	132-193	Guzel and Akgerman, 1999; Joung and Yoo, 1998
67	Orange 3	20	323.7-413.7	101.3-310.6	Cabral et al., 2007; Lee et al., 1999; Banchero et al., 2006
68	p-Coumaric acid	29	313–333	90–500	Murga et al., 2003
69	p-Dimethylaminoazobenzene	14	308.2-333.2	91-253	Gordillo et al., 1991
70	Penicillin G	18	313–333	100–350	Gordillo et al., 1999

71	Phenazopyridine	45	308–348	120–360	Asghari-Khiavi and Yamini, 2003
72	Photochromic Dye	19	308-328	105-256	Coimbra et al., 2005
73	p-Hydroxyazobenzene	14	308.2-333.2	91-253	Maeda et al., 2001
74	Piroxicam	9	313–332	100–220	Macnaughton et al., 1996
75	p-Quinone	18	308–318	90–290	Joung et al., 1998
76	Progesterone	11	313–333	90–240	Alessi et al., 1996
77	Propranolol	45	308–348	120–360	Asghari-Khiavi and Yamini, 2003
78	Propyl gallate	8	313–333	150–250	Cortesi et al., 1999
79	Protocatechualdehyde	24	313–333	100–500	Murga et al., 2002
80	Protocatechuic acid	24	313–333	100–500	Murga et al., 2002
81	Red 1	12	313.15-393.15	100-250	Shinoda and Tamura, 2003
82	Red 153	8	353.2-393.2	150-300	Lin et al., 2001
83	Red 60	45	313.15-423.15	98.5-335.4	Cabral et al., 2007; Lee et al., 1999
84	Red 73	15	343-383	120-280	Jinhua et al., 2010;Dong et al., 2010
85	Red 82	12	353.2-393.2	150-300	Lin et al., 2004
86	Salicylic acid	11	313–328	90–250	Stassi et al., 2000
87	Stigmasterol	19	308–333	90–300	Wong and Johnston, 1986
88	Sulfadimethoxine	19	313–333	130–490	Hampson et al., 1999
89	Sulfamerazine	18	313–333	150–470	Hampson et al., 1999
90	Syringic acid	27	313–333	90–500	Murga et al., 2004
91	Tebuconazole	12	323–338	100–300	Sahle-Demessie et al., 2003
92	Theobromine	23	313–353	190–350	Johannsen and Brunner, 1994
93	Theophylline	24	313–353	200–350	Johannsen and Brunner, 1994
94	Uracil	12	313–333	100–300	Burgos-Solórzano et al., 2004
95	Vanillic acid	28	313–333	90–500	Murga et al., 2004
96	Vitamin C	4	313–333	130–200	Cortesi et al., 1999
97	Yellow 119	15	353.2-393.2	150-300	Dong et al., 2010; Lin et al., 2001
98	Yellow 16	15	323.15-383.15	100-250	Tamura and Shinoda, 2004
99	Yellow 7	8	333.15-353.15	132-193	Guzel and Akgerman, 1999; Joung and Yoo, 1998
100	Zopiclone	21	313–333	100–250	Medina and Bueno, 2001

[a] N_p denotes number of data points

Tab. 2. The details of studied solute in supercritical carbon dioxide

No.	Solute	Formula	T_c (K)	P_c(bar)	ω	Mw(gr/mole)	n	T_b (K)
1	(Rac) Boc-piperazine	$C_{14}H_{27}N_3O_3$	954.30	19.53	0.807	285.38	47	381.05
2	(S) Boc-piperazine	$C_{14}H_{27}N_3O_3$	951.15	19.46	0.805	285.38	47	376.33
3	1,4-Naphthoquinone	$C_{10}H_6O_2$	594.32	73.48	0.3988	158.15	18	399.15
4	1,5-NDA	$C_{10}H_{15}N_2$	886.30	43.39	0.7141	158.20	27	628.88
5	1-methyl-aminonthraquinone	$C_{15}H_{11}NO_2$	1071.4	30.1895	0.9693	246.26	39	759.37
6	2-methyl-N-phenylacetamide	$C_9H_{11}NO$	761.01	35.01	0.625	149.19	22	383.2
7	3,3,4,5,7-Pentahydroxy flavone	$C_{15}H_{10}O_7$	837.59	85.78	0.4802	302.24	32	587.15
8	4-methyl-N-phenylacetamide	$C_9H_{11}NO$	761.01	35.01	0.625	149.19	22	421.7
9	7,8-Dihydroxy flavone	$C_{15}H_{10}O_4$	801.57	86.509	0.4713	254.24	29	558.1
10	9,10-Anthraquinone	$C_{14}H_8O_2$	812.48	87.624	0.4559	208.21	24	559.15
11	AC03	$C_{20}H_{22}N_2O_2$	1036.7	42.496	1.9388	322.4	46	744.35
12	Amical-48	$C_8H_8O_2SI_2$	619.11	73.924	0.5253	422.02	46	453.15
13	APAN	$C_{16}H_{13}N_3O$	1189.7	27.0985	1.0855	263.294	33	693.4
14	AQ2	$C_{15}H_{20}O_3$	631.07	75.57	0.4922	238.25	38	449-453
15	AQ3	$C_{15}H_{18}O_4Me$	576.58	70.457	0.4863	268.27	38	411-415
16	AQ4	$C_{15}H_{18}O_4Et$	560.80	68.92	0.4844	282.30	38	401-403
17	AQ5	$C_{15}H_{18}O_4Pr$	541.80	67.08	0.4822	296.23	38	388-389.5
18	AQ6	$C_{15}H_{18}O_4Bu$	533.204	66.25	0.4813	310.35	38	382.5-383
19	Artemisinin	$C_{15}H_{22}O_5$	592.93	71.77	0.5060	282.33	42	429.65
20	Ascorbyl palmitate	$C_{22}H_{38}O_7$	488.57	60	0.6312	414.53	67	389.65
21	Aspirin	$C_9H_8O_4$	600.45	73.86	0.4136	180.16	21	407.36
22	Azobenzene	$C_{12}H_{10}N_2$	792.9	25.8	0.496	182.22	24	566
23	Beclomethasoneipropionate	$C_{28}H_{37}ClO_7$	479.45	58.83	0.6654	521.04	73	391.15
24	Benzocaine	$C_9H_{11}NO_2$	533.15	67.36	0.4072	165.19	23	363.05
25	Bisacodyl	$C_{22}H_{19}NO_4$	554.76	67.84	0.5219	361.39	46	408.27
26	Blue 134	$C_{20}H_{22}N_2O_2$	940.6	19.1358	1.23165	322.401	46	677.33
27	Blue 14	$C_{16}H_{14}N_2O_2$	1143.8	27.1833	1.1876	266.3	34	803.30
28	Blue 3	$C_{17}H_{16}N_2O_3$	1237.29	29.2184	1.4985	296	38	453.6
29	Blue 60	$C_{20}H_{19}NO_3$	1159.75	20.4931	1.1775	321.37	43	826.22
30	Blue 79	$C_{24}H_{27}N_6O_{10}Br$	1982.6	10.631	0.79663	639.42	68	420.2
31	Blue 79:1	$C_{23}H_{25}N_6O_{10}Br$	2064.8	12.0396	0.85749	625.39	55	413.3
32	Budesonide	$C_{25}H_{34}O_6$	650.07	74.77	0.6033	430.53	65	499.65
33	Caffeine	$C_8H_{10}N_4O_2$	742.40	85.25	0.4506	194.19	24	510.28
34	Carbamazepine	$C_{15}H_{12}N_2O$	665.07	79.14	0.4634	236.27	30	464.22
35	Chlorothalonil	$C_8Cl_4N_2$	780.01	88.50	0.4208	265.91	14	523.4
36	Cholesterol	$C_{27}H_{46}O$	520.60	62.85	0.6614	386.65	74	421.16
37	Cholesteryl acetate	$C_{29}H_{48}O_2$	463.56	56.91	0.7032	428.69	79	387.94
38	Cholesteryl benzoate	$C_{34}H_{50}O_2$	498.89	60.06	0.7290	490.76	86	421.75
39	Cholesteryl butyrate	$C_{31}H_{52}O_2$	429.64	53.19	0.7520	456.76	85	372.15

40	Codeine	$C_{18}H_{21}NO_3$	511.74	61.38	0.7196	299.36	85	429.4
41	D1	$C_{14}H_{14}N_4O_2$	1148.49	21.0034	0.92634	270.12	34	488-489
42	D2	$C_{16}H_{18}N_4O_2$	1184.61	16.8241	0.95803	298.14	40	418-419
43	D3	$C_{16}H_{11}N_3O_3$	1322.78	25.5592	1.18618	293.13	33	529-530
44	DADPM	$C_{13}H_{14}N_2$	925.64	34.80	0.7614	198.27	29	672.15
45	DDT	$C_{14}H_9Cl_5$	550.42	68.59	0.4353	354.48	28	381.65
46	Diazepam	$C_{16}H_{13}ClN_2O$	570.06	70.14	0.4623	284.74	33	401.9
47	DY82	$C_{20}H_{19}N_3O_2$	1233.8	23.4282	1.238	333.384	44	879.17
48	Eflucimibe	$C_{29}H_{43}NO_2S$	491.01	59.81	0.6786	469.73	76	403.15
49	Erythromycin	$C_{37}H_{67}NO_{13}$	499.89	58.39	0.8952	733.93	118	464.4
50	Ferulic acid	$C_{10}H_{10}O_4$	649.006	78.21	0.4365	194.18	24	445.15
51	Flurbiprofen	$C_{15}H_{13}FO_2$	548.01	68.15	0.4492	244.26	31	383.9
52	Ketoprofen	$C_{16}H_{14}O_3$	520.23	65.38	0.4546	254.28	33	367.15
53	Medroxyprogesterone acetate	$C_{24}H_{34}O_4$	628.40	73.45	0.5928	386.54	62	480.6
54	Methimazole	$C_4H_6N_2S$	631.92	77.40	0.3868	114.17	13	418.82
55	Methyl gallate	$C_8H_8O_5$	697.91	82.59	0.4333	184.15	21	475.32
56	Methylparaben	$C_8H_8O_3$	596.91	73.66	0.4039	152.15	19	402.27
57	Metronidazole benzoate	$C_{13}H_{13}N_3O_4$	531.70	66.46	0.4563	275.27	33	375.15
58	Modified Yellow 119	$C_{15}H_{12}N_5O_4Cl$	1500.14	19.3213	1.44514	362.05	37	501.2
59	Mordant Brown	$C_{10}H_7NO_2$	881.95	45.2249	0.7111	173.168	20	602.34
60	Mordant Red 11	$C_{14}H_8O_4$	1170.67	49.3151	1.33176	240.211	26	811.55
61	Naproxen	$C_{14}H_{14}O_3$	610.16	74.12	0.4595	230.26	31	427.24
62	Nifedipine	$C_{17}H_{18}N_2O_6$	622.02	74.68	0.49	346.33	39	446
63	Nimesulide	$C_{13}H_{12}N_2O_5S$	598.38	72.87	0.4665	308.31	33	421.65
64	Nimodipine	$C_{21}H_{26}N_2O_7$	521.44	63.97	0.5706	418.44	56	398.15
65	N-phenylacetamide	C_8H_9NO	735.85	40.11	0.577	135.17	19	387.5
66	Orange 11	$C_{15}H_{11}NO_2$	1059.5	25.9513	0.94905	242	29	737.96
67	Orange 3	$C_{12}H_{10}N_5O_2$	1103.88	31.1752	0.99369	237.253	29	481.0
68	p-Coumaric acid	$C_9H_8O_3$	715.79	84.03	0.4325	164.16	20	486.48
69	p-Dimethylaminoazobenzene	$C_{14}H_{15}N_3$	839.8	21.1	0.635	225.29	32	384
70	Penicillin G	$C_{16}H_{18}N_2O_4S$	1034.6	67.7	0.5	334.39	41	736.31
71	Phenazopyridine	$C_{11}H_{11}N_5$	596.04	73.04	0.4394	213.24	27	412.15
72	Photochromic Dye	$C_{30}H_{30}N_3O$	1446.2	14.36	1.169	448.58	64	450
73	p-Hydroxyazobenzene	$C_{12}H_{10}N_2O$	877.2	30.2	0.720	198.22	25	642.812
74	Piroxicam	$C_{15}H_{13}N_3O_4S$	660.86	78.29	0.4870	331.35	36	469.15
75	p-Quinone	$C_6H_4O_2$	592.69	73.75	0.3715	108.09	12	390.15
76	Progesterone	$C_{21}H_{30}O_2$	529.95	64.98	0.5554	314.46	53	400.15
77	Propranolol	$C_{16}H_{21}NO_2$	509.94	63.903	0.4889	259.35	40	369.15
78	Propyl gallate	$C_{10}H_{12}O_5$	611.81	74.54	0.4424	212.2	27	423.15
79	Protocatechualdehyde	$C_7H_6O_3$	637.27	77.70	0.4008	138.12	16	426.48
80	Protocatechuic acid	$C_7H_6O_4$	702.07	83.29	0.4189	154.12	17	472.98

81	Red 1	$C_{16}H_{18}N_4O_3$	1242.6	6.7746	0.3829	314.15	41	881.37
82	Red 153	$C_{18}H_{15}N_5Cl_2S$	1418.5	18.0156	1.2971	404.32	41	440
83	Red 60	$C_{20}H_{13}NO_4$	1337.7	24.8506	1.56541	331.322	38	459.2
84	Red 73	$C_{18}H_{16}N_6O_2$	1475.2	13.137	1.14723	348.359	42	1044.9
85	Red 82	$C_{21}H_{21}N_5O_6$	1657.29	9.85163	0.96028	439.43	53	402.3
86	Salicylic acid	$C_7H_6O_3$	645.53	78.47	0.4028	138.12	16	432.24
87	Stigmasterol	$C_{29}H_{48}O$	533.14	63.85	0.6786	412.69	78	435.15
88	Sulfadimethoxine	$C_{12}H_{14}N_4O_4S$	672.42	79.31	0.4841	310.33	35	475.9
89	Sulfamerazine	$C_{11}H_{12}N_4O_2S$	720.96	82.65	0.4881	264.3	35	509.75
90	Syringic acid	$C_9H_{10}O_5$	697.40	82.27	0.4447	198.17	24	478.9
91	Tebuconazole	$C_{16}H_{22}ClN_3O$	516.77	64.34	0.5048	307.83	43	377.85
92	Theobromine	$C_7H_8N_4O_2$	905.38	86.34	0.4468	180.16	21	620
93	Theophylline	$C_7H_8N_4O_2$	801.41	88.02	0.4458	180.16	21	547.5
94	Uracil	$C_4H_4N_2O_2$	907.45	88.85	0.4230	122.09	12	609.65
95	Vanillic acid	$C_8H_8O_4$	710.24	83.62	0.43	168.15	20	482.61
96	Vitamin C	$C_6H_8O_6$	685.20	81.66	0.4272	176.12	20	465.15
97	Yellow 119	$C_{15}H_{13}N_5O_4$	1453.4	20.7554	1.45226	327.3	37	540
98	Yellow 16	$C_{16}H_{14}N_4O$	917.1	25.611	0.9046	278.309	35	646.52
99	Yellow 7	$C_{19}H_{16}N_4O$	1389.7	16.6055	1.05428	316.357	40	982.64
100	Zopiclone	$C_{17}H_{17}ClN_6O_3$	620.01	74.14	0.5168	388.808	44	451.15

4 Results and Discussion

The Accumulative AARD% values of each system of dyes, in order of appearance in Table 1, for proposed EOS and PR-EOS are shown in Fig. 1. As it can be seen, the new EOS has lower Accumulative AARD% values than PR-EOS. So, it can be concluded that the proposed EOS presented more accurate result for solubility prediction and correlation in supercritical carbon dioxide. Also as a key system (due to largest data points among other systems), Fig. 2 shows the AARD% values corresponding to system 11, AC03, at a range of temperatures. Again it can be concluded that the new EOS is more successful in solubility correlation than PR-EOS. The performance of New EOS for Drugs data is shown in Fig. 3. We provide Fig. 4 as pressure- composition graph of D_2, showing the fitted isotherms at 308K and the experimental points used. Studies on applicability and generality of the new EOS on other solutes (60 Drugs solubility data, 1417 data points) show that the EOS will reveal even more accurate results if the Eq. 22 extended to third order in term of M (pressure to temperature ratio). This extension and derivation of practical thermodynamics relationships from this proposed EOS will be discussed later. It's clear that the proposed EOS in this paper is able to predict and correlate the solubility of any solute in supercritical carbon dioxide.

5 Conclusion

In this study, solubility of thirty dyes and sixty drugs in supercritical carbon dioxide have been used for evaluation and assessment of the new proposed EOS accuracy in correlation of solubility data in supercritical fluids. The solubility data were correlated with two equation of state; PR-EOS together with two adjustable parameter van der Waals mixing and combining rules and Proposed EOS. As the results show the mean AARD for the new EOS is significantly lower than that obtained from PR-EOS. The new EOS presented more accurate prediction for solubility data in supercritical CO_2.

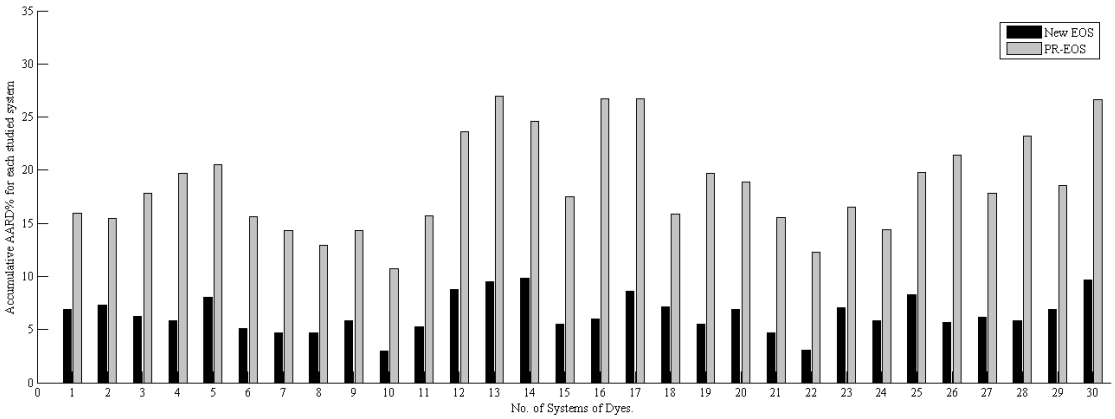

Fig. 1. The Accumulative AARD% values of each system, in order of appearance in Table 1, for proposed EOS and PR-EOS for Dyes.

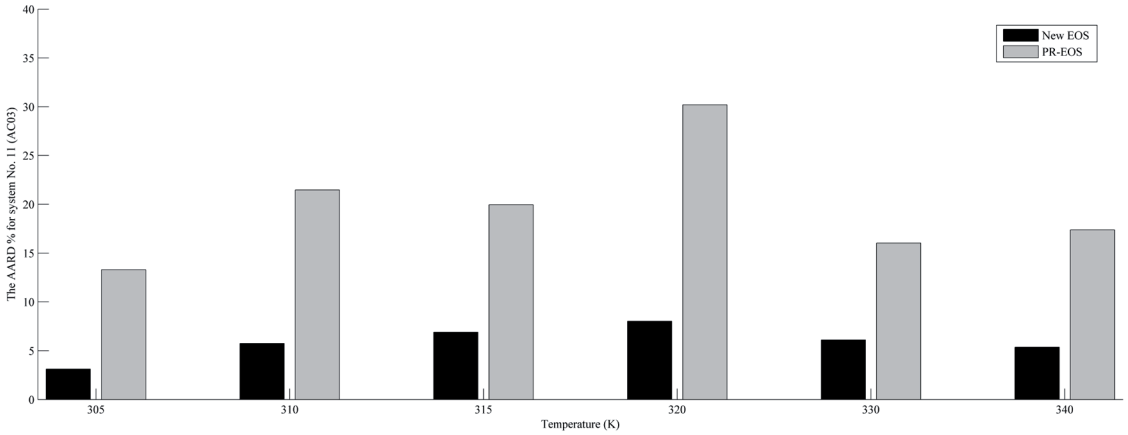

Fig. 2. The AARD% values corresponding to system 11, AC03, at a range of temperatures.

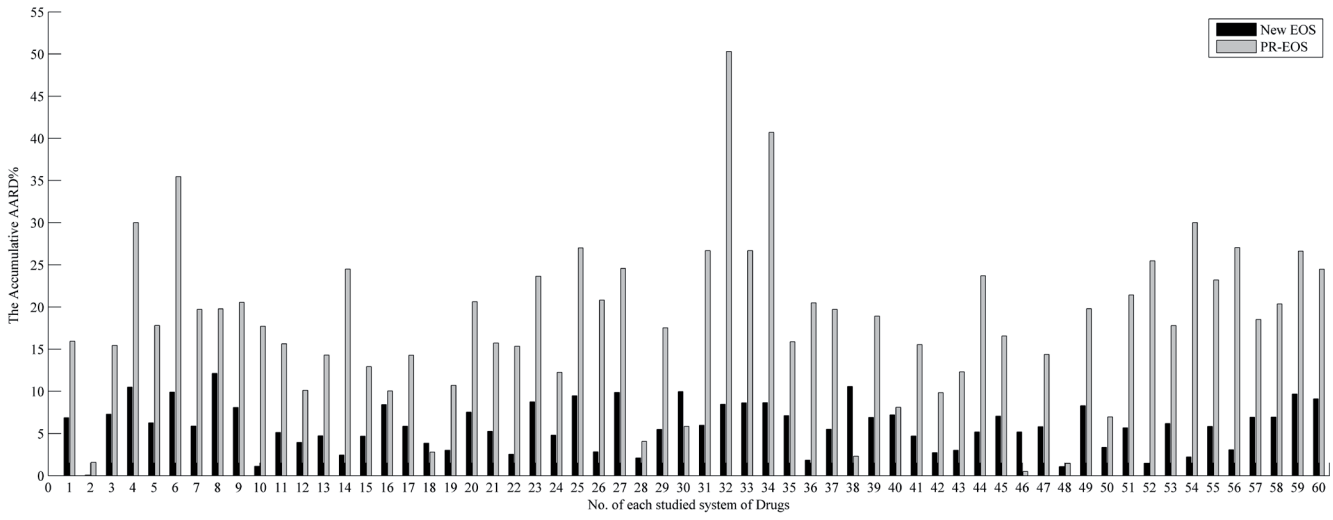

Fig. 3. The Accumulative AARD% values of each system, in order of appearance in Table 1, for proposed EOS and PR-EOS for Drugs.

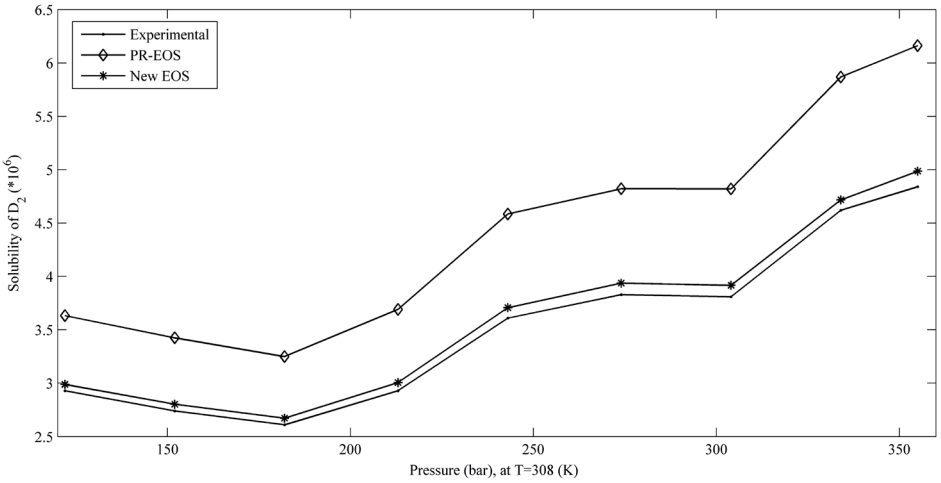

Fig. 4. The pressure- composition graph for D_2 at isotherm 308K.

Nomenclature

α	energy parameter of the cubic equation of state (Nm^4mol^{-2})
A	coefficients of new EOS
AARD	average absolute relative deviation (%)
b	volume parameter in the PR EOS and in the SRK EOS (m^3mol^{-1})
A, B, C, D …	virial coefficients
A', B', C', D',	virial coefficients
EOS	equation of state
GCM	group contribution method
k	coefficients of proposed EOS
k_{ij}	binary interaction parameters
l_{ij}	binary interaction parameters
M	proposed EOS parameter
Mw	molecular weight
N	number of data points
n	number of atoms
P	pressure (Pa)
PR	Peng-Robinson
R	ideal gas constant ($Jmol^{-1}K^{-1}$)
T	temperature (K)
ν	molar volume (cm^3mol^{-1})
vdW2	van der Waals mixing and combining rules with two adjustable parameters
y	mole fraction
Z	compressibility factor

Greek Symbols

α, β, γ	coefficients of Equation (19)
φ	fugacity coefficient
ω	Pitzer's acentric factor

Subscripts

1	solvent
2	solute
avg	average
b	boiling point
c	critical property
i, j	components
ps	pseudo
r	reduced

Superscripts

0, 1, 2	indices for new EOS coefficients
cal	calculated
exp	experimental
l	liquid
SCF	supercritical fluid
sat	saturation

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