A Simple Thermodynamic Model for the Solubility of Thermolabile Solids in Supercritical Fluids

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Abstract

An equation-of-state (EoS) scheme to correlate the solubility of solids in supercritical fluids is presented. The solute fugacity coefficient is obtained using the pure-solvent compressibility factor, and empirical solute-to-solvent parameter ratios of cohesion factors and covolumes. The proposed method is simpler than EoS conventional calculations since no iteration is required. We retain the link to classical cubic EoS and mixing rules and showcase the application employing both the Redlich-Kwong and Peng-Robinson EoS. The method uses two adjustable parameters, which are computed from experimental data for several binary systems and used to predict solubilities. The results have been favorably compared to those computed by other methods. The advantage of EoS-based models over empirical ones has been emphasized for cases where the solubilities are extrapolated beyond the range of experimental data. The proposal is advantageous for correlating solubility of thermolabile solids in supercritical fluids since no critical properties of the solute are required.

Keywords:

Solubility model; high-molar-mass solids; supercritical fluid; equation-of-state model

1. INTRODUCTION

The continuing development of supercritical fluid technology includes applications in biotechnology, chromatography, food industry, petrochemical industry, and textiles. In a typical application, a supercritical fluid (SFC) is used to extract or dissolve thermolabile compounds, such as active pharmaceutical ingredients, nutraceuticals, food additives, or dyes and pigments. These solutes are characterized by having a high molar mass thus are normally solid at room conditions. Furthermore, the extent to which they dissolve in the SCF is small. The challenge at hand is two-fold, on one hand, the accurate measurement of these solubilities and on the other hand the modeling or correlation of the often sparse data. A recent book (Santos et al., 2020) describes various applications of biorefining using supercritical fluids, with techniques such as micronization, coprecipitation, and fractionation to processes such as valorization of plant materials, and vanillin and carotenoids production. Other recent studies have also reviewed the state of the art concerning measurements and correlations for pharmaceuticals (Baghbana et al., 2018; Sodeifian et al., 2018; Jahromi and Roosta, 2019), for food components (de la Fuente et al., 2006; Topal et al., 2006), for dyes and pigments (Tamura and Alwi, 2015; Cui et al., 2018; Shi et al., 2018), for solid alkanes (Sedaghat and Esfandiarian, 2019), and in electronic applications such as liquid-crystal (LED) displays (Tamura and Fukamizu, 2019).

The work presented here focuses on models used to correlate experimental data of solubility of thermolabile compounds in SCF. Most of these models fall within two main categories: those based on equations of state (EoS), on one hand, and the so-called density-based models on the other hand.

Density-based models derive from the original work of Chrastil (1982). Although Chrastil provided a theoretical justification to his model, in practice the model and its modifications are used as empirical correlations. It is a handy equation and quite useful to correlate experimental solubility data. A good summary of its modifications and a critical analysis of them is presented by Sparks et al. (2008). Moreover, Sparks et al. (2008) proposed two modifications of their own, which contain 5 and 6 adjustable constants, respectively:

$$c_2^* = \rho_{r,1}^{e_0+e_1\rho_{r,1}} \exp\left(\alpha + \frac{\beta}{T_r} + \frac{\gamma}{T_r^2}\right) \quad (1)$$

$$c_2^* = \rho_{r,1}^{e_0+e_1\rho_{r,1}+\rho_{r,1}^2} \exp\left(\alpha + \frac{\beta}{T_r} + \frac{\gamma}{T_r^2}\right) \quad (2)$$

where notation used in the original reference has been used here; note that α and β here are different from the ones used below in our model. EoS-based models are a thermodynamically sound alternative for solubility calculations, but not devoid of implementation issues. When dealing with thermolabile, solid solutes, some of the limitations become evident: (a) EoS-based methods require the knowledge of the critical properties of the solute. However, these properties are rarely accessible from experiments, as they correspond to temperatures much above the thermal decomposition limits for organic matter, hence they have to be estimated; (b) To fine-tune the method, one or two empirical adjustable parameters are employed (usually referred to as binary interaction parameters or simply BIPs), which are determined by regression from experimental data; (c) As the BIPs depend on the method used to estimate the critical properties of the solute, they are presumably correcting shortcomings in both the EoS and in the estimation of the critical properties. That also implies that for a given set of experimental solubility data, the BIPs will depend on the method used to predict the critical properties. One might think that

the variation of critical-property estimation by the various available methods is unimportant, but this is not necessarily true. Karim (2008) estimated several properties (including critical properties) of disperse orange 30 dye. For critical temperature, he used five different methods and the values obtained varied from 892 [K] to 1811 [K]; for critical pressure the results varied from 1.33 [MPa] to 9.59 [MPa] using four different estimation methods. Those results show a dramatic difference in results for the various estimation methods, which emphasizes the advantages of using a method that is independent of the critical properties of the solute. Even using sound estimation methods, e.g., Kazakov et al. (2010), a contribution of the U.S. National Institute of Standards and Technology (NIST), the variability of the critical temperature and pressure will affect the values of the model parameters. The results from Karim (2008) mentioned above just dramatize this effect.

In this work, a new EoS-based method is proposed. The proposed model has the following key features:

1. The EoS parameters are grouped into two adjustable parameters in such a way that the solute's critical properties are not needed.
2. Since solubility is expected to be low, the infinite-dilution approximation is used to compute all concentration-dependent parameters, including the fugacity coefficient of the solute in the SCF phase.

The second feature represents a significant simplification of the computational aspect of the model since it eliminates the need for an iterative scheme. Using the infinite-dilution concept renders the compressibility factor and the fugacity coefficient of the solute in the SCF-phase independent of the mole fraction (solubility) of the solute. The conventional

iterative procedure is thus substituted by a once-through calculation. The modifications or simplifications proposed herein can be used with any EoS. In this work, we exemplify the procedure using the Redlich-Kwong and Peng-Robinson EoS as they are mathematically simple and widely used.

To benchmark the model, results are compared to the two empirical equations proposed by Sparks et al. (2008), namely, Eqs. (1) and (2) above.

2. THE PROPOSED MODEL

As mentioned above, the model proposed here can be applied to any equation of state (EoS), and it is presented here for the Redlich-Kwong EoS and the Peng-Robinson EoS. In both cases (or with any other EoS), the starting point for the calculation of the solubility of a low-sublimation-pressure solid in a supercritical fluid is (Prausnitz et al., 1998, p. 192):

$$y_2 = \frac{P_2^{sub}}{P\hat{\phi}_2^V} \exp\left(\frac{V_2^{sol}P}{RT}\right) \quad (3)$$

where P_2^{sub} and V_2^{sol} are the sublimation pressure and molar volume of the solid at the temperature T , while P is the total pressure. Every term on the RHS of equation (3), except $\hat{\phi}_2^V$, is known if the solid properties (P_2^{sub}, V_2^{sol}) are known. Therefore, the model presented herein focuses on the computation of $\hat{\phi}_2^V$. Hereinafter, the superscript V will be omitted to simplify the notation in the understanding that $\hat{\phi}_2$ refers to the vapor or supercritical fluid phase.

2.1. Redlich/Kwong EoS

The Redlich/Kwong EoS can be expressed as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (4)$$

The corresponding expression for $\hat{\phi}_2$ is:

$$\ln \hat{\phi}_2 = (Z-1) \frac{b_2}{b_1} - \ln(Z-B) + \frac{a}{bRT^{1.5}} \left[\frac{2(y_1 a_{12} + y_2 a_2)}{a} - \frac{b_2}{b} \right] \ln \frac{Z+B}{Z} \quad (5)$$

As seen, y_2 appears both explicitly and implicitly through Z , which depends on the composition of the supercritical phase. For the fluid-phase parameters a and b , standard van der Waals mixing rules are used:

$$a = y_1^2 a_1 + 2y_1 y_2 a_{12} + y_2^2 a_2 \quad (6)$$

and:

$$b = y_1 b_1 + y_2 b_2 \quad (7)$$

For the infinite-dilution limit ($y_2 \rightarrow 0, y_1 \rightarrow 1, a \rightarrow a_1, b \rightarrow b_1$, and $Z \rightarrow Z_1$), equation (2) reduces to:

$$\ln \hat{\phi}_2^\infty = (Z-1) \frac{b_2}{b_1} - \ln(Z-B) + \frac{A}{B} \left(\frac{2a_{12}}{a_1} - \frac{b_2}{b_1} \right) \ln \frac{Z+B}{Z} \quad (8)$$

When using the standard combination rule for a_{12} :

$$a_{12} = \sqrt{a_1 a_2} \quad (9)$$

equation (8) can be written as:

$$\ln \hat{\phi}_2^\infty = (Z-1) \frac{b_2}{b_1} - \ln(Z-B) + \frac{A}{B} \left(2 \sqrt{\frac{a_2}{a_1}} - \frac{b_2}{b_1} \right) \ln \frac{Z+B}{Z} \quad (10)$$

where A and B are defined at infinite dilution as:

$$A = \frac{\left(\frac{a_1}{\sqrt{T}} \right) P}{(RT)^2}, \quad a_1 = \Omega_a \frac{R^2 T_{c1}^{2.5}}{P_{c1}}, \quad A = \Omega_a \frac{P_r}{T_r^{2.5}} \quad (11)$$

$$B = \frac{b_1 P}{RT}, \quad b_1 = \Omega_b \frac{RT_{c1}}{P_{c1}}, \quad B = \Omega_b \frac{P_r}{T_r} \quad (12)$$

$$\Omega_a = \frac{1}{9(\sqrt[3]{2}-1)} = 0.427480, \quad \Omega_b = \frac{\sqrt[3]{2}-1}{3} = 0.086640 \quad (13)$$

The reduced properties are normalized with respect to the critical properties of the *solvent*.

The key feature of the proposed model is the recognition that in equation (10) the only two parameters that depend on the properties of the solute are the cohesion parameter a_2 and the covolume b_2 . In rigor, these should be calculated using the critical properties of the solute (which are essentially unknown). Furthermore, the values would be modulated using a BIP. Given both the uncertainty surrounding the determination of critical constants for high-molar-mass substances and the need to further adjust these numbers, it makes sense to define the parameters α and β , as:

$$\alpha \equiv \sqrt{\frac{a_2}{a_1}} \quad \text{and} \quad \beta \equiv \frac{b_2}{b_1} \quad (14)$$

The final equation for the infinite-dilution fugacity coefficient of the solute in the supercritical fluid phase is thus obtained:

$$\ln \hat{\phi}_2^\infty = \beta(Z-1) - \ln(Z-B) + \frac{A}{B}(\beta - 2\alpha) \ln \frac{Z+B}{Z} \quad (15)$$

Note that up to equation (13), the development is standard. If α and β are treated as the sole adjustable parameter in the model, the procedure is simplified two-fold: The equation (15) is no longer implicit in terms of the unknown (solubility), and the unknown parameters are lumped together into constants α and β . Hereinafter, this model will be referred to as the Redlich/Kwong version of the Estévez-Colpas-Müller model or simply ECM-RK.

2.2. Peng/Robinson EoS

The Peng/Robinson EoS can be expressed as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (16)$$

A derivation analogous to the previous one may be followed for the Peng-Robinson EOS. In

this case, the expression for $\hat{\phi}_2^\infty$, (cf. equation (5)), is:

$$\ln \hat{\phi}_2^\infty = (Z-1) \frac{b_2}{b_1} - \ln(Z-B) + \frac{A}{2\sqrt{2}B} \left[\frac{2a_{12}}{a_1} - \frac{b_2}{b_1} \right] \ln \frac{Z+B(1-\sqrt{2})}{Z+B(1+\sqrt{2})} \quad (17)$$

Using equation (9) above for a_{12} , the previous equation becomes:

$$\ln \hat{\phi}_2^\infty = (Z-1) \frac{b_2}{b_1} - \ln(Z-B) + \frac{A}{2\sqrt{2}B} \left[2\sqrt{\frac{a_2}{a_1}} - \frac{b_2}{b_1} \right] \ln \frac{Z+B(1-\sqrt{2})}{Z+B(1+\sqrt{2})} \quad (18)$$

Defining parameters α and β again as in equations (14), the equation for the infinite-dilution fugacity coefficient of the solute in the supercritical fluid phase is:

$$\ln \hat{\phi}_2^\infty = \beta(Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B} (\beta - 2\alpha) \ln \frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})} \quad (19)$$

Again, reduced properties are normalized with respect to the solvent critical properties

and A and B are defined at infinite dilution as:

$$A = \frac{a_1 P}{(RT)^2}, \quad a_1 = \Omega_a \frac{R^2 T_{c1}^2}{P_{c1}} \left[1 + (0.37464 + 1.54226\omega - 0.2699\omega^2) (1 - \sqrt{T_r}) \right]^2 \quad (20)$$

$$B = \frac{b_1 P}{RT}, \quad b_1 = \Omega_b \frac{RT_{c1}}{P_{c1}} \quad (21)$$

$$\Omega_a = 0.457235529, \quad \Omega_b = 0.077796074 \quad (22)$$

Hereinafter, this model will be referred to as the Peng-Robinson version of the Estévez-Colpas-Müller model or simply ECM-PR.

3. COMPUTATION OF α AND β FROM EXPERIMENTAL DATA

As mentioned, two types of computations were carried out. First, a limited database of α and β values was created and presented in section 3.1 for the nearly 130 isotherms analyzed by Caballero et al. (1992). Secondly, the proposed model was benchmarked by calculating the errors for the six systems analyzed by Sparks et al. (2008).

3.1. Database of α and β values

A database consisting of about 130 experimental isotherms (Caballero et al., 1992) was employed to regress values of α and β for combinations of five solvents and twelve solutes. The same molar mass (M), critical properties (P_c , T_c), and acentric factors (ω) used by Caballero et al. (1992) for the solvents, listed in Table 1, were used here for a fair comparison purpose. The values used by Caballero et al. (1992) for molar mass (M), Antoine constants (A_A , B_A), and molar volume (V^{sol}) of the solutes, listed in Table 2, were used here with no modification for the same reason. The Antoine equation used in this work, that gives P^{sub} in [Pa] when T is in [K], is:

$$\log P^{sub} = A_A + \frac{B_A}{T} \quad (23)$$

The values of solubility were predicted from the proposed model using the best set of parameters α and β . The parameters were obtained by minimizing the objective function used by Caballero et al. (1992), equation (22) of their publication:

$$OF_1 = \sqrt{\frac{1}{N_p} \sum_{i=1}^{N_p} (y_{i,calc} - y_{i,exp})^2} \quad (24)$$

in which N_p is the number of experimental points for each isotherm.

Table 1. Properties of the solvents as used by Caballero et al., (1992)

Solvent	CAS number	M [g/mol]	P_c [MPa]	T_c [K]	ω [–]	Ref. key (*)
Chlorotrifluoromethane	75-72-9	104.46	3.92	301.95	0.108	<i>a</i>
Carbon dioxide	124-38-9	44.01	7.38	304.25	0.225	<i>a</i>
Ethane	74-84-0	30.07	4.88	305.35	0.098	<i>a</i>
Ethylene	74-85-1	28.054	5.03	282.4	0.089	<i>b</i>
Fluoroform	75-46-7	70.013	4.88	299.15	0.275	<i>a</i>

(*) References are listed in Table 4 according to this reference key

Table 2. Properties of the solutes as used by Caballero et al., (1992)

solute	M [g/mol]	A_A [–]	B_A [K]	V^{sol} [L/mol]	Ref. key (*)
Benzoic acid	122.124	14.408	4618.1	0.0965	<i>c</i>
Naphthalene	128.174	13.583	3733.9	0.1103	<i>a</i>
2,3-Dimethylnaphthalene	156.23	14.0646	4302.5	0.1547	<i>c</i>
2,6-Dimethylnaphthalene	156.23	14.4286	4419.5	0.1547	<i>c</i>
1,4-Naphthoquinone	158.16	14.735	4739.4	0.1112	<i>a</i>
Hexamethylbenzene	162.276	13.1336	3855	0.1526	<i>c</i>
Fluorene	166.23	14.2046	4561.8	0.1393	<i>c</i>
Anthracene	178.234	12.147	4397.6	0.1426	<i>f,g</i>
Phenanthrene	178.24	14.631	4873.4	0.1512	<i>f,g</i>
Acridine	179.22	13.721	4740.1	0.1783	<i>a</i>
Hexachloroethane	236.74	10.6322	2600.94	0.1132	<i>d</i>
Triphenylmethane	244.34	14.785	5228	0.2409	<i>c</i>

(*) References are listed in Table 4 according to this reference key.

Table 3. Values of α and β for the ECM-PR and ECM-RK EoS (*)

Solvent	$T, ^\circ\text{C}$	ECM Peng-Robinson			ECM Redlich-Kwong			Ref. key (†)
		α	β	RMSE, %	α	β	RMSE, %	
1,4 Naphthoquinone								
CHF ₃	45	4.766	4.495	16.65	4.625	3.921	14.66	<i>a</i>
CHF ₃	55	4.450	3.688	11.06	4.200	3.004	13.35	<i>a</i>
C ₂ H ₆	35	3.931	3.808	4.91	3.981	3.573	4.87	<i>a</i>
C ₂ H ₆	45	3.900	3.680	3.32	3.918	3.387	3.10	<i>a</i>
C ₂ H ₆	55	3.993	3.848	9.24	3.984	3.503	8.48	<i>a</i>
C ₂ H ₆	70	3.862	3.528	6.86	3.813	3.135	6.11	<i>a</i>
CClF ₃	45	3.667	3.363	13.18	3.634	3.029	11.64	<i>a</i>
CClF ₃	55	3.583	3.108	7.42	3.503	2.723	5.80	<i>a</i>
CO ₂	45	5.221	5.664	8.71	5.127	5.075	6.40	<i>a</i>
CO ₂	55	5.233	5.610	4.08	5.012	4.799	1.50	<i>a</i>
CO ₂	70				5.005	4.729	0.90	<i>a</i>
2,3 Dimethylnaphthalene								
C ₂ H ₄	35	4.752	4.325	2.03	4.744	3.907	1.98	<i>e</i>
C ₂ H ₄	45	4.623	3.847	3.07	4.578	3.377	3.24	<i>e</i>
C ₂ H ₄	55	4.567	3.495	0.60	4.485	2.976	1.05	<i>e</i>
CO ₂	35	4.934	6.274	5.12	4.929	5.883	5.15	<i>e</i>
CO ₂	45	4.991	6.291	3.44	4.860	5.633	3.09	<i>e</i>
C ₂ H ₄	35	4.818	4.293	3.02	4.816	3.882	3.35	<i>e</i>
C ₂ H ₄	45	4.632	3.660	1.43	4.592	3.200	1.57	<i>e</i>
C ₂ H ₄	55	4.195	2.167	2.74	4.129	1.720	2.36	<i>e</i>
CO ₂	35	5.007	6.249	2.72	5.010	5.866	2.85	<i>e</i>
CO ₂	45	5.318	7.103	2.52	5.172	6.387	1.00	<i>e</i>
CO ₂	55	5.319	7.084	1.86	5.042	6.099	1.14	<i>e</i>
Acridine								
C ₂ H ₄	45	5.280	5.611	13.63	5.113	4.943	12.63	<i>a</i>
C ₂ H ₄	55	5.205	5.336	11.68	4.944	4.569	9.76	<i>a</i>
C ₂ H ₆	35	5.237	5.919	6.11	5.286	5.577	6.35	<i>a</i>
C ₂ H ₆	55	4.903	4.786	13.47	4.906	4.382	13.07	<i>a</i>
C ₂ H ₆	70				4.981	4.440	7.11	<i>a</i>
CClF ₃	45	4.432	4.305	13.02	4.393	3.895	11.95	<i>a</i>
CClF ₃	55	4.492	4.333	10.71	4.390	3.835	8.63	<i>a</i>
CO ₂	35	5.592	6.616	7.41	5.603	6.185	7.27	<i>a</i>
CO ₂	45	5.856	7.145	2.64	5.723	6.421	3.68	<i>a</i>
CO ₂	55	6.048	7.534	22.46	5.809	6.624	20.44	<i>a</i>
CO ₂	70	5.840	6.790	4.61	5.408	5.572	3.26	<i>a</i>
Anthracene								

Solvent	$T, ^\circ\text{C}$	ECM Peng-Robinson			ECM Redlich-Kwong			Ref. key (†)
		α	β	RMSE, %	α	β	RMSE, %	
C ₂ H ₄	50	5.182	4.631	3.69	5.144	4.149	3.43	<i>f</i>
C ₂ H ₄	70	5.275	4.667	9.52	5.144	4.044	9.04	<i>g</i>
C ₂ H ₄	85	5.622	5.203	6.75	5.434	4.493	6.56	<i>g</i>
C ₂ H ₆	30	4.413	4.082	8.88	4.467	3.795	8.99	<i>f</i>
C ₂ H ₆	35	4.343	3.925	7.84	4.388	3.630	8.51	<i>f</i>
C ₂ H ₆	50	4.501	4.081	6.49	4.514	3.726	6.48	<i>h</i>
C ₂ H ₆	70	4.713	4.322	7.99	4.677	3.884	7.76	<i>h</i>
CO ₂	30	5.060	5.930	5.77	5.113	5.613	6.10	<i>h</i>
CO ₂	34.85				5.132	5.553	13.89	<i>f</i>
CO ₂	44.85	5.501	6.893	5.67	5.346	6.130	7.63	<i>f</i>
CO ₂	50	5.317	6.296	4.90	5.150	5.572	5.96	<i>f</i>
CO ₂	70	5.579	6.593	6.62	5.171	5.446	6.89	<i>f</i>
Benzoic acid								
C ₂ H ₄	45	4.923	4.331	8.06	4.859	3.793	8.20	<i>e</i>
C ₂ H ₄	55	5.003	4.438	2.71	4.902	3.838	3.13	<i>e</i>
C ₂ H ₄	65	4.959	4.163	1.25	4.818	3.513	1.51	<i>e</i>
CO ₂	45	5.055	5.404	4.12	4.933	4.748	3.97	<i>e</i>
CO ₂	55	4.703	4.183	5.82	4.448	3.304	4.98	<i>e</i>
CO ₂	65	4.631	3.717	0.56	4.218	2.554	1.63	<i>e</i>
Fluorene								
C ₂ H ₄	25	5.128	4.691	9.03	5.155	4.297	9.06	<i>f</i>
C ₂ H ₄	45	5.090	4.476	8.37	5.071	4.030	7.64	<i>f</i>
C ₂ H ₄	70	5.220	4.438	2.11	5.113	3.877	1.76	<i>f</i>
CO ₂	30	5.127	6.122	8.22	5.175	5.789	10.07	<i>f</i>
CO ₂	35	5.201	6.277	8.03	5.194	5.841	8.08	<i>f</i>
CO ₂	50	5.298	6.397	3.77	5.142	5.700	2.36	<i>f</i>
CO ₂	70	5.354	6.294	3.18	5.001	5.299	1.09	<i>f</i>
Hexachloroethane								
CO ₂	35	3.884	5.229	2.63	3.872	4.924	2.63	<i>e</i>
CO ₂	45	4.042	5.445	3.03	3.906	4.846	2.16	<i>e</i>
CO ₂	55	4.463	6.340	41.13	4.297	5.699	41.27	<i>e</i>
C ₂ H ₄	25	4.265	4.243	4.02	4.270	3.890	4.09	<i>f</i>
Hexamethylbenzene								
C ₂ H ₄	45	4.360	4.348	2.64	4.319	3.920	2.49	<i>f</i>
C ₂ H ₄	70	4.329	4.085	4.82	4.209	3.548	5.07	<i>f</i>
CO ₂	30	4.385	6.029	14.17	4.396	5.719	15.45	<i>f</i>
CO ₂	50	4.236	5.526	5.14	5.269	8.381	68.37	<i>f</i>
CO ₂	70	4.288	5.543	6.17	4.010	4.741	8.39	<i>f</i>

Solvent	$T, ^\circ\text{C}$	ECM Peng-Robinson			ECM Redlich-Kwong			Ref. key (†)
		α	β	RMSE, %	α	β	RMSE, %	
Naphthalene								
C ₂ H ₄	12	4.202	4.110	11.93	4.277	3.910	12.46	<i>a</i>
C ₂ H ₄	12	3.952	3.507	1.88	4.016	3.296	1.97	<i>i</i>
C ₂ H ₄	25	4.304	4.240	5.84	4.317	3.898	5.36	<i>a</i>
C ₂ H ₄	25	4.270	4.148	1.31	4.289	3.823	1.29	<i>i</i>
C ₂ H ₄	25	4.317	4.241	8.25	4.331	3.902	7.64	<i>a</i>
C ₂ H ₄	25	4.484	4.771	6.55	4.479	4.373	5.98	(‡)
C ₂ H ₄	35	4.330	4.092	5.24	4.297	3.696	0.82	<i>j</i>
C ₂ H ₄	35	3.619	3.810	9.67	4.315	3.700	4.35	<i>j</i>
C ₂ H ₄	45	4.330	3.800	1.94	4.298	3.389	3.14	<i>h</i>
C ₂ H ₄	45	4.322	3.712	2.67	4.269	3.320	1.69	(‡)
C ₂ H ₄	45	4.528	4.250	2.55	4.196	3.036	2.88	<i>j</i>
C ₂ H ₄	45	3.685	3.865	8.15	4.478	3.780	2.79	<i>j</i>
C ₂ H ₄	50	4.091	2.799	0.34	4.226	2.595	22.82	<i>h</i>
C ₂ H ₄	50	4.392	3.322	20.16	3.957	2.144	0.19	(‡)
C ₂ H ₄	50				4.294	2.757	20.70	<i>j</i>
C ₂ H ₄	55	3.746	3.911	5.12	3.537	3.314	3.32	<i>h</i>
C ₂ H ₄	60	4.411	2.754	0.14	4.795	3.361	0.14	(‡)
C ₂ H ₆	20	3.832	4.183	8.84	3.948	4.143	8.42	<i>f</i>
C ₂ H ₆	25	3.577	3.443	5.52	3.650	3.292	6.53	<i>f</i>
C ₂ H ₆	35	3.794	3.853	9.67	3.833	3.614	10.38	<i>f</i>
C ₂ H ₆	35	3.875	4.060	8.48	3.921	3.837	8.99	<i>a</i>
C ₂ H ₆	35	3.771	3.800	9.63	3.808	3.557	10.34	(‡)
C ₂ H ₆	45	3.818	3.758	12.05	3.836	3.474	11.79	<i>h</i>
C ₂ H ₆	45	4.001	4.253	6.75	4.009	3.938	6.02	<i>a</i>
C ₂ H ₆	45	3.817	3.735	8.81	3.834	3.450	8.47	(‡)
C ₂ H ₆	55	4.156	4.118	6.65	4.144	3.752	6.95	<i>a</i>
CClF ₃	35	3.119	2.860	7.19	3.131	2.633	7.06	<i>a</i>
CClF ₃	45	3.195	2.991	5.50	3.159	2.690	4.75	<i>a</i>
CClF ₃	55	3.221	2.973	3.01	3.146	2.622	1.53	<i>a</i>
CO ₂	35	4.259	5.257	10.56	4.250	4.905	9.15	<i>a</i>
CO ₂	35	4.258	5.259	12.18	4.257	4.927	10.38	<i>a</i>
CO ₂	36	4.091	4.802	4.64	4.086	4.475	4.57	<i>a</i>
CO ₂	45	4.404	5.453	7.46	4.251	4.782	4.70	<i>a</i>
CO ₂	55	4.501	5.376	3.53	4.231	4.465	4.61	<i>i</i>
CO ₂	55	4.527	5.430	5.06	4.233	4.470	4.51	<i>a</i>
CO ₂	55	4.554	5.478	2.97	4.260	4.520	6.02	<i>k</i>
CO ₂	55				4.302	4.602	2.57	(‡)

Solvent	$T, ^\circ\text{C}$	ECM Peng-Robinson			ECM Redlich-Kwong			Ref. key (†)
		α	β	RMSE, %	α	β	RMSE, %	
Phenanthrene								
C ₂ H ₄	25	5.696	5.702	5.63	5.718	5.252	5.30	<i>h</i>
C ₂ H ₄	25	6.727	8.501	78.79	6.758	8.014	78.62	<i>f</i>
C ₂ H ₄	45	6.725	8.293	57.87	4.118	4.318	0.17	<i>e</i>
C ₂ H ₄	45	4.164	4.740	0.00	6.528	7.294	58.11	<i>e</i>
C ₂ H ₄	45	5.682	5.543	7.20	5.621	4.947	6.87	<i>f</i>
C ₂ H ₄	55	5.072	3.760	5.06	4.988	3.199	4.63	<i>g</i>
C ₂ H ₄	65	7.355	10.045	60.00	7.110	8.939	60.38	<i>g</i>
C ₂ H ₄	70	7.093	9.199	75.41	4.602	5.777	0.14	<i>a</i>
C ₂ H ₄	70	4.642	6.192	0.00	6.864	8.184	75.80	<i>f</i>
C ₂ H ₄	70	5.468	4.754	4.67	5.287	3.998	4.63	<i>h</i>
C ₂ H ₆	30	4.693	4.612	5.31	4.773	4.368	5.27	<i>f</i>
C ₂ H ₆	40	4.874	4.759	3.50	4.911	4.408	3.62	<i>f</i>
C ₂ H ₆	60	4.905	4.889	8.90	4.884	4.446	8.63	<i>f</i>
C ₂ H ₆	30				5.590	6.503	8.70	<i>f</i>
CO ₂	30	5.536	6.849	6.78	6.667	8.296	9.46	<i>f</i>
CO ₂	45	5.813	7.423	6.66	5.671	6.677	5.72	<i>e</i>
CO ₂	50	5.643	6.974	6.87	5.457	6.184	6.01	<i>f</i>
CO ₂	55	5.856	7.421	3.57	5.553	6.342	2.16	<i>e</i>
CO ₂	65	5.892	7.456	2.23	5.426	6.049	3.27	<i>e</i>
CO ₂	70				5.324	6.052	10.80	<i>f</i>
Triphenylmethane								
C ₂ H ₄	30	7.090	7.890	17.97	7.073	7.240	17.88	<i>f</i>
C ₂ H ₄	40	7.570	8.984	17.31	7.487	8.169	16.85	<i>f</i>
C ₂ H ₄	50	8.774	11.990	16.25	8.556	10.78	15.86	<i>f</i>
CO ₂	30	6.643	8.797	9.06				<i>f</i>
CO ₂	40	6.845	9.230	6.33	6.753	8.504	5.47	<i>f</i>
CO ₂	50	6.967	9.535	10.63	6.751	8.583	11.77	<i>f</i>

(*) Data are grouped by solutes, which are displayed in **boldface** before each group in a row across the table while the first column displays the solvents.

(†) References are listed in Table 4 according to this reference key.

(‡) These rows use combined data from different authors for a given system at a given temperature.

To assess the quality of the fit, the root-mean-squared error of the deviations between experimental and predicted values was obtained by:

$$RMSE = 100 \frac{OF_1}{\bar{y}_{exp}} \quad (25)$$

The results are presented in Table 3 for about 130 isotherms. The average values of RMSE shown therein are 8.85% and 9.10% for the ECM-PR and ECM-RK, respectively. As seen, both ECM models give similar RMSE; being the Redlich/Kwong EoS simpler, the ECM-RK seems to be preferable.

3.2. Benchmarking the model

To further test the model, calculations were made for 18 isotherms of the 6 systems analyzed by Sparks et al. (2008). Each system therein was a solute with carbon dioxide, the only solvent used in that case. For a fair comparison, the same objective function used in their work was used here:

$$OF_2 = \sum_{i=1}^{N_p} \frac{|y_{i,calc} - y_{i,exp}|}{y_{i,exp}} \quad (26)$$

Note that this is different from that defined in the previous section. The properties of the compounds used by Sparks et al. (2008) are displayed in Table 2 of their work and are not reproduced here. The following compounds were used both in section 3.1 and section 3.2: naphthalene, fluorene, anthracene, and carbon dioxide. The properties used for these compounds in each section are slightly different since they were obtained from different sources: those used in section 3.1 were from Caballero et al. (1992) while those in section 3.2 were from Sparks et al. (2008), as mentioned above. The comparison was then made based on the *percent average relative deviation* (PARD) defined by:

$$PAR D = \frac{100}{N_p} \sum_{i=1}^{N_p} \frac{|y_{i,calc} - y_{i,exp}|}{y_{i,exp}} = 100 \frac{OF_2}{N_p} \quad (27)$$

The α and β values computed for the 18 solubility isotherms of the six solutes in carbon dioxide, and the corresponding *PARDs*, are included in Table 5. Note that *RMSE* and *PARD* are different and not comparable. For the same set of constants α and β , *PARD* is typically about 1.5 times *RMSE*.

Table 4. References used in the previous three tables

Key	Reference
<i>a</i>	Schmitt and Reid (1986)
<i>b</i>	Lee et al. (1988)
<i>c</i>	Reid et al. (1987)
<i>d</i>	Martinelli et al. (1987)
<i>e</i>	Kurnik et al. (1981)
<i>f</i>	Johnston et al. (1982)
<i>g</i>	Kosal and Holder (1987)
<i>h</i>	Johnston and Eckert (1981)
<i>i</i>	Mitra et al. (1988)
<i>j</i>	Diepen and Scheffer (1953)
<i>k</i>	Tsekhanskaya et al. (1964)

Table 5. Comparison of the results of this work and those of Sparks et al. (2008)

Temperature		ECM-RK Model			ECM-PR Model			Sparks et al. (2008)		
[°C]	[K]	α	β	<i>PARD</i>	α	β	<i>PARD</i>	<i>PARD</i> eq. (1)	<i>PARD</i> eq. (2)	
Naphthalene										
35	308.15	4.3579	5.2640	12.87%	4.3634	5.6044	12.73%	10.57%	10.28%	
45	318.15	4.2481	4.8420	11.13%	4.4652	5.6783	11.64%	10.15%	7.15%	
55	328.15	4.1750	4.3759	11.39%	4.5182	5.4928	8.64%	13.00%	5.55%	
Fluorene										
35	308.15	5.3664	6.15	9.03%	5.3338	6.5020	10.73%	9.68%	9.16%	
50	323.15	5.1331	5.5512	6.20%	5.3126	6.3041	7.80%	4.75%	4.54%	
70	343.15	4.9602	5.0291	7.46%	5.445	6.3213	6.03%	2.41%	2.09%	
Hydroquinone										
59.85	333	4.8146	6.0284	10.19%	5.2112	7.2881	12.23%	5.50%	3.51%	
74.85	348	4.8534	6.8721	12.24%	5.2547	7.9653	13.08%	6.22%	5.62%	
89.85	363	3.5327	3.7143	10.70%	4.0128	4.8706	9.23%	8.51%	2.73%	
Anthracene										
30	303.15	5.0591	5.5009	4.72%	4.9776	5.7536	4.48%	9.48%	11.13%	
50	323.15	4.6341	4.3933	26.59%	5.0461	5.6652	20.27%	4.59%	2.87%	
70	343.15	5.1426	5.3982	8.03%	5.7783	7.1168	8.20%	7.55%	9.64%	
1,5-Naphthalenediamine (1,5-NDA)										
40	313.15	4.9873	5.5575	2.41%	5.0546	6.103	2.13%	5.20%	5.10%	
50	323.15	5.1304	6.0539	5.40%	5.4468	7.228	4.21%	5.99%	7.68%	
60	333.15	5.1305	6.0539	3.86%	5.8643	8.4323	3.08%	6.65%	4.14%	
Cholesterol										
35	308.15	5.9058	8.6858	7.70%	5.971	9.263	7.98%	7.55%	7.57%	
40	313.15	7.0864	10.811	12.73%	7.317	11.901	13.52%	14.37%	14.78%	
60	333.15	7.3937	10.66	24.87%	7.6409	11.635	27.33%	7.46%	7.55%	
Averages				10.42%				10.18%	7.76%	6.73%

4. RESULTS AND DISCUSSION

To illustrate the typical prediction capabilities of the proposed model, graphs have been prepared. Figure 1 shows results for fluorene + carbon dioxide at 35 [°C]. This system was chosen because it was studied both by Caballero et al. (1992) and Sparks et al. (2008) and thus we can compare both modeling approaches.

Figure 1. Solubility curves for fluorene in carbon dioxide at 35 [°C] using the ECM-PR model and eq. (2) (Sparks et al., 2008). The ECM-PR1 curve uses α and β from section 3.1 while ECM-PR2 curve uses α and β from section 3.2. Experimental data from Johnston et al. (1982).

Besides the experimental points from Johnston et al. (1982), the modeling curves have been included for comparison purposes. Let us mention first that curves labeled ECM-PR1 (in green, long dash line) and ECM-PR2 (in red, dotted line), represent the model being proposed in this contribution. Both correspond to the ECM-PR the only difference being the objective function used: ECM-PR1 was obtained from the objective function used in section 3.1 (eq. 24) while for ECM-PR2, eq. (26) from section 3.2 was used. Both curves are virtually identical meaning that the objective function used bears little weight on the results. (If no color is used in the printed version of the paper, both lines will be most likely indistinguishable.) They show a slight maximum at a pressure between 20 [MPa] and 30 [MPa]. This type of maxima is explained by Prausnitz et al. (1999) on p. 195 of their textbook, while discussing a similar graph for the naphthalene + carbon dioxide system

displaying Tsekhanskaya et al. (1968) data. They say that the maximum occurs at high densities when repulsive forces between solvent and solute become important; as the density (or pressure) rises further, the solute is "squeezed out" of the gaseous solution (sic). The third curve is what is substantially different. That was obtained from eq. (2) above, which corresponds to the six-constant, semiempirical model proposed by Sparks et al. (2008). To have a fair comparison of the different curves, the correlation coefficient has been calculated for all three curves and it is displayed along with the *RMSE* and the *PARD* in Table 6.

Table 6. Statistical comparison of curves in Figure 1

Model	<i>RMSE</i>	<i>PARD</i>	R^2
ECM-PR3.1	14.36%	10.73%	0.900
ECM-PR3.2	12.64%	11.41%	0.923
Sparks et al. (eq. 2)	7.55%	9.20%	0.972

Note that *PARD* for ECM-PR3.1 is lower than the corresponding value for ECM-PR3.2 because that was minimized to get the parameter values in section 3.1. Conversely, *RMSE* was lower for ECM-PR3.2 because that was minimized to get the parameters in section 3.2. All three statistical parameters in Table 6 are better for the bottom row because eq. (2) is a six-parameter equation and thus offers more flexibility in correlating or fitting the experimental data. However, that does not mean, necessarily, that it is the best choice, as explained now. Any empirical or semiempirical model should be an excellent tool to interpolate between experimental data points, i.e., to predict solubility within the range of the experimental data. However, they may do a poor job when they are used to extrapolate solubilities outside that range. At low pressures, the behavior of eq. (2) becomes

unpredictable and extreme caution should be used; in this case, it predicts a solubility of zero (rather than the correct value of 1) as pressure goes to zero.

Figure 2. Solubility curves for sorafenib tosylate in carbon dioxide at 338 [K] using the two ECM models, eq. (2) (Sparks et al., 2008), and Sodeifian et al. (2019). The objective function given by eq. (26) was used for both ECM models.

Figure 2 is a similar one but using the recent data of Sodeifian et al. (2020) for sorafenib tosylate + carbon dioxide at 338 [K]. The publication includes the solid density and sublimation pressure, which are necessary to use the models herein proposed. A fourth curve obtained from a published correlation from the Sodeifian group (Sodeifian et al., 2019) is included. Their correlation is:

$$\ln y_2 = a_0 + a_1 \frac{P^2}{T} + a_2 \ln \rho T + a_3 \rho \ln \rho + a_4 P \ln T + a_5 \frac{\ln \rho}{T} \quad (28)$$

The value of the a_i constants are available from Sodeifian et al. (2020). The units to be used were not available in either publication but they were kindly provided by the authors: P in

[MPa], T in [K], and ρ in [kg/m³]. We can foresee advantages in expressing eq. (28) in terms of reduced properties, the main ones being avoiding any confusion with the units and having all constants much closer in order of magnitude. Table 7 gives a comparison of the performance of the four models used in Figure 2. Interestingly, the ECM-RK seems (visually) to give a slightly better fit than the ECM-PR model, although statistical parameters indicate the contrary. Although statistics seem to indicate that the Sparks et al. (2008) (eq. 2) is the best of the three, Figure 2 shows that at low pressures (outside the range of experimental data) that model fails to give a good estimation of solubility. This comment also applies to the curve obtained from the Sodeifian et al. (2019) correlation. It is fair to say that ECM-RK and ECM-PR models do not include a dependence on temperature meaning that whenever more than one experimental isotherm are available, α and β are found for each isotherm. Sparks et al. (2008) and Sodeifian et al. (2019) do include a temperature dependence and thus a given set of parameters apply to several temperatures when several experimental isotherms were used to obtain such parameters. That may explain why the Sodeifian et al. (2019) curve in Figure 2 is below all experimental points. Their parameters were obtained fitting five isotherms, the one in Figure 2 being at the highest temperature. Quite possibly, for one or more of the other isotherms, the curve might be above all data points. That may explain the poor statistical values for the Sodeifian et al. (2019) correlation.

Table 7. Statistical comparison of curves in Figure 2

Model	$RMSE$	$PARD$	R^2
ECM-RK	14.21%	14.81%	0.879
ECM-PR	11.93%	17.16%	0.915
Sparks et al. (eq. 2)	4.33%	3.70%	0.989
Sodiefian et al. (2019)	39.37%	32.95%	0.070

Figure 3. Solubility curves for sodium valproate in carbon dioxide at 65 [°C] using the two ECM models, eq. (2) (Sparks et al., 2008), and Sodeifian et al. (2019): (a) narrow (detailed) range; (b) wide range.

Finally, another test for the model is provided by Figure 3, which is like Figure 2 but for the system sodium valproate + carbon dioxide at 65 [°C]. This publication also includes the solid density and sublimation pressure and therefore all four curves could be generated. All the comments made concerning Figure 2 apply here. We cannot emphasize enough that empirical correlations should be used within the range of the experimental data and that extrapolating beyond that should be done with great care. The value of equation-of-state models is their simplicity (just two adjustable constants in the model proposed here) and

the fact that they are based on a physically sound basis and thus they represent the actual behavior better. They should be certainly used whenever extrapolation beyond the range of experimental data is needed.

The graphical abstract included in this publication emphasizes further the last point made above. The three figures presented so far are semi-log plots. The graphical abstract is a reproduction of Figure 2 (sorafenib tosylate + CO₂ at 338 [K]) but in a log-log plot. The two empirical correlations deviate significantly from the behavior predicted by the ideal-gas law at pressures below a few bars (say, $P \lesssim 0.5$ [bar]). The ideal solubility is given by:

$$y_2^{id} = \frac{p^{sub}}{P} \quad (29)$$

and thus, inversely proportional to P . That is a straight line with slope -1 in a log-log plot. This is observed for the two ECM models (or any EoS-based model) in the graphical abstract. Conversely, the other two models have unpredictable behavior outside the range of experimental data.

5. CONCLUDING REMARKS

This contribution presents a simple, yet effective, way to model the solubility of solids in supercritical fluids. The model is based on a sound thermodynamic basis, on one hand, and does not require the knowledge or estimation of critical properties of the solid. Moreover, it uses just two adjustable parameters. The model can be formulated with any cubic equation of state and its use is shown here for two of the most popular and simple ones: the Redlich/Kwong and the Peng/Robinson equations of state. An ample database of the adjustable parameters α and β is presented for nearly 130 isotherms as shown in Table 3. Another 18 isotherms were used to compare the method to other sophisticated empirical

or semiempirical approaches. The proposed method based on EoS performed similarly to empirical equations containing 5 or 6 adjustable constants, which have no physical meaning. It was also shown that extrapolating the empirical equations beyond the range of the experimental data used to obtain the adjustable parameters is risky and highly advisable to refrain from doing so.

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Notation

A	dimensionless EoS constant in RK-EoS, eq. (11) and in PR-EoS, eq. (20)
A_A	Antoine's equation constant, eq. (23), dimensionless
a	EoS constant in RK-EoS, eq. (4), [$\text{J}\cdot\text{K}^{0.5}/\text{mol}^2\cdot\text{Pa}$]
a	EoS constant in PR-EoS, eq. (16), [$\text{J}/\text{mol}^2\cdot\text{Pa}$]
a_i	empirical constants in eq. (28), $i = 0, 1, \dots, 5$ (units of constants varies)
B	dimensionless EoS constant in RK-EoS, eq. (12) and in PR-EoS, eq. (21)
B_A	Antoine's equation constant, eq. (23), [K]
b	EoS constant in RK-EoS, eq. (4), and in PR-EoS, eq. (16), [m^3/mol]
c_2^*	normalized solubility of solute, eq. (17), dimensionless
e_0	empirical constant in Eqs. (1) and (2), dimensionless
e_1	empirical constant in Eqs. (1) and (2), dimensionless
e_2	empirical constant in Eq. (2), dimensionless
M	molar mass, [kg/mol]
N_p	number of data points in Eqs. (24) and (26), dimensionless
OF_1	objective function defined by Eq. (24), dimensionless
OF_2	objective function defined by Eq. (26), dimensionless
P	total pressure, [Pa]
$PARD$	Percent average relative deviation defined by Eq. (27)
P_2^{sub}	solute sublimation pressure, [Pa]
R	gas constant, 8.3144598 [$\text{J}/\text{mol}\cdot\text{K}$]
$RMSE$	Root mean square error defined by Eq. (25)
T	temperature, [K]
V	molar volume, [m^3/mol]
V_1^{sol}	solid solute molar volume, [m^3/mol]
y, y_2	mole fraction of the solute in the supercritical phase, [-]
y_i	solubility of solute for the i -th experimental point, [-]

$\bar{y}_{exp}$ in Eq. (25), average of all experimental solubilities, [-]
 Z compressibility factor in Eqs. (5), (8), (10), (15), (17), (18), and (19), [-]

Greek letters

α empirical constant in Eqs. (1) and (2), dimensionless
 α dimensionless ECM model parameter defined by Eq. (14), [-]
 β empirical constant in Eqs. (1) and (2), dimensionless
 β dimensionless ECM model parameter defined by Eq. (14), [-]
 γ empirical constant in Eqs. (1) and (2), dimensionless
 ρ density, [kg/m³]
 $\hat{\phi}_2^V, \hat{\phi}_2$ fugacity coefficient in Eqs. (3) and (5), dimensionless
 $\hat{\phi}_2^\infty$ fugacity coefficient at infinite dilution, Eqs. (8), (10), (17), (18) and (19), dimensionless
 Ω_a, Ω_b dimensionless numerical constants in Eqs. (13) and (22)
 ω acentric factor in Eq. (20), dimensionless

Subscripts

c critical property
 $calc$ calculated solubility value
 exp experimental solubility value
 r reduced property with respect to species 1
1 solvent
2 solute

Superscripts

$calc$ calculated solubility
 id ideal gas
 sub sublimation
 V vapor or supercritical phase

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