

Correlation and Prediction of the Solubility of Solid Solutes in Chemically Diverse Supercritical Fluids Based on the Expanded Liquid Theory

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Received July 20, 2013; revised August 20, 2013; accepted August 30, 2013

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ABSTRACT

For the proper design of any extraction procedure based on supercritical solvents, it is essential to have a sound knowledge of the solubility data of different compounds and the accurate way to represent it. The solute's solubility in a supercritical solvent is dependent on the solute, the solvent, and the operating conditions (temperature and pressure). Developing a comprehensive experimental data set is an onerous task and time consuming and, thus, the incentive to develop predictive tools is substantial. In this paper, a technique is presented and tested to correlate and predict solute's solubility in different supercritical fluids with a methodology based on the expanded liquid theory, in which the solid-fluid equilibrium is modeled using the local composition model of UNIQUAC in which the interaction parameters are related to the solvent reduced density with empiric equations. The most advantages of this model include: it does not require the knowledge of critical properties and sublimation pressure of solid solutes and does take into account the binary interaction between solid solute and solvent. The evaluation of the proposed model capabilities is done by testing it on a large data base consisting of experimental solubility data taken from literature of 33 binary systems solid-SC fluid. The results obtained for both correlation and prediction show good agreement with the experimental data used. For the comparison we have considered some literature models that account for effect of the system conditions (temperature and pressure) in addition to the sublimation pressure of the solute through their introduction of the enhancement factor and a model based on a modified Peng-Robinson equation of state.

Keywords: Solubility Modeling; Supercritical Fluids; Correlation; Prediction; Expanded Liquid; UNIQUAC

1. Introduction

During the past few years, widespread attention has been focused on supercritical fluids due to their potential application in extraction processes in foods processing, pharmaceuticals, flavors, chemicals and petroleum industries. The main advantages of supercritical fluid extraction over conventional extraction methods include increased speed, easy solvent separation and better recovery, and reduction in both solvent usage and solvent waste generation. The solubility of a solute in a supercritical fluid is perhaps the most important thermophysical property that must be determined and modeled for an efficient design of any extraction procedure based on supercritical solvents. The determination of solubilities

of a wide variety of solids and liquids of low volatility in supercritical fluids has received considerable attention in recent years. However, despite the vital importance of the solubility data of different compounds from chemical, biochemical, pharmaceutical and industrial points of view, there is still a lack of fundamental solubility and mass-transfer data available in the literature to facilitate the development of commercial-scale processes. Since the experimental determination of the solubilities of various solutes in supercritical fluids at each operating condition is tedious, time-consuming and not reported in literatures, there is a considerable interest in mathematical models that can accurately predict the solubilities of solid solutes in supercritical fluids [1]. Therefore it is essential to have a model that not only can accurately correlate but also predict phase equilibrium properties.

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Some of the models that have been used for correlating solubility data can be classified in two classes, equations of state based models (EOS) [2] and empirical models [3,4]. EOS based models require the prior knowledge of a certain number of parameters such as the critical properties (temperature and pressure), acentric factor and the sublimation pressure of the solid solute. These parameters are not available and specifically for many high molecular weight compounds and are calculated using group contribution methods, which could lead to solubility error prediction. Due to the lack of information on these properties, empirical models are often used for the correlation of experimental solubility data. These models are known as density-based models and consist of equations that contain constants that are empirically adjusted for each compound. Although simple, these models rely much on the knowledge of the thermodynamic behaviour of the supercritical solvent rather than of the solute, and are mostly capable of correlating rather than predicting the solubility. They are used for quantitative determination of the solute solubility in supercritical phase at equilibrium, and do not provide qualitative information about the solute-solvent interaction.

In a previous presentation [5], we have adopted a methodology for the correlation and the prediction of the solubility of 10 aromatic pollutants in the supercritical carbon dioxide. In this work we present an extension of the methodology to the solubility of other solids with different functional groups in different supercritical fluids namely carbon dioxide, ethylene and ethane. The methodology is based on the expanded liquid model theory [6,7] which does not require the knowledge of the solute critical properties and sublimation pressure. In this case the supercritical phase is considered as an expanded liquid and is modeled using excess Gibbs energy models such as Margules, Van Laar, and local composition based models *i.e.* Wilson, NRTL and UNIQUAC. In this study we focus on the use of the UNIQUAC model that has been widely used in modeling vapour-liquid and liquid-liquid equilibria data. This model does not only take the size and nature of the molecules into consideration, but also accounts for the strength of solute-solvent intermolecular forces. And because the primary concentration variable is the surface fraction rather than mole fraction, the UNIQUAC model is applicable to solutions containing small or large molecules, including polymers. To assess the correlative and predictive capabilities of this model, a database is built by consisting of the experimental solubility data of 33 binary systems solid-supercritical fluid where solid solutes have different functional groups.

2. Model Development

In the supercritical state, a fluid has a high density when

compared with a gas. In fact, the density of a supercritical fluid is closer to that of a liquid than that of a gas. Consequently, in theoretical treatments the supercritical fluid phase can be treated approximately as an expanded liquid. This allows the phase equilibria between the solute and the supercritical fluid to be represented thermodynamically by solid-liquid equilibrium relations and conventional activity coefficients. To estimate the solid solubility in the supercritical phase, the knowledge of the activity coefficients are required. These coefficients are determined from the knowledge of the component fugacities, thus when the equilibrium of the pure solid and the supercritical phase is reached, we have:

$$f_2^s = f_2^L \quad (1)$$

f_2^s is the fugacity of the solute in the solid phase considered as pure solid and equal to f_2^{os} because the solubility of supercritical fluid (SCF) in the solid phase is considered to be negligibly small. The f_2^L is the fugacity of the solid solute in the supercritical phase and is equal to:

$$f_2^L = \gamma_2 y_2 f_2^{ol} \quad (2)$$

Equation (1) could be written as follows:

$$f_2^{os} = \gamma_2 y_2 f_2^{ol} \quad (3)$$

where γ_2 , y_2 and f_2^{ol} are the activity coefficient, the solid solubility represented in mole fraction and the fugacity of the pure solid solute in the expanded liquid phase respectively. According to Prausnitz *et al.* [8], we have:

$$\ln \left(\frac{f_2^{os}}{f_2^{ol}} \right) = \frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) - \frac{\Delta C_p}{RT} \left(\frac{T - T_m}{T} \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T}{T_m} \right) \quad (4)$$

Prausnitz *et al.* [8] stated that, to a fair approximation, the heat capacity terms can be neglected. Equations (3) and (4) then combined to yield an expression for the solute solubility:

$$y_2 = \frac{1}{\gamma_2} \exp \left[\frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (5)$$

ΔH_2^f is the enthalpy of fusion, T_m is the melting point temperature of the solid solute. Since the solid solubility in the supercritical phase is very small, we can assume to be at infinite dilution condition. Consequently, the activity coefficient of the solid solute is the one at infinite dilution and the density of the solution is that of the pure solvent. Thus Equation (5) becomes:

$$y_2 = \frac{1}{\gamma_2^\infty} \exp \left[\frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (6)$$

The activity coefficient of the solid solute at infinite dilution γ_2^∞ was calculated using the UNIQUAC model which consists of two parts, a combinatorial part $\gamma_2^{C,\infty}$ that attempts to describe the dominant entropic contribution, and a residual part $\gamma_2^{R,\infty}$ that is due primarily to intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure-component data. The residual part, however, depends also on intermolecular forces; the two adjustable binary parameters a_{12} and a_{21} , therefore, appear only in the residual part [8]:

$$\ln \gamma_2^\infty = \ln \gamma_2^{C,\infty} + \ln \gamma_2^{R,\infty} \quad (7)$$

$$\ln \gamma_2^{C,\infty} = 1 - \frac{r_2}{r_1} + \ln \frac{r_2}{r_1} - q_2 \frac{z}{2} \left(1 - \frac{r_2 q_1}{r_1 q_2} + \ln \frac{r_2 q_1}{r_1 q_2} \right) \quad (8)$$

Here q and r are the surface area and volume parameters; z is the coordination number that is usually taken equal to 10. The residual part at infinite dilution is given by the following equation [8]:

$$\ln \gamma_2^{R,\infty} = q_2 (1 - \ln \tau_{12} - \tau_{21}) \quad (9)$$

where

$$\tau_{12} = \exp(-\Delta u_{12}/RT) = \exp(-a_{12}/T) \quad (10a)$$

and

$$\tau_{21} = \exp(-\Delta u_{21}/RT) = \exp(-a_{21}/T) \quad (10b)$$

Δu_{12} and Δu_{21} are characteristic energies and are related to the interaction parameters a_{12} and a_{21} through Equation (10). Finally combining Equations (9) and (10) leads to:

$$\ln \gamma_2^{R,\infty} = q_2 \frac{a_{12}}{T} + q_2 \left(1 - e^{-\frac{a_{21}}{T}} \right) \quad (11)$$

Equation (11) could be written in reduced form by introducing the reduced temperature, thus we obtain:

$$\ln \gamma_2^{R,\infty} = q_2 \frac{a'_{12}}{T_r} + q_2 \left(1 - e^{-\frac{a'_{21}}{T_r}} \right) \quad (12)$$

With $a'_{12} = \frac{a_{12}}{T_c}$ and $a'_{21} = \frac{a_{21}}{T_c}$, T_c is the solvent critical temperature.

The binary interaction parameters a'_{12} and a'_{21} are related to the energy of interaction between the solid solute and the solvent in the supercritical phase, and cannot be kept constant and specifically at high pressure conditions. Therefore to take into account the pressure and temperature effects, these parameters are assumed to be density dependent and were fitted to the following equations:

$$a'_{12} = \alpha_{12} \cdot \rho_r^{\beta_{12}} \quad (13a)$$

$$a'_{21} = \alpha_{21} \cdot \rho_r^{\beta_{21}} \quad (13b)$$

ρ_r is the reduced density of the solvent equal to ρ/ρ_{c1} where ρ_{c1} is its critical density, α_{12} , β_{12} , α_{21} and β_{21} are the regressed parameters of the model.

3. Database Compilation

By considering 33 system solid-SC fluid, an exhaustive solutes solubility database consisting of more than 2218 solubility data in supercritical fluids is built-up for the elaboration and validation of the proposed model. It is acknowledged that the systems studied do not include all the data available but should be sufficient to provide a thorough testing of the potential of Equations (6) to 13(b). The density of supercritical fluid solvents used in this work, is estimated using the Span and Wagner equation of state [10] when they are not reported in the solubility data sources, the physical properties of the solvents are given in **Table 1**. **Table 2** show the solutes and their thermodynamic properties obtained from literature used in this study. Description of the database is given in **Table 3** which lists the binary systems used together with the number of solubility data points, and the lower and upper limits of the operating conditions, solubility and the references. Detailed information about all the complete references from which experimental solubility data are taken are provided in **Table 4**.

4. Solutes Solubility Correlation

The surface area and volume parameters are calculated as the sum of the group volume and area parameters (R and Q) given by the UNIFAC group specifications [8]. These parameters and properties listed in **Table 2**, together with those of different fluids listed in **Table 1** are used to calculate the combinatorial part of the activity coefficient from Equation (8). In other hand, Equation (12) is used to calculate the residual part of the solid solute activity coefficient. Thermodynamic properties of the solid solute listed in **Table 2** are used together with Equations (7), (8), and (12) to estimate the solubility y_2 using Equation (6). The interaction parameters a'_{12} and a'_{21} are then regressed according to Equations 13(a) and 13(b). The best regression is based on minimizing the error between the regressed and experimental solubility data. The objective function used minimizes the sum of average absolute relative deviation (AARD) according to Equation (14):

$$\text{FOBJ} = \text{AARD}(\%) = \frac{100}{N} \sum_1^N \frac{|y_{2(\text{exp})} - y_{2(\text{reg})}|}{y_{2(\text{exp})}} \quad (14)$$

where N is the number of experimental solubility data of each solute.

Table 1. Solvents physical properties.

Solvent	T_{c1} (K)	P_{c1} (bar)	ω_1	ρ_{c1} (mol/cm ³) × 100	r_1	q_1
CO ₂	304.2 ^a	73.83 ^a	0.239 ^a	1.063 ^a	1.296 ^b	1.261 ^b
ethane	305.33 ^a	48.8 ^a	0.09 ^a	0.687 ^a	1.802	1.696
ethylene	382.35 ^a	50.4 ^a	0.089 ^a	0.764 ^a	1.488	1.574

^aFrom reference [8], ^bFrom reference [9].

Table 2. Solute species properties.

Solute	Formula	M (g/mol)	T_m (K)	ΔH_2^f (J/mol)	V_2^s (cm ³ /mol)	r_2	q_2
anthracene	C ₁₄ H ₁₀	178.23	492.5 [10]	28829.0 [11]	138.9 [11]	6.77	4.48
biphenyl	C ₁₂ H ₁₀	154.21	342.1 [10]	18601.0 [11]	132.0 [11]	6.04	4.24
6-caprolactam	C ₆ H ₁₁ NO	113.16	342.3 [12]	16096.0 [12]	162.0 [13]	4.67 [14]	3.736 [14]
1,10-decanediol	C ₁₀ H ₂₂ O ₂	174.3	347.1 [15]	43505.3 [16]	158.4 [17]	8.74	7.8
2,3-dimethylnaphtalene	C ₁₂ H ₁₂	156.23	377.8 [11]	25101.0 [11]	156.0 [11]	6.45	4.57
2,6-dimethylnaphtalene	C ₁₂ H ₁₂	156.23	383.2 [11]	25055.0 [11]	199.0 [11]	6.45	4.57
2,7-dimethylnaphtalene	C ₁₂ H ₁₂	156.23	369.0 [18]	23349.0 [18]	154.0 [18]	6.45	4.57
fluoranthene	C ₁₆ H ₁₀	202.2	383.3 [15]	18728.0 [12]	163.0 [11]	7.5	4.72
fluorene	C ₁₃ H ₁₀	116.23	387.9 [19]	19580.0 [19]	139.3 [19]	6.39	4.22
hexamethylbenzene	C ₁₂ H ₁₈	228.38	438.7 [19]	20640.0 [19]	152.7 [13]	7.59	5.8
lauric acid	C ₁₂ H ₂₄ O ₂	200.3	316.9 [12]	36650.0 [12]	229.0 [20]	8.94	7.47
myristic acid	C ₁₄ H ₂₈ O ₂	228.38	327.1 [15]	45362.8 [15]	257.5 [13]	10.29	8.55
naphtalene	C ₁₀ H ₈	128.17	353.2 [11]	19123.0 [11]	125.0 [11]	4.98	3.44
1-naphtol	C ₁₀ H ₈ O	144.2	368.1 [15]	23477.5 [15]	117.8 [21]	5.34	3.72
2-naphtol	C ₁₀ H ₈ O	144.2	396.0 [11]	17511.0 [11]	118.0 [11]	5.34	3.72
phenanthrene	C ₁₄ H ₁₀	178.23	372.2 [11]	16465.0 [11]	182.0 [11]	6.77	4.48
phenol	C ₆ H ₆ O	94.10	313.9 [11]	11289.0 [11]	89.0 [13]	3.55	2.68
pyrene	C ₁₆ H ₁₀	202.26	424.2 [19]	17111.0 [19]	158.5 [19]	7.5	4.72
resorcinol	C ₆ H ₆ O ₂	110.11	383.1 [15]	21291.6 [15]	86.7 [21]	3.91	2.96
stearic acid	C ₁₈ H ₃₆ O ₂	284.5	341.9 [15]	56569.2 [15]	302.4 [13]	12.99	10.71
triphenylene	C ₁₈ H ₁₂	228.29	470.9 [15]	24190.0 [18]	175.0 [20]	8.57	5.52
triphenylmethane	C ₁₉ H ₁₆	244.3	365.6 [19]	20920.0 [19]	240.9 [19]	9.512	6.588

5. Solutes Solubility Prediction

In order to evaluate the predictive ability of the proposed model, the solubility data for each considered component are split with specific tool in two sets. The first data set is the training set on which the minimization routine is performed and the interaction parameters are regressed. This data set contains 70% of the data randomly picked up from the experimental solubility data for each com-

ponent. The second data set, namely the test set, contains the remaining 30% data and is intended for testing the generalized capabilities of the UNIQUAC model. The interaction parameters have been regressed using the training solubility data set, and then used directly to predict the solid solubility y_2 using the test data set. The predictive ability of the model is then assessed by comparing the obtained AARD values for each data set and so for each component.

Table 3. Database description.

Binary systems	<i>N</i>	<i>T</i> -range (K)	<i>P</i> -range (bar)	ρ_i range	Solubility order	References
naphtalene-CO ₂	242	308 - 338.05	75.4 - 400	0.51 - 1.98	7E-4 - 6E-2	L1 - L17
naphtalene-ethylene	166	285 - 323	54.5 - 303.9	0.52 - 1.99	3E-4 - 8E-2	L1, L6, L61, L62
naphtalene-ethane	48	308 - 328.2	48.1 - 250	0.56 - 1.99	8E-4 - 5E-2	L24, L59
anthracene-CO ₂	206	298 - 343	92.6 - 470	0.66 - 2.0	3E-6 - 3E-4	L20, L23, L28, L29, L30, L31, L32, L33, L34
anthracene-ethane	13	308 - 343	104.3 - 345.6	1.49 - 1.99	7E-5 - 6E-4	L24
anthracene-ethylene	27	323 - 358	104.4 - 414.7	0.75-1.97	1E-5 - 9E-4	L59
biphenyl-CO ₂	57	308 - 330.6	80 - 379.46	0.55 - 1.99	4E-4 - 6E-2	L9, L5, L12
biphenyl-ethane	8	308 - 318.3	70.5 - 180	1.32 - 1.94	1E-2 - 4E-2	L24
6-caprolactam-CO ₂	32	307 - 324	101 - 208	1.5 - 1.81	2E-2 - 7E-2	L46
2,3-dimethylnaphtalene-CO ₂	25	308 - 328	99 - 280	0.68 - 1.96	3E-4 - 9E-3	L21, L25
2,3-dimethylnaphtalene-ethylene	18	308 - 328	77 - 280	0.64 - 1.93	3E-4 - 5E-2	L21
2,6-dimethylnaphtalene-CO ₂	23	308 - 328.2	79 - 280	0.63 - 1.96	3E-4 - 9E-3	L8, L21
2,6-dimethylnaphtalene-ethylene	18	308 - 328	78 - 280	0.62 - 1.94	2E-4 - 2E-3	L21
2,7-dimethylnaphtalene-CO ₂	10	308.2 - 328.2	88 - 249	0.69 - 1.91	7E-4 - 1E-2	L8
fluoranthene-CO ₂	68	308 - 348	86 - 354.6	0.62 - 1.99	9E-6 - 1E-3	L35, L26
fluorene-CO ₂	146	308 - 343	80.9 - 483.4	0.6 - 1.98	6E-5 - 9E-3	L18, L19, L23
phenanthrene-CO ₂	281	308 - 343	82.2 - 414.5	0.56 - 2.0	3E-5 - 4E-3	L12, L17, L18, L19, L20, L21, L22, L24, L25, L26, L63
phenanthrene-ethylene	42	298 - 343	69.9 - 280	0.45 - 1.49	3E-5 - 1E-2	L59, L21, L19
phenanthrene-ethane	17	313 - 333	69.9 - 264	0.76 - 1.95	2E-4 - 6E-3	L19
pyrene-CO ₂	235	308 - 343	83.4 - 483.4	0.78 - 1.99	1E-5 - 9E-4	L18, L19, L20, L27
pyrene-ethane	15	333 - 333	100.2 - 314.5	1.37 - 1.98	2E-4 - 1E-3	L20
triphenylene-CO ₂	53	308 - 328	85 - 355.6	0.83 - 1.99	1E-6 - 5E-5	L35, L27
triphenylmethane-CO ₂	111	308 - 328	73.7 - 414.5	0.507 - 1.99	3E-5 - 4E-3	L19, L38
lauric acid-CO ₂	24	308 - 318	77 - 260	0.53 - 1.94	2E-5 - 5E-2	L43, L44, L45
palmitic acid-CO ₂	27	308 - 328	91 - 248	1.1 - 1.9	3E-5 - 2E-3	L4, L52, L53
myristic acid-CO ₂	30	308 - 318	128.5 - 226.5	1.47 - 1.89	1E-3 - 1E-2	L43, L44
stearic acid-CO ₂	28	308 - 338	90 - 237	0.94 - 1.91	2E-5 - 1E-3	L56, L60, L57, L58
Resorcinol	26	308 - 338	121.6 - 405.3	0.84 - 1.97	1E-4 - 9E-4	L55
phenol-CO ₂	73	309 - 333.2	79.3 - 249.43	0.51 - 1.91	1E-3 - 6E-3	L40, L41,
1,10-decanediol	15	318 - 328	133.7 - 307.3	1.26 - 1.91	3E-4 - 8E-4	L47
1-naphtol-CO ₂	64	308 - 328	88.7 - 296.5	0.54 - 1.98	6E-5 - 2E-3	L33, L51
2-naphtol-CO ₂	48	308.05 - 343.2	100 - 363.6	0.65 - 1.99	8E-5 - 2E-3	L24, L37, L29
2-naphtol-ethane	22	308 - 343.2	61 - 364	0.56 - 1.98	2E-5 - 1E-3	L24

Table 4. References for solubility data.

L1: Russian journal of physical chemistry 1964; 38: 9	L30: Ind. Eng. Chem. Res. 1987, 26, 7, 1476-1482
L2: J. Supercritical Fluids. 1996; 9: 3	L31: J. Chem. Eng. Data 1996, 41, 97-100
L3: J. Chem. Eng. Data 1998; 43: 400-402	L32: J. Chem. Eng. Data 1997, 42, 636-640
L4: J. Chem. Eng. Data 1999; 48: 951-957	L33: J. Chem. Eng. Data 1995, 40, 953-858
L5: J. Chem. Eng. Data 1980; 25, 4, 326-329	L34: Utilisation des fluides supercritiques pour l'extraction des fullerènes, thesis presented by Valérie Quillet, 1996: Bordeaux I, France
L6: J. Supercritical. Fluids 1988; 1: 1	L35: J. Chem. Eng. Data 2000, 45, 53
L7: J. Chem. Eng. Data 1989, 36: 4, 430-432	L37: Ind. Eng. Chem. Res 26, 1, 1987, 56-65
L8: J. Chem. Eng. Data 1993, 38, 3,	L38: J. Supercritical Fluids 2004, 32, 115-121
L9: Fluid Phase Equilibria 1992; 81:321-341	L39: Fluid Phase Equilibria 2004, 226, 9-13
L10: Fluid Phase Equilibria 1995, 107, 189-200	L40: J. Chem. Eng. Data 1980, 25, 257-259
L11: Ind. Eng. Chem. Res. 2000, 39, 4609-4614	L41: Hwahak Konghak Journal 1993, 31, 6, 637
L12: J. Supercritical. Fluids 1995, 8, 1, 15-19	L43: J. Chem. Eng. Data 1988, 33, 3, 327-333
L13: J. chem. Eng. Data 1988, 33, 1, 35-37	L44: J. Chem. Eng. Data 2008, 53, vol. 11
L14: J. Chem. Eng. Data 1985, 30, 1	L45: J. Am. Oil. Chem. Soc. 1992, 69, p. 1069
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L18: J. Chem. Eng. Data 1990, 35: 355-360	L52: J. Chem. Eng. Data 1991, 36, 4, 430-432
L19: Ind. Eng. Chem. Fundamentals 1982, 21, 3	L53: J. Chem. Eng. Data 1988, 33, 230-234
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L21: J. Chem. Eng. Data 1981, 26, 1, 47-51	L56: J. Chem. Eng. Data 1993, 38, 506-508
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L23: Phys. Chem. 1984, 88, 865-869	L58: J. Chem. Thermodynamics 2010, 42, 193-197
L24: J. Chem. Eng. Data 1986, 31, 2, 204-212	L59: AIChE journal 1981, 27, No 5, 773-779
L25: J. Chem. Eng. Data 2001, 46, 5, 1156-1159	L60: J. Chem. Eng. Data 1989, 34, 184-187
L26: J. Chem. Eng. Data 1996, 41, 1466-1469	L61: J. Amer. Chemic. Socie 1953, 57, 575-578
L27: Ind. Eng. Chem. Res 1995, 34, 340-346	L62: J. Amer. Chemic. Socie 1948, 70, 4085-4089
L28: J. Chem. Eng. Data 1987, 32, 148-150	L63: J. Chem. Eng. Data 1986, 31, 3, 303-308
L29: Fluid Phase Equilibria 2003, 207, 183-192	

6. Results and Discussion

6.1. Solubility Data Correlation

The analysis of the correlation model results is done through statistical calculations. **Table 5** provides the quantitative results of the regression for the UNIQUAC model. The AARD is included for each binary system and is listed together with the adjustable parameters values. Each component parameters are obtained by fitting them on its own solubility data available in the database.

For all investigated systems the resultant AARD values are lower than 20% (except for the system phenol-CO₂). The model achieves an overall AARD of 12.16 on a range of 2.8 to 29.7. These results are indicative of a good correlation performance of the proposed model and also show that the calculated solubility data are in good agreement with the experimental ones.

In order to compare more clearly, the experimental data and correlated data in this work are compared in **Figures 1-3** with naphthalene in SC CO₂ at $T = 308$ K,

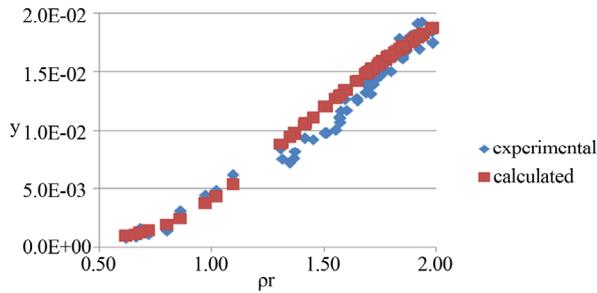


Figure 1. Experimental and correlated solubility versus reduced density of naphthalene-CO₂ system at 308 K.

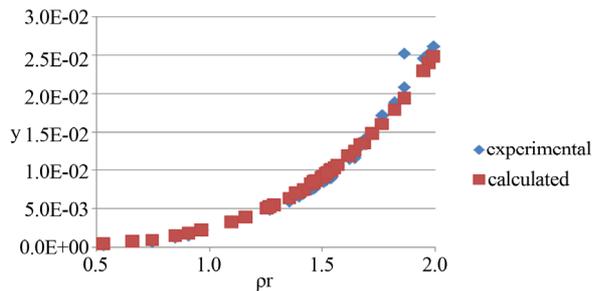


Figure 2. Experimental and correlated solubility versus reduced density of naphthalene-ethylene system at 298 K.

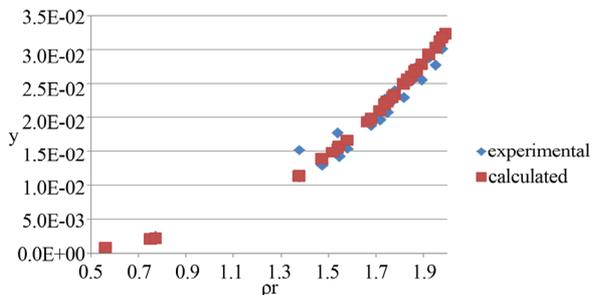


Figure 3. Experimental and correlated solubility versus reduced density of naphthalene-ethane system at 308 K.

naphthalene in SC ethylene at $T = 298$ K, and naphthalene in SC ethane at $T = 308$ K respectively. These systems are arbitrarily taken from the database for illustration. From the figures, we see that it is good accordance with experimental and calculated ones, and the precision of the model in this work is very acceptable.

6.2. Comparison with Literature

We have considered for the comparison some literature models that account for effect of the system conditions (temperature and pressure) in addition to the physical properties as sublimation pressure of the solute through their introduction of the enhancement factor and a model based on a modified equation of state.

6.2.1. Wang and Tavlarides Model

Based on a dilute solution theory, Wang and Tavlarides

[22] proposed the following model:

$$\frac{1}{T[\ln(E) - \ln(Z)]} = R \left(\frac{c}{b} + \frac{V_1}{b} \right), \left(V_1 = \frac{1}{\rho_1} \right) \quad (15)$$

where Z is the compressibility factor, E is the *enhancement factor* that is defined as the enhancement of actual mole fraction solubility of the solid solute y_2 over the solubility in an ideal gas P_2^s/P , i.e., $y_2 = \frac{EP_2^s}{P}$. P_2^s

and P are the sublimation vapor pressure and total pressure respectively. By introducing reduced variables, the dimensionless form of Equation (15) is given by:

$$\frac{1}{T_r[\ln(E) - \ln(Z)]} = \alpha \left(\beta + \frac{1}{\rho_r} \right) \quad (16)$$

where $\alpha = \frac{T_{c1} R}{\rho_{c1} b}$; $\beta = c \rho_{c1}$.

6.2.2. Méndez-Santiago and Teja Models

Based on the theory of dilute solutions, Méndez-Santiago and Teja [23] began with the Henry's constant and presented a simple linear relationship for the solubility of solids in supercritical fluids as given below:

$$T \ln E = A_1 + B_1 \rho \quad (17)$$

To apply the model to compounds whose sublimation vapor pressure is unknown, a Clausius-Clapeyron-type expression for the sublimation pressure $\ln P_2^s = A + \frac{B}{T}$

and $E = \frac{y_2 P_2^s}{P}$ are substituted into Equation (17) resulting in the following expression:

$$T \ln(y_2 P) = A' + B' \rho + C' T \quad (18)$$

The dimensionless form of Equations (17) and (18) are given below [4]:

$$T_r \ln E = T_r \ln \frac{y_2 P}{P_2^s} = \alpha + \beta \rho_r \quad (19)$$

where:

$$\alpha = \frac{A_1}{T_{c1}}; \quad \beta = \frac{B_1 \rho_{c1}}{T_{c1}}$$

$$T_r \ln(y_2 P_r) = \alpha' + \beta' \rho_r + \gamma' T_r \quad (20)$$

where:

$$P_r = \frac{P}{P_{c1}}; \quad \alpha' = \frac{A'}{T_{c1}}; \quad \beta' = \frac{B' \rho_{c1}}{T_{c1}}; \quad \gamma' = C' - T_r \ln P_{c1}$$

The linear behavior of Equation (17) is well observed in the range (0.5 - 2) of reduced density of the super-

Table 5. Regression parameters and average deviation of the model.

Binary systems	N	α_{12}	β_{12}	α_{21}	β_{21}	AARD (%)
anthracene-CO ₂	206	2.380	-0.210	-0.360	0.598	14.58
anthracene-ethylene	27	2.284	-0.356	-0.277	0.841	8.06
anthracene-ethane	13	1.840	-0.711	-0.053	0.844	6.87
biphenyl-CO ₂	57	1.620	-0.450	-0.107	0.930	16.39
biphenyl-ethane	8	1.303	-0.403	-0.066	1.942	8.99
6-caprolactam	32	1.630	0.851	-0.330	1.940	5.66
1,10-decanediol-CO ₂	15	1.803	-0.357	-0.090	-0.370	3.94
2,3-dimethylnaphthalene-CO ₂	25	0.680	-0.370	2.424	-2.160	19.71
2,3-dimethylnaphthalene-ethylene	18	0.525	-0.827	3.659	-2.390	13.04
2,6-dimethylnaphthalene-CO ₂	23	0.900	-0.560	0.802	-0.702	9.68
2,6-dimethylnaphthalene-ethylene	18	0.513	-0.890	3.240	-2.440	15.97
2,7-dimethylnaphthalene-CO ₂	10	1.192	-0.332	0.271	-1.579	2.78
fluoranthene-CO ₂	68	1.310	-0.150	1.209	-2.010	12.55
fluorene-CO ₂	146	1.040	-0.370	1.174	-1.300	6.87
lauric acid-CO ₂	24	0.680	-0.600	2.480	-2.090	11.48
myristic acid-CO ₂	30	1.260	-0.470	0.377	-2.150	15.42
naphthalene-CO ₂	242	0.920	-0.090	0.757	-2.450	16.57
naphthalene-ethylene	166	0.741	-0.490	1.327	-1.779	19.26
naphthalene-ethane	48	0.718	-0.705	0.675	-1.194	12.01
1-naphtol-CO ₂	64	1.350	-0.280	2.695	-1.960	16.05
2-naphtol-CO ₂	48	1.530	-0.114	1.735	-2.260	12.31
2-naphtol-ethane	22	1.660	-0.115	1.550	-1.916	17.46
palmitic acid-CO ₂	27	1.530	-0.380	6.295	-42.14	10.42
phenanthrene-CO ₂	281	1.970	-0.350	0.053	1.950	13.15
phenanthrene-ethylene	42	2.060	-0.370	-0.120	1.810	16.31
phenanthrene-ethane	17	2.040	-0.180	-0.230	1.470	14.67
phenol-CO ₂	73	1.460	-0.200	0.990	-1.530	29.70
pyrene-CO ₂	235	2.190	-0.370	-0.061	1.890	4.78
pyrene-ethane	15	1.870	-0.460	-0.060	1.750	1.16
resorcinol-CO ₂	26	3.120	-0.290	-0.020	3.250	6.71
stearic acid-CO ₂	28	1.120	-0.320	0.461	-0.500	8.49
triphenylene-CO ₂	53	3.370	-0.300	-0.800	-1E-4	4.90
triphenylmethane-CO ₂	111	1.800	-0.170	-0.270	0.690	15.08

critical solvent [23], for this reason we have omitted from the database all data points over this range of density (see **Table 3**).

6.2.3. Schmitt and Reid Model

By the assumption that: the system pressure is much greater than the sublimation pressure of the solute, that

the solute is incompressible, and that no solvent is dissolving in the solid phase, the solubilities of solids in supercritical solvents are usually correlated with the equation below [24]:

$$y_2 = \left(\frac{P_2^s}{P} \right) \frac{\exp\left(\frac{v_2^s}{RT} (P - P_2^s) \right)}{\Phi_2^{sf}} \quad (21)$$

v_2^s is the molar volume of the solute (Table 2), the fugacity coefficient of the solute in the supercritical phase (Φ_2^{sf}) is determined from an equation of state applicable to the solute-solvent mixture. The Peng-Robinson equation of state, *i.e.* PR-EOS is a commonly used approach for correlating solubility in supercritical fluids.

Schmitt and Reid [24] used this equation of state for modeling solid solubilities in supercritical fluids but not in the traditional manner due to the lack of the critical properties values and the low accuracy of their estimation. In fact they eliminated the binary interaction parameter and they assumed the solid solute parameters “ a_2 ” and “ b_2 ” independent of temperature and they eliminated the terms with y_2 in the combining and mixing rules since the values of y_2 were sufficiently small. Thus they propose the simplified equation below for the fugacity coefficient:

$$\begin{aligned} \ln \Phi_2^{sf} = & (b_2/b_1)(Z-1) - \ln [P(V-b_1)/RT] \\ & - (a_1/8^{0.5} RTb_1) \left[2(a_2/a_1)^{0.5} - (b_2/b_1) \right] \\ & \times \ln \left[(V + 2.414b_1) / (V - \sqrt{2}b_1) \right] \end{aligned} \quad (22)$$

For the supercritical solvent, the parameters a_1 and b_1 are given by:

$$\begin{aligned} a_1 = & 0.4572R^2 T_{c1}^2 / P_{c1} \\ \times \left[& 1 + (0.3746 + 1.5423\omega_1 - 0.2699\omega_1^2) \left(1 - (T/T_{c1})^{0.5} \right) \right]^2 \\ b_1 = & 0.0778RT_{c1} / P_{c1} \end{aligned}$$

Equation (21) becomes,

$$\begin{aligned} \ln y_2 = & \ln [P_2^s/P] + \frac{(P - P_2^s)v_2^s}{RT} \\ & - \left[(b_2/b_1)(Z-1) - \ln [P(V-b_1)/RT] \right] \\ & - (a_1/8^{0.5} RTb_1) \left[2(a_2/a_1)^{0.5} - (b_2/b_1) \right] \\ & \times \ln \left[(V + 2.414b_1) / (V - \sqrt{2}b_1) \right] \end{aligned} \quad (23)$$

The experimental solubility data are regressed by using Equation (23) to determine the parameters of the solute a_2 and b_2 for each binary system considered. These parameters are expressed in $Pa \text{ (m}^3/\text{mol)}^2$ and m^3/mol

respectively. The Equation (23) is dimensionally consistent and already dimensionless, but the parameters “ a_2 ” and “ b_2 ” are not. For comparison on the same basis the dimensionless parameters are as follow:

$$a_2' = (a_2 \rho_{c1}^2 / P_{c1}) \quad \text{and} \quad b_2' = (b_1 \rho_{c1})$$

6.3. Analysis and Discussion

As mentioned in the previous section, the three first correlations used for comparison require the knowledge of the sublimation pressure. Table 6 gives the coefficients for the estimation of the sublimation pressure of the different solutes taken from literature and the temperature range of applicability.

To compare all the correlations on the same basis, the average absolute relative deviation (AARD) is determined for each system's solute using each model. Table 7 display the parameters of the comparison models and shows in the last column the AARD produced by each equation for the different fluid-solute systems considered. The lowest error fit is marked with (*), the proposed model gives the lowest AARD for 11 binary systems and provides a better fit than the modified EOS for 24 binary systems. From this comparison we want to emphasize that the proposed UNIQUAC model provides better quantitative capabilities with one common EOS which does not require the knowledge of solute critical properties.

Judging from the mean AARD values given in Table 8, we can see clearly that the UNIQUAC model gives good results compared to the other models. The best fit is achieved by the Mendez-Teja model with three parameters given by Equation (20). Whereas, the largest values of AARD and the highest mean AARD are achieved by the model of Wang-Tavlarides (Equation (16)). However, as acknowledged by the authors [22], this model somewhat oversimplified a real system since the interaction between solute and solvent molecules is assumed to follow an interaction behavior similar to the potential well model. In this theory, the system consists of a free volume and a constant solvent cluster volume (*i.e.*, they assume that this volume does not vary with temperature and pressures); the solute thus is either a quasi-gas type (moving in the cluster) or an ideal gas type. As a result, the model developed produces a large error for the supercritical fluid solubility.

6.4. Solubility Prediction

6.4.1. Binary Systems

In order to evaluate the predictive capabilities of the UNIQUAC model and to overcome the over-fitting problem which may alter the model generalization capabilities, solubility data for each considered component

Table 6. Coefficients for sublimation pressure estimation.

Solute	$P^s (Pa) = 10^{\left(\frac{A-B}{T}\right)}$		T-range (K)	Reference
	A	B		
anthracene	14.755	5313.7	308 - 343	[24]
biphenyl	14.804	4367.4	308 - 343	[24]
6-caprolactam	15.480	4811.1	307 - 324	[25] ^a
1,10-decanediol	20.901	7217.0	308 - 328	[26] ^a
2,3-dimethylnaphtalene	14.065	4302.5	308 - 328	[27]
2,6-dimethylnaphtalene	14.417	4415.9	308 - 328	[27]
2,7-dimethylnaphtalene	14.464	4386.7	308 - 328	[28]
fluoranthene	14.795	5357.0	298 - 358	[29]
fluorene	14.205	4561.8	308 - 343	[27]
lauric acid	22.022	7322.0	295 - 314	[15]
myristic acid	20.861	7291.0	311 - 325	[15]
naphthalene	13.865	3823.1	250 - 340	[15] ^a
1-naphtol	10.683	3148.9	308 - 328	[24]
2-naphtol	14.815	4923.9	308 - 343	[24]
palmitic acid	22.341	8069.0	308 - 328	[20]
phenanthrene	14.343	4776.7	300 - 360	[15] ^a
phenol	13.689	3586.4	309 - 333	[20]
pyrene	13.395	4904.0	308 - 398	[30]
stearic acid	21.021	7957.0	308 - 338	[31]
triphenylene	14.462	5804.1	300 - 340	[20]
triphenylmethane	14.781	5228.0	308 - 328	[19]

^aData interpolated in this work.

were split into two sets. The first set of solubility data obtained from randomly sampling 70% of the experimental data, served for the optimization of the model adjustable parameters and for training the model. The second set of solubility data was then used to test its predictive capabilities. In this step we have considered only solutes for which solubility data points are more than 20. **Table 9** summarizes the key information on the two data sets, namely, the training and the test data sets together with the correlation and prediction results. This table lists the number of solubility data points used for each component and deviations in term of the AARD values obtained for both the training and the test data sets. To assess the predictive ability of the model, the two AARD values are compared. To be predictive, the model should respect the following rule: the AARD values for both data sets should be of the same order of magnitude for

each component. **Table 9** shows that the AARD values obtained for the test data set are in accordance with those of the training data set and are generally of the same order of magnitude. This results implies that the proposed model do not show any over-fitting problem or over prediction of the experimental solubility data. Therefore we can conclude that the predictive ability of the model is well demonstrated.

6.4.2. Ternary Systems

The study of mixed-solute systems is important because most potential applications of supercritical fluid extraction involve the removal of a desired compound from a matrix of components. However, in this section an attempt is made to predict the solubilities of mixed compounds in supercritical carbon dioxide. Experimental data provided by: Kosal and Holder [32] for mixed an

Table 7. Comparison with the literature models considered.

System	N	α	β	α'	β'	γ'	a'_2	b'_2	AARD%
anthracene-CO ₂	206								
Equation (19)		4.10	4.73						14.88
Equation (20)				-33.09	4.58	15.57			14.41*
Equation (16)		16.17	0.65						21.44
Equation (23)							8.7E-5	1.24E-4	16.74
UNIQUAC model									14.58
anthracene-ethylene	27								
Equation (19)		6.33	5.22						14.30
Equation (20)				-32.12	5.33	12.80			7.60*
Equation (16)		18.05	0.776						21.80
Equation (23)							1.26E-4	1.56E-4	17.05
UNIQUAC model									8.06
anthracene-ethane	13								
Equation (19)		3.42	5.05						10.38
Equation (20)				-33.06	4.77	15.76			5.66*
Equation (16)		15.00	0.602						22.64
Equation (23)							1.19E-4	1.54E-4	10.96
UNIQUAC model									6.87
biphenyl-CO ₂	57								
Equation (19)		3.87	4.04						17.69
Equation (20)				-35.57	4.19	24.15			14.48
Equation (16)		17.58	0.910						13.11*
Equation (23)							8.39E-5	1.4E-4	19.14
UNIQUAC model									16.39
biphenyl-ethane	8								
Equation (19)		3.11	4.42						9.81
Equation (20)				-40.01	4.97	27.71			5.76
Equation (16)		15.06	0.705						3.77*
Equation (23)							1.0E-4	1.41E-4	6.59
UNIQUAC model									8.99
6-caprolactam-CO ₂	32								
Equation (19)		-0.08	7.96						6.95
Equation (20)				-29.20	6.89	14.50			7.51
Equation (16)		9.71	0.08						12.71
Equation (23)							6.36E-5	4.33E-5	16.40
UNIQUAC model									5.66*

Continued

1,10-decanediol-CO ₂	15							
Equation (19)		5.40	4.55				4.22	
Equation (20)				-45.09	4.37	28.71	3.03*	
Equation (16)		20.29	0.859				6.60	
Equation (23)						1.08E-4	1.47E-4	6.07
UNIQUAC model								3.94
2,3-dimethylnaphtalène-CO ₂	25							
Equation (19)		2.68	4.74				20.05	
Equation (20)				-27.72	4.56	14.76	19.74	
Equation (16)		12.57	0.493				26.07	
Equation (23)						7.19E-5	1.14E-4	32.97
UNIQUAC model								19.71*
2,3-dimethylnaphtalene-ethylene	18							
Equation (19)		2.82	5.72				16.78	
Equation (20)				-42.37	6.48	24.85	14.62	
Equation (16)		12.67	0.373				16.37	
Equation (23)						9.26E-5	1.10E-4	17.80
UNIQUAC model								13.04*
2,6-dimethylnaphtalène-CO ₂	23							
Equation (19)		4.23	3.77				12.75	
Equation (20)				-31.54	3.90	19.42	11.78	
Equation (16)		17.16	0.885				11.85	
Equation (23)						8.66E-5	1.57E-4	13.56
UNIQUAC model								9.68*
2,6-dimethylnaphtalene-ethylene	18							
Equation (19)		2.73	5.59				11.77	
Equation (20)				-38.84	6.13	21.93	10.31*	
Equation (16)		14.28	0.521				13.81	
Equation (23)						8.64E-5	1.12E-4	10.41
UNIQUAC model								15.97
2,7-dimethylnaphtalène-CO ₂	10							
Equation (19)		4.87	3.44				8.52	
Equation (20)				-30.31	3.63	19.05	6.73	
Equation (16)		18.66	1.004				9.95	
Equation (23)						9.79E-5	1.74E-4	12.62
UNIQUAC model								2.78*
fluoranthene-CO ₂	68							

Continued

Equation (19)		6.73	4.42				18.38	
Equation (20)				-29.06	4.28	13.99	11.21*	
Equation (16)		24.59	1.06				35.14	
Equation (23)						1.49E-4	1.96E-4	24.30
UNIQUAC model								12.35
fluorene-CO ₂	146							
Equation (19)		4.74	3.97					7.59
Equation (20)				-29.77	3.97	16.87		7.59
Equation (16)		19.63	0.99					15.23
Equation (23)						9.59E-5	1.53E4	13.80
UNIQUAC model								6.87*
lauric acid-CO ₂	24							
Equation (19)		4.39	6.83					13.56
Equation (20)				-37.51	6.66	21.85		11.06*
Equation (16)		19.63	0.55					14.77
Equation (23)						1.39E-4	1.54E-4	14.66
UNIQUAC model								11.48
myristic acid-CO ₂	30							
Equation (19)		7.41	5.72					14.66
Equation (20)				-48.06	5.72	32.48		14.65*
Equation (16)		25.65	0.82					17.20
Equation (23)						1.88E-4	2.13E-4	15.12
UNIQUAC model								15.45
naphtalene-CO ₂	242							
Equation (19)		3.39	3.31					19.45
Equation (20)				-34.37	3.68	24.12		11.79
Equation (16)		15.55	0.948					11.13*
Equation (23)						6.77E-5	1.34E-4	14.37
UNIQUAC model								16.57
naphthalene-ethylene	167							
Equation (19)		3.24	4.18					16.02
Equation (20)				-32.94	4.54	20.65		1.28
Equation (16)		14.00	0.655					10.53*
Equation (23)						8.43E-5	1.37E-4	16.46
UNIQUAC model								19.26
naphthalene-ethane	48							
Equation (19)		2.65	3.70					15.19

Continued

Equation (20)				-32.25	3.85	22.23		12.47	
Equation (16)		14.22	0.833					10.15*	
Equation (23)							8.03E-5	1.37E-4	14.12
UNIQUAC model									12.01
1-naphtol-CO ₂	64								
Equation (19)		4.02	3.83						20.41
Equation (20)				-35.10	3.86	21.15			17.99
Equation (16)		18.48	1.015						18.27
Equation (23)							7.32E-5	1.18E-4	23.33
UNIQUAC model									16.05*
2-naphtol-CO ₂	48								
Equation (19)		3.71	4.53						14.08
Equation (20)				-30.50	4.30	15.73			11.91*
Equation (16)		15.55	0.948						84.51
Equation (23)							8.28E-5	1.24E-4	18.93
UNIQUAC model									12.31
2-naphtol-ethane	22								
Equation (19)		2.68	4.13						8.74
Equation (20)				-33.93	4.10	18.27			8.68*
Equation (16)		13.55	0.704						16.68
Equation (23)							8.4E-5	1.26E-4	10.92
UNIQUAC model									17.46
Palmitic acid-CO ₂	27								
Equation (19)		8.26	5.34						7.85
Equation (20)				-52.37	5.32	35.22			7.70*
Equation (16)		26.65	0.86						14.10
Equation (23)							2.03E-4	2.34E-4	13.15
UNIQUAC model									10.42
phenanthrene-CO ₂	281								
Equation (19)		4.92	4.37						13.57
Equation (20)				-32.20	4.40	18.06			13.37
Equation (16)		20.59	0.96						17.34
Equation (23)							1.07E-4	1.64E-4	17.27
UNIQUAC model									13.15*
phenanthrene-ethylene	42								
Equation (19)		4.08	5.83						12.55
Equation (20)				-31.68	5.64	15.03			9.55*

Continued

Equation (16)		16.54	0.55					21.72
Equation (23)						1.35E-4	1.66E-4	16.80
UNIQUAC model								16.31
phenanthrene-ethane	17							
Equation (19)		2.21	5.81					16.13
Equation (20)				-30.77	5.83	14.73		15.11
Equation (16)		13.80	0.49					19.45
Equation (23)						1.09E-4	1.31E-4	17.85
UNIQUAC model								14.67*
phenol-CO ₂	73							
Equation (19)		2.12	3.23					28.34
Equation (20)				-36.15	3.65	25.92		24.84*
Equation (16)		12.32	0.82					26.54
Equation (23)						4.66E-5	1.01E-4	26.38
UNIQUAC model								29.70
pyrene-CO ₂	235							
Equation (19)		5.66	4.89					9.60
Equation (20)				-31.67	4.79	14.92		6.41
Equation (16)		20.75	0.85					14.44
Equation (23)						1.14E-4	1.52E-4	11.24
UNIQUAC model								4.78*
pyrene-ethane	15							
Equation (19)		5.34	4.95					2.89
Equation (20)				-30.24	4.95	13.83		2.89
Equation (16)		20.55	0.87					1.99
Equation (23)						1.49E-4	1.7E-4	6.07
UNIQUAC model								1.16*
resorcinol-CO ₂	26							
Equation (19)		2.83	4.38					6.02
Equation (20)				-33.73	4.42	17.67		5.05*
Equation (16)		11.67	0.61					66.21
Equation (23)						4.58E-5	7.38E-5	65.60
UNIQUAC model								6.71
stearic acid-CO ₂	28							
Equation (19)		10.55	4.59					8.80
Equation (20)				-53.95	5.16	35.78		7.53*
Equation (16)		24.25	0.65					30.96

Continued

Equation (23)							1.98E-4	2.08E-4	31.30
UNIQUAC model									8.49
triphenylene-CO ₂	53								
Equation (19)		8.15	5.04						12.84
Equation (20)					-32.91	5.03	17.78		4.77*
Equation (16)		26.18	1.01						20.40
Equation (23)							1.59E-4	1.92E-4	14.19
UNIQUAC model									4.90
triphenylmethane-CO ₂	111								
Equation (19)		7.46	4.42						13.18
Equation (20)					-32.29	4.42	22.69		13.17
Equation (16)		35.63	1.68						10.90*
Equation (23)							1.65E-4	2.22E-4	24.71
UNIQUAC model									15.09

Table 8. AARD range and mean AARD.

	Solvent CO ₂		Solvent ethane		Solvent ethylene		Mean AARD	Mean AARD	Mean AARD
	minima	maxima	minima	maxima	minima	maxima	(solvent CO ₂)	(solvent ethylene)	(solvent ethane)
Equation (19)	4.20	28.34	2.9	16.3	11.7	16.8	13.34	14.3	10.5
Equation (20)	3.03	24.84	2.9	15.1	7.6	14.6	11.21	10.7	8.40
Equation (16)	6.60	84.51	1.99	22.6	10.5	21.8	22.68	16.8	12.4
Equation (23)	6.07	65.60	6.07	17.85	10.4	17.8	20.27	15.7	11.1
UNIQUAC model	2.78	29.70	1.16	17.46	8.06	19.2	11.70	14.5	10.19

thracene and phenanthrene, Pennisi and Chimowitz [26] for mixed 1,10-decanediol and benzoic acid, Iwai *et al.* [33] for mixed 2,6- and 2,7-dimethylnaphthalenes are used. The solubility data of the considered compounds are very small and have an order of 10^{-6} - 10^{-3} . As a consequence, we can assume that the density of the supercritical phase is that of the pure solvent, and the activity coefficient of each solute is the one at infinite dilution. In this case the only interaction parameters that are taken into account are those of solutes-CO₂. Therefore predicted solubilities are estimated using Equations (6) to 13(b) and interaction parameters listed in **Table 5** are directly implemented to estimate the solubility of each component in the mixture.

The interpolation results are given in **Table 10**, the absolute average relative deviation (AARD) obtained are generally low confirming the predictive ability of the model but have an order of magnitude considerably higher than those for the solutes in binary systems. This can be attributed to the fact that effect of solute-solute interactions is not always negligible and assuming an

infinite dilution of all solutes can be inaccurate in some systems. However, there is significant experimental evidence to suggest that solute-solute interactions are important even in dilute solutions [34-36].

7. Conclusion

In this work, we have proposed the correlation and prediction of the solubility of solid solutes with different functional groups in chemically diverse supercritical fluids with a methodology based on the expanded liquid theory, in which the solid-fluid equilibrium is modeled using the local composition model of UNIQUAC. For the elaboration of the model we have considered 33 systems solid-SC fluid to built-up an exhaustive solutes solubility database consisting of more than 2218 experimental solubility data in supercritical fluids taken from literature. The proposed model achieves an overall AARD of 11.85 on a whole database and on a range of 1.16 to 29.7, these results show that the calculated solubility data are in

Table 9. Prediction capabilities of the model.

System	Training set		Test set	
	N	AARD%	N	AARD%
anthracene-CO ₂	144	14.51	62	14.70
anthracene-ethylene	18	8.36	9	7.57
biphenyl-CO ₂	39	15.15	18	20.27
6-caprolactam-CO ₂	22	6.18	10	4.76
2,3-dimethylnaphthalene-CO ₂	17	16.93	8	21.42
2,6-dimethylnaphthalene-CO ₂	16	8.10	7	15.24
fluoranthene-CO ₂	47	11.33	20	16.22
fluorene-CO ₂	102	6.48	44	7.86
lauric acid-CO ₂	16	10.06	8	20.48
myristic acid-CO ₂	20	12.98	10	18.79
naphthalene-CO ₂	169	16.36	73	17.28
naphthalene-ethylene	116	18.50	50	21.20
naphthalene-ethane	33	10.16	15	16.42
1-naphthol-CO ₂	44	15.76	20	17.05
2-naphthol-CO ₂	33	8.32	15	21.22
2-naphthol-ethane	15	18.24	7	17.20
palmitic acid-CO ₂	18	10.54	9	12.23
phenanthrene-CO ₂	196	13.44	85	12.54
phenanthrene-ethylene	29	16.90	13	15.68
phenol-CO ₂	51	26.18	22	47.01
pyrene-CO ₂	164	4.71	71	5.04
Resorcinol-CO ₂	18	6.51	8	7.17
stearic acid-CO ₂	19	7.87	9	11.15
triphenylene-CO ₂	37	5.05	16	5.66
triphenylmethane-CO ₂	77	16.73	34	11.90

Table 10. Prediction results for solutes considered in ternary systems.

Solute	N	T-range (K)	P-range (bar)	ρ_r range	AARD (%)
anthracene	10	308 - 318	104 - 242	1.19 - 1.92	27.0
phenanthrene	10	308 - 318	104 - 242	1.19 - 1.92	15.5
2,6-dimethyl naphthalene	12	308 - 318	90 - 247	0.72 - 1.92	18.1
2,7-dimethyl naphthalene	12	308 - 318	90 - 247	0.72 - 1.92	16.9
1,10-decanediol	10	308 - 318	164 - 307	1.64 - 1.99	26.2

good agreement with the experimental ones. Comparison between the considered literature correlations and the proposed model was justified using comparative criteria. The model's performance is similar and sometimes superior to the literature models considered. The advantages of this model include the following: it does not require the knowledge of critical properties of the solutes and does take into account the binary interaction between solid solute and solvent. Moreover the predictive capabilities of the proposed model were well demonstrated both for solid-solvent and mixed solids-solvent systems.

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