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Determining sublimation pressures from solubility data of solids in different solvents

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Abstract

Solvent effects in the calculation of the sublimation pressure of pure solids using high pressure solubility data are discussed. Three binary gas–solid systems containing anthracene, napthalene and phenanthrene as solutes and carbon dioxide, ethane, ethylene, fluoroform, chlorotrifluoromethane as solvents are considered in the study. The Peng–Robinson EoS with the mixing rules proposed by Wong and Sandler are used to evaluate the fugacity coefficient φ^S included in the classical solubility equation which relates the mole fraction of a dissolved solid in a compressed gas phase. The sublimation pressure P^S of the solid is considered as a parameter to be determined by regression analysis of experimental solubility data (TPy), and theoretically it should be independent of the solvent. The results show that the determination of sublimation pressure using high pressure solubility data is reliable and produce unique values of sublimation pressure independent of the solvents in the mixtures.

Keywords: Sublimation pressure; Gas–solid equilibrium; Genetic algorithms; Wong–Sandler mixing rule; Supercritical fluids

1. Introduction

Accurate prediction of phase equilibria in gas–solid mixtures is needed in many industrial applications, especially in separation processes such as supercritical fluid extraction. For this reason, it is essential to use reliable models that can correlate and predict phase equilibrium properties. One of the common approaches used in the literature to correlate and predict phase equilibrium is the so-called *equation of state method*. The use of this method requires an equation of state that well relates the variables temperature, pressure and volume and appropriate mixing rules to express the dependence of the equation of state parameters on concentration. There are several industrially important EoS being the most popular ones the so-called cubic equations derived from the equation first proposed by van der Waals. A review by one of the authors gives a detailed picture of the present use and applications of this type of equations [1]. All practical cubic equations when applied to mixtures involve the use of mixing rules which include empirical binary interaction parameters k_{ij}'s usually calculated from experimental phase equilibrium data. In applications of EoS to complex mixtures even modern mixing rules require more than one interaction parameter to obtain good correlation and prediction of phase equilibrium properties [2].

Phase equilibrium calculations of a solid dissolved in a compressed gas, at a pressure P and a temperature T can be performed using the fundamental equation of phase equilibria which leads to a simple equation that relates solubility y, pressure P, and temperature T. The equation also contains other properties such as the sublimation pressure P^S, the molar volume of the solid v^S and the fugacity coefficient of the solid component in the high pressure gas φ^S [3]. Of all these properties involved in the calculation of the solubility of the solid in the high pressure gas, the sublimation pressure has received low attention in the literature, although it is directly related to the solubility. The molar volume does not have a strong influence on the calculations and the fugacity coefficient φ^S can be estimated from an appropriate

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Abbreviations: EoS, equation of state; PR, Peng–Robinson equation of state; WS, Wong–Sandler mixing rule; VL, van Laar model for G^{ex}

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Nomenclature

a_i, a_j, b_i, b_j	constants for pure components in the equation of state
a_{ij}, b_{ij}	interaction constants in the equation of state for a mixture
a_{m}, b_{m}	constants for mixtures in the equation of state
f_2^{gas}	fugacity of the solute in the gas phase
f_2^{sol}	fugacity of the solute in the solid phase
F	objective function
F_i	parameter in the $\alpha(T_{\mathrm{r}}, \omega)$ function
k_{ij}	binary interaction parameters in the PR equation of state
M	molecular weight
N	number of points in a data set
P	pressure
P_{c}	critical pressure
P_2^{S}	sublimation pressure of the pure solid
R	universal gas constant
T	system temperature
T_{c}	critical temperature
T_{r}	reduced temperature
v	molar volume
v_2^{sol}	solid molar volume
y_i	mole fraction component i in vapor phase
Z	compressibility factor

Greek letters

$\alpha(T_{\mathrm{r}}, \omega)$	temperature function in an EoS
Δ	deviation
φ_2	fugacity coefficient of solute
φ_2^{S}	fugacity coefficient at sublimation pressure P_2^{S}
ω	acentric factor

Super/subscripts

exp	experimental
calc	calculated
S	sublimation
sol	solid phase
vap	vapor phase

equation of state and mixing rules. The sublimation pressure is usually small for common industrially important solids and in many cases available experimental techniques cannot be used to obtain accurate values.

In another communication, the authors have proposed to evaluate the sublimation pressure of a solid from solubility data of the solid in a high pressure gas [4]. They determined the sublimation pressure of several solids (naphthalene, biphenyl, anthracene, phenanthrene and pyrene), using solubility data of those solids in high pressure carbon dioxide. However, that study did not considered in a detailed form the influence of the solvent, if there is any, in determining the sublimation pressure of a given solid. This article considered this situation and analyzes the influence of different solvents (carbon dioxide, ethane, ethylene, fluoroform and chlorotrifluoromethane) in determining the sublimation pressure of anthracene, naphthalene and phenanthrene. In theory the calculated sublimation pressures should be independent of the solvent used, but this statement must be proved.

2. Solubility calculations

The theory of solid solubility in a compressed gas is found in standard books [3,5], so a summary only is given in what follows. The fundamental equation of phase equilibria establishes that at a given temperature and pressure, the fugacity of a component, for instance the solid solute, in the gas phase must be equal to the fugacity of the same component in the solid phase. If subscript 2 stands for the solid component, then:

$$f_2^{\mathrm{sol}} = f_2^{\mathrm{gas}} \tag{1}$$

If the solid phase is considered to be a pure substance, then:

$$P^{\mathrm{S}}\varphi_2^{\mathrm{sol}} = y_2\varphi_2^{\mathrm{gas}}P \tag{2}$$

Since the sublimation pressure is normally low, ideal gas behavior for the gas phase over the pure solid can be assumed, and $\varphi_2^{\mathrm{S}} \approx 1$. Also, the volume of the solid is considered to be pressure independent, the mole fraction of the solute in the gas phase, or solubility, at the temperature T and pressure P for component 2 is [5]:

$$y_2 = \frac{P_2^{\mathrm{S}}\,\mathrm{e}^{(v_2^{\mathrm{sol}}/RT)(P-P_2^{\mathrm{S}})}}{P\varphi_2} \tag{3}$$

Here, P_2^{S} is the sublimation pressure of the pure solid, v_2^{sol} the solid molar volume, all at the temperature T and φ_2 is the fugacity coefficient of solid (2) at the pressure P.

The fugacity coefficient is calculated from standard thermodynamic relations as [5]:

$$RT\ln(\varphi_i) = \int_v^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{v}\right]\mathrm{d}v - RT\ln Z \tag{4}$$

The Peng–Robinson EoS (PR) [6], with the mixing rules proposed by Wong and Sandler [7], are used as the thermodynamic model to evaluate the fugacity coefficient φ_2. The excess Gibbs free energy that appears in the Wong–Sandler (WS) mixing rules is represented by the van Laar model (VL). Therefore, the model contains three parameters (the van Laar constants A_{12} and A_{21} and the k_{12} parameter included in the mixing rule). This model is designed here as PR/WS/VL.

Table 1 shows the Peng–Robinson equation. Table 2 shows the Wong–Sandler mixing rules for the PR EoS that are used in this work [3]. In those equations a_{m} and b_{m} are the equation of state constants with k_{ij} as adjustable parameter, $\Omega = 0.34657$ for the Peng–Robinson EoS, and $A_{\infty}^{\mathrm{E}}(x)$ is calculated assuming that $A_{\infty}^{\mathrm{E}}(x) \approx A_0^{\mathrm{E}}(x) \approx G_0^{\mathrm{E}}(x)$. For the excess Gibbs free energy $G_0^{\mathrm{E}}(x)$, is calculated using the van Laar model (see Table 2) that has been shown to perform well in high pressure phase equilibrium calculations [4].

Table 1
The Peng–Robinson EoS

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

$$a = 0.457235\left(\frac{R^2T_c^2}{P_c}\right)\alpha(T_r)$$

$$b = 0.077796\left(\frac{RT_c}{P_c}\right)\alpha(T_r)^{0.5} = [1 + F_i(1 - T_r^{0.5})]$$

$$F_i = 0.37646 + 1.54226\omega - 0.26992\omega^2$$

For mixtures

$$P = \frac{RT}{v-b_m} + \frac{a_m}{v(v+b_m)+b_m(v-b_m)}$$

The expressions for the fugacity coefficient using the PR equation with WS mixing and combination rules (Table 2) can be found elsewhere [2]. The problem is then reduced here to determine the parameters A_{12} and A_{21} in the van Laar model, the k_{12} parameter included in the combining rule for $(b - a/RT)_{12}$, and the sublimation pressure P_2^S that appears in the solubility Eq. (3), using available high pressure TPy data for gas–solid systems.

The optimization procedure requires an objective function that is defined here as:

$$F = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{y_2^{\text{calc}} - y_2^{\text{exp}}}{y_2^{\text{exp}}}\right|_i \qquad (5)$$

In this equation N is the number of points in the experimental data set and y_2 is the mole fraction of the solid solute in the gas phase, both experimental (exp) and calculated (cal) values. The optimization problem, that is the determination of the sublimation pressure and the EoS parameters was solved using genetic algorithms, as explained elsewhere by the authors [4]. For more details on genetic algorithms, the books of Davis [8] and of Goldberg [9] are recommended.

3. Cases studied

Binary system containing anthracene, napthalene and phenanthrene as solute in various solvents (carbon dioxide, ethane, ethylene, fluoroform and chlorotrifluoromethane) were considered in the study. The data consisted of 38 isotherms and a total of 435 PTy data points. The binary systems studied are the following: (i) napthalene as solute with the following five solvents: carbon dioxide, ethane, ethylene, fluoroform and chlorotrifluoromethane; (ii) phenanthrene as solute with the following four solvents: carbon dioxide, ethane, fluoroform and chlorotrifluoromethane; (iii) anthracene as solute with the following three solvents: carbon dioxide, ethane and fluoroform.

Table 2
The Wong–Sandler mixing rules for the PR EoS and the van Laar model

The Wong–Sandler mixing rules for the PR EoS

$$b_m = \frac{\sum_i^N\sum_j^N y_iy_j(b-(a/RT))_{ij}}{1-\sum_i^N (y_ia_i/b_iRT)-(A_\infty^E(y)/\Omega RT)}$$

$$\left(a - \frac{a}{RT}\right)_{ij} = \frac{1}{2}[b_i + b_j] - \frac{\sqrt{a_ia_j}}{RT}(1 - k_{ij})$$

$$a_m = b_m\left(\sum_i^N \frac{y_ia_i}{b_i} - \frac{A_\infty^E(y)}{\Omega}\right)$$

For a binary mixture

$$b_m = \frac{y_1^2(b-a/RT)_1+2y_1y_2(b-a/RT)_{12}+y_2^2(b-a/RT)_2}{1-(y_1a_1/b_1RT)-(y_2a_2/b_2RT)-(A_\infty^E(y)/\Omega RT)}$$

$$\left(b - \frac{a}{RT}\right)_{12} = \frac{1}{2}[b_1 + b_2] - \frac{\sqrt{a_1a_2}}{RT}(1 - k_{12})$$

$$a_m = b_m\left(\frac{y_1a_1}{b_1RT} + \frac{y_2a_2}{b_2RT} + \frac{G_0^E(y)}{\Omega}\right)$$

The van Laar model

$$\frac{G^E}{RT} = \sum_i^N y_i\frac{\sum_j^N y_jA_{ij}}{1-x_i}\left[1 - \frac{y_i\sum_j^N y_jA_{ij}}{y_i\sum_j^N y_jA_{ij}+(1-y_i)x_i\sum_j^N y_jA_{ji}}\right]^2$$

For a binary mixture

$$\frac{G^E}{RT} = \frac{(A_{12}/RT)y_1y_2}{y_1(A_{12}/A_{21})+y_2}$$

Table 3 shows the basic properties of the compounds involved in the study. In the table, M is the molecular weight, T_c the critical temperature, P_c the critical pressure and ω is the acentric factor. The last column shows the literature reference from where these properties were obtained.

Table 4 shows details of the phase equilibrium data considered in this study. In this table, N indicate the number of experimental data. For naphthlene as solute, the temperature and the pressure vary from 308 to 338 K and from 0.8 to 36.1 MPa, respectively. Napthalene solubility in the supercritical solvents covers a range from 5.0×10^{-5} to 13.4×10^{-1}. For systems containing phenanthrene as solute, temperature and pressure vary from 308 to 333 K and from 6.9 to 41.5 MPa, respectively. Phenanthrene solubility in the supercritical solvents varies from 9.0×10^{-5} to 8.0×10^{-3}. For systems containing anthracene as solute, temperature and pressure vary from 308 to 343 K and from 9.0 to 48.4 MPa, respectively. For these systems anthracene solubility in the supercritical solvents varies from 0.3×10^{-6} to 7.7×10^{-4}. These details are of special importance because the thermodynamic model used must be able to correlate the data in this wide range of pressure and solubility. The Peng–Robinson EoS with the mixing rules of Wong and Sandler, including the van Laar model for the excess Gibbs free energy, have shown the required flexibility to model the systems under study.

In obtaining the optimum value of the sublimation pressure P_2^S using the solubility data of the solid solutes described in Table 4, the interaction parameter k_{12} included in the combining rule for $(b - a/RT)_{12}$ and the van Laar parameters A_{12} and A_{21} included in the van Laar model of the Wong–Sandler mixing rules are also calculated. These parameters are not directly related to the sublimation pressure, but their values determine the acceptancy of the model used as a good correlating tool for the solubility of the solid in the compressed gas phase.

4. Results and discussion

The accuracy of the model and the method used to calculate the sublimation pressure is evaluated by considering the deviations between experimental and calculated values of the solubility of the solid in the high pressure gas. If these deviations are within acceptable defined ranges, then the model and the calculated sublimation pressure are considered to be acceptable and the value of the sublimation pressure is accepted as the true value of this property. This statement has been checked using data of substances for which the sublimation pressures are known and using mixture data of the studied solids in different type of solvents. The deviations are expressed in relative and

Table 3
Properties of the gases and solids considered in this work

Compound	Formula	M	T_c (K)	P_c (Pa)	ω	Reference
Anthracene	$C_{14}H_{10}$	178.2	873.0	2.90	0.486	[10]
Naphthalene	$C_{10}H_8$	128.2	748.4	4.05	0.302	[10]
Phenanthrene	$C_{14}H_{10}$	178.2	869.0	2.90	0.471	[10]
Carbon dioxide	CO_2	44.0	304.2	7.38	0.224	[10]
Ethane	C_2H_6	30.1	305.3	4.88	0.098	[11]
Ethylene	C_2H_4	28.1	282.3	5.04	0.086	[10]
Fluoroform	CHF_3	70.0	299.2	4.95	0.272	[11]
Chlorotrifluoromethane	$CClF_3$	104.5	302.0	3.92	0.180	[11]

In the table, M is the molecular weight, T_c the critical temperature, P_c the critical pressure and ω is the acentric factor. The last column shows the literature reference from where these properties were obtained.

Table 4
Details on the phase equilibrium data for the systems considered in this study

Systems	Reference	T (K)	N	Range of date	
				P (MPa)	y_2 ($\times 10^3$)
Napthalene + carbon dioxide	[12]	308	9	8.6–25.6	75–193
		328	16	8.2–28.8	13–539
		333	19	10.8–29.2	52–981
		338	7	15.1–23.3	247–791
Napthalene + ethane	[13]	308	15	5.0–36.2	25–348
		318	12	5.1–36.4	6–585
		328	14	5.6–36.4	1.2–1340
	[14]	308	6	3.5–20.8	1–31.9
		318	8	4.9–25.0	5–467
Napthalene + ethylene	[15]	308	10	0.8–6.3	0.5–0.38
		323	9	0.8–6.3	1.6–5.1
		338	9	1.2–5.7	3.8–6.6
Napthalene + fluoroform	[13]	308	6	6.0–35.2	24–92
		318	6	6.0–35.2	8–134
		328	6	6.6–35.2	12–185
Napthalene + chlorotrifluoromethane	[13]	308	7	5.0–35.6	28–79
		318	7	5.0–35.6	11–109
		328	7	5.1–36.1	10–158
Phenanthrene + carbon dioxide	[16]	313	26	10.7–35.7	4.2–23.4
		323	30	11.0–34.1	2.9–31.0
		333	30	11.1–35.0	2.0–40.8
Phenanthrene + ethane	[13]	308	6	7.1–35.5	4.0–60.4
	[13]	318	6	7.1–35.5	2.0–80.1
	[14]	333	7	6.9–41.5	1.9–75.3
Phenanthrene + fluoroform	[13]	308	4	8.0–36.4	1.4–12.8
		318	4	8.0–36.4	0.9–17.2
Phenanthrene + chlorotrifluoromethane	[13]	308	4	7.5–30.1	2.3–8.8
		318	4	7.5–30.1	2.3–11.0
Anthracene + carbon dioxide	[14]	323	10	9.0–41.5	0.03–1.72
		343	9	11.8–41.5	0.14–3.49
	[16]	313	30	11.8–33.8	0.27–0.92
		323	30	12.1–35.0	0.22–1.45
		333	30	13.2–35.6	0.22–1.83
Anthracene + ethane	[14]	308	4	10.4–48.4	0.76–1.96
		323	10	10.4–44.9	1.01–3.72
		343	7	13.8–41.5	2.38–7.68
Anthracene + fluoroform	[13]	328	8	9.1–29.8	0.09–0.67
		343	8	11.1–29.9	0.12–1.28

In the table the temperature values have been rounded to the closest integer.

absolute forms, as follows:

$$\Delta y_2\% = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{y_2^{\mathrm{cal}} - y_2^{\mathrm{exp}}}{y_2^{\mathrm{exp}}}\right]_i \tag{6}$$

$$|\Delta y_2\%| = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{|y_2^{\mathrm{cal}} - y_2^{\mathrm{exp}}|}{y_2^{\mathrm{exp}}}\right]_i \tag{7}$$

For systems containing napthalene as solute. Relative deviations in the solubility calculation vary from −4.5% to 11.8% and the absolute deviations vary from 3.8% to 15.0%. Of the 18 isotherms studied, 14 of them present absolute deviations in solubility calculations less than 12%. For systems containing phenanthrene as solute, relative deviations in solubility calculation vary from 0.12% to 7.5%, while absolute deviations vary from 2.8% to 15.5%. Among the 10 isotherms studied, 8 of them present deviations less than 11%. For the systems containing anthracene as solute, the model reproduces the solubility of those binary systems with relative and absolute deviations less than 10% for each temperature. Maximum relative and absolute deviations are 8.5% and 9.8%, respectively. All these numbers are, according to the literature, within acceptable margins for modeling and correlation [4].

Table 5
Optimum interaction parameters and sublimation pressures of the solid solutes at all temperatures studied

Naphthalene+	T (K)	N	k_{12}	A_{12}	A_{21}	P_S ($\times 10^{-2}$ MPa)
Carbon dioxide	308	9	0.08246	2.3636	2.9801	0.271
	328	16	0.03474	3.3385	0.6743	1.606
	333	19	0.09084	2.3069	0.8090	2.407
	338	7	0.08246	2.5812	0.8334	3.379
Ethane	308	15	0.00599	1.4056	4.2086	0.289
	318	12	0.00166	1.2636	4.0199	0.719
	328	14	0.00116	0.8772	2.6481	1.590
	308	6	0.00933	1.4480	3.4662	0.309
	318	8	0.00105	1.2785	5.4031	0.709
Ethylene	308	10	0.03607	0.8978	4.7469	0.290
	323	9	0.01441	1.4484	4.7248	0.992
	338	6	0.00227	19.338	3.1670	3.215
Fluoroform	308	6	0.01269	3.2929	4.8148	0.303
	318	6	0.00102	3.0262	5.6050	0.710
	328	6	0.00113	2.9046	3.7365	1.693
Chlorotrifluoromethane	308	7	0.06872	2.9431	4.8734	0.299
	318	7	0.00865	2.9971	2.9239	0.704
	328	7	0.00689	2.7775	2.5381	1.606
Phenanthrene+	T (K)	N	k_{12}	A_{12}	A_{21}	P_S ($\times 10^{-1}$ MPa)
Carbon dioxide	313	26	0.15278	4.4016	0.7769	0.91
	323	30	0.13675	4.3624	0.6390	2.68
	333	30	0.12064	4.3134	0.3690	6.95
Ethane	318	6	0.05826	2.2808	0.7398	1.55
	328	6	0.04067	2.4154	0.2315	4.25
	333	7	0.00654	2.8740	1.6235	6.99
Fluoroform	318	4	0.08355	4.2362	2.2035	1.65
	328	4	0.04313	4.2374	1.7869	4.28
Chlorotrifluoromethane	318	4	0.07217	4.5303	1.8871	1.52
	328	4	0.06784	4.2105	2.4829	4.22
Anthracene+	T (K)	N	k_{12}	A_{12}	A_{21}	P_S (MPa)
Carbon dioxide	323	8	0.15841	4.5915	1.3495	1.89
	343	9	0.12618	4.7562	0.8112	19.10
	313	30	0.18943	5.0434	1.1887	0.61
	323	30	0.16442	4.9834	1.8708	2.05
	333	30	0.14092	5.3397	2.4917	6.38
Ethane	308	4	0.13724	2.8096	0.7879	0.31
	323	10	0.10313	2.6295	1.2021	2.07
	343	7	0.07617	2.4484	1.6324	18.60
Fluoroform	328	8	0.14997	5.1904	2.8337	3.67
	343	8	0.12645	4.5861	2.8297	18.80

Table 6
Relative deviations between calculated and experimental values of the sublimation pressure for all cases studied

	T (K)	% ΔP_S
Naphthalene+		
Carbon dioxide	308	7.5
	328	−0.3
	333	1.6
	338	2.0
Ethane	308	1.1
	318	−2.4
	328	0.7
	308	−5.7
	318	−0.9
Ethylene	308	0.7
	323	7.1
	338	6.8
Fluoroform	308	−3.5
	318	−1.0
	328	−5.8
Chlorotrifluoromethane	308	−2.1
	318	−0.2
	328	−0.3
Phenanthrene+		
Carbon dioxide	313	0.3
	323	−4.1
	333	−1.7
Ethane	318	−0.3
	328	−0.7
	333	−2.4
Fluoroform	318	−6.8
	328	−1.3
Chlorotrifluoromethane	318	1.4
	328	0.1
Anthracene+		
Carbon dioxide	323	7.8
	343	−2.6
	313	0.2
	323	−0.1
	333	0.1
Ethane	308	4.3
	323	−1.0
	343	0.1
Fluoroform	328	−0.6
	343	−1.0

Tables 5 and 6 show the results obtained using PR/WS/VL model for gas–solid systems considered in this study. In Table 5, the first three columns list the system, temperature and number of experimental data (N), respectively. The fourth column lists the interaction parameter k_{ij}, and the fifth and sixth column list the van Laar A_{12} and A_{21} parameters, respectively. The seventh column lists the calculated sublimation pressure. Table 6 shows the relative deviations between experimental and calculated values of the sublimation pressure for all cases studied. The relative deviations between estimated and experimental sublimation pressures are defined as:

$$\%\Delta P^{\text{sub}} = \frac{P^{\text{S}}_{\text{cal}} - P^{\text{S}}_{\text{exp}}}{P^{\text{S}}_{\text{exp}}} \quad (8)$$

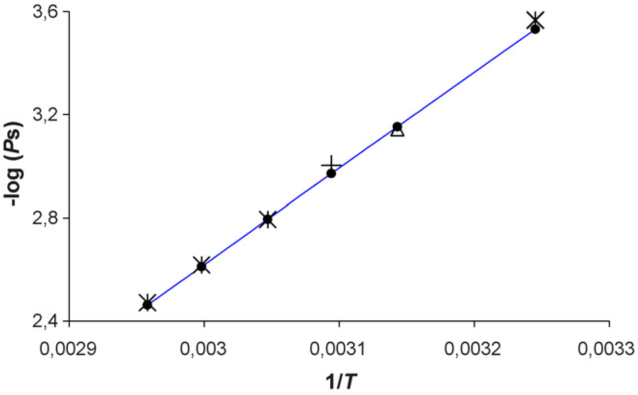

Fig. 1. Calculated sublimation pressure of naphthalene of all isotherms with different solvents: (*) CO_2 for T = 308, 328, 333 and 338 K; (+) ethylene for T = 323 K; (△) ethane for T = 318 K.

As we can see in Table 6, for systems which contain naphthalene as solute the proposed method predicts sublimation pressure with individual deviations between −5.7% and 7.5%. For systems containing phenanthrene as solute individual deviations are between −6.8 and 1.4. For systems which contain anthracene as solute individual deviations are between −2.6 and 7.8.

Fig. 1 shows the calculated sublimation pressure of napthalene for all isotherms with different solvents. The symbols in the figure are (*) CO_2 for T = 308, 328, 333 and 338 K; (+) ethylene for T = 323 K; and (△) ethane for T = 318 K. In the figure, the sublimation pressure is in bar and T in Kelvin. The results shown in Fig. 1 indicate that the proposed method is reliable enough to estimate the sublimation pressure of solids using solubility data of the solid in high pressure gases. The method could also be used to model the solid solubility in those cases in which the sublimation pressure is not available.

Fig. 2 shows relative individual deviations among experimental values of sublimation pressure the systems which contain anthracene as solute and those obtained using the proposed genetic algorithm method. In Fig. 2 the symbol (*) represents anthracene + CO_2, (△) anthracene + ethane, and (●)

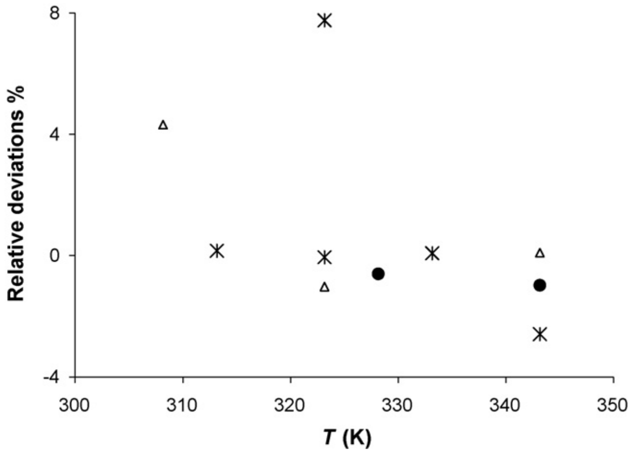

Fig. 2. Relative individual deviations among experimental and calculated values of sublimation pressure for the systems which contain anthracene as solute: (*) anthracene + CO_2; (△) anthracene + ethane; (●) anthracene + fluoroform.

anthracene + fluoroform. As seen, the highest relative deviation (8%) is at $T = 323$ K for the system anthracene + CO_2 when experimental data obtained of [14] are used.

From all these results it is clear that the sublimation pressure is calculated with acceptable accuracy and that the solvent used does not affect the calculated value for a given solid. The predicted values are within experimental errors found in measuring this property [17].

5. Conclusions

Sublimation pressure of solid from high pressure solubility data are calculated. Based on the results and discussion presented in this study, the following main conclusions are obtained:

(i) The low deviations between experimental and calculated values of the sublimation pressure show that the thermodynamic model PR/WS/VL is appropriate to estimate the sublimation pressure of solids.
(ii) The genetic algorithms method has shown to be a good tool to solve the optimization problem studied here, providing accurate global optimum.
(iii) It appears that, within experimental uncertainties on literature data used herein, the solvent in the mixture does not affect the calculated value of the sublimation pressure for a given solid.

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