Available online at www.sciencedirect.com

Computers and Chemical Engineering 29 (2005) 1885–1890

Computers & Chemical Engineering

www.elsevier.com/locate/compchemeng

Thermodynamic modelling of supercritical fluid–solid phase equilibrium data

M.D. Gordillo*, M.A. Blanco, C. Pereyra, E.J. Martínez de la Ossa

Department of Chemical Engineering, Food Technology and Environmental Technologies, Faculty of Sciences,
University of Cádiz, 11510 Puerto Real (Cádiz), Spain

Received 30 September 2004; received in revised form 29 March 2005; accepted 4 April 2005
Available online 6 May 2005

Abstract

The design and development of processes involving supercritical fluids depend on how easy the phase equilibrium can be accurately modelled and predicted. In the work described herein, the supercritical fluid–solid equilibrium has been considered. Modelling the fluid–solid equilibrium is associated with a number of drawbacks, even when it is possible to obtain the experimental solubility data for the solute in the supercritical fluid. In most cases it is necessary to introduce additional adjustment parameters into the model. The developed program, realized in Visual Basic® language, is based on the fitting of two parameters – the binary interaction parameter (k_{12}) and the solid sublimation pressure (P_2^{sat}). This program can be used for any fluid–solid equilibrium even when both parameters are known or supposed. The model has been applied to several systems and, as example, in this work, the Penicillin G-CO_2 phase equilibrium data are shown. The results obtained allow affirm that the thermodynamic model applied to fluid–solid equilibrium calculations is useful to predict the behaviour of this system.

Keywords: Group contribution method; Critical state; Thermodynamic modelling; Fluid–solid equilibrium; Equation of state

1. Introduction

The interest in the supercritical fluid extraction lies in the possibility developing a process for the antibiotics separation and purification that is able to simplify the number of stages of the actual production process, thus minimizing the economical cost of industrial production and reducing the risk of environmental impact by eliminating the use of organic solvents, besides which increasing the quality of the extracted product. This aspect is of vital important if we think about the nature of the product and its use by humans. Obviously, the first step in order to evaluate the possibilities of the supercritical extraction as an alternative process for the extraction of liquid solvents is to determine the solubility of the penicillins in supercritical solvent and its variation under pressure and temperature (Gordillo, Blanco, Molero, & Martínez de la Ossa, 1999).

Many of the current models are unable to predict the supercritical fluid–solid equilibrium near to the key region for the conditions in which the solvent functions. Another significant problem is that, in most cases, the solute molecules are voluminous and polar, while the solvent molecules are often small and of low polarity.

For these reasons, modelling the fluid–solid equilibrium is associated with a number of drawbacks, even when it is possible to obtain the experimental solubility data for the solute in the supercritical fluid. In most cases it is necessary to introduce additional adjustment parameters into the model.

The thermodynamic development of the system is accompanied by complex mathematical relationships as well as iterative calculations. Cubic equations of state are the basic tools for supercritical fluid–solid equilibria calculations (Coutsikos, Magoulas, & Kontogeorgis, 2003).

There are many properties that affect the results of calculations of solid solubilities in supercritical carbon dioxide using equations of state and mixing rules. Besides the crit-

---

* Corresponding author. Tel.: +34 956016458; fax: +34 956016411.
E-mail address: dolores.gordillo@uca.es (M.D. Gordillo).

0098-1354/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compchemeng.2005.04.001

Nomenclature

a, b	EOS mixture parameter
a_{ij}	PR EOS cross-energy parameter
k_{ij}	binary interaction parameter
P	pressure
R	universal gas constant
T	temperature
v, V	molar volume
y	mole fraction in supercritical phase

Greek letters

α	PR EOS parameter $\alpha = \alpha\,(T, T_c, \omega)$
ϕ	fugacity coefficient
ω	acentric factor

Subscripts

c	critical
1	CO_2
2	solute
i, j	component index

Superscripts

sat	saturated value
S	solid phase
F	supercritical fluid phase

Abbreviations

AARD	average absolute relative deviation
EOS	equation of state
GCM	group contribution method
LB	Lorentz–Berthelot
MR	mixing rules
PR	Peng–Robinson
VdW	Van der Waals

ical constants, the sublimation pressures of solids also have a significant influence on the results of the calculations. The sublimation pressures of high molecular weight compounds are too small for accurate experimental measurement. Reverchon et al. suggested that the sublimation pressure should be considered as an adjustable parameter (Reverchon, Della Porta, Taddeo, Pallado, & Stassi, 1995). Cortesi et al. and Huang et al. have reported data for the sublimation pressures of solids obtained in this way (Cortesi, Kikic, Alessi, Turtoi, & Garnier, 1999; Huang, Tang, Tao, & Chen, 2001).

The aforementioned problem is more marked in the case of organic compounds for which data do not exist above the melting temperature. In such cases the boiling and critical temperature values do not have physical meaning and, moreover, they are parameters that can only be adjusted on the basis of experimental data or can be considered for the correlation of the empirical data obtained.

In this way, it is essential to use a calculation program considering all those considerations. The program developed in this work can be used with three equations of state, two mixing rules and several group contribution methods.

2. Thermodynamic model

In this work, Peng–Robinson (PR) equation of state (EOS) with Van der Waals (VDW) and Lorentz–Berthelot (LB) mixing rules (MR) have been used.

Several group contribution methods (GCM) for normal boiling temperature (necessary to estimate the critical temperature by some methods), critical temperature and critical pressure of Penicillin G have been used to analyze the reliability of this correlation method and to study the influence of each parameter. Critical parameters have been estimated using Ambrose (Reid, Prausnitz, & Sherwood, 1977), Constantinou–Gani (Constantinou & Gani, 1994), Lydersen (Reid, Prausnitz, & Poling, 1987), Joback (Reid et al., 1987) and Somayajulu (Somayajulu, 1989) group contribution methods with Joback, Miller and Meissner methods for the estimation of boiling temperature (Lyman, Reehl, & Rosenblatt, 1990; Reid et al., 1977, 1987). The acentric factor has been calculated by the Constantinou–Gani group contribution method (Constantinou & Gani, 1995) or by the Lee–Kesler correlation (Walas, 1995). The calculation of the solid molar volume has been achieved by the Immirzi and Perini group contribution method (Lyman et al., 1990). The estimated properties of Penicillin G obtained using all possible combinations of GCM are shown in Table 1. In the case of CO_2 the physical properties are known from experimental measurements ($T_c = 304.21$ K, $P_c = 73.8$ MPa and $\omega = 0.225$) (Walas, 1995).

The Fugacity Method for calculating the phase equilibrium (Fotoug and Shukla, 1996) is based on the equality of chemical potentials, for each component in each phase, at fixed temperature and pressure. We consider a binary fluid mixture consisting of components 1 (carbon dioxide) and 2 (solid). In this way, the solubility of a solid in supercritical carbon dioxide from its thermodynamic definition is

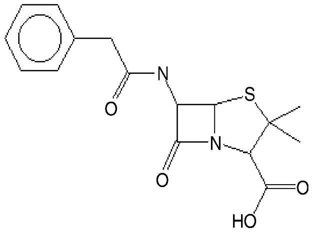
$$y_2 = \frac{P_2^{\mathrm{sat}}}{\hat{\phi}_2^{\mathrm{F}} P} \exp\frac{(P - P_2^{\mathrm{sat}})\upsilon_2^{\mathrm{S}}}{RT}. \qquad (1)$$

The calculation of the solubility y_2 therefore requires a knowledge of the solid sublimation pressure (P_2^{sat}), solid molar volume (υ_2^{S}) and the equation of state (with its associated mixing rules) for the calculation of $\hat{\phi}_2^{\mathrm{F}}$. The fugacity coefficient is the property calculated by a thermodynamic model. The other properties of the solid (P_2^{sat} and υ_2^{S}) should be obtained from independent information.

For determining fluid–solid phase equilibria using an equation of state approach, the EOS must be able to describe both the fluid-phase and the solid phase behaviour reliably (Fotoug and Shukla, 1996). Many cubic equations of state exist in the literature for modelling fluid–solid equilibrium data. In this paper, we adopt the Peng–Robinson equation of

Table 1
Properties of Penicillin G using different combinations of group contribution methods

Properties of Penicillin G (CAS Number 000061-33-6)



Combination of GCM	T_b (K)	T_c (K)	P_c (bar)	V_c ($cm^3\ mol^{-1}$)	ω
Ambrose + Meissner	718.60	907.30	23.5	940	1.315
Ambrose + Miller	853.92	1078.16			
Ambrose + Fedors		902.78	23.5	940	1.325
Constantinou–Gani[a]	640.80	809.27	21.2	727	1.003
Joback	974.18	1224.35	25.2	869	1.424
Lydersen + Meissner	718.60	901.63	22.9	899	1.381
Lydersen + Miller	853.92	1071.41			
Somayajulu + Meissner	718.60	902.27	25.1	862	1.446
Somayajulu + Miller	853.92	1072.18			

[a] Note that the groups used to predict the properties with the Constantinou–Gani GCM are not those recommended by the authors.

state (PR EOS), which contains two parameters to describe properties of the pure fluids and it can be shown that it is better to modelling equilibria data at high pressures. In this work, the mixture parameters are given by the simple Van der Waals mixing rules (VDW MR) and by the Lorentz–Berthelot mixing rules (LB MR), as given by Eqs. (2)–(9). In order to calculate the fugacity coefficient, a binary interaction parameter k_{ij}, that it is part of the mixing rules, must be obtained by fitting the experimental solubility data.

Mixing rules

$$a\alpha = \sum_i \sum_j y_i y_j (a\alpha)_{ij}; \quad b = \sum_i y_i b_i \tag{2}$$

Van der Waals mixing rules

$$(a\alpha)_{ij} = (1 - k_{ij})\{(a\alpha)_i (a\alpha)_j\}^{1/2} \tag{3}$$

Lorentz–Berthelot mixing rules

$$(a\alpha)_{ij} = 0.45724 R^2 T_{cij}^2 \frac{\alpha_{ij}}{P_{cij}} \tag{4}$$

$$T_{cij} = (1 - k_{ij})(T_{ci} T_{cj})^{1/2} \tag{5}$$

$$V_{cij} = \left(\frac{{V_{ci}}^{1/3} + {V_{cj}}^{1/3}}{2} \right)^3 \tag{6}$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \tag{7}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \tag{8}$$

$$\alpha_{ij} = (\alpha_i \alpha_j)^{1/2}. \tag{9}$$

The algorithm of the program is shown in Fig. 1. As it is shown, this algorithm requires binary equilibrium data. These solubility data of Penicillin G in supercritical carbon dioxide, expressed as solid mole fraction, were published in our previous study (Gordillo et al., 1999). The solubility was measured in pressure range from 100 to 350 bar and in temperature range from 313 to 333 K.

The program developed has been realized in Visual Basic® language. The necessary properties of the both compounds: critical temperature and pressure, molar volume and acentric factor are introduced as a file, i.e., *components file*. The experimental data are introduced as a file, i.e., *experimental data file*. A components file exists for each group contribution method used to estimate these properties and the experimental data file is the solubility data for all pressure and a constant temperature. Once both files have been opened, the program presents in screen the range of saturation pressure and of binary interaction parameter that we want to use and with which increments. Next we can choose the equation of state that we want to use. After carrying out the calculations, the calculated solubility data, for each P_2^{sat} and with the value of k_{12} that minimizes the error, are shown in the screen. Each calculation begins with the initial values of the compositions taken from the experiment. The program also proved useful when both parameters were known and, in addition, can be used for any fluid–solid equilibrium (Gordillo, 2001).

3. Results and discussion

In an effort to study the influence of the GCM on the thermodynamic model, all of the possible combinations of GCM with the PR EOS and VDW and LB MR were analyzed. The results obtained are shown in Tables 2 and 3 respectively. The

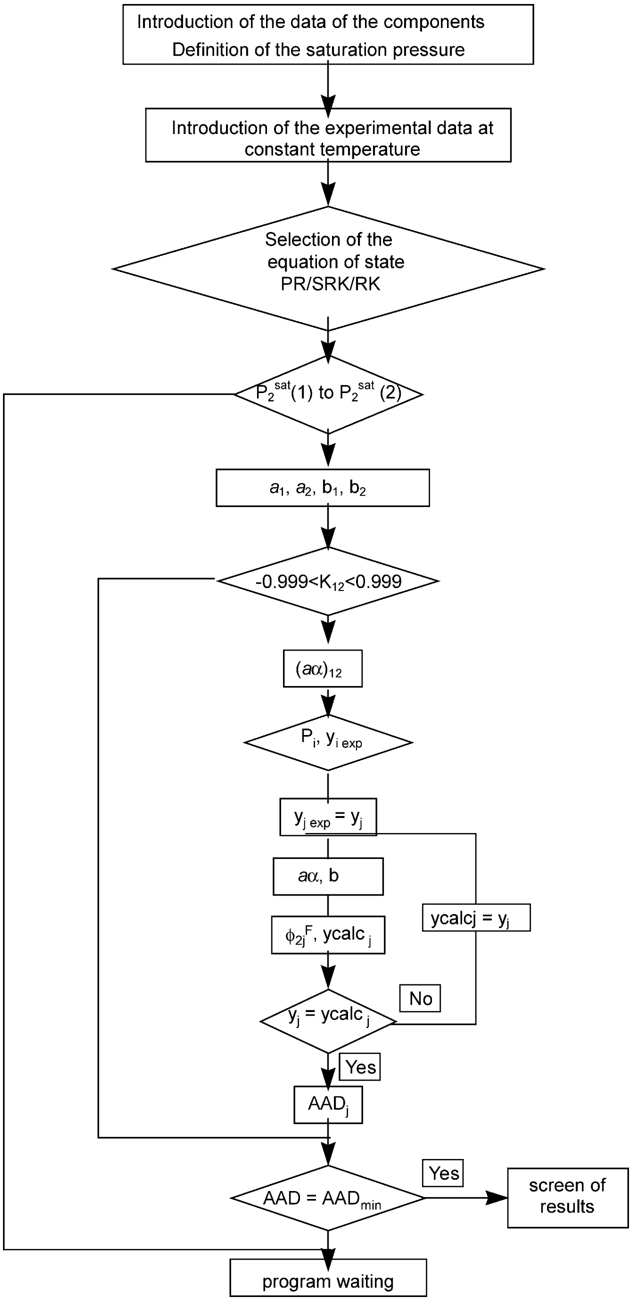


Fig. 1. Algorithm of the program.

values of R^2 in the lineal adjustment of k_{12} with temperature and the adjustment of the sublimation pressure to the Clapeyron equation are also shown in these Tables. For a given EOS and a MR, similar trends and AARD values are obtained with all GCM and the agreement between calculated and experimental data can be considered very good. These results only differ notably in the P_2^{sat} values, and in the adjustment of k_{12} with temperature.

The best results in terms of data values, trends, lineal adjustment of k_{12} with temperature and adjustment of P_2^{sat} to the Clapeyron equation were obtained with the PR EOS and LB MR, but significant differences do not exist between all the GCM used. In the case of VDW MR it is difficult to obtain good adjustments of k_{12} with the temperature.

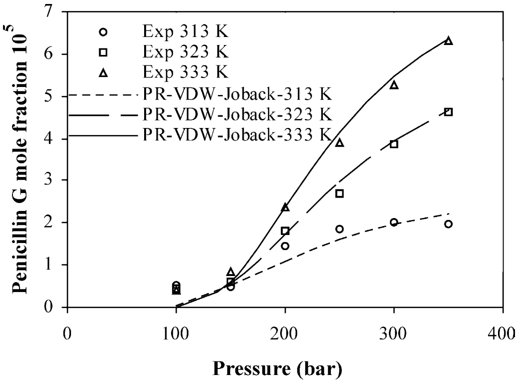


Fig. 2. Solubility of Penicillin G in supercritical carbon dioxide: experimental data and results obtained by the thermodynamic model with the PR EOS, VDW MR and Joback GCM.

Of these methods, the easiest to use are the Joback and Constantinou–Gani GCM since they do not require any other GCM to estimate the critical temperature. However, as the group parameter tables of Constantinou–Gani GCM did not have the groups needed for Penicillin-G in the referenced paper; we have used groups that Constantinou–Gani would not have used.

For this reason, and as examples, experimental solubility data of Penicillin G together with those calculated with the EOS of PR with VDW and LB MR and the GCM of Joback are shown in Figs. 2 and 3 respectively.

We have also studied Disperse Blue 14-CO_2 (Gordillo, Pereyra, & Martínez de la Ossa, 2003, 2005) and Palmitic Acid-CO_2 systems (Gordillo, Pereyra, & Martínez de la Ossa, 2004). The solubility data were measured and correlated with this model.

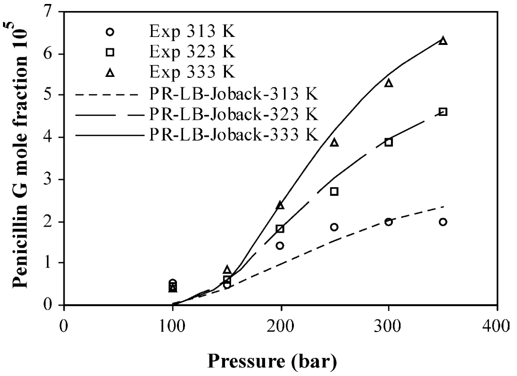


Fig. 3. Solubility of Penicillin G in supercritical carbon dioxide: experimental data and results obtained by the thermodynamic model with the PR EOS, LB MR and Joback GCM.

Table 2
Results of the modelling of the Penicillin G-CO_2 phase equilibrium with the PR EOS and the VDW MR

GCM-T	k_{12}	AARD (%)	P_2^{sat} (bar)	GCM-T	k_{12}	AARD (%)	P_2^{sat} (bar)
Amb + Meis-313	−0.352		5.0×10^{-11}	Lyd + Meis-313	0.047		1.3×10^{-10}
Amb + Meis-323	−0.403	22	1.3×10^{-10}	Lyd + Meis-323	0.001	23	2.6×10^{-10}
Amb + Meis-333	−0.264	5[a]	5.0×10^{-9}	Lyd + Meis-333	0.056	5[a]	4.0×10^{-9}
	$R^2 = 0.3916$		$R^2 = 0.8818$		$R^2 = 0.0233$		$R^2 = 0.8900$
Amb + Mill-313	0.003		5.6×10^{-13}	Lyd + Mill-313	0.015		4.7×10^{-13}
Amb + Mill-323	0.016	22	7.7×10^{-12}	Lyd + Mill-323	0.022	22	5.6×10^{-12}
Amb + Mill-333	0.088	6[a]	2.9×10^{-10}	Lyd + Mill-333	0.098	6[a]	2.8×10^{-10}
	$R^2 = 0.8616$		$R^2 = 0.9877$		$R^2 = 0.9128$		$R^2 = 0.9806$
Amb + Fed-313	−0.120		4.0×10^{-12}	Som + Meis-313	0.056		1.7×10^{-10}
Amb + Fed-323	−0.063	22	1.3×10^{-10}	Som + Meis-323	0.019	21	4.7×10^{-10}
Amb + Fed-333	0.002	7[a]	2.5×10^{-9}	Som + Meis-333	0.104	6[a]	1.2×10^{-8}
	$R^2 = 0.9986$		$R^2 = 0.9994$		$R^2 = 0.3171$		$R^2 = 0.9033$
Constantinou-313	−0.197		1.6×10^{-10}	Som + Mill-313	0.055		1.9×10^{-12}
Constantinou-323	−0.214	22	1.6×10^{-10}	Som + Mill-323	0.075	21	3.0×10^{-11}
Constantinou-333	−0.109	5[a]	5.0×10^{-9}	Som + Mill-333	0.150	6[a]	8.7×10^{-10}
	$R^2 = 0.6095$		$R^2 = 0.7344$		$R^2 = 0.8995$		$R^2 = 0.9934$
Joback-313	0.094		1.6×10^{-13}				
Joback-323	0.106	23	2.4×10^{-12}				
Joback-333	0.178	7[a]	1.3×10^{-10}				
	$R^2 = 0.8547$		$R^2 = 0.9838$				

[a] At pressures above 200 bar.

Table 3
Results of the modelling of the Penicillin G-CO_2 phase equilibrium with the PR EOS and the LB MR

GCM-T	k_{12}	AARD (%)	P_2^{sat} (bar)	GCM-T	k_{12}	AARD (%)	P_2^{sat} (bar)
Amb + Meis-313	−0.571		4.8×10^{-12}	Lyd + Meis-313	−0.631		2.0×10^{-12}
Amb + Meis-323	−0.465	22	1.3×10^{-10}	Lyd + Meis-323	−0.483	23	1.1×10^{-10}
Amb + Meis-333	−0.290	8[a]	5.0×10^{-9}	Lyd + Meis-333	−0.333	8[a]	3.0×10^{-9}
	$R^2 = 0.9803$		$R^2 = 0.9973$		$R^2 = 1.0000$		$R^2 = 0.9986$
Amb + Mill-313	−0.539		2.5×10^{-13}	Lyd + Mill-313	−0.597		1.0×10^{-13}
Amb + Mill-323	−0.439	22	9.3×10^{-12}	Lyd + Mill-323	−0.502	25	3.5×10^{-12}
Amb + Mill-333	−0.307	7[a]	3.5×10^{-10}	Lyd + Mill-333	−0.349	8[a]	2.0×10^{-10}
	$R^2 = 0.9937$		$R^2 = 0.9997$		$R^2 = 0.9821$		$R^2 = 0.9971$
Amb + Fed-313	−0.608		4.0×10^{-12}	Som + Meis-313	−0.518		2.6×10^{-11}
Amb + Fed-323	−0.508	21	1.0×10^{-10}	Som + Meis-323	−0.433	21	4.4×10^{-10}
Amb + Fed-333	−0.371	7[a]	2.5×10^{-9}	Som + Meis-333	−0.277	8[a]	1.2×10^{-8}
	$R^2 = 0.9919$		$R^2 = 0.9997$		$R^2 = 0.9719$		$R^2 = 0.9951$
Constantinou-313	−0.582		6.3×10^{-11}	Som + Mill-313	−0.521		1.0×10^{-12}
Constantinou-323	−0.614	21	1.6×10^{-10}	Som + Mill-323	−0.424	22	2.9×10^{-11}
Constantinou-333	−0.443	5[a]	5.0×10^{-9}	Som + Mill-333	−0.295	7[a]	8.7×10^{-10}
	$R^2 = 0.5845$		$R^2 = 0.8881$		$R^2 = 0.9934$		$R^2 = 0.9997$
Joback-313	−0.543		3.6×10^{-14}				
Joback-323	−0.411	24	3.4×10^{-12}				
Joback-333	−0.286	8[a]	1.4×10^{-10}				
	$R^2 = 0.9998$		$R^2 = 0.9983$				

[a] At pressures above 200 bar.

4. Conclusions

The thermodynamic model developed, that involves the use of the binary interaction parameter and the solid sublimation pressure as adjustment parameters, provides good results in all cases studied for the Penicillin G-CO_2 equilibrium.

The Peng–Robinson equations of state provide good predictions for the solid-fluid equilibrium of the Penicillin G-CO_2 system. Significant differences were not observed in the values of AARD and the trends obtained with each EOS and MR used in this work. Differences are, however, observed in the values of the two adjustment parameters used: the binary interaction parameter and the solid sublimation pressure. For a given GCM, when different EOS and MR are used, the influence in the binary interaction parameter obtained is more marked than the influence in the sublimation pressure.

And for the PR EOS with LB MR, when different GCM are used, the influence is more marked in the sublimation pressure values than in the binary interaction parameter. Using the VDW MR, different values of both adjustment parameters are obtained for each GCM used.

In most cases, when the LB MR are used, the parameter k_{12} increases lineally with temperature and the solute sublimation pressure is adjusted correctly to the Clapeyron equation.

The results obtained in predicting the solubility of the Penicillin-CO_2 system show that the correlations with the three equations, the two MR and the several combination of GCM give similar results. Better adjustment of k_{12} with the temperature and P_2^{sat} to Clapeyron equation are obtained when the LB MR are used. This equilibrium can be correlated with anyone of the GCM studied in this work using the LB MR and the PR EOS.

But, it can be affirmed that different values for the physical properties are obtained with each GCM. Therefore, the choice of a GCM that estimates values very different from the critical parameters is more important than the choice of EOS or MR among those used in this work.

References

Constantinou, L., & Gani, R. (1994). New group contribution method for estimating properties of pure compounds. *AIChE Journal*, *40*(10), 1697.

Constantinou, L., & Gani, R. (1995). Estimation of the acentric factor and the liquid molar volume at 298 K using a new group contribution method. *Fluid Phase Equilibria*, *103*, 11.

Cortesi, A., Kikic, I., Alessi, P., Turtoi, G., & Garnier, S. (1999). Effect of chemical structure on the solubility of antioxidants in supercritical carbon dioxide: experimental data and correlation. *Journal of Supercritical Fluids*, *14*, 139.

Coutsikos, P., Magoulas, K., & Kontogeorgis, G. M. (2003). Prediction of solid–gas equilibria with the Peng–Robinson equation of state. *Journal of Supercritical Fluids*, *25*, 197.

Fotoug, K., & Shukla, K. (1996). A comparative study of numerical methods for calculating phase equilibria in fluid mixtures from an equation of state. *Chemical Engineering Science*, *51*, 3763.

Gordillo, M.D. (2001). Ph. D. Thesis, University of Cádiz, Spain.

Gordillo, M. D., Blanco, M. A., Molero, A., & Martínez de la Ossa, E. (1999). Solubility of the antibiotic Penicillin G in supercritical carbon dioxide. *Journal of Supercritical Fluids*, *15*, 183.

Gordillo, M. D., Pereyra, C., & Martínez de la Ossa, E. (2003). Measurement and correlation of solubility of Disperse Blue 14 in supercritical carbon dioxide. *Journal of Supercritical Fluids*, *27*, 31.

Gordillo, M. D., Pereyra, C., & Martínez de la Ossa, E. (2004). Supercritical fluid–solid phase equilibria calculations by cubic equations of state and empirical equations: Application to the palmitic acid-carbon dioxide system. *Journal of Chemical and Engineering Data*, *49*, 435.

Gordillo, M. D., Pereyra, C., & Martínez de la Ossa, E. (2005). Solubility estimations for Disperse Blue 14 in supercritical carbon dioxide. *Dyes and Pigments*, *67*, 167.

Huang, C., Tang, M., Tao, W., & Chen, Y. (2001). Calculation of the solid solubilities in supercritical carbon dioxide using a modified mixing model. *Fluid Phase Equilibria*, *179*, 67.

Lyman, W. J., Reehl, W. F., & Rosenblatt, D. H. (1990). *Handbook of chemical property estimation methods*. Washington: American Chemical Society.

Reid, R. C., Prausnitz, J. M., & Sherwood, T. K. (1977). *The properties of gases and liquids*. New York: McGraw-Hill Book Company.

Reid, R. C., Prausnitz, J. M., & Poling, B. E. (1987). *The properties of gases and liquids*. New York: McGraw-Hill Book Company.

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

Somayajulu, G. R. (1989). Estimation procedures for critical constants. *Journal of Chemical and Engineering Data*, *34*, 106.

Walas, S. M. (1995). *Phase equilibra in chemical engineering*. Butterworth Publishers.