

Correlation of the Binary Interaction Factor for Polar Solutes Dissolved in Supercritical Carbon Dioxide

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Abstract

This contribution is focused on supercritical solutions of many polar solutes in carbon dioxide (nonpolar solvent) when the molar polarization of the solute at infinite dilution is accurately known. A database containing experimental solubility measurements for many solutes is used in this study where isotherms are known between 308 and 343 K. A mathematical model is developed to compute the solubility of solids in supercritical fluids, particularly in carbon dioxide. As a result, a new correlation of the binary interaction (k_{ij}) is proposed. This new relationship considers the k_{ij} term as a function of the dipole moment and the solute carbon number.

Keywords: Solubility; supercritical fluid; binary interaction; optimization; dipole moment.

1. Introduction

Solubility data are essential for the assessment and development of new applications for supercritical fluids. One of the great advantages of supercritical fluids is that the solute's solubility may be adjusted by changing the operating pressure and temperature. Therefore, since the solubility is a function of the temperature and the pressure, a large solubility database must be generated for each solute.

Recently, many supercritical applications concerning the extraction of organic compounds have been published by several authors. Among them, we notice the work of Mohamed et al. (2000) who have studied the reduction in the cholesterol content of butter oil using supercritical ethane extraction.

In the environmental field, the desorptive behavior of many organics, such as naphthalene and phenanthrene from soil using supercritical carbon dioxide, is also investigated by several authors, namely, Erkey et al. (1993).

Concerning the extraction of essential oils via this technique, Ueno et al. (2008) have extracted valuable compounds from citrus seed using supercritical carbon dioxide. In addition, oil samples are obtained from coriander using supercritical extraction as mentioned by Ravi et al. (2007).

The numerical optimisation of supercritical phase equilibria can be performed via several methods. Cubic equations of state (EoS's) is shown as the most used method where their use is strongly related to binary interaction and critical properties definitions (Stamataki and Tassios, 1998). For other applications, we find in the literature non-cubic EoS's which have been successfully applied to correlate the pVT -behavior of a supercritical solution (Kraska et al, 2002). For quantitative determination of the solute mole fraction in supercritical solution at equilibrium, the Chrastil method is also used for correlating solubilities (Ksibi, 2004).

Here, we assume that the key features of the solute-solvent interactions of relevance are captured in the interactions between only two molecules at a time. A

considerable fraction of the interaction energy in such a pair is expected to come from dipole-induced dipole interactions. This assumption requires the knowledge of binary interaction parameters k_{ij} .

Moreover, we present firstly the phase equilibrium equations and followed by an optimization technique which can determine precisely the binary interaction factor. Finally we depict the accuracy of the developed correlation by comparing it predictions with estimated values of binary interaction coefficients for many isotherms and solutes dissolved in carbon dioxide.

2. Solubility Optimization

The calculation of the solubility of a compound in a supercritical fluid has included both correlative and predictive approaches. Three models are commonly used in the literature to establish correlations for binary systems' solubility data. These models are those of Chrastil and those deduced from the Redlich- Kwong -Soave and Peng – Robinson EoS's.

The solute properties necessary to effectively correlate solubilities based on an EOS include the molar volume and the saturated vapor pressure (as a function of temperature). The prediction of solubility using the chosen EOS model assumes that the solute phase remains pure. This assumption is thought to be quite reasonable for solid solutes. However, in the case of liquid solutes, it is likely that carbon dioxide will dissolve into the liquid solute at the same time as the liquid is dissolving into the supercritical carbon dioxide. Indeed, McHugh and Krukoni provide the necessary equations to handle this phase equilibrium of the liquid solute within the supercritical fluid.

The solubility can be expressed by equating the fugacity terms of the solute (2) at each state as written:

$$f_i^{(V)}(T, P, y_i) = f_i^{(S)}(T, P, x_i) \quad (1)$$

Here y_i and x_i denote the mole fraction of vapor and solid phases respectively, and i the considered substance of the solution.

$$f_i^s = P_i^{sat} \phi_i^{sat} \exp\left(\int_{P_i^{sat}}^P \frac{V_i^s}{RT} \cdot dP\right) \quad (2)$$

$$\text{and } f_i^F = \phi_i \cdot y_i \cdot P \quad (3)$$

Therefore we obtained the expression of the solute mole fraction as a function of the pressure and the temperature:

$$y_i = \frac{P_i^{sat} \cdot \phi_i^{sat}}{\phi_i^f \cdot P} \exp\left(\frac{V_i^s (P - P_i^{sat})}{RT}\right) \quad (4)$$

Here ϕ_i^{sat} and ϕ_i^f are the fugacity coefficients of the saturated pure vapor and the supercritical state of the solute, respectively. The coefficient ϕ_i^{sat} is equal to 1, and ϕ_i^f is calculated using the chosen EOS.

Numerous EoS's are proposed in the literature where their use is strongly related to the domains of the operating parameters and the nature of the chemical components. The best known EoS for pure compounds are the cubic equations of state, such as Redlich - Kwong - Soave (RKS) EOS (1972) and Peng - Robinson (PR) EOS (1976). These two PVT relationships can accurately describe the supercritical phase of carbon dioxide. Valderrama has summarized the use of cubic equations of state, especially the RKS EOS for supercritical fluid and mixtures. These equations can be written respectively as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (5)$$

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (6)$$

The phase equilibrium calculation for a given mixture involves both suitable EoS and mixing rules which define the EoS corrective terms (a , b) of the solution. The most used are those of Van der Waals (VDW), where k_{ij} is the binary interaction parameter:

$$a = \sum_i \sum_j y_i \cdot y_j \cdot a_{ij} \quad (7)$$

$$\text{and } b = \sum_i y_i \cdot b_i \quad (8)$$

Here b_i and a_{ii} are constants depending on the substance nature. The term a_{ij} is defined as:

$$a_{ij} = (a_{ii} \cdot a_{jj})^{0.5} (1 - k_{ij}) \quad (9)$$

The knowledge of the vapor pressure P^{sat} of the solute is also an essential step in the calculation of solubility. If the model is not available as a function of temperature, it is still possible to attempt to fit the solubility data, but the quality of fitting is likely to be poor.

Indeed, several works yield accurate vapor pressure from the triple point up to the critical point. Rogalski et al. (1990) give adequate representations of both the saturated vapor pressure expression and the molar volume estimation for different ranges of operating conditions. The

mathematical relationships of vapor tension given in the literature depend highly on the state of the solute state at ambient conditions. Generally, these equations are based on the Antoine equation.

Two kinds of models depending on the acentric factor are summarized in the following:

$$\frac{P^{sat}}{P} = \exp(f_0 + \omega \cdot f_1) \quad (10)$$

and

$$\frac{P^{sat}}{P} = \exp(f_0 + \omega \cdot f_1 + \omega^2 \cdot f_2) \quad (11)$$

The most used functions f_0 and f_1 of Eqn (10) are given by Schreiber and Pitzer (1995):

$$f_0 = 0.90387412 - \frac{3.8754024}{T_r} - 10.021469 \times 2.3 \ln(T_r) + 2.9715283 T_r \quad (12)$$

$$f_1 = 2.0095293 - \frac{8.66162}{T_r} - 30.391841 \times 2.3 \ln(T_r) + 6.6520983 T_r \quad (13)$$

According to the second model, Eqn (11), Ambrose and Walton (1989) gave expressions of f_0 , f_1 , and f_2 as follows :

$$f_0 = \frac{1}{T_r} (-5.97616(1-T_r) + 1.29874(1-T_r)^{1.5} - 0.60394(1-T_r)^{2.5} - 1.068415(1-T_r)^5) \quad (14)$$

$$f_1 = \frac{1}{T_r} (-5.03365(1-T_r) + 1.11505(1-T_r)^{1.5} - 5.41217(1-T_r)^{2.5} - 7.46628(1-T_r)^5) \quad (15)$$

$$f_2 = \frac{1}{T_r} (-0.64774(1-T_r) + 2.41539(1-T_r)^{1.5} - 4.26979(1-T_r)^{2.5} + 3.25259(1-T_r)^5) \quad (16)$$

3. k_{ij} correlation

As can be seen, the EOS corrective coefficients (a , b) require the interaction parameters for the phase behavior description. Many papers, such as Pauvonic et al. (1981) and Bartle et al. (1992) have given averaged values of this binary interaction. They have used numerous couples of supercritical solvent and solute presented in the literature, and then by linear fitting, they have obtained empirical correlations for the binary interaction factor k_{ij} . The latter is estimated as a function of physical properties of the solution such as molecular polarity, weight, etc...

Moreover, the binary interaction parameter is fitted numerically from experimental solubility data by Ksibi (1999). The numerical calculation of this parameter is based on both modified Peng-Robinson and Redlich-Kwong-Soave EoS's coupled with Van der Waals (VDW) mixing rules.

To achieve this goal at a reasonable computing time, it is necessary to have recourse to optimisation methods. We proceeded numerical calculation by the means of two methods of optimization to determine the k_{ij} parameter as a dimensionless coefficient bounded between $[0,1]$. Here, we seek to minimize the number of evaluations of the function by maintaining a constant reduction of step time.

The golden section number is the positive solution of the quadratic equation $t^2+t-1=0$. The “golden section search” optimization technique is suitable to determine the interaction parameter k_{ij} by a limited number of iterations. This fast and inexpensive method gives the optimal value of k_{ij} within few iterations.

The quadratic method is often used as a last stage in algorithms depending mainly on other methods, since the physical functions are generally parabolic when in proximity to a minimum. This method requires the evaluation of the function in three points, x_1 , x_2 , and x_3 . It predicts then the minimum of the parabola passing through these 3 points. The function is evaluated with this new point while replacing one of the three others. The new point x_4 is predicted, still by quadratic interpolation by using the new set of three points. While intervening using the quadratic method formulation in order to accelerate convergence, we establish a new algorithm where we reiterate on the calculation of binary coefficient of interaction optimal k_{ij} (x_4) by varying the whole parameter D while minimizing the truncation error, as follows:

$$x_4 = \frac{(x_1 + x_2)}{D} + \frac{(f(x_1) - f(x_2))(x_2 - x_3)(x_3 - x_1)}{D(x_2 - x_3)f(x_1) + (x_3 - x_1)f(x_2) + (x_1 - x_2)f(x_3)} \quad (17)$$

In this work, attention is focused on the dependency of the binary interaction on the dipole moment of the solute as the carbon dioxide is a non-polar molecule. The binary interaction is implemented via numerous databases of solubility and several models of vapor pressure, Eqs. (10) and (11), where the numerical code chooses the adequate one by judging an appropriate convergence criterion.

The performance of the correlations is quantified by a squared absolute average relative deviation (SAARD). This approach is the most widely used assessment for evaluating the success of the numerical model. An SAARD is calculated according to Eqn (18):

$$SAARD\% = \frac{1}{N} \sum \left(\frac{Y_{calc} - Y_{exp}}{Y_{exp}} \right)^2 \times 100 \quad (18)$$

4. Results and discussions:

The first test case is the supercritical solution of limonene and carbon dioxide at equilibrium which is studied numerically by using both PR and RKS EoS's coupled with VDW mixing rules. The solubility computation using k_{ij} optimization from experimental data is shown in Figure 1. The solid line depicts the solubility at equilibrium estimated from Eqn (4). Therefore, a good agreement with solubility measurements can be noticed and the averaged relative deviation of experimental points is less than 7 % in most cases.

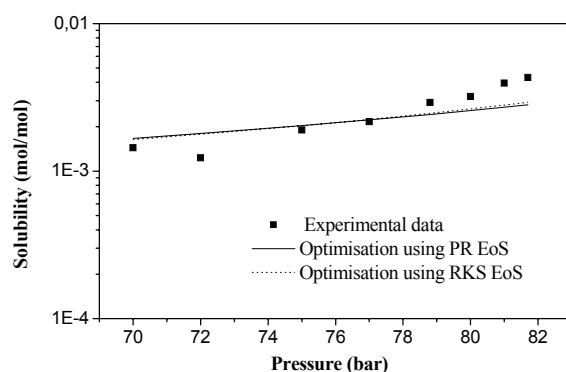


Figure 1. Solubility of limonene in supercritical CO_2 : Comparison between calculated and experimental data at $T= 313 K$.

Here we note that at high pressure, the estimated solubility value is strongly altered by the k_{ij} model and error increases.

As a second example of a solute, the solubility of naphthalene in supercritical carbon dioxide is calculated as a function of the pressure. Figure 2 shows the mole fraction for the isotherm (308 K) at different pressures. The numerical fitting used the experimental data given by several works. A good agreement of the calculated solubility is noticed when compared with the experimental value at the same pressure and temperature.

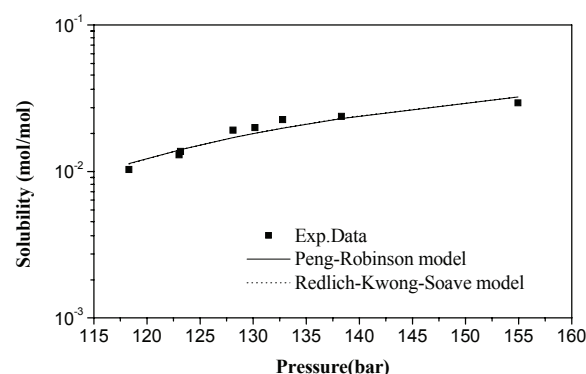


Figure 2. Solubility of naphthalene in supercritical CO_2 : Comparison between calculated and experimental data at $T= 308 K$.

In order to compare the results obtained by the quadratic method and those of the golden section, we plot on Figure 4 a curve giving the variation of the solubility of the benzoic acid in supercritical CO_2 to a temperature $T= 318.15 K$, by choosing the PR model and by applying these two optimization methods. The value of the binary interaction and the precision found by the method of golden section are respectively 0.116 and 9.37 %. On the other hand, by the quadratic method one found a value of k_{ij} equal to 0.136 and a precision of 5.8 %. According to Figure 3, the quadratic method is the most suitable among the two used techniques; it provides a coefficient with a better precision. Indeed, this method behaves generally well, but suffers sometimes from instabilities which can be serious. Among these instabilities we can state the fact that at any step, three points can determine a parabola with a maximum rather than a minimum, and then the method diverges.

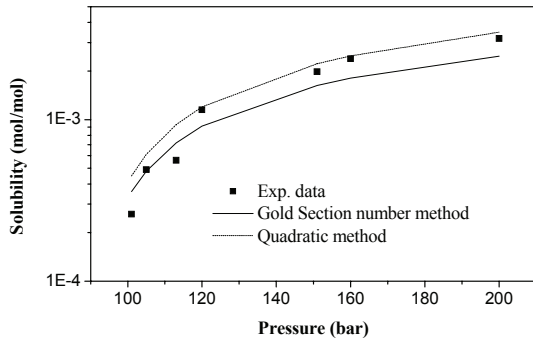


Figure 3. Solubility of benzoic acid in carbon dioxide at $T=320$ K: comparison between numerical models.

Additionally, we show the importance of the employment of an exact correlation of the binary interaction by calculating the solubility of the benzoic acid in supercritical CO_2 for the temperature 318.15 K, following two determination techniques of the parameter k_{ij} . In the first approach, the dissolved fraction is obtained by using numerical optimisation of k_{ij} and in the second one, the solubility is simply estimated at a zero value of the parameter of the binary interaction ($k_{ij} = 0$).

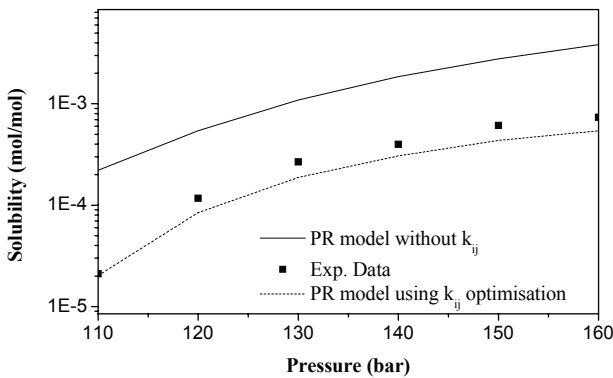


Figure 4. Solubility of benzoic acid in carbon dioxide: comparison between two optimization methods using the PR EoS.

After calculating different data of k_{ij} and correlating them for several temperature ranges, this parameter is studied as a function of the variable x which reflects the size of the solute molecule (carbon number N_c) and its dipole moment μ . This parameter is expressed as:

$$\xi = \mu / N_c^3 \quad (19)$$

To vary this variable we need to diversify the dipole moment and the carbon number, which means to study phase equilibria of different solutes in the supercritical carbon dioxide.

Several experimental works concerning usual solutes in carbon dioxide are implemented and satisfactory comparison between the calculated solubilities and the measured ones is obtained in each case. Therefore we list in Table 1 the averaged values of k_{ij} determined for the formed solutions. This table can be represented by a graph where

the binary interaction factor is plotted as a function of variable ξ , Figure 5. This empirical correlation is written as follows:

$$K_{ij} = C_1 + C_2 \times \exp(-100\xi) \text{Cos}\left(100\sqrt{\xi}\right) \quad (20)$$

where $C_1 = 0.25$ and $C_2 = 0.15$.

Table 1. Values of k_{ij} for different solutes dissolved in supercritical CO_2 .

Solute	N_c	μ (Debye)	T(K)	k_{ij}		
Naphthalene	10	0	308	$1.30418 \cdot 10^{-1}$		
Acridine	10	2.29		$5.34000 \cdot 10^{-2}$		
Vanilline	8	3.57		$7.54979 \cdot 10^{-2}$		
phenanthrene	14	0.228		$0.74700 \cdot 10^{-1}$		
Cholesterol	27	2.01		$4.38000 \cdot 10^{-1}$		
salicylic Acid	7	1.76		$3.14090 \cdot 10^{-1}$		
β -carotene	40	5.20		$1.51832 \cdot 10^{-1}$		
Anthracene	14	0.575		$2.37729 \cdot 10^{-1}$		
Aspirine	9	7.13		$2.08800 \cdot 10^{-1}$		
Fluorene	13	0.6		$0.08000 \cdot 10^{-1}$		
Limonene	10	0.27	313	$2.88974 \cdot 10^{-1}$		
Triethylene glycol	6	2.01		$2.36640 \cdot 10^{-1}$		
Cholesterol	27	2.01		$4.14300 \cdot 10^{-1}$		
salicylic Acid	7	1.76		$2.87280 \cdot 10^{-1}$		
Anthracene	14	0.575		$1.28169 \cdot 10^{-1}$		
DDT	8	0.74		$1.09700 \cdot 10^{-1}$		
Naproxen	14	4.69		$2.23000 \cdot 10^{-1}$		
Benzoic Acid	7	1.7		$1.30610 \cdot 10^{-1}$		
Caffeine	8	5.11		$1.58340 \cdot 10^{-3}$		
Naphthalene	10	0		$9.53498 \cdot 10^{-2}$		
Limonene	10	0.27	318	$4.30435 \cdot 10^{-1}$		
Acridin	13	2.29		$0.49900 \cdot 10^{-1}$		
Vanillin	8	3.57		$5.36146 \cdot 10^{-2}$		
phenanthrene	14	0.228		$0.69300 \cdot 10^{-1}$		
Cholesterol	27	2.01		$4.16100 \cdot 10^{-1}$		
Salicylic Acid	7	1.76		$2.60757 \cdot 10^{-1}$		
Anthracene	14	0.575		$1.27203 \cdot 10^{-1}$		
Aspirin	9	7.13		$2.05600 \cdot 10^{-1}$		
Naphthalene	10	0		323	$6.61626 \cdot 10^{-2}$	
Limonene	10	0.27			$3.79439 \cdot 10^{-1}$	
phenanthrene	14	0.228	$0.66200 \cdot 10^{-1}$			
Tri-ethyl-gly	6	2.01	$1.79196 \cdot 10^{-1}$			
Cholesterol	27	2.01	$4.18000 \cdot 10^{-1}$			
DDT	8	0.74	$1.10000 \cdot 10^{-1}$			
Naproxen	14	4.69	$2.23000 \cdot 10^{-1}$			
Benzoic Acid	7	1.7	$1.26104 \cdot 10^{-1}$			
Caffeine	8	5.11	$1.53943 \cdot 10^{-1}$			
Naphthalene	10	0	$4.99390 \cdot 10^{-2}$			
Acridin	13	2.29	328	$0.51400 \cdot 10^{-1}$		
phenanthrene	14	0.228		$0.70700 \cdot 10^{-1}$		
Salicylic Acid	7	1.76		$1.87047 \cdot 10^{-1}$		
Limonene	10	0.27		333	$3.35510 \cdot 10^{-1}$	
Triethylene glycol	6	2.01			$1.70091 \cdot 10^{-1}$	
Cholesterol	27	2.01			$4.21900 \cdot 10^{-1}$	
DDT	8	0.74			$1.05400 \cdot 10^{-1}$	
Naproxen	14	4.69			$2.29000 \cdot 10^{-1}$	
Benzoic Acid	7	1.7			343	$1.42288 \cdot 10^{-1}$
Acridin	13	2.29				$0.58700 \cdot 10^{-1}$
β -carotene	40	5.20	$1.23254 \cdot 10^{-1}$			
Fluorene	13	0.6	$0.01900 \cdot 10^{-1}$			

The curve corresponding to Eqn (20) and experimental data for several dilute supercritical solutions at various temperatures are illustrated in Figure 5. According to this Figure, the estimated binary interaction values via Eqn (20) are in agreement with those estimated from experimental data of solubility.

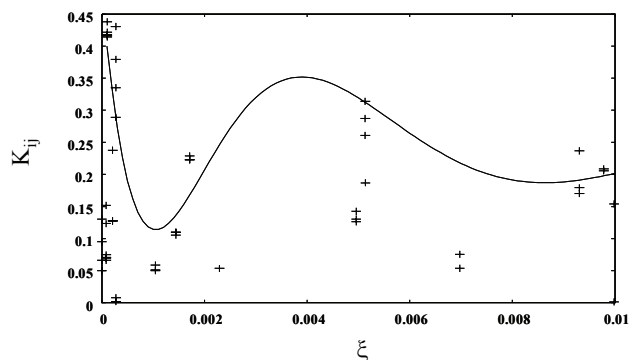


Figure 5. Variation of binary interaction coefficient as a function of ξ : (+ values of k_{ij} estimated from solubility data, — correlation 20).

We can divide the latter curve into three zones: a first part for the little polar compounds where the binary interaction factor is inversely proportional to the dipole moment (an increase in the dipole moment involves a reduction in factor of interaction); the second zone includes binary interaction for molecule solutes with moderate polarity where the factor of binary interaction increases by increasing the values of dipole moment. Finally, the k_{ij} factor undergoes a lowering for high polar molecules. Therefore the factor of interaction is proportional to the dipole moment; i.e. when μ increases k_{ij} increases, and, it is inversely proportional to the intermolecular distance, and consequently inversely proportional to the number of carbon of the solute.

5. Conclusion

This study shows numerically the effect of both the molecular structure and the polarity of the dissolved solute in supercritical carbon dioxide by means of an optimization of the binary interaction coefficient.

Published isotherms have judiciously been selected to develop the correlation using several saturation pressure models and optimization techniques. Detailed error calculations have been carried out for different thermodynamic models that include both Peng-Robinson and Redlich-Kwong-Soave equations of state taking into account Van Der Waals's mixing rules.

This work is a significant contribution in two ways: firstly, it provides a specific correlation that gives excellent values of solubility; secondly, it proposes a new formulation that can be extended to other mixing rules and may result in a fully predictive method.

6. Nomenclature

a	attractive term
b	covolume
f	fugacity
k_{ij}	binary interaction coefficient
M	molar weight
n	mole number
N_c	carbon number
N	number of experimental data
P	pressure
R	perfect gas constant
T	temperature
V	molar volume
y	solubility
x	liquid mole fraction

ϕ	fugacity coefficient
μ	dipole moment of the solute
ω	acentric factor

Indices

c	critical
cal	calculated
exp	experimental
F	fluid phase
sat	saturation
s	solid phase
r	reduced
1	supercritical solvent
2	solute

7. References

- Ambrose, D. Walton, J. (1989). Vapour pressures up to their critical temperatures of normal alkanes and 1-alkanols. *J. Pure & Appl. Chem.* 61, 1395-1403.
- Bartle, K.D. Clifford, A.A., Shilstane, G.F. (1992). Estimation of solubilities in supercritical carbon dioxide: A correlation for the peng-robinson interaction parameters. *J. of supercritical fluids*, 5(3), 220-225.
- Chrastil, J. (1982) Solubility of solids and liquids in supercritical gases. *J. Phys. Chem.* 86 (15), 3016-3021.
- Erkey C., Madras G., Orejuela M., Akgerman A. (1993). Supercritical carbon dioxide extraction of organics from soil. *Environmental Science & Technology*, 27(6), 1225-1231.
- Kraska T., Leonhard K. O., Tuma D., Schneider G. M., (2002). Correlation of the solubility of low-volatile organic compounds in near- and supercritical fluids. Part I: applications to adamantane and β -carotene. *J. of Supercritical Fluids* 23 (3), 209-224.
- Ksibi, H. (1999). Modélisation de la solubilité d'un produit organique dans une solution supercritique, *Revue Entropie*, 222, 34-39.
- Ksibi H., (2004). The solvent - solute interaction in supercritical solution at equilibrium: Modelling and related industrial applications. *Int. J. of Thermodynamics*, 7(3), 131-140.
- Ksibi H., Ben Moussa A. (2007). Prediction of critical parameters of cholesterol and its binary interaction coefficient in the supercritical carbon dioxide. *Int. J. of Thermodynamics*. 10 (1), 47-52.
- McHugh, M. A., Krukonic, V. J. (1994). *Supercritical Fluid Extraction: Principles and Practice*, ed. Butterworths
- Mohamed, R. S.; Saldana, M. D. A.; Socantaype, F. H.; Kieckbusch, T. G. (2000). Reduction in the cholesterol content of butter oil using supercritical ethane extraction and adsorption on alumina. *J. of Supercritical Fluids* 16(3), 225-233.
- Paunovic, R.; Jovanovic, S.; Mihajlov, A. (1981). Rapid computation of binary interaction coefficients of an equation of state for vapor-liquid equilibrium calculations: application to the Redlich-Kwong-Soave equation of state. *Fluid Phase Equilibria*, 6, 141-148.

- Ravi R., Prakash M. and Bhat K. (2007). Aroma characterization of coriander (*Coriandrum sativum* L.) oil samples, *Eur Food Res Technol* 225, 367–374.
- Rogalski, M., Carrier, B., Solimando, R., Peneloux, A., (1990). Correlation and prediction of physical properties of hydrocarbons with the modified Peng-Robinson equation of state. 2. Representation of the vapor pressures and of the molar volumes, *Ind. Eng. Chem. Res.*, 29(4), 659-666.
- Kenneth S. Pitzer, Donald R. Schreiber (1988). Improving equation-of-state accuracy in the critical region; equations for carbon dioxide and neopentane as examples. *Fluid Phase Equilibria*. 41(1-2),1-17.
- Stamataki S., Tassios D. (1998). Performance of cubic EOS at high pressures, *Oil & Gas Science and Technology* -53(3), 367- 377.
- Ueno H., Tanaka M., Machmudah S., Sasaki M. and Goto M.(2008). Supercritical Carbon Dioxide Extraction of Valuable Compounds from Citrus junos Seed, *Food and Bioprocess Technology*, 1(4), 357-363.
- Valderrama, J. O. (2003). The state of the cubic equations of state, *Ind. Eng. Chem. Res.* 42, 1603-1618.