

CALCULATION MIXING RULE AND MODIFICATION SEMI-EMPIRICAL MODELS FOR SOLUBILITY MODELING IN SUPERCRITICAL CARBON DIOXIDE

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Received July 27, 2018; Accepted October 2 April 24, 2019

Abstract

In this work, Soave-Redlich-Kowang (SRK) and Peng-Robinson (PR) equations of state with Huran-Vidal mixing rules was used to estimate the solubility of Tributyl phosphate (TBP) in supercritical CO₂. Since there were no available data for critical properties of TBP, A new method for evaluating of C₂ (Huran-Vidal mixing rule parameter) is recommended as a function of temperature and pressure. Also for solubility modeling by semi-empirical correlation, the new forms of Chrastil equation with variable coefficients were used which resulted in 6% of AARD%. The amounts of AARD% were obtained 8.97% for SRK-EOS and 17.01% for PR-EOS. Finally, the modeling of solubility for 21 compounds (The solubility data were obtained from literatures) by these methods has been investigated. Results show that the AARD% for the models with Charstil and modified Charstil are 12.07 and 11.17 respectively. Also the AARD% for SRK and PR-EOS are 14 and 19.85 respectively.

Keywords: Solubility Modeling; Group Contribution Method; Equation of State; Semi-Empirical Model; Extraction.

1. Introduction

One of several important advantages of supercritical fluid extraction (SFE) is the enhancement of extraction efficiency and the selectivity enhancement by tuning the pressure and/or temperature. Another advantage of SFE is a higher diffusivity and lower viscosity of a liquid, and much stronger solvent power than a gas [1]. Solubility is the concentration or mole fraction of a substance in the supercritical phase at a particular temperature and pressure when it is in equilibrium with the pure substance. For quantitative analysis, it is important that good solubility speeds up to initial stages of extraction and reduces the time of the process to some extent. The solubility of extracted compounds needs to be known if an efficient SFE process is to be designed [2]. There is some different models to estimate solubility data and these models generally fall into the following categories: i) A density-based approach, ii) A solubility parameter approach where the SCF is treated as a liquid, iii) An equation of state (EOS) approach where the SCF is treated as a high-pressure gas [9]. The simplest available models for EOS are based on cubic equations of state, which require a minimum number of parameters. The general form of EOS is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{\phi(b,T) + \phi(b,T) \times v + v^2} \quad (1)$$

where $\phi(b,T)$ and $\phi(b,T)$ are function of temperature and the co-volume b of the molecules of solute [3].

Critical properties (T_c , P_c) and the acentric factor (ω) of the solute and solvent are required for calculating of constant parameters, but these properties are not available for many of

compounds (Because large number of low-volatile natural substances decompose when heated before T_c is reached). Therefore, these parameters have been estimated by group contribution method (GCM) [4]. For example, application of group contribution method to approximate critical temperature leads in $T_c=388.6$ K for ethane, although the real value of T_c is 305.42 K. This error leads in consecutive errors in the calculations of solubility model [5]. Otherwise semi-empirical correlations are widely used and they are useful tools for experimental data correlation. These models are based on the simple error minimization and use only density of pure supercritical carbon dioxide and operational pressure and temperature. Thus, there is no need to calculate critical and thermo physical properties of the involved solutes. Several equations have been presented by different authors, covering from three to six parameters [6-7].

In this study, we investigated the modeling solubility of tributyl phosphate (TBP) in supercritical CO_2 (SC- CO_2). Also experimental data for solubility modeling are collected from Y. Meguro *et al.* literature [1]. Three models were used to estimate the solubility of TBP in SC- CO_2 : Peng-Robinson equation of state (PR-EOS), Soave Redlich-Kowan equation of state (SRK-EOS) and modified Chrastil equation. According to obtained results, the proposed models present much more accurate estimation/prediction for in solubility. So, in order to accelerate the industrial processes, the proposed models can be employed and strongly recommended. TBP, belong to organ phosphorous compounds, is a liquid at ambient temperature, and this compound has widely employed in solvent extraction of metal ions because of their high extractability acid aqueous solution and high radiochemical stability.

2. Theory

2.1. Equation of state models

The solubility of a solid (2) in a SCF (1) system can be calculated using the following equation:

$$y_2 = \frac{f_2^{ol}}{\phi_2^v P} = \frac{P_2^{sat}}{P} \frac{\exp\left(\frac{v_2^l (P - P_2^{sat})}{RT}\right)}{\phi_2^v} \quad (2)$$

where y_2 is the mole fraction of the solute in SCF phase; P_2^{sat} is the saturation pressure of the pure liquid at the system temperature; ϕ_2^v is the fugacity coefficient of solute in SCF at the system temperature and pressure, and v_2^l is the molar volume of the pure solute.

In this work, cubic EOSs (PR-EOS and SRK-EOS) will be used to estimate ϕ_2^v . The pressure-explicit form of SRK-EOS and PR-EOS respectively are:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (3) \quad P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (4)$$

Solvent properties (critical constants and acentric factor) are usually well known for solvent (CO_2), so its parameters can be calculated in the usual way:

$$A_1 = \frac{a_1 P}{R^2 T^2} = \eta_1 \alpha_1 \frac{P_{r1}}{T_{r1}^2} \quad (5) \quad B_1 = \frac{b_1 P}{RT} = \eta_2 \frac{P_{r1}}{T_{r1}} \quad (6)$$

$$\alpha_1(T_{r1}) = [1 + m_1(1 - \sqrt{T_{r1}})]^2 \quad (7)$$

$$m_1 = \lambda_0 + \lambda_1 \omega_1 + \lambda_2 \omega_1^2 \quad (8)$$

The critical constants and acentric factor of the solute are not known, and then B_2 must be estimated. Constants of two EOSs for CO_2 are shown in Table 1.

Table 1. Constants of PR-EOS and SRK-EOS for CO_2

	η_1	η_2	λ_0	λ_1	λ_2
PR-EOS	0.45724	0.07796	0.379	1.485	-0.1644
SRK-EOS	0.42748	0.08664	0.48	1.57	-0.176

The co-volume B_2 of the solute can be assumed as equal to the known molar volume of the liquid:

$$B_2 = v_2^L \frac{P}{RT} \quad (9)$$

The mixing rules proposed by Huron and Vidal were applied:

$$B_m = \sum_i y_i B_i = y_1 B_1 + y_2 B_2 \quad (10)$$

$$\frac{A_m}{B_m} = \sum_i y_i \left(\frac{A_i}{B_i} - \frac{\ln \gamma_i^\infty}{\ln 2} \right) = \sum_i y_i C_i \quad (11)$$

γ_i^∞ is the activity coefficient at infinite pressure. We can neglect γ_1^∞ of the solvent, which is almost pure, therefore:

$$C_1 \cong \frac{A_1}{B_1} \quad (12) \quad \text{and for } C_2: \quad C_2 = \frac{A_2}{B_2} - \frac{\ln \gamma_2^\infty}{\ln 2} \quad (13)$$

Thus:

$$\frac{A_m}{B_m} = y_1 \frac{A_1}{B_1} + y_2 C_2 \quad (14)$$

As critical values and acentric factor for the TBP solute are not available, C_2 cannot be calculated from Eq. (13). In contrast with most of previous works which have used group contribution methods, this study tries to propose a new mathematical model to estimate C_2 values without using critical properties. Jafari Nejad *et al.* investigated EOSs for correlation solubility of TBP in supercritical CO_2 but they used thermodynamic properties of TBP (critical temperature, critical pressure and Pitzer's acentric factor) that obtained from fitting solubility experimental data [8]. Modeling results for C_2 values (by using Matlab 7 and Eviews 3.1 software) in terms of temperature and pressure are shown in Figures. 1(a) and 1(b) which refer to SRK-EOS and PR-EOS, respectively.

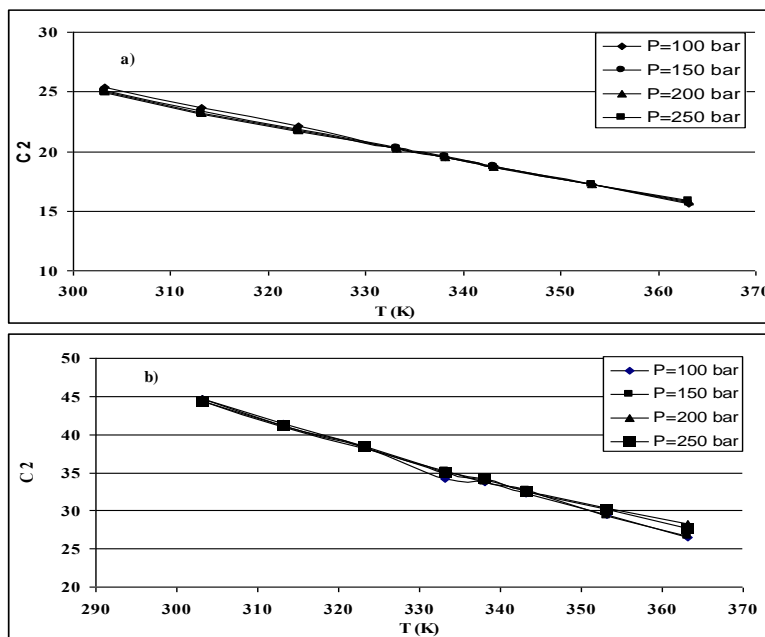


Figure 1. Variations of C_2 with temperature and pressure for (a) SRK-EOS and (b) PR-EOS

According to the above illustration C_2 is a function of temperature and pressure. We found that C_2 has:

1. A linear relationship with temperature at constant pressure,
2. and a logarithmic relationship with pressure at constant temperature.

Then the best model for C_2 is presented as:

$$C_2(T, P) = \alpha(T) - \beta(T) \ln\left(\frac{P}{P_{ref}}\right) \quad (15)$$

In which T is temperature (K); P is pressure (bar); $P_{ref} = 100\text{bar}$, $\alpha(T)$ and $\beta(T)$ are defined as:

$$\alpha(T) = a_1' T + b_1' \quad (16)$$

$$\beta(T) = a_2' T + b_2'$$

After modeling C_2 using software tools and experimental data, constants coefficients in Eq. (16) for SRK-EOS and PR-EOS are calculated and shown in Table 2.

Table 2. Constants of Eq. (16)

Equation of state	a_1'	b_1'	a_2'	b_2'
PR-EOS	0.8568	66.32	1.1432	-64.319
SRK-EOS	0.16196	74.3774	0.0314	10.9083

This function for C_2 has never been reported before in the literature. Using the Huron-Vidal mixing rules with the above approximation, the fugacity coefficient of the solute in gas phase will be calculated. An iterative procedure is required to calculate the solute concentration in the gas phase because the fugacity coefficient is a function of y_2 . P_2^{sat} varies strongly with T and has a direct effect on y_2 , so it must be determined separately at each temperature or expressed as a function of temperature:

$$\ln(P_2^{sat}) = 36.85 - \frac{11790}{T} \quad (17)$$

where P_2^{sat} is vapor pressure (bar) and T is temperature (K).

2.2. Density-based model

The Chrastil model [9] is based on the assumption of the formation of a solvate-complex between molecules of solvent and solute at equilibrium was used as a semi-empirical model. Eq. (18) leads to the linear relationship between the solubility of the solute, $S(g \text{ solute}/L \text{ solvent})$, and the density of the solvent, $\rho(g/L)$, for a given temperature, $T(K)$:

$$\ln S = k \ln \rho + \frac{a}{T} + b \quad (18)$$

where a , b , and k are the adjustable parameters of the model. The constant k is an association factor that represents the number of CO_2 molecules in the complex; a depends on the vaporization and salvation enthalpies of the solute; b depends on the molecular weights of the solute and solvent.

The parameters a , b , and k are obtained performing a multiple linear regression on the experimental solubility data. The advantages of the Chrastil model, it is simple to use and require a maximum of three fitting parameters to cover all temperature, pressure, and densities in supercritical region, thus it was successfully used to correlate system considered in this study. In contrast with the previous reports which have considered constant coefficient, we developed a new technique what the value of k is considered as function of temperature and simulation shows that the dependency is linear as follow:

$$k = n_1 T + n_2 \quad (19)$$

Using Eq. (19) in Eq. (18), modified Chrastil equation would be as:

$$\ln S = (n_1 T + n_2) \ln \rho + \frac{a}{T} + b \quad (20)$$

Constants in Eq. (20) after modeling with using software tools and experimental values are calculated and shown in Table 3:

Table 3. Constants of TBP for Eq. (20)

n_1	0.037721
n_2	-2.4929
a	17 630.75
b	-123.0075

The error for these models was estimated by average absolute relative deviation (AARD) between experimental (y_{exp}) and calculated (y_{calc}) solubility data according to the following equation:

$$\text{AARD}(\%) = \frac{1}{n} \left| \sum \frac{y_{2,\text{exp}} - y_{2,\text{calc}}}{y_{2,\text{exp}}} \right| \times 100 \quad (21)$$

where n is the number solubility of data used.

3. Results and discussion

After modeling C_2 for SRK and PR equations of state, estimate critical properties of TBP, and calculating the coefficient of density-based equations, y_2 is calculated in different operation conditions and shown in Figures 2, 3. Figure 2(a) shows that under about 333.15 K, vapor pressure is more effective which causes the solubility to be increased as the temperature increases. However, between temperature 333.15 K and 363.15 K, the fluid density is more on y_2 and it decreases the solubility.

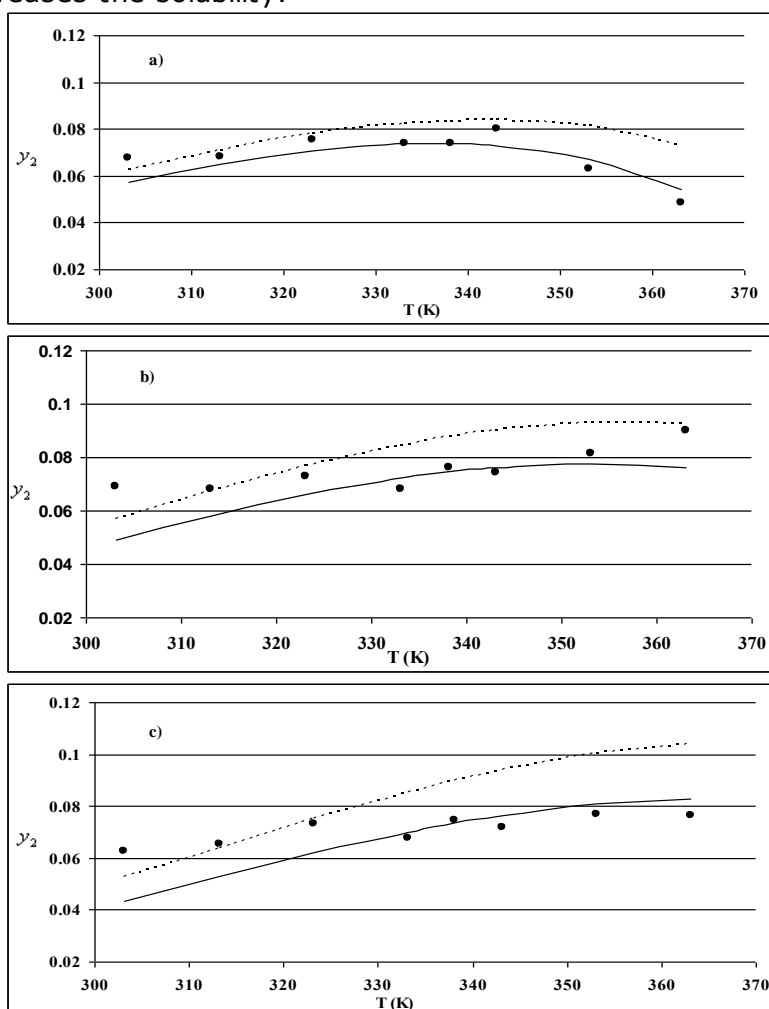


Figure 2. Solubility of TBP in SC-CO₂ at (a) P=150 bar, (b) P=200 bar and (c) P=250 bar (•) Experimental [4], (—) Calculated by SRK-EOS, (---) Calculated by PR-EOS

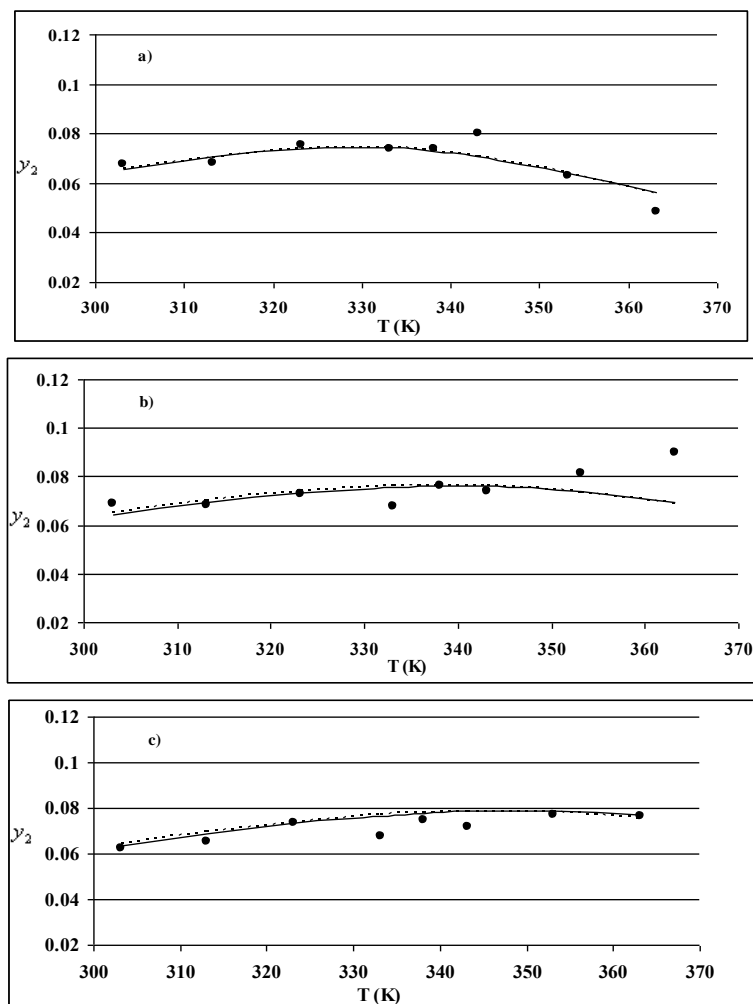


Figure 3. Solubility of TBP in SC-CO₂ at (a) P=150 bar, (b) P=200 bar and (c) P=250 bar (●) Experimental [4], (—) Calculated by Modified Chrastil Model, (---) Calculated by Modified Semi-Empirical Model

Other figures show the same results. As other researches such as Bordet *et al.* [3] has reported, equations of state have a considerable error in comparison with experimental results near the critical point ($T=30^{\circ}\text{C}$) in different pressures, as may be observed clearly in Figs. 2(a), 2(b), and 2(c). This shows that considering the high sensitivity of supercritical fluid density to temperature and pressure around the critical point, equations of state are not able to predict the solubility in this area accurately. As the error of SRK-EOS is lower than PR-EOS, the SRK-EOS predicts TBP solubility in supercritical CO₂ more accurately. The density based model derived from experimental data regression (It is just mathematical model) has an acceptable correlation near the critical point and is observed clearly in Figures 3(a), 3(b), and 3(c). According to these figures, when variable coefficients form of Chrastil is used, the result had very low errors (around 6%). This kind of model is simple because it resulted from the fit of just four parameters. The error of Chrastil (constant and variable coefficients) in addition to the errors for PR-EOS and SRK-EOS are listed in Table 4.

Table 4. The amount of AARD% for TBP solubility in SC-CO₂

AARD%	SRK-EOS	PR-EOS	Chrastil model	
			Modified form	Main form
	8.97	17.01	5.99	6.40

The usages of C_2 instead of GCM for substances for which the critical properties and acentric factor are not available, and temperature-dependent variable coefficients for semi-empirical equations in this study, are compared with Coimbra *et al.* [10] results. Coimbra *et al.* have estimated critical temperature and pressure for photochromic dye using GCM and have used the main form for semi-empirical equations. AARD% of the models is presented in Table 5.

Table 5. AARD% for modeling photochromic dye solubility

Chrastil model	SRK-EOS	PR-EOS
7.9	28.14	24.65
6.9	13.7	18.15

The results show a better solubility modeling for the usage of C_2 in comparison with the use of GCM for critical properties. The accuracy of the proposed model was evaluated using 21 published solubility data (about 350 data points) sets by calculating the average of absolute relative deviation. The error of Chrastil equation (constant and variable coefficients) in addition to the errors for PR-EOS and SRK-EOS are listed in Table 6.

Table 6. AARD% obtained for the prediction solubility in supercritical solvent

	Chrastil equation	Modified Chrastil	SRK-EOS	PR-EOS	Number of Data Points
Anthracene- CO ₂	18.04	17.83	17.22	15.73	23
Anthracene-Ethane	9.94	9.30	7.78	8.18	27
Fluorene- CO ₂	21.72	21.70	10.02	11.59	30
Fluorene-Ethylene	8.10	6.91	21.07	30.16	24
Naphthalene-Ethane	13.93	11.40	30.34	42.44	23
Pyrene- CO ₂	23.43	20.28	16.41	26.07	21
Pyrene-ethylene	7.98	7.93	12.93	15.92	15
Phenanthrene- C ₂ H ₄	11.15	10.63	15.74	20.25	15
Phenanthrene- CO ₂	5.86	4.28	9.87	9.30	21
Phenanthrene-Ethylene	2.55	1.39	3.02	2.94	6
Triphenylmethane- CO ₂	9.65	8.90	34.38	43.33	19
Ascorbyl Palmitate- CO ₂	5.07	4.46	6.32	6.41	8
BHA- CO ₂	8.30	3.78	16.50	29.52	6
Dodecyl Gallate- CO ₂	5.58	1.50	7.12	10.59	8
Propyl Gallate- CO ₂	3.60	2.29	3.98	6.00	8
2,3-Dimethylnaphthalene- CO ₂	13.19	11.65	8.86	22.62	15
2,6-Dimethylnaphthalene- C ₂ H ₄	10.03	10.39	18.01	26.66	18
2,6-Dimethylnaphthalene- CO ₂	9.38	8.89	10.79	22.13	15
Benzoic acid- C ₂ H ₄	8.88	8.86	3.35	4.29	15
Benzoic acid- CO ₂	9.81	9.22	5.93	13.53	15
Hexachloroethane- CO ₂	15.30	14.53	6.58	23.41	15
AARD%	12.07	11.17	14.00	19.85	-

4. Conclusions

The critical properties of a solute are required for modeling of the solubility by the equation of state. For many compounds, the critical properties are not available. So, group contribution method is utilized as a common method to estimate these properties. But, it leads to the consecutive errors in calculations of the solubility modeling. As critical values and acentric factor for the TBP solute are not available, in contrast with most of previous works which have used group contribution methods, this study tries to propose a new mathematical model to estimate C_2 values without using critical properties. As a result for TBP, photochromic dye and other solvents solubility modeling, it been concluded that using C_2 as a function of temperature and pressure results in good predictions of solubility in supercritical state and has the ability to be used in modeling accurately. A new four-constant empirical equation was developed for correlation of solute solubility in supercritical phase and validated by about 350 experimental data point collected from literature. The comparison between proposed model and published

models shows that the proposed model gives much more accurate results in solubility calculations than previously published models. Thus we strongly suggested using the same coefficients for the density-based models in future researches.

References

- [1] Meguro Y, Iso S, Sasaki T, Yoshida Z. Solubility of Organophosphorus Metal Extraction in Supercritical Carbon Dioxide. *Anal. Chem.* 1998; 70(4): 774-779.
- [2] Ozel MZ, Bartle KD, Clifford AA, Burford MD. Extraction, Solubility and Stability of Metal Complexes Using Stainless Steel Supercritical Fluid Extraction System. *Anal. Chim. Acta.* 2000; 417(2): 172-184.
- [3] Bordet F, Passarello JP, Chartier T, Tufeu R, Baumard JF. Modeling Solutions of Hydrocarbons in Dense CO₂ gas. *J. Eur. Ceram. Soc.* 2001; 21(9): 1219-1227.
- [4] Melo SABV, Melo RLFV, Costa GMN, Alves TLM. Solubility of L-Dopa in Supercritical Carbon Dioxide: Prediction Using a Cubic Equation of State. *J. Supercrit. Fluids.* 2005; 34(2): 231-236.
- [5] Joback KG, Reid RC. Estimation of Pure-Component Properties from Group-Contributions. *Chem. Eng. Commun.* 1987; 57(1-6): 233-243.
- [6] Murga R, Sanaz MT, Beltran S, Cabezas JL. Solubility of Three Hydroxycinnamic Acids in Supercritical Carbon Dioxide. *J. Supercrit. Fluids.* 2003; 27(3): 239-245.
- [7] Asgarpour Khansary M, Amiri F, Hosseini A, Hallaji Sani A, Shahbeig H. Representing Solute Solubility in Supercriticalcarbon Dioxide: A Novel Empirical Model. *Chem. Eng. Res. Des.* 2015; 93: 355-365.
- [8] Jafari Nejad Sh, Mohammadikhah R, Abolghasemi H, Moosavian MA, Maragheh MG. A Novel Equation of State (EOS) for Prediction of Solute Solubility in Supercritical Carbon Dioxide: Experimental Determination and Correlation. *Can. J. Chem. Eng.* 2009; 87(6): 930-938.
- [9] Chrastil FJ. Solubility of Solids and Liquids in Supercritical Gases. *Phys. Chem.* 1982; 86(15): 3016-3021.
- [10] Coimbra P, Gil MH, Duarte CMM, Heron BM, de Sousa HC. Solubility of a Spiroindolinonaphthoxazine Photo Chromic Dye in Supercritical Carbon Dioxide: Experimental Determination and Correlation. *Fluid. Phase. Equilib.* 2005; 38(1): 120-128.

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