

Modeling the Solubility of Spiroindolinonaphthoxazine Photochromic Dye in Supercritical Carbon Dioxide

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Abstract

In this report, two methods were developed to estimate the solubility of Spiroindolinonaphthoxazine Photochromic dye in supercritical CO₂. First method used Soave-Redlich-Kowang (SRK) and Peng-Robinson (PR) equations of state with Huran-Vidal mixing rules while second method used based-density models (recommended by Mendez and Chrastil) for a direct relation between solubility and solvent density. Since there were not any data for critical properties of Photochromic dye, a new method for evaluating of C₂ (mixing rule parameter), as a function of temperature and pressure, was recommended. This method in comparison with others such as group contribution methods, predicts good result. The amounts of Average Absolute Relative Deviation (%AARD) were obtained 13.7% for SRK-EOS and 18.15% for PR-EOS. Also, a based-density modified equation is used with variable coefficients which results %AARD about 6% employing Chrastil modified model and 6.2% employing Mendez modified model.

Keywords: Solubility, Supercritical fluid, Spiroindolinonaphthoxazine Photochromic dye, cubic equation of state.

1. Introduction

Many applications of supercritical fluid technology have continuously been developed for the processing of food, pharmaceutical, polymer and specific chemicals [1, 2].

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. Also SFE can minimize the amount of solvent waste [3, 4].

Carbon dioxide is the most commonly used supercritical fluid. The critical temperature and pressure of carbon dioxide is relatively low (304 K and 73.7 bar), non-toxic, non-flammable, non-explosive and readily available at low cost [5-7].

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. High solubility is also an indication of favorable partition between the SCF and a liquid or other matrix. If an efficient SFE process is to be designed, the solubility of extracted compounds needs to be known. Generally, it is important in designing operating conditions to obtain an extract of the desired composition [8-10].

After several decades of SCF research in industry and academic, there are only a few methods available for correlating solid solubility in dense carbon dioxide [11]. There are some different models to estimate solubility data. 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 [12].

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 $\varphi(b,T)$ are function of temperature and the co-volume b of the molecules of solute [13].

Critical properties (T_C , P_C) and the acentric factor (ω) of the solute and solvent are required for calculate its parameters for the pure components, these properties are almost not available for many of compounds and a large number of low-volatile natural substances decomposes when heated before T_C is reached, therefore, they have been estimated by group contribution method (GCM) [10,14]. For example, application of GCM, to approximate critical temperature (Joback et.al [15]) leads in $T_C = 498.0$ K for Chloroethane, although the real value of T_C is 460.4 K. This error leads in consecutive errors in the calculations of solubility model.

Otherwise semi-empirical correlations are widely used and they are useful tools for experimental data correlation [11, 16].

In this study, we investigated the modeling solubility of Spiroindolinophthoxazine Photochromic dye in supercritical CO_2 (SC- CO_2) in 308, 318, 328 K and pressure range of 10 to 26 MPa. A variety of systems display photochromism, prominent amongst these are Diheterourylethenes, Azobenzenes and Spiroindolinophthoxazines. Fundamental to the application of photochromic dye is its incorporation/impregnation into polymeric host materials, e.g. simple plastics and fibers and more complex functional polymers. A recent method to impregnate a polymer with dye or other additives is by supercritical fluid impregnation technique [6]. The Spiroindolinophthoxazine molecular structure is shown in Fig (1):

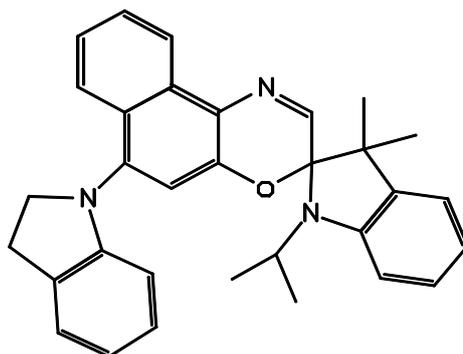


Fig (1): Molecular structure of Spiroindolinophthoxazine

2. Theoretical models to correlate solubility in supercritical CO_2

In this study four models were used to estimate the solubility of Photochromic dye in SC- CO_2 : Peng-Robinson equation of state (PR-EOS), Soave Redlich-Kowan equation of state (SRK-EOS), Chrastil equation [17], and Mendez-Santiago and Teja [18] correlation based on density of supercritical fluid.

2.1 Equation of state models

Let us consider a binary system, where component 1 is the supercritical solvent and component 2 is the solute (Photochromic dye), which is present as a pure solid, in equilibrium with the gas phase. The general method for evaluation of y_2 starts with the phase equilibrium necessary condition written in terms of equal fugacities of species 2 in both liquid and vapor phase:

$$f_2^{0S} = f_2^v \quad (2)$$

Where f_2^{0S} the fugacity of pure component 2 in solid phase and f_2^v is the fugacity of solute in vapor phase (SCF). $f_2^{0S}(P)$ Can be expressed through its vapor pressure and a poynting factor:

$$f_2^{0S}(P) = f_2^{0S}(P_2^{Sub}) \exp\left(\frac{v_2^S(P - P_2^{Sub})}{RT}\right) \quad (3)$$

We assumed that $f_2^{0S}(P_2^{Sub}) = P_2^{Sub}$.

The fugacity of the solute in the gas phase (f_2^v) is expressed as the product of the partial pressure (Py_2) and a fugacity coefficient (ϕ_2^v):

$$f_2^v = Py_2 \phi_2^v \quad (4)$$

Combining the Eq. (3) and (4), the solubility of solid in the fluid phase is obtained as:

$$y_2 = \frac{f_2^{0S}}{\phi_2^v P} = \frac{P_2^{Sub}}{P} \frac{\exp\left(\frac{v_2^S(P - P_2^{Sub})}{RT}\right)}{\phi_2^v} \quad (5)$$

The fugacity coefficient ϕ_2^v , at supercritical conditions can be calculated by using an equation of state.

In this work, the 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:

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

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (7)$$

Solvent properties (critical constants and acentric factor) are usually well known for solvent (CO₂), so its parameters can be calculated in the usual way:

$$A_1 = \frac{a_1 P}{R^2 T^2} = \eta_1 \alpha_1 \frac{P_{r_1}}{T_{r_1}^2} \quad (8)$$

$$B_1 = \frac{b_1 P}{RT} = \eta_2 \frac{P_{r_1}}{T_{r_1}} \quad (9)$$

$$\alpha_1(T_{r_1}) = [1 + m_1(1 - \sqrt{T_{r_1}})]^2 \quad (10)$$

$$m_1 = \lambda_0 + \lambda_1 \omega_1 + \lambda_2 \omega_1^2 \quad (11)$$

Table (1): Constants of PR and SRK EOS

	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 critical constants and acentric factor of the solute are not known usually, so B_2 must be estimated:

The co-volume b_2 of the solute can be assumed as equal to the known molar volume of the liquid [10]:

$$B_2 = v_2^L \frac{P}{RT} \quad (12)$$

The mixing rules proposed by Huron and Vidal were applied:

$$B_m = \sum_i y_i B_i = y_1 B_1 + y_2 B_2 \quad (13)$$

$$\frac{A_m}{B_m} = \sum_i y_i \left(\frac{A_i}{B_i} - \frac{\ln \gamma_i^\infty}{\ln 2} \right) = \sum_i y_i C_i \quad (14)$$

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

$$C_1 \cong \frac{A_1}{B_1} \quad (15)$$

And for C_2 :

$$C_2 = \frac{A_2}{B_2} - \frac{\ln \gamma_2^\infty}{\ln 2} \quad (16)$$

Thus:

$$\frac{A_m}{B_m} = y_1 \frac{A_1}{B_1} + y_2 C_2 \quad (17)$$

As critical values and acentric factor for the Photochromic dye solute are not available, C_2 can not be calculated from Eq. (17). In contrast with most of previous works which have used group contribution methods, this study tries to propose a mathematical model to estimate C_2 values without using critical properties. Modeling results for C_2 values in terms of temperature and pressure are shown in Figures (2) and (3) which refer to SRK-EOS and PR-EOS, respectively. According to the above illustration C_2 is a function of temperature and pressure. The model which best fits to the experimental results is presented as:

$$C_2(T, P) = \alpha(T) - \beta(T) \ln\left(\frac{P}{P_{ref}}\right) \quad (18)$$

in which T is temperature (K), P is pressure (bar) and $P_{ref} = 105 \text{ bar}$. $\alpha(T)$ and $\beta(T)$ are defined as:

$$\begin{aligned} \alpha(T) &= a_1' T + b_1' \\ \beta(T) &= a_2' T + b_2' \end{aligned} \quad (19)$$

After modeling C_2 using software tools and experimental data [6], constants coefficients in Eq. (19) for SRK-EOS and PR-EOS are calculated and shown in Table (2).

Table (2): Constants of Eq. (19)

Equation of state	a_1'	b_1'	a_2'	b_2'
PR-EOS	0.89	147.6	0.6	169.3
SRK-EOS	0.216	2.2	0.167	42.5

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 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^{Sub} varies strongly with T and has a direct effect on y_2 , so it must be determined separately at each temperature as Table (3).

Table (3): P_2^{Sub} vs T [6]

T (K)	$P_2^{Sub} \times 10^{13}$ (Pa)
308	0.72
318	3.81
328	18.3

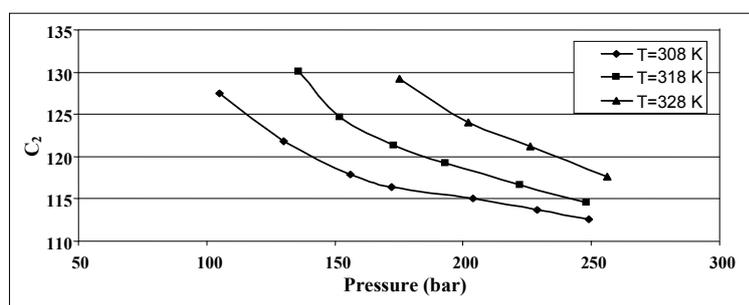


Fig (2): Variations of C_2 with Temperature and Pressure for PR-EOS

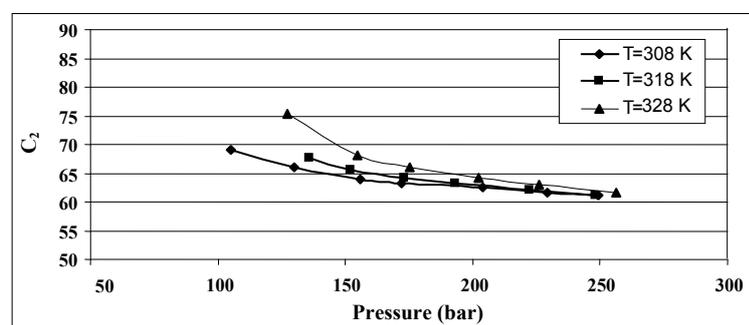


Fig (3): Variations of C_2 with Temperature and Pressure for SRK-EOS

2.2 A density-based models

Two semi empirical models have been used for data correlation. The first one, was the Chrastil model [17], is based on the assumption of the formation of a solvate-complex between molecules of solvent and solute at equilibrium. Eq. (20) leads to the linear

relationship between the solubility of the solute, $S(\frac{gr \text{ solute}}{Lit \text{ solvent}})$, and the density of the solvent, $\rho(\frac{gr}{Lit})$, for a given temperature, $T(k)$:

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

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 solvation 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.

The second semi-empirical correlation used, was the Mendez et al [18]. Based on the theory of dilute solutions, Mendez-Santiago and Teja proposed a simple linear expression to correlate the solubility of solids in a SCF:

$$T \ln(yP) = A' + B' \rho + C' T \quad (21)$$

where A' , B' and C' are constants, considered as temperature independent, and obtained by a multiple linear regression of solubility experimental data.

In contrast with the previous reports which have considered constant coefficient, we developed a new technique what the values of k , B' is considered as function of temperature and simulation shows that the dependency is linear as follows:

$$k = n_1 T + n_2; \quad B' = c_1 T + c_2 \quad (22)$$

Using Eq. (22) in Eq. (20), Chrastil equation would be as:

$$\ln S = (n_1 T + n_2) \ln \rho + \frac{a}{T} + b \quad (23)$$

After modeling with using software tools and experimental data, constants in Eq. (23) are calculated and shown in Table (4):

Table (4): Constants for Eq. (23)

n_1	0.037721
n_2	-2.4929
a	17630.75
b	-123.0075

As similar with using Eq. (22) in Eq. (21), modified Mendez et al equation would be as:

$$T \ln(yP) = A' + (c_1 T + c_2) \rho + C' T \quad (24)$$

Constants in Eq. (24) are calculated and shown in Table (5):

Table (5): constants for Eq. (24)

c_1	-0.002
c_2	5.4597
A'	40.1975
C'	-14716.699

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:

$$AARD(\%) = \frac{1}{n} \left| \sum \frac{y_{2,exp} - y_{2,calc}}{y_{2,exp}} \right| \times 100 \quad (25)$$

where n is the number solubility of data used.

3. Results and Discussion

After modeling C_2 for SRK and PR equation of states, and calculating the coefficient of based-density equations, y_2 is calculated in different operation conditions and shown in Figures (4) to (9).

As observed in results, solubility of Photochromic dye is increased first by increasing of temperature and then decreased. Increasing the temperature causes an increase in solute vapor pressure and also decreasing the supercritical fluid density.

EOS have a considerable error comparing with experimental results near the critical point ($T=30^\circ\text{C}$) in different pressures, as may be observed clearly in Figures (4). This shows that considering the high sensitivity of supercritical fluid density to temperature and pressure around the critical point, equation of states are unable to predict the solubility in this area accurately.

As the error of SRK-EOS is less than PR-EOS, SRK-EOS predicts Photochromic dye solubility in supercritical CO_2 more accurately.

The density based models derived from experimental data regression (and is just a mathematical model) have an acceptable correlation as observed clearly in Figures (7), (8), and (9). According to these Figures, Chrastil and Mendez equations show convenient nearly similar behavior and, when variable coefficients are used, result in very low errors (around 6%). These equations are simple because they result from the fit of just four parameters.

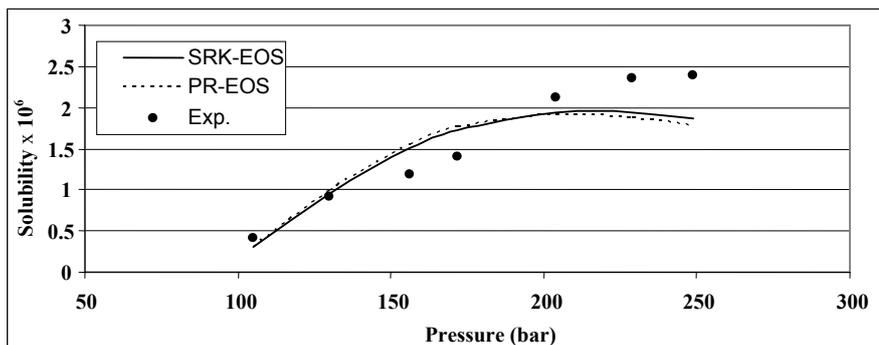


Figure (4): Solubility of Photochromic dye in SC- CO_2 at $T=308\text{ K}$

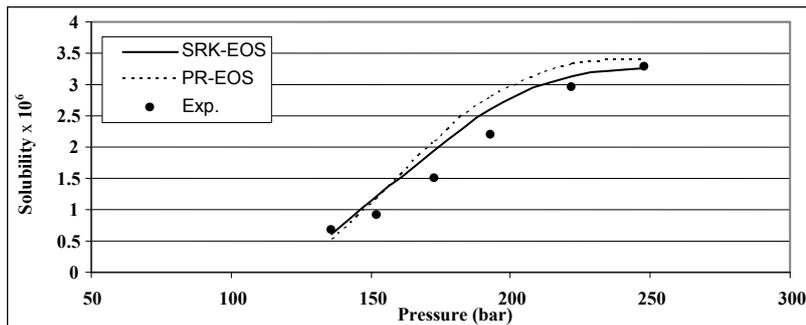


Figure (5): Solubility of Photocromic dye in SC-CO₂ at T=318 K

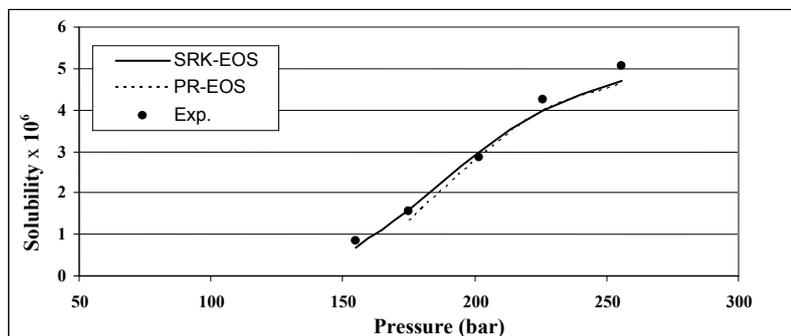


Figure (6): Solubility of Photocromic dye in SC-CO₂ at T=328 K

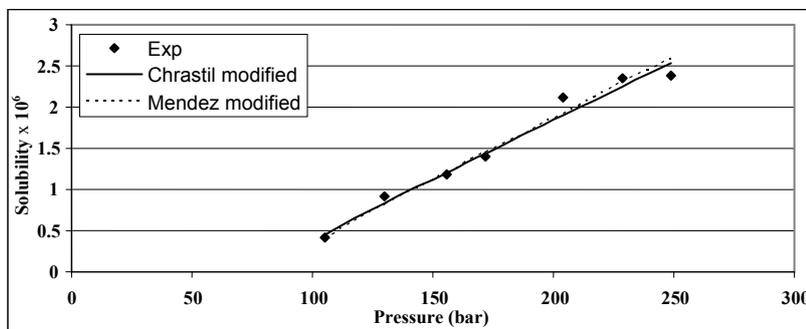


Figure (7): Solubility of Photocromic dye in SC-CO₂ at T=308 K

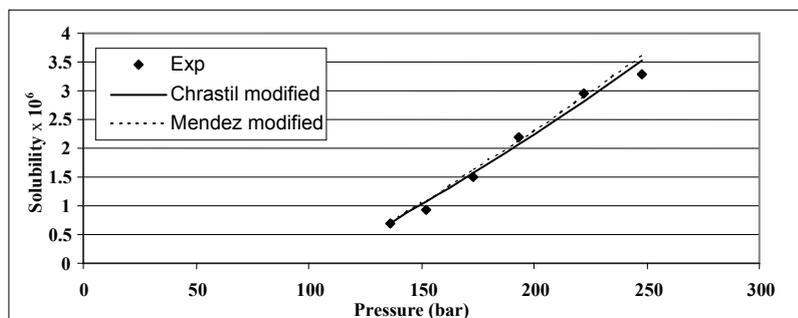


Figure (8): Solubility of Photocromic dye in SC-CO₂ at T=318 K

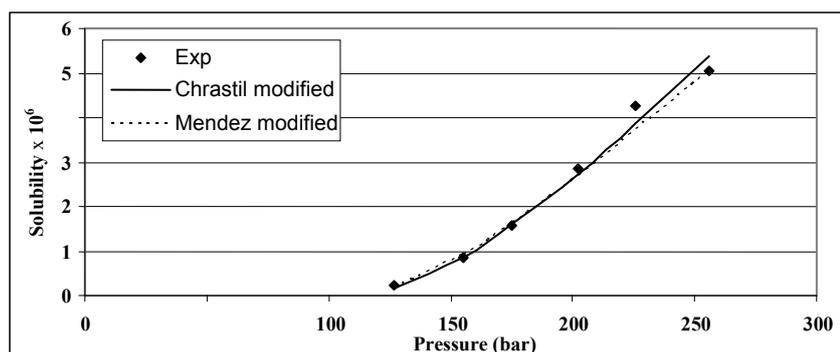


Figure (9): Solubility of Photochromic dye in SC-CO₂ at T=328 K

The usages of C₂ 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 Meguro et al [4] results for Tributyl Phosphate solubility modeling in supercritical carbon dioxide. %AARD of the models are presented in Table (6).

Table (6): %AARD for modeling TBP solubility

	Chrastil Model	SRK-EOS	PR-EOS
Meguro et al.	6.4	--	--
In this study	5.99	8.97	17.01

Phenanthrene solubility for various temperatures and pressures are studied by Keith, et al. [19]. For solubility modeling of Phenanthrene in SC-CO₂ using SRK-EOS and PR-EOS, the value of %AARD for C₂ and Phenanthrene T_c and P_c are compared in Table (7).

Table (7): %AARD for modeling Phenanthrene solubility

Equation of State	With C ₂	With Critical Properties
SRK-EOS	12.33	9.87
PR-EOS	14.16	9.30

The usages of C₂ instead of GCM and temperature-dependent variable coefficients for semi-empirical equations in this study are compared with Coimbra et al [6] results for Spiroindolinonaphthoxazine photochromic dye solubility modeling in supercritical carbon dioxide. 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 are presented in Table (8).

Table (8): The amount of %AARD for the prediction of Photocromic dye solubility in SC-CO₂

	SRK-EOS		PR-EOS		Chrastil model		Mendez model	
	Coimbra	This Work	Coimbra	This Work	Coimbra	This Work	Coimbra	This Work
%AARD	28.14%	13.7%	24.65%	18.15%	7.9%	6.9%	6.3%	6.2%

4. Conclusions

It may be observed that the AARD is increased when main forms of based-density models (constant coefficients) are used. As variable coefficients are used in density-based models, %AARD is decreased considerably which approves the convenient modeling and overlap of B' and k. Thus we suggest the same coefficients for the based-density model in future researches.

As a result of photochromic dye, TBP and Phenanthrene solubility predictions, we may conclude 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.

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