



# A five-parameter empirical model for correlating the solubility of solid compounds in supercritical carbon dioxide

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## ABSTRACT

The correlation of solute solubility in supercritical fluids is crucial for the development of supercritical applications. Many models have been developed to calculate the solubility of solid compounds. In this work, a new five-parameter empirical model was proposed for correlating solute solubility in supercritical carbon dioxide (SCCO<sub>2</sub>). The new model successfully correlated solute solubility of 45 compounds (1130 data points) in SCCO<sub>2</sub>, which were collected from literature published between 2010 and 2015. A comparison of the 14 most common empirical models (Chrastil, Adachi-Lu, del Valle–Aguilera, Sparks, Gordillo, Jouyban, Garlapati-Madras, Ch-Madras, Kumar-Johnston, Méndez Santiago-Teja, Hozhabr, Keshmiri, Khansary) and the proposed model showed that the overall average absolute relative deviation of the proposed model is the lowest (5.16%).

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## 1. Introduction

In recent years, Supercritical fluids (SCF) have caught much attention due to their potential applications in chemical, food, pharmaceutical, and polymer processing industries [1]. They are indeed widely used for extraction and purification. Carbon dioxide (CO<sub>2</sub>) is the preferred supercritical solvent for applications since it is nontoxic, nonflammable, non-explosive and recyclable. Moreover its critical properties are at relatively unworried temperature and pressure (304.12 K and 7.38 MPa, respectively) [2,3].

It is well known that the experimental determination of solubility of solid compounds in a SCF at various temperatures and pressures is expensive and time-consuming [4]. Consequently, the development of correlations to predict the solubility is a necessarily step. Such correlations may indeed be used to perform predictions at pressures and temperatures [5] where no data are available and are thus very useful to design new processes.

The models [6] classically used to correlate the solubility of solid

solutes are either equations of state or semi-empirical equations. Well-established models like cubic equations of state [7–9] not only need the knowledge of the critical temperature and pressure but also solid properties [2,10–12], which cannot be readily determined experimentally. Such parameters are however of the highest importance since in many cases, uncertainty and errors on numerical values of the solute properties are responsible for large deviations between experimental and calculated solubilities [13]. On the other hand, empirical models, which do not need solid properties, but instead density of solvent are widely used in prediction of solubility data.

In this work, after a short review of the commonly used semi-empirical models, a new five-parameter empirical model is presented to correlate the solubility of some solid compounds in SCCO<sub>2</sub>. The accuracy of the proposed model is compared to that of other correlations available in the open literature using the solubility data of 45 different compounds in SCCO<sub>2</sub>. Such data were collected in scientific papers published between 2010 and 2015. The results highlight the superiority of the proposed model over the other 14 models considered in this work to correlate the solute solubility.

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## 2. Reviews of commonly used empirical models

One of the first density-based models, in which it is assumed that a solvate complex is formed between the solute and the solvent molecules at equilibrium, was proposed by Chrastil (1982) [14]. As shown by Eq. (1), such a model couples the solubility of the solute ( $y_2$  in mole fraction) together with the density of the pure solvent ( $\rho_1$  in  $\text{kg}\cdot\text{m}^{-3}$ ):

$$y_2 = \rho_1^k \exp\left(\frac{a}{T} + b\right) \quad (1)$$

$k$  is the association number, which describes the average number of SCF molecules in the solvated complex,  $a$  is the sum of the heat of solvation and heat of vaporization of the solute,  $b$  is a function of the association number and molecular weights of the solute and supercritical fluid, and  $T$  is the absolute temperature in K.

With such a model, there is a necessary linear relationship between  $y_2$  and  $\rho_1$  in an isothermal log–log graph. Other limitations are also exhibited by Chrastil's model. For instance, if the solute solubility is greater than  $200 \text{ kg m}^{-3}$  [15], the model is no longer applicable. Based on these confinements, several modified forms of Chrastil's equation have been developed.

A modification was made by Adachi and Lu (1983) [16] considering the quantity  $k$  to be density-dependent. The model can be written as follows:

$$y_2 = \rho_1^{(e_0 + e_1\rho_1 + e_2\rho_1^2)} \exp\left(\frac{a}{T} + b\right) \quad (2)$$

$e_0$ ,  $e_1$ , and  $e_2$  are the model parameters which can be obtained by regression of experimental data. In comparison with Eq. (1), in Eq. (2) the association number  $k$  is a density second-order polynomial equation which makes it possible to significantly increase the accuracy of such a model.

The del Valle–Aguilera model (1983) [17] was developed by taking into account the enthalpy of vaporization change with temperature. They obtained:

$$y_2 = \rho_1^k \exp\left(\frac{a}{T} + b + \frac{m}{T^2}\right) \quad (3)$$

where  $m$  is a new model parameter.

Sparks et al. (2008) [15] derived an equation that combined together Adachi–Lu model with del Valle–Aguilera model by considering both the density impact on the association number  $k$  and the change of the enthalpy of vaporization with the temperature. The obtained equations can be expressed as:

$$y_2 = \rho_1^{(e_0 + e_1\rho_1)} \exp\left(\frac{a}{T} + b + \frac{m}{T^2}\right) \quad (4)$$

$$y_2 = \rho_1^{(e_0 + e_1\rho_1 + e_2\rho_1^2)} \exp\left(\frac{a}{T} + b + \frac{m}{T^2}\right) \quad (5)$$

Gordillo et al. (1999) [18] proposed a 6-parameter empirical model to calculate the solubility in  $\text{SCCO}_2$ . Their equation writes:

$$\ln(y_2) = e_0 + e_1P + e_2P^2 + e_3PT + e_4 + e_5T^2 \quad (6)$$

where  $P$  is the system pressure in MPa and  $T$  the temperature in K.

Jouyban et al. (2002) [5] also proposed a 6-parameter empirical model:

$$\ln(y_2) = e_0 + e_1P + e_2P^2 + e_3PT + e_4\frac{T}{P} + e_5 \ln \rho_1 \quad (7)$$

A recent modification of Chrastil's model was proposed by Garlapati and Madras (2010) [19]. Their model correlates the solubilities of solids as a function of temperature and density of  $\text{SCCO}_2$ . The Garlapati–Madras model can be written as:

$$\ln(y_2) = e_0 \ln \rho_1 + e_1 \rho_1 \ln \rho_1 + e_2 \ln(\rho_1 T) + \frac{a}{T} + b \quad (8)$$

On the basis of solvate complex theory, Ch and Madras (2010) [6] introduced a new semi-empirical equation with four parameters:

$$y_2 = \left(\frac{P}{P^*}\right)^{(k-1)} \exp\left(\frac{a}{T} + m\rho_1 + b\right) \quad (9)$$

where  $P^*$  is a reference pressure, 0.1 MPa.

Kumar and Johnston (1988) [20] found that many experimental data exhibited a linear dependence of  $\ln y_2$  with respect to  $\rho_1$  and derived the following equation:

$$\ln(y_2) = k\rho_1 + \frac{a}{T} + b \quad (10)$$

Based on the dilution theory [2,3,6], Méndez-Santiago and Teja (1999) [21] took pressure into consideration directly, and obtained the following model:

$$\ln(Py_2) = k\frac{\rho_1}{T} + \frac{a}{T} + b \quad (11)$$

Hozahabr et al. (2014) [3] worked on the expression developed by Méndez-Santiago–Teja and inserted an additional constant. Their new empirical equation which shows a linear relationship between  $\ln y_2$  and  $\rho_1$  in a certain range of pressure and temperature writes:

$$\ln(y_2) = e_0 + \frac{e_1}{T} + \frac{e_2\rho_1}{T} - e_3 \ln P \quad (12)$$

Being aware of the non-linear relationship between  $\ln y_2$  and temperature as well as pressure, and of the possible linear relationship between  $\ln y_2$  and  $\ln \rho_1$ , Keshmiri et al. [22] (2014) proposed the following model to correlate solute solubility in  $\text{SCCO}_2$ :

$$\ln(y_2) = e_0 + \frac{e_1}{T} + e_2P^2 + \left(e_3 + \frac{e_4}{T}\right) \ln \rho_1 \quad (13)$$

Recently, Khansay et al. (2015) [2] presented the following empirical model which contains 5 parameters:

$$\ln(y_2) = \frac{e_0}{T} + e_1P + e_2\frac{P^2}{T} + e_3 \ln \rho_1 + e_4 P \ln \rho_1 \quad (14)$$

## 3. Presentation of the new model

In order to illustrate the various relationships that can experimentally be found between  $y_2$  and  $\rho_1$ , 3 sets of experimental data were selected. The plot of  $\ln y_2$  versus  $\ln \rho_1$  for tetraethylene glycol bis (n-octyl) dimethyl diphosphate [23] can be seen in Fig. 1. Such a figure highlights that for such a system  $\ln y_2$  varies linearly with  $\ln \rho_1$ . The plot of  $\ln y_2$  versus  $\rho_1/T$  for bisphenol A [24] can be seen in Fig. 2 and suggests a linear relationship between the two quantities for such a system. In the end, the relationship between  $\ln y_2$  and  $\rho_1 \ln \rho_1$  for azadirachtin [30] is depicted in Fig. 3. Once again a linear relationship is obtained. In conclusion depending on the system considered, it is possible to observe one of the following behaviors:

I: Linear relationship between  $\ln y_2$  and  $\ln \rho_1$  in isothermal conditions.

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