An improved density-based model for the solubility of some compounds in supercritical carbon dioxide

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ARTICLE INFO

ABSTRACT

The ability to correlate the solubility of solutes in supercritical fluids (SCF) is of great importance for the design and evaluation of any supercritical process. The empirical equations are quite successful in correlating the solubility of compounds in the SCF. In this work, a new density-based semi-empirical model was proposed to correlate some compounds in supercritical carbon dioxide. Solubility data from 54 different compounds were collected from literature published in the last ten years and the different empirical models (Chrastil, Adachi-Lu, del Valle-Aguilera, Kumar-Johnston, Méndez Santiago-Teja, Gordillo, Jouyban, Sparks, Garlapati-Madras, and Ch-Madras) were evaluated. The results showed that, the proposed model produced the least global average absolute relative deviation (5.91%) compared to all other empirical models considered in this study.

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1. Introduction

In recent years, supercritical fluid technology has been becoming increasingly popular in petroleum, food, pharmacy and chemical industries. This is because the supercritical fluid (SCF) has a large density, a low viscosity and a high diffusivity, which can be very adequate for extraction. Carbon dioxide is the most commonly used supercritical fluid. The critical properties of carbon dioxide are respectively low (T_c = 304.2 K and P_c = 7.38 MPa) and it is non-toxic, non-flammable, non-explosive and readily available at low cost [1,2]. In this work, the solubility of some compounds in the supercritical carbon dioxide (SC-CO$_2$) has been considered.

In an extraction or reaction process, it is crucial to obtain the solubility of solutes in the SCF in order to determine the optimal operating conditions. The experimental determination of solubility of compounds in the SCF at various temperatures and pressures is expensive and time-consuming. Therefore, correlation and prediction of solubility is essential [3]. In general, there are two sorts of models used to correlate and predict the solubility. One is based on theoretical models such as equations of state, another is semi-empirical equations. Theoretical models like cubic equation of state need complicated computational procedures and the knowledge of solute critical properties, acentric factor and sublimation pressures [4–6]. However, semi-empirical models, which are based on simple error minimization using least-square methods, do not need

solute properties, and they only need temperature, pressure, density of solvent such as SC-CO$_2$ and solubility data. The most common semi-empirical equations are based on solvent density.

In this study, our focus was on correlating the solubility of some compounds in SC-CO$_2$ using the 11 most common semi-empirical models [7–15,52] and a new density-based model was proposed. The model parameters for each equation were also presented. The accuracy of the new and previously published semi-empirical models were evaluated using solubility data of 54 different compounds in SC-CO$_2$, which were collected from the literatures published in the last ten years. The results showed that the proposed model provided the least global average absolute relative deviation compared to all existing models considered in this study.

2. Review of density-based models

Chrastil [7] assumed that a solvate complex was formed between the solute and solvent molecules at equilibrium and presented the first density-based model as follows:

$$c_2 = \rho_1^k \exp\left(\frac{a}{T} + b\right) \tag{1}$$

where c_2 is the solute solubility in the solvent in kg m^{-3}, ρ_1 is the density of the solvent in kg m^{-3}, k is the average association number, a is a function of the enthalpy of solvation and enthalpy of vaporization, b is a function of the average association number and molecular weight of the solute and solvent, and T is the operating temperature in K.

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However, Chrastil's model has some limitations. For example, it is not applicable to the higher solubility (greater than $100–200\,kg\,m^{-3}$) and a wide range of temperatures [10,16]. Therefore, there were several modified forms of Chrastil's equation.

Adachi and Lu [8] correlated the average association number k to a second-order polynomial of the solvent density, achieving a lower error in the correlation of the solute solubility. The Adachi-Lu model can be shown as follows:

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2\rho_1^2)}\exp\left(\frac{a}{T}+b\right) \tag{2}$$

where e_0, e_1, and e_2 are model parameters, respectively, which can be obtained by the fitting of experimental data.

On the basis of Eq. (1), del Valle and Aguilera [9] took into consideration the change in the enthalpy of vaporization with temperature and obtained the following modified equation:

$$c_2 = \rho_1^k\exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{3}$$

where m is the model parameter.

Since the Adachi-Lu equation (Eq. (2)) corrected the effect of density on solubility and the del Valle-Aguilera equation (Eq. (3)) corrected the effect of temperature on solubility, Sparks et al. [10] conducted a combination of Eq. (2) and Eq. (3) and proposed the following equations, respectively.

$$c_2 = \rho_1^{(e_0+e_1\rho_1)}\exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{4}$$

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2\rho_1^2)}\exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{5}$$

The latest Chrastil's modification was done by Garlapati and Madras [11]. They found a linear relation between $\ln y_2$ and $\ln(\rho_1 T)$ in a certain range of density and temperature and presented the following equation:

$$\ln y_2 = e_0\ln\rho_1 + e_1\rho_1\ln\rho_1 + e_2\ln(\rho_1 T) + \frac{a}{T} + b \tag{6}$$

where y_2 is the solubility of the solute in the SCF in mole fraction.

Kumar and Johnston [12] presented a new density-based model according to a linear relationship between $\ln y_2$ and ρ_1:

$$\ln y_2 = k\rho_1 + \frac{a}{T} + b \tag{7}$$

A widely used density-based model based on the theory of dilute solutions was proposed by Méndez-Santiago and Teja [13]. This model is excellent for determination of consistency of solubility data across different isotherms. However, the model must need previously the knowledge of solute sublimation pressure. In many instances, the sublimation pressure of the solute is not available. In order to solve this problem, a two-constant Antoine equation for solute sublimation pressure is substituted and the final model can be expressed as follows:

$$\ln(Py_2) = k\frac{\rho_1}{T} + \frac{a}{T} + b \tag{8}$$

where P is the system pressure in MPa.

Another different density-based model was presented by Jouyban et al. [14]. Though the use of this model was low [16], the model was in good agreement with experimental solubility data, which can be confirmed in the ensuing text. The Jouyban model can be written as

$$\ln y_2 = m_0 + m_1P + m_2P^2 + m_3PT + m_4\frac{T}{P} + m_5\ln\rho_1 \tag{9}$$

where m_i ($i = 0, 1,\ldots,5$) are the model constants.

Based on the theory of response surface, Gordillo et al. [15] proposed another empirical model which contained only temperature and pressure:

$$\ln y_2 = m_0 + m_1P + m_2P^2 + m_3PT + m_4T + m_5T^2 \tag{10}$$

Based on the association theory, Ch and Madras [52] have presented a four parameter model very recently:

$$y = \left(\frac{P}{P*}\right)^{(k-1)}\exp\left(\frac{a}{T}+m\rho_1+b\right) \tag{11}$$

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

3. Improved density-based model

Reviewing published experimental solubility in SC-CO$_2$ and previously presented empirical models indicate the existence of:

(a) Non-linear relationship between $\ln c_2$ and $\ln\rho_1$ over a wide range of temperatures and pressures.
(b) Non-linear relationship between $\ln c_2$ and temperature in isopycnic condition.
(c) When the system temperature increases under isobaric conditions, the average association number k will certainly decrease due to the increase of the thermal motion of its molecules; on the other hand, when the system pressure increases under isothermal conditions, k will increase as a result of shortening distance as well as increasing collision between molecules. Once k changes, the enthalpy of solvation and enthalpy of vaporization will change.

Taking into account all the above factors and in order to provide a better correlation, the following density-based empirical equation is proposed for the solubility of some compounds in SC-CO$_2$:

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2/\ln T)}\exp\left(\frac{a+m\rho_1}{T}+b\right) \tag{12}$$

4. Methodology

In this study, the density of SC-CO$_2$ for all models was determined with PR EoS [17]. Solubility of a solute is calculated by means of Eq. (13):

$$c_2 = \frac{\rho_1 MW_2 y_2}{MW_1(1-y_2)} \tag{13}$$

where MW_2 is molar weight of the solute in g mol^{-1}, MW_1 is the molar weight of CO$_2$ in g mol^{-1}, the other symbols are the same as stated above.

The model parameters for each compound with each equation were determined by using MATLAB 7.01 by the minimization of experimental and calculated solubility with the following objective function:

$$OF = \sum_i^N \left|\frac{y_i^{calc}-y_i^{exp}}{y_i^{exp}}\right| \tag{14}$$

where N is the number of solubility data points, y_i^{calc} and y_i^{exp} is the calculated and experimental solubility for experimental point i, respectively.

The goodness of the calculations was evaluated by the absolute average relative deviation defined as follows:

$$AARD\ (\%) = \frac{100}{N}\sum_i^N \left|\frac{y_i^{calc}-y_i^{exp}}{y_i^{exp}}\right| \tag{15}$$