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Representing solute solubility in supercritical carbon dioxide: A novel empirical model

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ABSTRACT

In this paper, a new empirical model proposed for mathematical representation of solutes solubility in supercritical carbon dioxide. The accuracy of the proposed model is compared to previously published models in literature using experimental data of dyes and drugs collected from literature (more than 2400 data points). According to obtained results, the proposed model presents much more accurate estimation/prediction for in solubility. So, in order to accelerate the industrial processes, the proposed model can be employed and strongly recommended.

Keywords: Supercritical fluid; Carbon Dioxide; Solubility; Empirical model; Prediction; Correlation

1. Introduction

Chemical and petroleum, pharmaceutical, food, biotechnology, biomedical, nuclear, material and polymer processing industries can be mentioned as example of industries use supercritical fluid (SCF) technology for extraction and separation widely (Cabral et al., 2007; Dong et al., 2010; Park and Bae, 2002; Giorgi et al., 2000; Srinivasan et al., 2002; Said-Galiyev et al., 2003; Guney and Akgerman, 2002; Subramanian et al., 1997; Guzel and Akgerman, 2000; Macnaughton et al., 1996; Murga et al., 2002; Ajzenberg et al., 2000; Jafari Nejad et al., 2011, 2012). In fact, in recent years, this technology has attracted considerable attention and widely applied.

Supercritical fluids, particularly supercritical carbon dioxide which is one of the most common SCF, have unique physical and chemical properties and usually low toxicity. This process is categorized as rapid processes due to high diffusivity and lower viscosity in SCF mediums. By setting the operating condition i.e. temperature, pressure and density, which itself results in a variation in solvating power as indicated by Tabernero et al. (2010), a desired selectivity can be obtained. Of the most interesting properties of supercritical carbon dioxide are the relatively low critical temperature and pressure of 304 K and 73.7 bar, low costs, nontoxicity, no flammability, and recyclability with no environmental hazard (Saus, 1995; Fasihi et al., 2004).

The design of SCF processes will be facilitated and possible provided that the solubility data and mathematical modeling of these solubility data are available and known (Lucien and Foster, 2000; Bae and Hur, 1996; Haarhaus et al., 1995; Joung et al., 1998). In fact, a better understanding of the process can be achieved by the mathematical modeling in any process of interest (Asgarpour Khansary et al., 2014), and here it can be used for the representation of solubility at interested pressures and temperatures.

The mathematical modeling of solubility data of solutes in supercritical fluids process can involve three main categories:

i. A single solute in a supercritical fluid,
ii. Mixed solutes in a supercritical fluid, and
iii. A single solute in mixed supercritical fluids or supercritical fluid plus an organic solvent.

Also, based on the method of mathematical modeling, different equations for representation of solubility data in supercritical carbon dioxide can be obtained. Generally, these models are classified into two groups; theoretical or semi-empirical equations such as models based on equations of

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Table 1 – Empirical models for solute solubility representation in supercritical fluids.

Model	Equation[a]	Reference
Chrastil	$\ln S = k \ln \rho + A + \frac{B}{T}$ (1)	Chrastil (1982)
Kumar and Johnston	$\ln y_2 = A + B\rho + \frac{C}{T}$ (2)	Kumar and Johnston (1988)
del Valle and Aguilera	$\ln S = A + \frac{B}{T} + C \ln \rho + \frac{D}{T^2}$ (3)	del Valle and Aguilera (1988)
Méndez-Santiago and Teja	$T \ln(y_2 P) = A + B\rho + CT$ (4)	Méndez-Santiago and Teja (2000)
Bartle et al.	$\ln\left(\frac{y_2 P}{P_{ref}}\right) = A + \frac{B}{T} + C(\rho - \rho_{ref})$ (5)	Bartle et al. (1991)
Yu et al.	$y_2 = A + BP + CP^2 + DPT(1 - y_2) + ET + FT^2$ (6)	Yu et al. (1994)
Sung and Shim	$\ln y_2 = A + \frac{B}{T} + \left(C + \frac{D}{T}\right) \ln \rho$ (7)	Sung and Shim (1999)
Gordillo et al.	$\ln y_2 = A + BT + CT^2 + DPT + EP + PT^2$ (8)	Gordillo et al. (1999)
Jouyban et al.	$y_2 = A + BP + CP^2 + DPT + \frac{ET}{P} + F \ln \rho$ (9a)	Jouyban et al. (2002)
	$\ln \rho = -27.091 + 0.609\sqrt{T} + \frac{3966.170}{T} - \frac{3.445P}{T} + 0.402\sqrt{P}$ (9b)	
Adachi and Lu	$\ln y_2 = (A + B\rho) \ln \rho + \frac{C}{T} + D$ (10)	Adachi and Lu (1983)
Garlapati and Madras (2009)	$\ln y_2 = A \ln(\rho T) + \frac{B}{T} + C$ (11)	Garlapati and Madras (2009)
Garlapati and Madras (2010)	$\ln y_2 = A + (B + C\rho) \ln \rho + \frac{D}{T} + E \ln(\rho T)$ (12)	Garlapati and Madras (2010)
Jafari Nejad et al.	$\ln y_2 = A + BP^2 + CT^2 + D \ln \rho$ (13)	Jafari Nejad et al. (2010)

[a] The coefficient of these models are indicated by A–F, and k.

state, and empirical equations such as density based equations.

Using theoretical models such as cubic equation of state requires complicated computational procedures and methods, and also the knowledge of the solid properties including critical properties, acentric factor, molar volumes and sublimation pressure, which often cannot be easily determined experimentally and should be calculated using some group contribution method. It is obvious that uncertainty and errors on numerical values of the solute properties can affect solubility predictions (Garnier et al., 1999). The physical basis of these models can be regarded as one the most important reasons why such models may appear in some literatures.

To overcome some of the mentioned obstacles, most researchers tend to use empirical models such as density-based models of Chrastil, Bartle, Méndez-Santiago–Teja, etc., or the Ziger–Eckert semi-empirical model. 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, which are necessary to determine solids solubility.

In this paper, after reviewing most efficient published solubility models in literature, a new accurate model for solute solubility in supercritical carbon dioxide has been proposed. These density based correlations have been presented in the following section in detail. The accuracy and performance of proposed model and previous models are critically verified and examined using a large number of solute solubility in supercritical CO_2 data (more than 2400 data points), collected from literatures for the calculations. For an in-depth comparison, four statistical parameters have been defined. The results demonstrated that, using the proposed empirical model, much accurate solubility calculations could be achieved with readily available independent variables temperature, pressure and density of pure supercritical CO_2. Thus, the proposed model could be used for solubility calculation at interested pressures and temperatures in industry.

2. A brief literature review and presentation of new model

Conveniently, using the density of the supercritical solvent, the solute solubility data can be correlated and modeled. Historically, by assuming association of one molecule of solute with k molecules of solvent and a complex formation, Chrastil (1982) derived an equation that relates the solubility of solute in a supercritical fluid with the density of the pure supercritical fluid and the absolute temperature as shown by Eq. (1) in Table 1.

In Chrastil Model (Eq. (1)) A, B and k are the model constants which are obtained from experimental data fitting by means of an efficient error minimizing technique such Least Square Method, Objective Function minimization using Evolutionary Algorithms (Genetic Algorithm, etc.) which are widely available in literatures (for an example of GA application refer to Asgarpour Khansary and Hallji Sani, 2014). It is worthwhile to mention that k is an association number and represents the average number of CO_2 molecules in the solvated complex, the constant B depends on vaporization and solvation enthalpies of the solute, and the constant A depends on molecular weight of the solute, molecular weight of supercritical fluid and also k. Also in Eq. (1), S ($g\,m^{-3}$), is the solubility of the solute in the

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