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Correlation of solute solubility in supercritical carbon dioxide using a new empirical equation

Sare B. Hozhabr, Seyed Hossein Mazloumi*, Javad Sargolzaei

Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

ABSTRACT

A new empirical equation is proposed to correlate solute solubility in supercritical carbon dioxide (SCCO₂). The new empirical model has four parameters per each solute that can be obtained by correlation of the experimental solubility data. The input variables of the equation are pressure, temperature and density of pure SCCO₂. The new equation is applied for correlation of solubility of 24 compounds in SCCO₂ at wide range of temperatures and pressures. The overall percent of absolute average relative deviation (%AARD) of the new equation for correlation of the experimental data is 6.54%. Comparison of the results of the present model with a three-parameter and a four-parameter empirical model demonstrates good accuracy of the new empirical model.

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Keywords: Solubility; Supercritical carbon dioxide; Empirical equation; Four-parameter model; Density

1. Introduction

The correlation of solubility data in supercritical fluids is an essential step in the design of various processes such as separations, purifications, and pharmaceuticals. In the recent years, huge attentions have been focused to develop theoretical, semi empirical or empirical models to correlate the experimental data of solubility data in supercritical fluids (Gordillo et al., 1999; Jouyban et al., 2002; Jafari Nejad et al., 2010). The importance of modeling of solubility data in supercritical fluids will be more understandable if one notes that the generation of experimental data of solute solubility in supercritical phase is tedious and time expensive. One of the most important supercritical fluids is supercritical carbon dioxide with some unique features; it is nonexplosive, nontoxic, inflammable, its critical properties are at relatively unworried temperature and pressure (304 K and 73.7 bar, respectively) and it is readily available at low cost (Jouyban et al., 2002; Jafari Nejad et al., 2010).

A variety of models have been proposed to calculate the solubility of solids in SCFs that can be categorized in three groups; empirical equations (Gordillo et al., 1999; Jouyban et al., 2002; Jafari Nejad et al., 2010; Chrastil, 1982; Del Valle and Aguilera, 1988; Bartle et al., 1991; Méndez-Santiago and Teja,

2000), methods based on activity coefficient models (Su and Chen, 2007), and equation of state approach (Yazdizadeh et al., 2012; Huang et al., 2001, 2007). However one may compensate the two first methods in one method as semi-empirical or empirical models. The equation of state method is more complicated and requires more computations and inputs. Alternatively, the empirical and semi-empirical methods are rather simple with good accuracy even more than the equation of state method. The independent variables of the empirical and semi-empirical methods are often pressure, temperature and density of pure SCFs, so parameters of the equations are not substance-dependent. These equations include a number of constants that can be obtained by correlation of experimental data. Several empirical equations have been proposed by various authors and it has been increased in the recent years (Jouyban et al., 2002). The models of Gordillo et al. (1999), Adachi and Lu (1983), Del Valle and Aguilera (1988), Sparks et al. (2008), Kumar and Johnston (1988), Garlapati and Madras (2010), Tang et al. (2011), Ch and Madras (2010), Jouyban et al. (2002), Méndez Santiago–Teja (MT), Jafari Nejad et al. (2010) are some example works in this categories.

The aim of the present study is to introduce a new empirical equation with good accuracy and reasonable number of parameters.

* Corresponding author at: Department of Chemical Engineering, Ferdowsi University of Mashhad, P.O. Box 9177948944, Iran. Tel.: +98 511 8805055.

E-mail addresses: s.h.mazloumi@um.ac.ir, hmazloumi@gmail.com (S.H. Mazloumi).

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Nomenclature

AARD	average-absolute-relative deviation
α_1, α_2 and C	constants in Eq. (7)
A', B' and C'	constants in Eq. (8)
a, b	constants in Eq. (5)
B_0 – B_3	constants in Eq. (6)
D_0 – D_5	the model constants in Eq. (1)
ΔH	sum of the enthalpies of vaporization and salivation of solute (J mol^{-1})
ΔH_{sub}	enthalpy of sublimation of the solute (J mol^{-1})
J_0 – J_3	the model constants in Eq. (3)
M_0 – M_5	the model constants in Eq. (2)
N	the number of experimental data points
p	pressure (bar)
p_{ref}	standard pressure of 1 bar
ρ	density (kg m^{-3})
ρ_{ref}	a reference density assumed as 700 (kg m^{-3})
R	ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
MW_{SCF}	molecular weight of supercritical fluid (kg kg mol^{-1})
MW_{solute}	molecular weight of solute (kg kg mol^{-1})
SFE	supercritical fluid extraction
SCF	supercritical fluid
SCCO ₂	supercritical carbon dioxide
S_0 – S_3	constants in Eq. (9)
T	temperature (K)
y_2	the mole fraction solubility of the solute
y_2^{cal}	the calculated solubility of solute
y_2^{exp}	the experimental solubility of solute

2. Theoretical

As mentioned, various empirical and semi-empirical models have been proposed by several authors with different number of constants from three to six. In most cases the constants are obtained by correlation of the experimental data of solubility in supercritical phase.

Gordillo et al. (1999) proposed an empirical model which has 6 constants. It is expressed as:

$$\ln y_2 = D_0 + D_1P + D_2P^2 + D_3PT + D_4T + D_5T^2 \quad (1)$$

where y_2 , P and T are the mole fraction of the solute, pressure and temperature, respectively. D_0 – D_5 are the model constants. Jouyban et al. (2002) model that is an empirical model is as follow:

$$\ln y_2 = M_0 + M_1P + M_2P^2 + M_3PT + \frac{M_4T}{P} + M_5 \ln \rho \quad (2)$$

where ρ is the density of pure SCCO₂ and M_0 – M_5 are the model constants.

Jafari Nejad et al. (2010) introduced a four-constant empirical equation:

$$\ln y_2 = J_0 + J_1P^2 + J_2T^2 + J_3 \ln \rho \quad (3)$$

where J_0 – J_3 are the model constants.

Solute solubility, S (kg m^{-3}), in SCF can be calculated using y_2 as:

$$S = \frac{\rho MW_{\text{solute}} y_2}{MW_{\text{SCF}}(1 - y_2)} \quad (4)$$

where MW is molecular weight.

At the side of the empirical equations, several semi-empirical models have been developed using thermodynamic framework (Escobedo-Alvarado et al., 2001). Based on thermodynamic relationships, Chrastil (1982) derived an expression for the solubility of a solute in a SCF:

$$\ln S = k \ln \rho + \frac{a}{T} + b \quad (5)$$

where S is the solubility of the solute in the supercritical, ρ is the density of the pure supercritical fluid, k is the association number, a is the ratio of the sum of the enthalpies of vaporization of the solute to the gas constant ($\Delta H/R$) and b is a constant related to the molecular weight of the solute and solvent. However, these parameters (k , a and b) are obtained by fitting of the experimental solubility data.

A modification of Eq. (5) is proposed by Del Valle and Aguilera (1988) in which one more term was added:

$$\ln S = B_0 + \frac{B_1}{T} + B_2 \ln \rho + \frac{B_3}{T^2} \quad (6)$$

where B_0 – B_3 are the adjustable parameters.

Bartle et al. (1991) semi-empirical model to correlate the solubility of solute in SCF is:

$$\ln \left(\frac{y_2 p}{p_{\text{ref}}} \right) = \alpha_1 + \frac{\alpha_2}{T} + C(\rho - \rho_{\text{ref}}) \quad (7)$$

where p_{ref} (1 bar) and ρ_{ref} (700 kg m^{-3}) are reference pressure and density, respectively. C , α_1 and α_2 are empirical constants.

Méndez-Santiago and Teja (2000) suggested a simple equation for correlation of the solubility data in SCF derived from the theory of dilute solutions:

$$T \ln(y_2 p) = A' + B' \rho + C' T \quad (8)$$

where A' , B' and C' are model constants that can be get by a regression of solubility experimental data. Rearrangement of Eq. (8) and inserting a new constant, the new empirical equation to correlate the solubility data in SCF is introduced as follows:

$$\ln y_2 = S_0 + \frac{S_1}{T} + \frac{S_2 \rho}{T} - S_3 \ln P \quad (9)$$

where S_0 – S_3 are the model constants that can be obtained by fitting of experimental solubility data. The new equation shows the non-linear relationship between $\ln y$ and pressure at isothermal conditions, non-linear relationship between $\ln y$ and temperature at isobaric conditions, linear relationship between $\ln y$ and ρ at a certain range of pressure and temperature.

3. Results and discussion

To demonstrate the accuracy of the new correlation the solubility data of various compounds in supercritical CO₂ have been collected from the literature. Density data were obtained from the same source as the solubility data. Table 1 includes

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