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Semi-empirical correlation of solid solute solubility in supercritical carbon dioxide: Comparative study and proposition of a novel density-based model

Corrélation semi-empirique de solubilité des solutés solides dans le dioxyde de carbone supercritique: étude comparative et proposition d'un nouveau modèle basé sur la densité

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ABSTRACT

A comprehensive data set on experimental solubility of 210 solid solutes in supercritical CO_2 counting 5550 data points has been used for comparison of the correlation performance of 21 empirical models. On the basis of the comparison results a new eight-parameter density-based model has been proposed. The comparison shows that the three-parameter models are the least accurate. The results also show that models that relate the logarithm of the solubility to the logarithm of solvent density and temperature are more accurate than models that include the pressure. When comparing the overall correlating performance in terms of average absolute relative deviation the proposed model is by far the best with an average absolute relative deviation lying in the range 0.17 −81.99% and an average value of 8.88%.

1. Introduction

Supercritical fluid (SCF) technologies have been gaining an increasing attention in process engineering during the past decades due to its various advantages. Carbon dioxide is the most commonly used SCF because it is environmentally benign, nontoxic, nonflammable, cheap, and readily available. As a green solvent, supercritical carbon dioxide ($scCO_2$) finds applications in many conventional and novel emerging technologies such as dry dyeing processing techniques, which operate without wastewater emissions, efficient environmentally friendly and benign new green biotechnological processes, and so forth [1,2]. The accurate knowledge of the phase behavior of the systems involved and, in particular, of the solubility of the solid solutes in high-pressure $scCO_2$ is crucial to the design, optimization, and operation of such processes. The solid solutes of interest, such as dyes or pharmaceuticals, are generally high molecular weight complex molecules and in their majority low volatile solids. This implies that very often their experimental physical properties, such as critical properties and sublimation pressure, are not readily available in the literature. The experimental measurement of the solubility of such compounds in $scCO_2$ is laborious and costly. To avoid expensive and tedious experiments, flexible and robust predictive models are the ideal targets. In the absence of such an ideal predictive model, however,

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simple and accurate enough correlative models are very useful in engineering applications such as used in commercial process simulators. This is the reason why both types of modeling have been and still remain a goal for many research works.

Three major modeling approaches have been used to model the solubility of a solid solute in an SCF for predictive or correlative purposes: equations of state (EoSs) and activity coefficient models, computational intelligence techniques, and density-based semiempirical equations. It should be mentioned that the three approaches rely more or less on experimental data and, therefore, their use outside the range of experimental data from which the models have been obtained is not safe.

EoSs are the straightforward and obvious methods as the solubility is a phase equilibrium problem. Simple cubic EoS with various mixing rules has been extensively used for calculation of solid solute solubility in $scCO_2$ (to cite just few, see, for example, Refs. [3–12]). Detailed review of the use of cubic EoSs in this context has been given by Yazdizadeh et al. [10]. The use of cubic EoSs requires critical properties, acentric factor to compute fugacity coefficient, which is needed along with the sublimation vapor pressure, and the molar volume of the solid solute to compute the solubility. In the absence of experimental values of these solid solute parameters, they are estimated using group contribution (GC) methods. Sublimation vapor pressure, which is very low, and experimental value, unavailable for many solids, may also be considered as an adjusted parameter to be fitted to solubility data as used in Refs. [8,13,14]. The accuracy of the correlation or prediction using the cubic EoS depends greatly on the method used to estimate these solid solute properties [3,4,11]. The effect of mixing rules has been investigated by Yazdizadeh et al. [9,10] in two comparative studies. The first one [9] concerned 52 solid solutes and compared two cubic EoSs combined with four mixing rules and showed a global superiority of Esmaeilzadeh–Roshanfekr EoS [15] combined with Wong–Sandler mixing rule [16] and a global average absolute deviation of 9%. In the second one [10] 23 compounds were considered, five cubic EoSs combined with four mixing rules and the results showed a global best performance of a modified Esmaeilzadeh–Roshanfekr EoS [17] with Wong–Sandler mixing rule [16] and a global average absolute deviation of 7%. Sang et al. [8] considered three cubic EoSs combined with five mixing rules where they used a modification of the calculation procedure by introducing some approximations. They proposed two- and three-adjustable-parameter models for the calculation of the fugacity coefficient. Accordingly, the only solid solute parameter required was the molar volume. They showed that the three-adjustable-parameter model gave a global average absolute deviation of 5.5% for the same data set used in Ref. [10].

Despite their success for fluid mixtures, theoretical –sound state of the art statistical thermodynamic models have not been used for modeling complex molecules such as pharmaceuticals. Statistical associating fluid theory (SAFT)-type models use fluid-specific parameters that usually are fitted to pure fluid experimental data. In common fluids, experimental vapor pressures and liquid densities are typically used. However, for the majority of pharmaceutical complex chemicals such extended experimental data do not exist [18]. Most SAFT-type models require five parameters for each pure associating compound (three for nonassociation ones). Three parameters for nonassociating fluids: the segment number, the interaction energy, and the hard core segment diameter. Two other parameters for associating fluids are the association energy and the affective association volume. These parameters are calculated using GC methods, such as proposed by Tihic et al. [19,20] or estimated from vapor pressure and liquid-density data over extended temperature ranges [21,22]. In the absence of such data for specific compounds, such as polymers and pharmaceuticals, GC methods, such as GC-SAFT [23,24], GC-SAFT variable range (SAFT-VR) [25–32], and GC-SAFT-γ [33–35], are used for the estimation of required properties. As regards modeling the solubility of complex solid molecules in $scCO_2$ using noncubic EoS only few works are reported. This is due to the lack of sufficient experimental data as this family of EoSs uses fluid-specific parameters that usually are fitted to pure fluid experimental data [18]. Tsivintzelis et al. [18] have used nonrandom hydrogen bonding theory to predict the solubility of pharmaceuticals in SCFs. SAFT models have also been used to predict or correlate the solubility of solids in SCFs [36–38].

Activity coefficient models, such as universal functional activity coefficient, the regular solution theory-based models, and more sophisticated models, such as conductor-like screening model (COSMO), cannot be used for high-pressure phase equilibrium calculations without being coupled with another model, namely, an EoS [18]. COSMO-based approach has been used to predict solubility of solids in $scCO_2$ [39–42]. The only experimental data required for solutes are the melting temperature and the melting enthalpy of the solid solute.

Computational intelligence techniques such as artificial neural networks, adaptive neurofuzzy inference system, and least square support vector machine are considered as powerful modeling tools that can map complex highly nonlinear input/output relationships of any systems. This ability has made them suited for a wide range of engineering applications. Applications of such techniques to correlate solubility of various solid solutes in $scCO_2$ have been reported: Refs. [43–51] for artificial neural networks, Refs. [52,53] for least square support vector machine, and Ref. [54] for adaptive neurofuzzy inference system.

The review of the EoS and computational intelligence approaches in modeling the solubility of solid solutes in supercritical solvents reveals that both approaches, whether used for predictive or correlative purposes, with the exception of the COSMO model, rely on experimental data of phase equilibrium and the physical properties of pure solid solute. As regards the EoS approach, phase equilibrium data are required for fitting at least one binary interaction parameter used by mixing rules, fitting other required pure solute properties, or for the validation of models. Regarding computational intelligence methods, experimental data are necessary for training and validation of the model. Pure component properties for complex multifunctional solid solutes, such as pharmaceuticals, are

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