Fluid Phase Equilibria 308 (2011) 35–43

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Comparison the capability of artificial neural network (ANN) and EOS for prediction of solid solubilities in supercritical carbon dioxide

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ARTICLE INFO

Article history:
Received 12 March 2011
Received in revised form 29 May 2011
Accepted 3 June 2011
Available online 12 June 2011

Keywords:
Solid solubilities
Supercritical carbon dioxide
Artificial neural network
Cubic equation of state
Mixing rules

ABSTRACT

The aim of this study is develop a feed-forward multi-layer perceptron neural network (MLPNN) model to predict the solid solubilities of aromatic hydrocarbons, aliphatic carboxylic acids, aromatic acids, heavy aliphatic and aromatic alcohols in the supercritical carbon dioxide.

Different networks are considered and trained using 627 data sets; the accuracy of the network is validated by 343 testing data sets. The networks were different regarding to network parameters, such as number of hidden layer, hidden neurons and training algorithm. Using validating data set, the network that is having the lowest absolute average relative deviation percent (AARD%), mean square error (MSE) and the highest regression coefficient (R^2) is selected as an optimal configuration.

To verify the network generalization, 100 different data sets of 23 binary systems have been considered. In the present work, 970 experimental data points of different works (up to now) which covers a wide range of temperatures and pressures have been used. Statistical analyses show that the artificial neural network (ANN) predictions have an excellent agreement (AARD% = 0.98, MSE = 2.8×10^{-5} and $R^2 = 0.99813$) with the experimental data set.

Also, accuracy of the cubic Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations of state by using six mixing rules, namely, the Wong–Sandler (WS) rule, the Orbey–Sandler (OS) rule, the van der Waals one fluid rule with one (VDW1) and two (VDW2) adjustable parameters, the covolume dependent (CVD) rule and the Esmaeilzadeh–As'adi–Lashkarbolooki (EAL) mixing rule for the prediction of solubility of solids in supercritical carbon dioxide has been compared with a developed neural network model. To base this comparison on a fair basis, same experimental data points of 23 different compounds has been used for both optimization of equations of state parameters and training, validation and testing of neural network. Results show that developed optimal ANN model is more accurate compared to the PR and SRK EOSs with mentioned mixing rules for the same compounds.

1. Introduction

Recently, the use of ANNs in many technical fields such as chemical and pharmaceutical areas has been increased due to their flexibility and ability to model linear and nonlinear systems without prior knowledge of an empirical model [1,2]. Thus, ANNs have a higher advantage over traditional fitting methods and experimental correlations for some chemical applications [3].

ANNs have shown their strength in modeling of very complicated and multi-variable dependent processes. Izadifar and Abdolahi [4] showed that the predictions of the ANNs model are better than that of the mathematical model in the some cases.

It should be noted that the application and capability of neural networks for modeling of processes demands a large number of experimental data involving a used range of all variables.

The solubility is one of the most important physicochemical properties of chemical/pharmaceutical compounds.

Nowadays, supercritical fluids have attracted great interest in the development of alternate processes to substitute traditional ones such as solvent extraction, distillation, and wiped film evaporation. Supercritical-fluid technology offers numerous advantages compared to conventional processes, such as high transfer rates, reduced number of unit operations, and lower operating costs [5,6].

Carbon dioxide is widely used in supercritical fluid applications because it has mild critical conditions (T_c = 304.25 K, P_c = 7.38 MPa), is inexpensive, nonflammable, nontoxic and readily available. The solubility of a solute in the supercritical fluid is the most important thermo-physical property that needs to be determined and modeled as a first step to developing any supercritical fluids application. In addition, experimental studies are very expensive and

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doi:10.1016/j.fluid.2011.06.002

Table 1
Summary of the mixing rules used in this work.

Mixing rules	Functional form	Refs.
Wong–Sandler	$a = RT\frac{QD}{1-D}$ $b = \frac{Q}{1-D}$ $a = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}$ $D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{G^{ex}}{CRT}$ $b - \frac{a}{RT} = \sum\sum x_i x_j \left(b - \frac{a}{RT}\right)_{ij}$ $\left(b - \frac{a}{RT}\right)_{ij} = \left(b_i - \frac{a_i}{RT} + b_j - \frac{a_j}{RT}\right)\frac{(1-k_{ij})}{2}$	[15,16]
Orbey–Sandler	$a_m = bRT\left[\frac{G^{ex}}{C^*RT} + \sum_{i=1}^{n} x_i \frac{a_i}{b_i RT}\right]$ $b_m = \frac{RT\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (b-(a/RT))_{ij}}{RT-(\sum_{i=1}^{n} x_i (a_i/b_i)+(G^{ex}/C^*))}$ $\left(b - \frac{a}{RT}\right)_{ij} = \left(\frac{b_i+b_j}{2}\right) - \left(\frac{\sqrt{a_i a_j}}{RT}\right)(1-k_{ij})$	[17]
CVD	$a = \sum\sum x_i x_j a_{ij} \left(\frac{b}{b_{ij}}\right)^{m_{ij}}$, $b = \sum x_i b_i$ $a = \sqrt{(a_i a_j)}$, $b = \sqrt{(b_i b_j)}$	[18]
VDW1	$a = \sum\sum x_i x_j (a_i a_j)^{0.5}(1-k_{ij})$, $b = \sum x_i b_i$	[13]
VDW2	$a = \sum\sum x_i x_j (a_i a_j)^{0.5}(1-k_{ij})$, $b = \sum\sum x_i x_j \left(\frac{b_i+b_j}{2}\right)(1-l_{ij})$	[13]

time consuming. Many researchers have tried to predict the thermodynamic properties by theoretical methods. EOS is an important and effective tool for calculations of thermodynamic properties and the phase equilibrium of pure and fluid mixtures. Accurate and simple EOSs are widely used for theoretical and practical studies in chemical process design, the petroleum industry, reservoir fluids, etc. Due to numerous industrial designs which are based on the results of these theoretical models, accuracy of them is a very important issue.

On the other hand, the conventional thermodynamics cannot predict the solubility of highly polar substances correctly and its predictions have a large inaccuracy [7]. Application of the EOS models is often limited while artificial intelligence (e.g. ANN) is found more popularity for prediction of various processes. The artificial intelligence models have lower inaccuracy, cost, and time-consumption [8].

ANNs are efficient tools which can be trained with experimental information to map input and output data regardless to complexity of their relation. Previous study showed that ANN model predictions are low sensitive to noisy and incomplete data compared to analytical approaches, thus they are found more popularity compared to analytical approaches [9,10]. Because of the nonlinear nature of solubility, ANN method could be considered as an alternative tool for solubility modeling [11].

In this work, a feed-forward MLPNN with Levenberg–Marquardt training algorithm has been developed in order to investigate its capability in prediction the solubilities of solids in supercritical carbon dioxide. The proposed ANN model results have been compared with two EOSs by using VDW1, VDW2, CVD, WS, OS, and EAL mixing rules. A database containing experimental solubility data for 100 data sets of 23 binary systems have been used in this study for validating model results.

2. Equation of state and mixing rules

As discussed in this study, the cubic Peng–Robinson (PR) [12] and Soave–Redlich–Kwong (SRK) [13] equations of state have been used to calculate the solid solubilities of 23 solutes in supercritical CO_2, by using six mixing rules, namely, VDW1, VDW2, CVD, WS, OS and EAL. Table 1 shows a summary of the VDW1, VDW2, CVD, WS

Table 2
Summary of the EAL mixing rule.

EOS and combination rule	PR	SRK
$P = \frac{RT}{v-b} - \frac{a}{(v+c_1 b)(v+c_2 b)}$	$c_1 = 1-\sqrt{2}$, $c_2 = 1+\sqrt{2}$	$c_1 = 0$, $c_2 = 1$
$S_1 = \sum\sum x_i x_j \left(b - \frac{a}{RT}\right)_{ij}$	$b = \frac{S_2}{S_1}\left[\frac{1.5}{1+2\alpha_m} - 0.5\right]$	$b = \frac{S_2}{S_1}\left[\frac{2}{1+\alpha_m} - 1\right]$
$S_2 = \sum\sum x_i x_j \left(b^2 + (c_1+c_2)\frac{a}{RT}\right)_{ij}$	$\alpha_m = \frac{a}{bRT}$	$\alpha_m = \frac{a}{bRT}$
$\left(b - \frac{a}{RT}\right)_{ij} = \left[\frac{(b_i-(a_i/RT))+(b_j-(a_j/RT))}{2}\right](1-k_{ij}^a)$	$a_{ij} = \sqrt{(a_i a_j)}$	$a_{ij} = \sqrt{(a_i a_j)}$
$\left(b^2 + (c_1+c_2)\frac{a}{RT}\right)_{ij} = \left(b_{ij} + (c_1+c_2)\frac{a_{ij}}{RT}\right)$	$b_{ij} = \frac{b_i+b_j}{2}$	$b_{ij}^{3/4} = \frac{b_i^{3/4}+b_j^{3/4}}{2}$
$a_m = \frac{a}{bRT} = \sum_{i=1}^{N} x_i a_i - \frac{G^{ex}}{CRT}$		
$C = \frac{1}{c_1-c_2}\ln\frac{1+c_1}{1+c_2}$		

[a]The k_{ij} is the binary interaction parameter.