Fluid Phase Equilibria 433 (2017) 174–183

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Prediction of limiting activity coefficients for binary vapor-liquid equilibrium using neural networks

Hesam Ahmadian Behrooz [a, *], R. Bozorgmehry Boozarjomehry [b]

[a] Chemical Engineering Faculty, Sahand University of Technology, Tabriz, Iran
[b] Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form
28 October 2016
Accepted 28 October 2016
Available online 1 November 2016

Keywords:
Artificial neural network
Limiting activity coefficient
Binary systems
VLE

ABSTRACT

The activity coefficient at infinite dilution is a representative of the limiting non-ideality of a solute in a mixture. Various methods for the prediction of infinite dilution activity coefficients (IDACs) have been developed. Artificial neural networks are powerful mapping tools for nonlinear function approximations. Accordingly, an artificial neural network model is proposed for the prediction of the IDACs of binary systems where the properties of the individual components are used as inputs to the network. The input parameters of the neural network are the mixture temperature, critical temperature, critical pressure, critical volume, molecular weight, dipole moment and the acentric factor of both solute and solvent. The output of the neural model is the natural logarithm of the activity coefficients at infinite dilution of the solute.

Two different approaches can be adopted, based on the available experimental in the literature: different solutes in a specific solvent and a series of solutes in various solvents. For the first case, the input parameters corresponding to the solvent can be eliminated from the network inputs without affecting the model performance. Five different examples were investigated to evaluate the performance of the proposed model where networks with minimum absolute average deviation were reported as the optimum structures.

An artificial neural network trained with comprehensive dataset collected from literature with more than 1891 experimental data was used for IDAC prediction where the predicted results from the neural models are in close agreement with available experimental data with a squared correlation coefficient of R^2=(0.9993, 0.9976 and 0.9977) for training, validation and test data, respectively. The results were also compared with the predictions of the modified UNIFAC method for non-aqueous systems and COSMO-SAC method for aqueous systems where the NN model performs very well in comparison to physically-based models. Due to the convincing agreement between experimental values and predicted values for limiting activity coefficients, a multilayer perceptron form of the feed-forward neural networks with 7 or 13 neurons in the input layer (depending on the type of the available experimental data) and one hidden layer can be accurately used to predict the IDACs of a solute in a binary VLE system where only solute and solvent properties are required.

1. Introduction

The infinite dilution activity coefficient (IDAC (γ^{∞})) is a thermodynamic property which is of great practical importance in separation processes, prediction of multicomponent vapor-liquid equilibrium [1] and more particularly in calculating the parameters needed in the expressions for the excess Gibbs energy. This also verifies the great efforts made in both experimental techniques and theoretical models developed to accurate prediction of IDAC [2].

IDAC of a solute in a solvent can be measured based on a number of experimental methods such as gas-liquid chromatography (GLC) [3], relative GLC [4], non-steady-state GLC method (NSGLC) [5], differential ebulliometry method [6], gas stripping method [7] and dew point method [8]. However, due to the expenses incurred in these experimental techniques and their time-consuming nature,

* Corresponding author.
E-mail addresses: ahmadian@sut.ac.ir (H. Ahmadian Behrooz), brbozorg@sharif.edu (R.B. Boozarjomehry).

http://dx.doi.org/10.1016/j.fluid.2016.10.033
0378-3812/

different mathematical models for the prediction of IDACs [9] have been proposed including group contribution methods (such as UNIFAC (UNIQUAC functional group activity coefficients) [10], ASOG (analytical solution of groups) [11]), SPACE (Solvatochromic Parameters for Activity Coefficient Estimation) equation [12], the MOSCED models [13], linear solvation energy relationships (LSER) [14] and free energy perturbation simulations [15].

Quantitative structure-property relationship (QSPR) models are an alternative approach of estimating IDAC where different types of molecular descriptors derived from the molecular structure are used to develop multiple linear regression and neural network models to predict IDAC [16]. Although in these models only the knowledge of the chemical structure is required without depending on any experimental properties [17], however, various ways of calculating physicochemical descriptors [18] is a challenging task.

Artificial neural network (ANN) is one of the popular methods of dealing with nonlinear systems theoretic modeling, where the available experimental data can be used to develop NN models that can be used as a predictor.

Chow et al. [19] used the fragmented structural information to estimate the aqueous activity coefficients of aromatic organic compounds using a neural network approach. Giralt et al. [20] developed quantitative structure–property relations for the prediction of aqueous infinite dilution activity coefficient of organic compounds using the integration of self-organizing maps with a modified fuzzy ARTMAP neural system. Nami and Deyhimi [21] evaluated the performance of predicting IDACs for organic solutes in ionic liquids using a multilayer feed-forward ANN.

In order to be able to develop an accurate enough neuromorphic model, selection of appropriate input parameters is a critical issue. After the selection of the appropriate input parameters, a gathering of a rich enough database is the other important factor in the successful implementation of the ANN-based prediction methods. Accordingly, availability of a large amount of experimental data on IDACs of various solutes and solvents [2] is the main motivation for the development of predictive ANN models of the IDAC.

In this work, IDACs are predicted using neural network approach. In Section 2 the details of the proposed methodology, including a brief overview of ANNs followed by the description of the proposed method as well as the data used in its development and validation are discussed in detail. In section 3, the proposed methodology is applied to various examples to evaluate the performance of the method in the prediction of IDACs against the experimental data and conclusions are drawn at the end.

2. Materials and methods

2.1. Artificial neural networks

The thermodynamic behavior of a solute in a liquid phase solvent is affected by so many factors that make the development of a complete mathematical model impossible. Such complicated systems can be handled effectively with the ability of the ANNs in learning and recognizing complex and highly nonlinear functional relationships between inputs and outputs [22].

The interconnection of simple computational elements called neurons can represent an ANN which can mimic the computational abilities of biological systems [23,24]. ANNs are capable of performing many tasks [25] among which is the function approximation that can be used to map the input space to the output space. Multilayer perceptron (MLP) with feed-forward network architecture is one of the most popular ANNs in use in this regard. This type of network consists of three main fully interconnected layer types including an input, one or more hidden layer(s) and an output layer as shown in Fig. 1. A neuron in each layer is connected to the

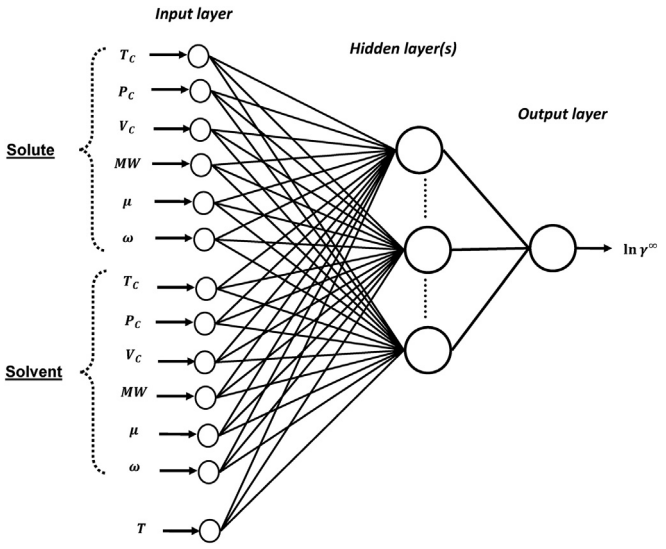

Fig. 1. Schematic of MLP with feed-forward network architecture.

neighborhood neurons as shown in Fig. 2. For the jth neuron, weighted sum of all the inputs (x_i) plus the bias (b_j) is passed through a transfer function (φ) to produce the output of the jth neuron (y_j) according to the formula (1):

$$y_j = \varphi\left(\sum_{i=1}^{n} w_{ji}x_i + b_j\right) \tag{1}$$

where w_{ji} = synaptic weight corresponding to ith synapse of jth neuron, x_i = ith input signal to jth neuron; n = number of input signals to jth neuron.

Sigmoid type transfer function is the most common transfer function in the MLPs used by the neurons located in the hidden layer(s). The weights and biases are randomly initialized and their values are corrected in the training process of the NN using a learning algorithm [26]. A trained ANN (i.e. an ANN with appropriate weight and bias values) is capable of predicting the output corresponding to an unseen input within the range of the input data used in the training step. Accordingly, the range of the data used in the training step can affect the neural network prediction capabilities.

2.2. Neural network synthesis

Two different approaches can be adopted for the selection of the type of data used in the synthesis of the ANN model for the prediction of IDAC:

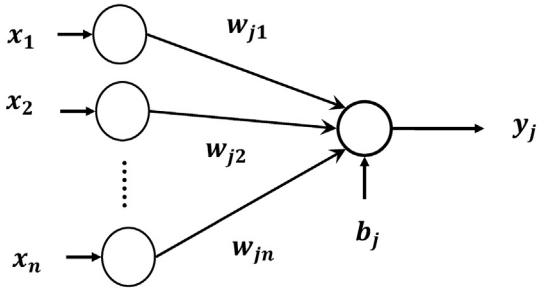

Fig. 2. A simple neuron with its connections.