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Studies on the Applicability of Artificial Neural Network (ANN) in Prediction of Thermodynamic Behavior of Sodium Chloride Aqueous System Containing Non-Electrolytes

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***Abstract*—**In this study a ternary system containing sodium chloride as solute, water as primary solvent and ethanol as the antisolvent was considered to investigate the application of artificial neural network (ANN) in prediction of sodium solubility in the mixture of water as the solvent and ethanol as the antisolvent. The system was previously studied using by Extended UNIQUAC model by the authors of this study. The comparison between the results of the two models shows an excellent agreement between them (R^2=0.99), and also approves the capability of ANN to predict the thermodynamic behavior of ternary electrolyte systems which are difficult to model.

***Keywords*—**Thermodynamic modeling, ANN, solubility, ternary electrolyte system.

I. Introduction

THE study of systems containing salts play a major role in industrial applications. Specially having the comprehensive knowledge about solubility is of fundamental importance in design of separation processes like crystallization, optimization of a distillation column, and adsorption towers. The solubility data of electrolyte systems are available in literature for many solute salts. But in the case of aqueous or organic-aqueous mixture solvents the data are scarce, unreliable, and in most of cases are unavailable [1].

The thermodynamic modeling of electrolyte systems especially solvent electrolyte systems is important since they are applied in many applications like crystallization and liquid-liquid extraction [2], [3]. Several thermodynamic models have been developed for the investigation of vapor-liquid and solid-liquid equilibrium systems [4]. It is worth noting that most of such models are based on the statistical mechanics. Many researches have been performed to study and model the thermodynamic behavior of electrolyte systems containing non-electrolytes as cosolvents using the empirical and semi-empirical thermodynamic models [4]-[7]. Most of the equations which were used in these modeling studies are not applicable for a wide range of conditions in various processes, because they are only appropriate for a certain set of conditions and they could be used under some assumptions. Therefore the significance of techniques which are directly based on data and their development to predict the result of processes seems to be obvious. Among these techniques, Artificial Neural Network (ANN) is an excellent tool to predict the results of processes using experimental data. Similar studies have proved this fact [8]-[10].

The purpose of this study is to simulate the thermodynamic behavior of an electrolyte system composed of NaCl and water mixed with ethanol using ANN and comparing the results with the results of previous published research of the authors of this study [7]. ANN has many applications in various fields, including finance and economics, robotics, material science, chemistry and chemical engineering, etc. [11]. Because of the capability of ANN in simulation of several processes, the number of researches about its applications in chemical engineering has been increased recently.

In this contribution we tried to train a network with an appropriate architecture to simulate the NaCl solubility in the mixture of water and ethanol based on the data provided in our previous publication [7]. To train the multi-layer perceptron (MLP) network which employs the Levenberg -Marquardt (LM) learning algorithm, data resulted from our previous study were used. The agreement between the results of these two modeling systems was measured through the statistical parameters.

II. Theory

Neural networks (NNs) which are inspired by biological systems are computer algorithms comprised of elements called neurons. They are applied for information processing purposes. Actually, they are neurocomputers which possess parallel distributed processors [12]. Neurons are the main elements of neural networks which are connected to the networks by a set of connections, called assigned weights. The performance of a network is strongly dependent on weights values. The neurons are organized in input, output, and the hidden layers. A neural network performs the modeling affair in a way that receives the input, sums them with their weights and adds a bias to the result of summation, then sends the results as an argument to the transfer function.

There are several types of neural networks, where multi-

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layer perception (MLP) is the most common one [13]. The MLP network has one input layer, one output layer, and usually one hidden layer. The number of input and output variables of the network depends on the type of process [14]. As mentioned in majority of cases a network with one hidden layer leads to satisfactory results. Therefore, the number of hidden layer is considered one in this paper. Each neuron in a layer is usually connected to the neurons of the latter one.

The network training is done by assigning a pattern to the input pattern, after that the results of activation level calculation are propagated forward toward the output layer. Calculation units sum the inputs and utilize a function to calculate the output. Finally the output of the network is achieved in the output layer. The improvement of network convergence is done by the addition of a constant term by the bias units of the input and hidden layers to the weighted sum. When the network outputs are compared to the target values, the errors of hidden units are determined, and then their weights are manipulated to minimize the error. This procedure is shown in Fig. 1. Generally it can be claimed that the reduction of global error is the consequent of weight and bias adjustment using training algorithms.

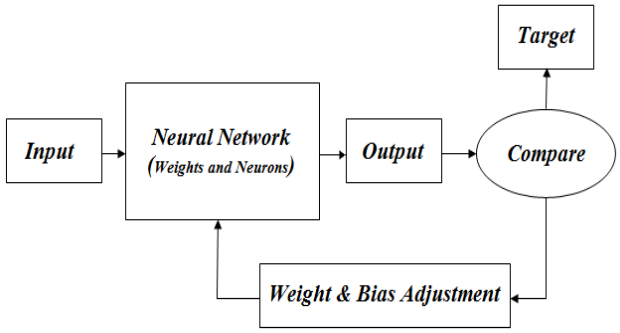

Fig. 1 A schematics of ANN model and weight and bias adjustment

The neuron k can be expressed mathematically using (1) and (2):

$$u_k = \sum_{j=1}^{m} w_{kj} x_j \tag{1}$$

$$y_k = \varphi(u_k + b_k) \tag{2}$$

where x_j is the input signal, w_{kj} is the neuron's weight, u_k is the linear combiner output due to input signals, b_k is its bias, φ is the activation function, and $y_k$is the output signal of neuron.

MLP neural network is used in the current study, where it is trained by the Levenberg Marquardt (LM) algorithm. The transfer functions of hidden and output layers are linear. The current training algorithm has provided the lowest error value; consequently, the optimal number of hidden layer neurons has been achieved. The operating parameter is the ethanol content, so the input layer of the network has 1 neuron. The output is NaCl solubility, which results in one neuron in the output layer. The number of hidden layer neurons is achieved by the training of several networks with different number of hidden layer neurons and the comparison between the results of predictions for the desired output. The number of hidden layer's neurons is equal to 14 in this network. The adequacy criterion for the optimized number of neurons is determined by the calculation of mean squared error (MSE) between the network output and the training data.

III. The Thermodynamic Modeling

In our previous work Extended UNIQUAC model was applied to describe the behavior of solutions containing electrolytes. The current version of Extended UNIQUAC model that was presented there was first introduced by [5], [15]. Water is the only solvent in the system and ions, non electrolytes (including alcohols) and dissolved gases are considered as solutes [6].

Equation (3) is the expression for the solute activity coefficient:

$$\ln \gamma_i^* = \ln \frac{\gamma_i^C}{\gamma_i^{C\infty}} + \ln \frac{\gamma_i^R}{\gamma_i^{R\infty}} + \ln \gamma_i^{*D-H} \tag{3}$$

where the terms for the combinatorial (γ_i^C), residual (γ_i^R) and Debye-Hückel (γ_i^{*D-H}) that are three parts of the activity coefficient will be introduced later [6].

The combinatorial contribution of the activity coefficient of solute *i* is given by (4):

$$\ln \gamma_i^C = \ln(\frac{\phi_i}{x_i}) + 1 - \frac{\phi_i}{x_i} - \frac{Z}{2} q_i \left[\ln(\frac{\phi_i}{\theta_i}) + 1 - \frac{\phi_i}{\theta_i} \right] \tag{4}$$

where $Z = 10$ is co-ordination number, x_i is mole fraction, Φ_i is volume fraction and θ_i is the surface fraction of solute *i* where:

$$\phi_i = \frac{x_i r_i}{\sum_i x_i r_i}$$
$$\theta_i = \frac{x_i q_i}{\sum_i x_i q_i} \tag{5}$$

The residual part of activity coefficient is as following:

$$\ln \gamma_i^R = q_i \left[1 - \ln(\sum_k \theta_k \psi_{ki}) - \sum_k \frac{\theta_k \psi_{ik}}{\sum_l \theta_l \psi_{ik}} \right] \tag{6}$$

where:

$$\psi_{kl} = \exp(-\frac{u_{kl} - u_{ll}}{T}) \tag{7}$$

It is worth noting that the interaction energy parameters are independent of composition while u_{kl} and u_{ll} are temperature dependent parameters [6].

The electrostatic contribution of the activity coefficient is given by (8):

$$\ln \gamma_i^{D-H} = b - z_i^2 \frac{A\sqrt{I}}{1 + b\sqrt{I}} \quad (8)$$

where b is a constant term, A is Debye-Hückel parameter which is a function of pressure and temperature and I is ionic strength, while the appropriate equations of these parameters can be found in references [15].

The components of the current system are water, sodium chloride and ethanol.

The procedure of the thermodynamic modeling of NaCl solubility in the mixture of ethanol and water is completely described in our previous work [7].

IV. Results and Discussion

The input variables of NNs significantly affect their efficiency, since they reflect the physical principles of the studied system. The input data have been normalized between zero and one prior to training step. The input variable in this study is the ethanol content. The structure of an ANN network comprises of three layers, including: input, hidden, and the output. There is one node in input layer corresponded to one input operating variable. The inputs are directly sent from the input nodes to the hidden layer (considered one) by the weights, where the main data processing is performed there by the calculation of inputs weighted summation. The output layer has one node since there is only one output variable, NaCl solubility in the mixture of water and ethanol. It is worth noting that a set of initial values are assigned to weights which are corrected during the training through the comparison between experimental data and the model results. The minimization of errors is done as the result of their back propagation.

80% of all of data produced by the thermodynamic modeling are randomly selected for the training and the rest were used for the network testing. The hidden layer neuron number is determined through the minimization of difference between the validation set of data and the results of network calculations. LM algorithm presented more accurate results during the training compared to scaled conjugate gradient, gradient descent with momentum, adaptive learning rate back-propagation, and resilient back-propagation. Therefore, the current network was trained using LM algorithm. After the training the network was tested by the new set of data which were not used during the training. Fig. 2 represents the graphical comparison between the thermodynamic modeling data and the results of ANN modeling. The value of correlation coefficient was 0.999, which denotes that the model output follows the target properly. It can be said that there is an excellent agreement between the data produced by the thermodynamic modeling and the results of modeling.

The standard deviation (SD) for the results of ANN modeling is equal to 0.072. The values of standard squared error (SSE), mean squared error (MSE), root mean squared error (RMSE), R^2, and SD are reported in Table I.

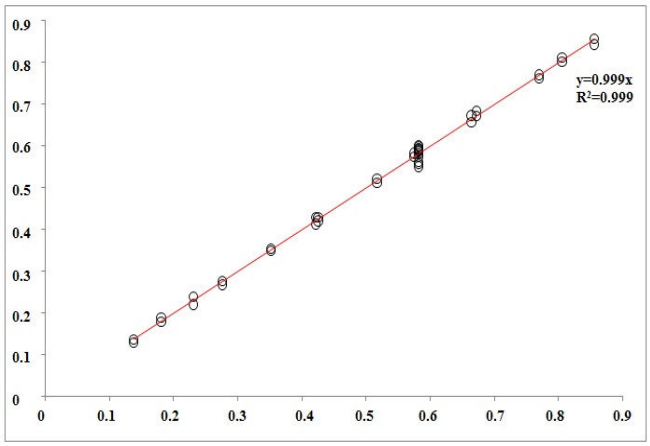

Fig. 2 Comparison of data produced by the thermodynamic modeling and predicted values by ANN for NaCl solubility in the mixture of water and ethanol

TABLE I
Statistical Parameters for ANN

R^2	0.9999999
SD	0.0719699
SSE	6.94E-06
MSE	2.305E-08
RMSE	0.0001518

The high value of R^2 and the reported errors show that the output variations are shown well by the target. The results of modeling approved the fact that ANN is an appropriate tool to predict the NaCl solubility in the mixture of water and ethanol.

Fig. 3 shows the evaluation of network error in training, validation, and testing as a function of learning epochs. The MSE became constant after 347 epochs which denotes the network convergence. Therefore the acceptable error was achieved by 347 epochs.

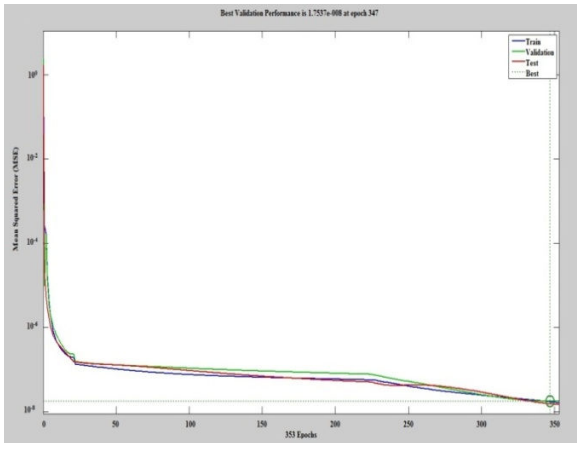

Fig. 3 Evolution of MSE values of training, validation and test errors during ANN training

V. Conclusion

In this study the solubility of NaCl in the mixture of water and ethanol was predicted by ANN and the results were compared with the results of the thermodynamic modeling

which was performed by the authors in another published research. The high values of correlation of coefficient, R^2, revealed that this approach well fitted the data that was provided by the thermodynamic modeling and can be applicable for prediction of the solubility of NaCl in the mixture of water and ethanol.

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