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PREDICTION OF VAPOR LIQUID EQUILIBRIUM (VLE) DATA FOR BINARY SYSTEMS; CASE STUDY: METHANE/TETRAFLUOROMETHANE

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ABSTRACT

In this research, the ability of multilayer perceptron neural networks to estimate vapor liquid equilibrium data have been studied. Isothermal vapor-liquid equilibrium (VLE) data for the binary mixture of methane (R50) + tetrafluoromethane (R14) have been investigated at (159.61, 161.58, 169.38, 173.90, and 178.93) K. Two different models with one hidden layer consisted of five hidden neurons are developed as the optimal structures. For this binary system, uncertainties of ANN models were 0.14, 0.26%. In addition, the abilities of ANNs are shown by comparisons with Margules, van Laar, and some other correlations.

Keywords: vapor liquid equilibrium, artificial neural network, binary systems, refrigerant, thermodynamics, methane.

1. INTRODUCTION

The modeling and control of equipment for different chemical processes require the vapor liquid equilibrium (VLE) data [1]. The VLE data is usually estimated by thermodynamic models based on the fundamental phase equilibrium criterion of equal chemical potential in both phases [2]. This process is based on the gamma- phi calculation method. This method requires the knowledge of activity and fugacity coefficients in the liquid (γ) and gas (ϕ) phases for all of the components. Several activity coefficient models such as NRTL, ASOG, UNIFAC, UNIQUAC, Wilson, and their modified forms have been devised to evaluate VLE [3-5]. Another method is based on equations of states (EoS). These methods are applied well to hydrocarbon systems. However, it is difficult to apply EoS for systems containing polar compounds [6]. Because of complexity, these approaches are not suitable for the rapid prediction of vapor liquid equilibrium.

Artificial neural network (ANN) is an empirical tool, which is analogous to the behavior of biological neural structures. ANN is a model based on some experimental results that is proposed to predict the required data because of avoiding more experiments [7]. They have the ability to identify underlying highly complex relationships with input-output data. In fact, they define several empirical relations, each for a part of the data [8]. Multi-layer networks are quite strong. For instance, a two-layer network, where the first and the second layers have sigmoid and linear functions respectively, can be trained to approximate any function (with a finite number of discontinuities) arbitrarily well [9]. Speed, simplicity, and capacity of learning are other advantages of ANNs compared to the classical methods. Therefore, they can be suitably used to predict VLE data non-iteratively for any set of input parameters. Furthermore, this method does not require values of pure component or interaction properties.

Recently, ANNs are used in the multifarious instances of thermo dynamical problems. In the context of VLE data, predictions by ANNs, can sign to the suggested networks to estimate compressibility factor for the vapor and liquid phases as a function of temperature and pressure for several refrigerants [10], prediction of activity coefficient of liquid phase [11], Prediction of High Pressure Vapor-liquid Equilibrium [12], calculation of VLE data for a light hydrocarbon mixture [13], benzene + hexane system [14], methane + ethane and ammonia + water systems and systems containing polar compounds [6], carbon dioxide + difluoromethane system [15], tert-butanol + 2-ethyl-1-hexanol and n-butanol + 2-ethyl-1-hexanol systems [16], apply three multi-layer networks to calculate logarithm of activity coefficient (γ) based on sign (positive or negative) of $ln\ \gamma$ [17], and estimation of VLE data for binary and ternary systems using Radial Base Function (RBF) neural networks [8], etc.

In this research, multi-layer perceptron networks are used to estimate vapor-liquid equilibrium data. Following two network models were considered for this study. The developed networks are trained and evaluated by using the experimental data reported by Zhu *et al*., [18]. A part of experimental data was used to train the networks and the rest was used to evaluate the performance of the networks. Experimental data and predicted values by ANNs are compared. Then, these models have been evaluated in contrast with the convenient correlations as Margules, van Laar, and etc. Then, results shown graphically and deviations are presented. Networks have been shown quite well behavior.

2. ARTIFICIAL NEURAL NETWORKS

An ANN can be considered as a black box consisting of a series of complicated equations for the calculation of outputs based on a given series of input values. One of the major advantages of ANN is efficient handling of highly nonlinear relations in data, even when the exact nature of such relation is unknown [19].

Commonly neural networks are trained; so that a particular input leads to a specific target output. The network is adjusted based on a comparison between the network outputs and the targets (real values of outputs), until the network outputs match the target [9].

The most popular ANN is the feed-forward multi-layer ANN which uses back-propagation learning algorithm. Feed-forward neural network usually has one or more hidden layers and an output layer. Scaled data is introduced into the input layer of the network and then is propagated from input layer to hidden layers and finally to the output layer.

Each layer consists of some cells, known as neurons. A parameter W_{ij} (known as weight) is associated with each connection between two cells. Each neuron in hidden or output layer firstly acts as a summing junction, which combines and modifies the inputs from the previous layer using the following equation [19]:

$$A_j = b_j + \sum_{j=1}^{n} X_j W_{ij} \quad (1)$$

$$Y_j = S(A_j) \quad (2)$$

Where,

X_j = inputs to j^{th} neuron (outputs from previous layer),
W_{ij} = weights representing the strength of the connection between the i^{th} neuron in the previous layer and j^{th} neuron
b_j = bias associated with j^{th} neuron
A_j = net input of j^{th} neuron in hidden or output layer.

Each neuron consists of a transfer function. Output of a neuron is determined by transforming its net input using a suitable transfer function, namely S in this work. Generally, the transfer functions for function approximation are sigmoidal function, hyperbolic tangent and linear function, that sigmoidal function is widely used for nonlinear relationship. Y_j (The output of j^{th} neuron) is also an element of inputs to neurons in the next layer [20, 21].

There are many variations of the back-propagation algorithm. The simplest implementation of back-propagation learning, updates the network weights and biases in the direction in which the performance function decreases most rapidly - the negative of error gradient. An iteration of this algorithm can be written as:

$$V_{k+1} = V_k - \alpha_k g_k \quad (3)$$

Where,

V_k = vector of current weights and biases
g_k = current gradient α_k is the learning rate
V_{k+1} = vector of new weights and biases.

The objective is to find the values of the weights and biases that they minimize differences between the targets and the predicted outputs in order to minimize the mean square errors (MSE). MSE is the average squared error between the network predicted outputs and the target outputs.

The Levenberg-Marquardt algorithm is one of the best training rules designed to approach second-order network training speed [9]. This algorithm trains a neural network 10 to 100 faster than the usual gradient descent back-propagation method and uses the following update rule:

$$V_{k+1} = V_k - [J^T J + \mu\ I]^{-1} J^T e \quad (4)$$

Where J is the Jacobian matrix contained first derivatives of the network errors with respect to the weights and biases, e is a vector of network errors, and I is always a ones square matrix that is the same size as the $J^T J$. The Jacobian matrix can be computed through a standard back-propagation technique. The scalar μ decreases after each successful step (reduction in performance function) and increases only when a tentative step would increase the performance function. In this way, the performance function will reduce at any iteration of algorithm [20].

In the learning process, there are several variables that have influence on the ANN training. These variables are the number of iterations, learning rate, the momentum coefficient, number of hidden layers and the number of hidden neuron. To find the best set of these variables and parameters, all of those must be varied and the best combination should be chosen [9].

3. DEVELOPMENT OF ANN MODELS

Following two network models were considered for this study. In the first model, the vapor phase composition of first compound (y_1) depends on temperature, pressure and liquid phase composition (T, P, x_1). In the second model, the liquid phase composition of first compound (x_1) and the temperature (T) were given as input to the network. The network predicted the vapor phase composition (y_1) and the pressure (P). The models 1 and 2 were evaluated for the binary system. A simple scheme of developed networks is shown in Figure-1. To compare these models, feed-forward multi-layer perceptron networks with one hidden layer are used for both models. It has been proven that utilizing hyperbolic tangent sigmoid and linear transfer functions in the hidden and outer layers respectively will produce better results.

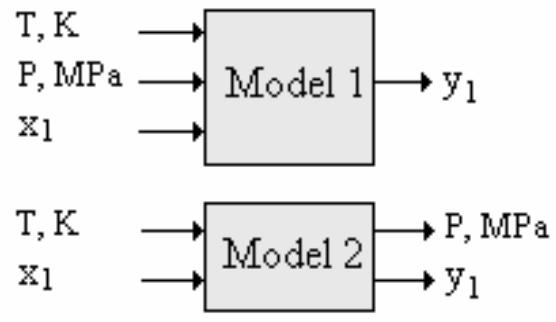

Figure-1. The developed neural models.

The input and output data are normalized in the range of [-1, 1], before import to networks. Then the Levenberg-Marquardt back-propagation algorithm that represents a simplified version of Newton's method is applied as the training algorithm in this study. This algorithm appears to be the fastest method for training moderate-sized feed-forward neural networks up to several hundred weights [9]. The mean squared error (MSE) as an excellent criterion for evaluating the performance of the neural network is used. Furthermore, the network was trained in MATLAB 7.0 environment.

The optimum performance of networks is obtained empirically by changing the number of neurons in the hidden layer, as the minimal number of neurons for which the prediction performance is sufficient without leading to over fitting or an unreasonably long computational time. If there are a few neurons in the hidden layer, the performance of the network will not be satisfactory. However, if there are too many, convergence will be very slow and may be compromised by local minima or over fitting. Effects of neurons number on the train and test errors for the both models are shown in Figures 2 and 3.

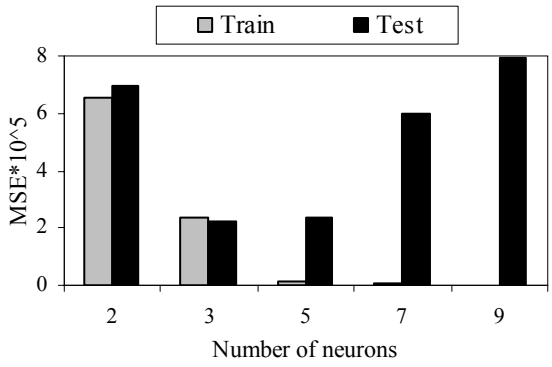

Figure-2. Effect of neurons number on mean square errors (MSE) in the first model.

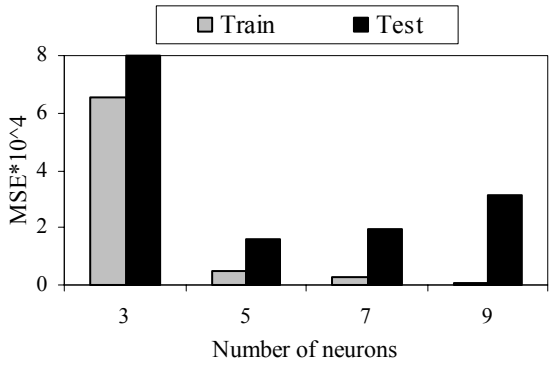

Figure-3. Effect of neurons number on mean square errors (MSE) in the second model.

For both models, MSEs are decreased with increasing neurons number in the hidden layer. It is because of increasing adjustable parameters. Nonetheless, inordinate increasing caused to over fitting (increasing the testing errors). Finally, two models containing five hidden neurons are selected as the optimum structures. The models structures are shown in Figures 4 and 5.

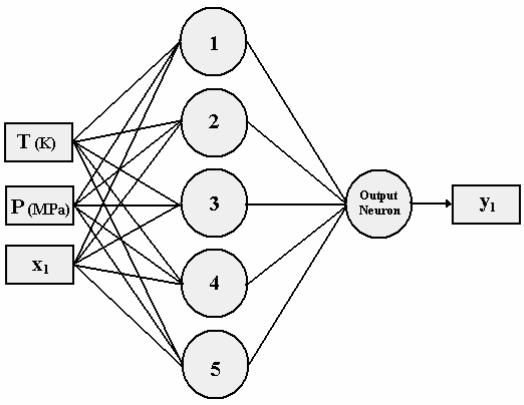

Figure-4. The schematic of the first model.

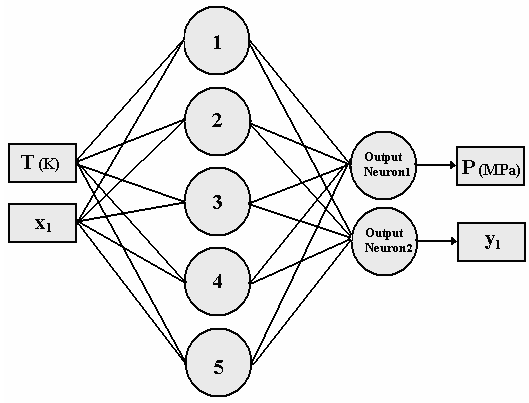

Figure-5. The schematic of the second model.

4. RESULTS AND DISCUSSIONS

The training and evaluating errors for binary system using models, in addition their adjustable parameters number are reported in Table-1. The admirable agreement between experimental data and predicted results by using neural models are shown, obviously. The small uncertainty of results in the training and testing stages are shown in Figures 6(a), 6(b) and 6(c), too.

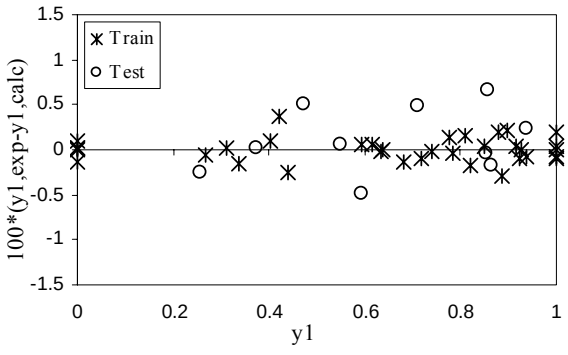

Figure-6(a). Deviations of the vapor phase composition of first compound for Model 1.

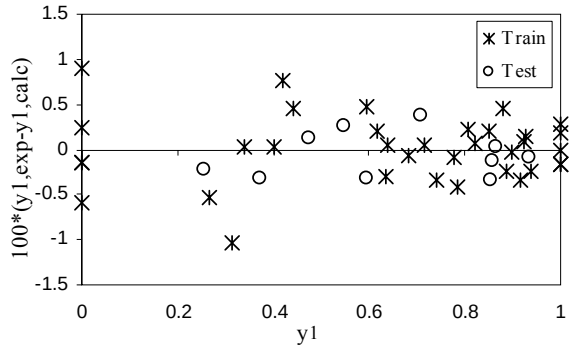

Figure-6(b). Deviations of the vapor phase composition of first compound for Model 2.

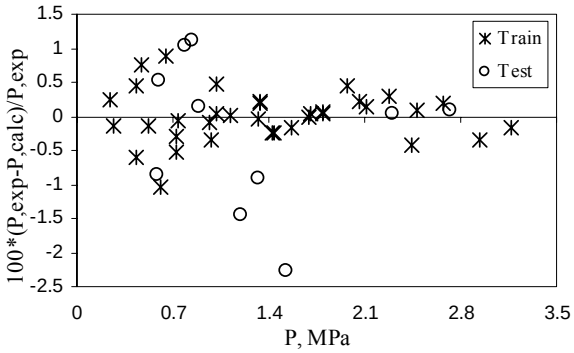

Figure-6(c). Deviations of pressure for Model 2.

Figure-6. Deviations of models against with the used experimental data in the training and testing stages.

Table-1. Deviations of training and testing stages for models 1, 2 and their adjustable parameters number.

Model 1: (20 weights and 6 Biases)	**MSE (y_1)**[a]		**AD (y_1)%**[b]	
Train	1.79E-06		0.10	
Test	1.33E-05		0.29	
Model 2: (20 weights and 7 biases)	MSE(y_1)	MSE(P)	AD(y_1)%	AAD(P)%[c]
Train	1.37E-05	5.55E-05	0.28	0.65
Test	6.27E-06	1.83 E-04	0.22	0.84

[a] $MSE(u)=\frac{1}{n}\times\sum_{i=1}^{n}(u_i^{\exp.}-u_i^{calc.})^2$, [b] $AD(u)\%=\frac{100}{n}\times\sum_{i=1}^{n}\left|u_i^{\exp.}-u_i^{calc.}\right|$, [c] $AAD(u)\%=\frac{100}{n}\times\sum_{i=1}^{n}\left|u_i^{\exp.}-u_i^{calc.}\right|/u_i^{\exp.}$

As it is clear, the values of absolute deviation of (y_1) in the training and testing stages for both models are about 1%. The absolute deviation of (y_1) is defined as the following to avoid dividing by zero in the relative error ($y_1^{calc.}$-$y_1^{exp.}$)/$y_1^{exp.}$, when mole fraction of the first compound in the vapor phase is zero. Deviations of pressure for the second Model in the training and testing stages are about 1 and 2.5%, respectively.

$$AbsoluteDeviation\% = (y_1^{calc.} - y_1^{\exp.}) \times 100 \quad (5)$$

In addition, some models of the excess Gibbs energy and subsequent activity coefficients are used to correlate VLE data. Then their results are used as a criterion to evaluate the ANNs abilities. The three-suffix Margules and van Laar equations are selected because they are mathematically easier to handle than the newer ones (Wilson, NRTL, and UNIQUAC) [22]. These equations include two empirical constants, to represent activity coefficient data. The equations are rearranged in a linear form to evaluate their constants.

Three-suffix Margules:

$$G^E = x_1 x_2 [A + B(x_1 - x_2)] \quad (6)$$

$$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3 \quad (7)$$

$$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3 \quad (8)$$

Linear form:

$$G^E / x_1 x_2 = (A - B) + 2Bx_1 \quad (9)$$

Van Laar:

$$G^E = Ax_1 x_2 / [x_1 (A/B) + x_2] \quad (10)$$

$$RT \ln \gamma_1 = A\left(1 + Ax_1/(Bx_2)\right)^{-2} \quad (11)$$

$$RT \ln \gamma_2 = B\left(1 + Bx_2/(Ax_1)\right)^{-2} \quad (12)$$

Linear form:

$$x_1 x_2 / G^E = 1/A + (1/B - 1/A)x_1 \quad (13)$$

Where,

G^E = excess Gibbs energy
y_i = activity coefficient of component *i*
x_i = liquid phase mole fraction of component *i*
A, and *B* = adjustable parameters of correlations.

The excess Gibbs energy data are produced from *TPxy* experimental data of binaries by using equations 14 and 15. It is supposed that the liquid phase properties are independent of the pressure variations [3].

$$\gamma_i = y_i \hat{\phi}_i P / (x_i \phi_i^{sat} P_i^{sat}) \qquad i = 1,2 \quad (14)$$

$$G^E = RT \sum_{i=1}^{2} x_i \ln \gamma_i \quad (15)$$

Where P, R, T, y_i, P_i^{sat}, $\hat{\phi}_i$, and ϕ_i^{sat} are pressure, the gases constant, temperature, the vapor phase mole fraction of component i, vapor pressure of component i, fugacity coefficient of component i in the vapor phase, fugacity coefficient of pure i at T and saturation pressure, respectively. The vapor pressures of pure components are given in Table-2 [18].

Table-2. Vapor pressure of pure compounds.

T, K	P, MPa	Component	T, K	P, MPa
159.61	1.566	Tetrafluoromethane	159.61	0.243
161.58	1.694		161.58	0.269
169.38	2.275		169.38	0.413
173.90	2.671		173.90	0.517
178.90	3.170		178.90	0.651

The fugacity coefficients are calculated by using the virial equation in the vapor phase [23]. For binary systems activity coefficient calculate as below:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^{sat}} + \frac{B_{ii}(P - P_i^{sat}) + P\delta_{12}(1 - y_i)^2}{RT} \qquad i = 1,2 \qquad (16)$$

$$\delta 12 = 2B_{12} - B_{11} - B_{22} \qquad (17)$$

Where B_{ii} are the second virial coefficients. These coefficients are calculated by using the Pitzer equations extended for mixture by Prausnitz [3]. Samples of the correlations at 159.61K are shown in Figures 7.a, b. In addition, for the binary system in the whole ranges of temperature, deviations between correlation results and experimental data for vapor phase mole fraction of first compounds (y_1) are shown in Figure-8. As it is clear, these results are in the lower accuracy than the ANNs estimations. The quantitative comparisons of these models as well as some other models used in the literatures for these systems are presented in Table-3. The P, x, y diagrams for the mixture of methane + tetrafluoromethane at various temperatures are shown in Figures 9.a, b, where the experimental VLE data at (159.61, 161.58, 169.38, 173.90, and 178.93) K are shown as black dash lines. The symbols indicated the calculated results by the ANN models. Results show the ability of ANNs in contrast with Margules, van Laar, and others. Models 1, 2 produced acceptable results for the binary system. Once the ANN models were trained, estimation of the vapor liquid equilibria data becomes a straight forward process without any iteration, which it saves computational time considerably. While conventional methods based on EoSs have usually iterative calculation as other complexity, too. In addition, developed networks do not require any pure component parameter or the binary interaction parameters, or the mixing rules as required in conventional methods. The deviations with PRP and PRM models are relatively low. But the complexities of these models cause that the ANNs will be recommended as straight forward tools to estimate VLE data.

Table-3. Comparison of different methods in the estimation of the first compounds vapor phase mole fraction.

Model	**Temp. range** (K)	**AD** (y_1)% [c]
ANN Model 1[a]	159.61-178.93	0.14
ANN Model 2[a]	159.61-178.93	0.26
Margules [a]	159.61-178.93	3.44
Van Laar [a]	159.61-178.93	2.74
PR EoS with the Panagiotopoulos-Reid mixing rule (PRP)[b]	293.16-353.18	0.28
PR EoS with the modified Panagiotopoulos-Reid mixing rule (PRM) [b]	293.16-353.18	0.36
[a] (This work result), [b] (Zhu *et al*., 2007), [c] $AD(u)\% = \frac{100}{n} \times \sum_{i=1}^{n} \left| u_i^{\exp.} - u_i^{calc.} \right|$		

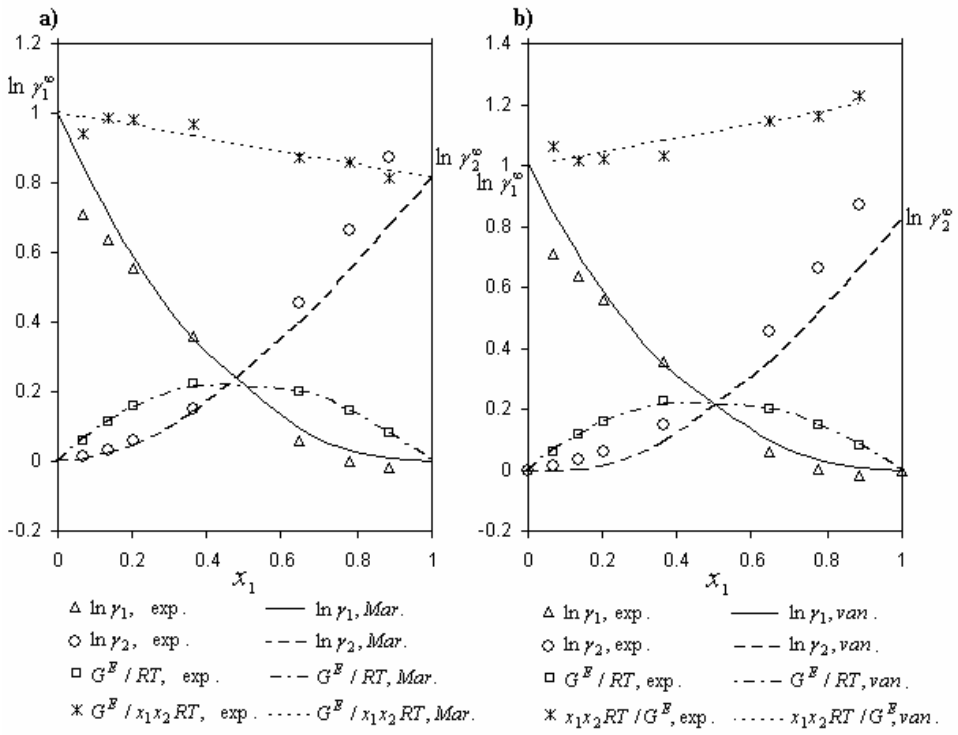

Figure-7. Correlations of liquid phase properties at 159.61K using (a) Margules and (b) van Laar equations.

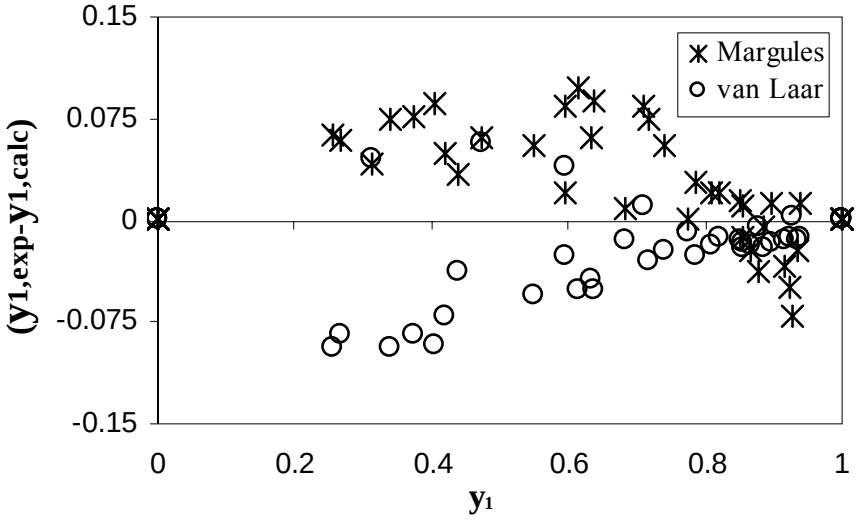

Figure-8. Deviations between correlations results and experimental data in the whole ranges of temperature (159.61-178.93).

5. CONCLUSIONS

The ability of Artificial Neural Networks based on back-propagation algorithm to predict vapor liquid equilibria data for binary system of methane-tetrafluoromethane. Therefore, two models with different number of inputs and outputs have been investigated. In addition, the three-suffix Margules and van Laar equations are used to correlate VLE data. Then their results are used as a criterion to evaluate the ANNs abilities. Predicted results by using the developed networks are very close to experimental. So deviations in the estimation of the first compounds vapor phase mole fraction with models 1, 2 were 0.14, 0.26%. Results for developed neural models were acceptable and more accurate than Margules and van Laar correlations. All of these results prove that Artificial Neural Networks can be a successful tool to predict vapor liquid equilibria data, if developed efficiently.

Nomenclature

A	Net input of neurons (Eq.1)	(-)
A	Correlation constant	(-)
B	Correlation constant	(-)
B	The second virial coefficients (Eqs.16, 17)	(m^3)
$AD\ \%$	Percent of absolute deviation	(-)
$AAD\ \%$	Percent of average absolute deviation	(-)
b	Bias associated with neurons	(-)
e	Error	(-)
g	Gradient of error	(-)
G^E	Excess Gibbs energy	(J / mol)
I	Ones square matrix	(-)
J	the Jacobian matrix	(-)
n	Number of data points	(-)
P	Pressure	MPa
Psat	Vapor pressure	MPa
R	Universal Gas Constant (8.31415)	J/mol K
T	Temperature	K
S	Transfer function	(-)
V	Vector of weights and biases	(-)
W	Connection weights between neurons	(-)
x	Mole fraction of compounds in the liquid phase	(-)
X	Input of neurons	(-)
y	Mole fraction of compounds in the vapor phase	(-)
Y	Output of neurons	(-)
Greek symbols		
α	Learning rate	(-)
γ	Activity coefficient	(-)
ϕ	Fugacity coefficient	(-)
μ	Scalar parameter in the LM algorithm	(-)
Subscripts		
i	Neuron number	(-)
j	Neuron number	(-)
k	Iteration number	(-)
Superscript		
calc.	Calculated values by using ANN	(-)
exp.	Experimental values	(-)
^{T}	Transpose matrix	(-)

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