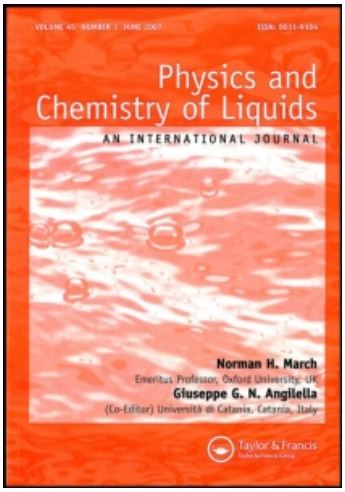

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Prediction dielectric constant of different ternary liquid mixtures at various temperatures and compositions using artificial neural networks

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Prediction dielectric constant of different ternary liquid mixtures at various temperatures and compositions using artificial neural networks

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Artificial neural networks (ANNs) were successfully developed for the modeling and prediction dielectric constant of different ternary liquid mixtures at various temperatures ($-10^{\circ}C \leq t \leq 80^{\circ}C$) and over the complete composition range ($0 \leq x_1, x_2, x_3 \leq 1$). A three-layered feed forward ANN with architecture 7-16-1 was generated using seven parameters as inputs and its output is dielectric constant of media. It was found that properly selected and trained neural network could fairly represent the dependence of dielectric constant of different ternary liquid mixtures on temperature and composition. For the evaluation of the predictive power of the generated ANN, an optimized network was applied for predicting the dielectric constant in the prediction set, which were not used in the modeling procedure. Squared correlation coefficient (R^2) and root mean square error for prediction set are 0.9997 and 0.2060, respectively. The mean percent deviation (MPD) for the property in the prediction set is 0.8892%. The results show nonlinear dependence of dielectric constant of ternary mixed solvent systems on temperature and composition is significant.

Keywords: Artificial neural networks; Dielectric constant; Ternary mixtures

1. Introduction

The dielectric constant is an important property of matters and liquids in particular, in connection with the transport phenomena in solution, e.g. transport of liquids through membranes either in biological systems or in industrial applications [1, 2]. Drug solubility in mixed solvents, acid dissociation constants of drugs, chemical stability of pharmaceuticals and the concentration of a drug in plasma from mixed solvent vehicles could be explained considering dielectric constant of the solvent system [3]. The utility of the dielectric constant for interpretation of solvent–solute behavior motivates the desire for an availability of this data. Solvent effects described through their dielectric properties may play an important role in the chemical reactivity and equilibrium. In general, the dielectric constant can be a very useful parameter to

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consider when reaction environment needs to be optimized to achieve better control over the chemical reaction [4]. The dielectric properties of the liquid mixtures seem of particular interest for both theoretical and practical reasons and as a rule cannot be predicted from the dielectric properties of the components. Much of the work reported in the literature in this field has employed binary mixtures, while ternary (and upper) solvent systems has been only slightly reviewed in spite of their more representative behavior of real system in actual use [5–10].

Artificial neural networks (ANNs) have become popular due to their success where complex nonlinear relationships exist amongst data [11–14]. Artificial neural networks are biologically inspired computer programs designed to simulate the way in which the human brain processes information. Artificial neural networks gather their knowledge by detecting the patterns and relationships in data and learned (or trained) through experience, not from programming. The wide applicability of ANNs stems from their flexibility and ability to model nonlinear systems without prior knowledge of an empirical model. Neural networks do not need an explicit formulation of the mathematical or physical relationships of the handled problem. These give ANNs an advantage over traditional fitting methods for some chemical application. For these reasons in recent years, ANNs have been used for a wide variety of chemical problems such as simulation of mass spectra, ion interaction chromatography, aqueous solubility and partition coefficient, simulation of nuclear magnetic resonance spectra, prediction of bioconcentration factor, solvent effects on reaction rate, prediction normalized polarity parameter in mixed solvent systems and dissociation constant of acids [15–31].

The correlation of dielectric constant for various organic compounds with molecular structure has been proposed using ANNs [2,4,7]. But there is no similar model for correlation of dielectric constant of liquid mixtures with temperature and composition.

In this work, for inspection of nonlinear relation of dielectric constant of different ternary liquid mixtures with temperature and composition, an ANN model, for a first time, was generated for prediction the property in various temperatures and compositions and the results were compared with the calculated values based on very recently proposed models.

2. Theory

A detailed description of theory behind neural networks has been adequately described by different researchers [11–14]. There are many types of neural networks designed by now and new ones are invented every week, but the behavior of a neural network is determined by transfer functions of its neurons, by learning rule, and by the architecture itself. An ANN is formed from artificial neuron or processing elements (PE), connected with coefficients (weights), which constitute the neural structure and are organized in layers. The first layer is termed the input layer, and the last the output layer. The layers of neurons between the input and output layers are called hidden layers. The number of neurons in the input and output layers are defined by system's properties. The number of neurons in the hidden layer could be considered as an adjustable parameter, which should be optimized. The input layer receives the experimental or theoretical information and the output layer produces the calculated values of dependent variables. Artificial neural networks allow one to estimate the relationships between input variables and one or several output dependent variables. The use of ANNs consists of

two steps: ''training'' and ''prediction''. In the training phase the optimum structure, weight coefficients and biases are searched for. These parameters are found from training and validation data sets. After the training phase, the trained network can be used to predict (calculate) the outputs from a set of inputs. There are many types of network architectures, but the type that has been most useful for prediction studies is the multiplayer feed-forward network with back-propagation (BP) learning rule [14]. Information from inputs is fed forward through the network to optimize the weights between neurons. The ANN reads the input and target values in the training data set and changes the values of the weighted links to reduce the difference between the calculated output and target values. The error between output and target values is minimized across many training cycles until network reaches specified level of accuracy. If a network is left to train for too long, however, it will overtrain and lose the ability to generalize [29–31].

3. Experimental

3.1. *Data set*

A reliable database is critically important for the training of ANNs. Six ternary liquid mixtures including *N*,*N*-dimethylformamide + 2-methoxyethanol + 1,2-dimethoxyethane ($-10^{\circ}C \leq t \leq 20^{\circ}C$), *N*,*N*-dimethylformamide + 2-methoxyethanol + 1,2-dimethoxyethane ($25^{\circ}C \leq t \leq 80^{\circ}C$), 2-methoxyethanol + 1,2-dimethoxyethane + water ($-10^{\circ}C \leq t \leq 80^{\circ}C$), ethane-1,2-diol + 1,2-dimethoxyethane + water ($-10^{\circ}C \leq t \leq 80^{\circ}C$), ethane-1,2-diol + 2-methoxyethanol + water ($30^{\circ}C \leq t \leq 50^{\circ}C$), 1,2-dichloroethane + 2-methoxyethanol + 1,2-dimethoxyethane ($-10^{\circ}C \leq t \leq 80^{\circ}C$) at various temperatures and compositions have been used [5–10]. The data set was randomly divided into three groups: a training set, a validation set and a prediction set consisting of 1361, 202 and 202 data, respectively. The training and validation sets were used for the model generation and the prediction set was used for evaluation of the generated model, because a prediction set is a better estimator of the ANN generalization ability than a validation (monitoring) set [29–31].

3.2. *Neural network generation*

The specification of a typical neural network model requires the choice of the type of inputs, the number of hidden layers, the number of neurons in each hidden layer and the connection structure between the input and output layers. The inputs of ANNs are dielectric constants and mole fractions of constituents of ternary mixed solvent system and temperature. A three-layer network with a sigmoidal transfer function was designed. The initial weights were randomly selected between 0 and 1. Before training, the input and output values were normalized (or scaled) between 0.1 and 0.9. After training of the optimized ANN, the data sets were unscaled. The optimization of the weights and biases was carried out according to resilient BP algorithm for BP of error [32]. For evaluation prediction power of the network, the trained ANN was used to predict dielectric constant of the data set included in the prediction set. The performances of training, validation and prediction of ANNs are evaluated by

the mean percentage deviation (MPD) and root-mean square error (RMSE), which are defined as follows:

$$\mathrm{MPD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}})}{P_i^{\mathrm{exptl}}}\right| \tag{1}$$

$$\mathrm{RMSE} = \sqrt{\sum_{i=1}^{N}\frac{(P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}})^2}{N}} \tag{2}$$

where P_i^{exptl} and P_i^{calcd} are experimental and calculated values of dielectric constant and N denote the number of data points.

Individual percent deviation (IPD) and residual are defined as follows:

$$\mathrm{IPD} = 100 \times \left(\frac{P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}}}{P_i^{\mathrm{exptl}}}\right) \tag{3}$$

$$\mathrm{Residual} = P_i^{\mathrm{calcd}} - P_i^{\mathrm{exptl}}. \tag{4}$$

The processing of the data was carried using Matlab 6.5 [33]. The neural networks were implemented using Neural Network Toolbox Ver. 4.0 for Matlab [32].

4. Results and discussion

There are no rigorously theoretical principles for choosing the proper network topology; so different structures were tested in order to obtain the optimal hidden neurons and training cycles [30]. Before training the network, the number of nodes in the hidden layer was optimized. In order to optimize the number of nodes in the hidden layer, several training sessions were conducted with different numbers of hidden nodes (from 1 to 20). The root mean square error of training (RMSET) and validation (RMSEV) sets were plotted *versus* the number of iterations for different number of neurons at the hidden layer and the minimum value of RMSEV was recorded as the optimum value. Plot of RMSET and RMSEV *versus* the number of nodes in the hidden layer has been shown in figure 1. It is clear that 16 nodes in hidden layer is optimum value, because its RMSEV is minimum.

This network consists of seven inputs (including dielectric constants and mole fractions of constituents of ternary liquid mixtures and temperature) and one output for dielectric constant. Then an ANN with architecture 7-16-1 was generated. It is interesting to note that training of the network was stopped when the RMSEV started to increase i.e. when overtraining begins. The overtraining causes the ANN to loose its prediction power [29–31]. Therefore, during training of the networks, it is desirable that iterations are stopped when overtraining begins. To control the overtraining of the network during the training procedure, the values of RMSET and RMSEV were calculated and recorded to monitor the extent of the learning in various iterations. Results demonstrated that overtraining is not seen in this work (figure 2).

The generated ANN was then trained using the training set for the optimization of the weights and biases. For evaluation of the predictive power of the generated ANN,

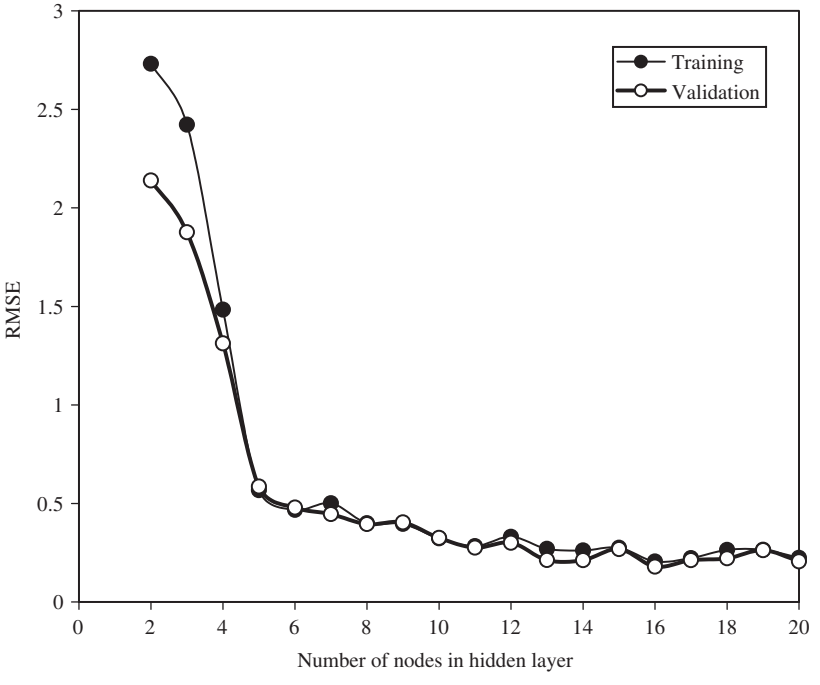

Figure 1. Plot of RMSE for training and validation sets *vs*. the number of nodes in hidden layer.

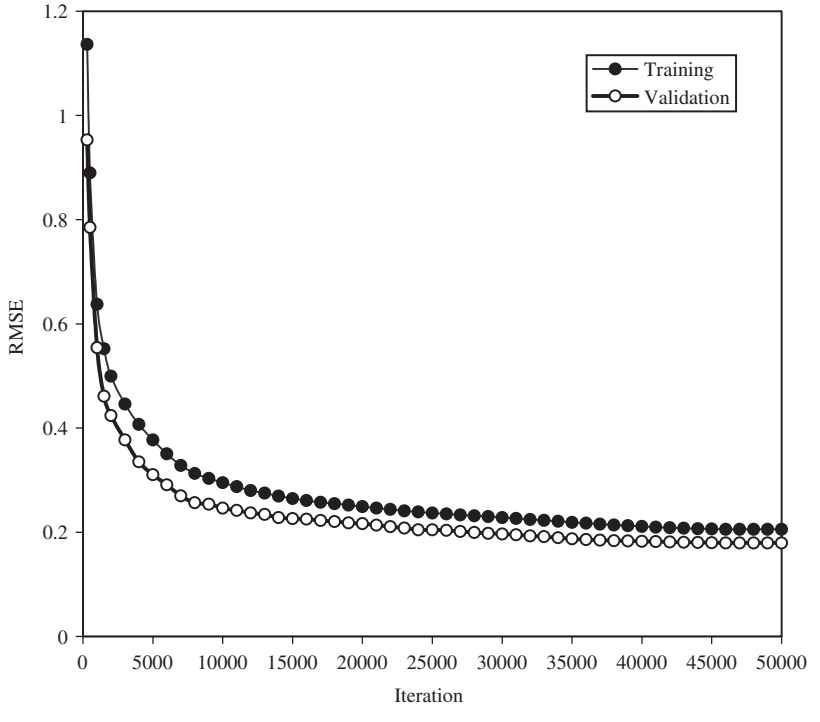

Figure 2. Plot of RMSE for training and validation sets *vs*. the number of iterations.

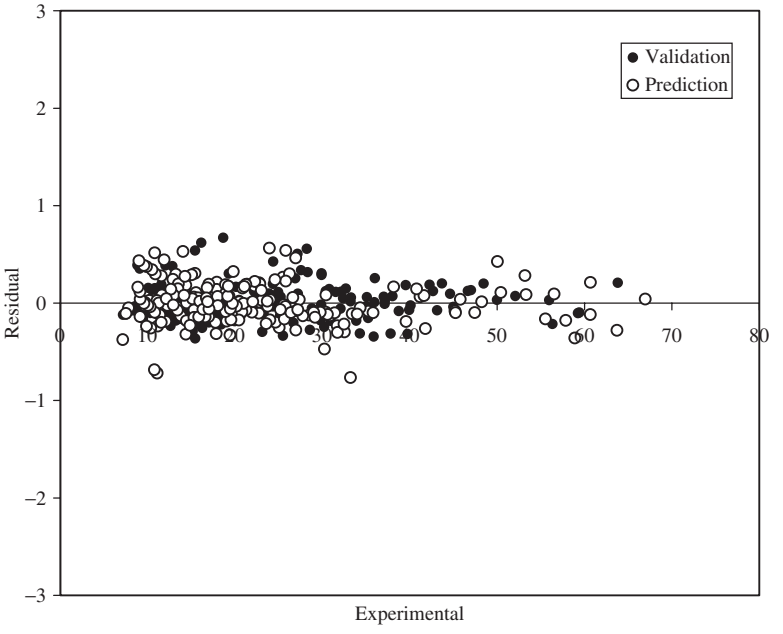

Figure 3. Plot of the residual for calculated values of dielectric constant from the ANN model *vs*. the experimental values of it for validation and prediction sets.

an optimized network was applied for predicting the dielectric constant in different ternary mixed solvent systems at various temperatures and compositions in the prediction set (including 202 data), which were not used in the modeling procedure. The calculated values of the dielectric constant in various compositions and temperatures for training, validation and prediction sets using the ANN model were obtained. The correlation equation for all of the calculated values of dielectric constant from ANN model *versus* the experimental values is as follows:

$$\varepsilon(\text{cal}) = 0.99967\varepsilon(\text{exp}) + 0.00736 \tag{5}$$

$$N = 1765;\ R^2 = 0.9998;\ \text{MPD} = 0.8116;\ \text{RMSE} = 0.2030;\ F_{1,1764} = 8910076.33.$$

As can be seen, the calculated values of dielectric constant (ε) are in good agreement with those of the experimental values. Similarly, the correlation of the calculated values of dielectric constant *versus* the experimental values of it in prediction set gives equation (6):

$$\varepsilon(\text{cal}) = 0.99810\varepsilon(\text{exp}) + 0.04401 \tag{6}$$

$$N = 202;\ R^2 = 0.9997;\ \text{MPD} = 0.8892;\ \text{RMSE} = 0.2060;\ F_{1,201} = 728169.3.$$

Plot of the residual for calculated values of dielectric constant in validation and prediction sets *versus* the experimental values of it has been illustrated in figure 3. The results demonstrate that the maximum value of the residual for the calculated values of dielectric constant in the prediction set is 0.7644.

Table 1. Statistical parameters obtained by the ANN model for total, training, validation and prediction sets.

Type of data set	N	R^2	MPD	RMSE	F
Total	1765	0.9998	0.8116	0.2030	8910076.3
Training	1361	0.9998	0.8091	0.2058	7256273.0
Validation	202	0.9998	0.7506	0.1795	875280.1
Prediction	202	0.9997	0.8892	0.2060	728169.3

N is number of data set; R is the correlation coefficient between the calculated and experimental values of dielectric constant; MPD is mean percent deviation; RMSE is root mean square error and F is the statistical F-value.

As can be seen the model did not show proportional and systematic error, because the slope ($a = 0.99810$) and intercept ($b = 0.04401$) of the correlation equation are not significantly different from unity and zero, respectively, and the propagation of errors in both sides of zero are random (figure 3).

Table 1 compares the results obtained using the ANN model. The correlation coefficient (R), RMSE, MPD and F-value of the model for total, training, validation and prediction sets show potential of the ANN model for prediction of dielectric constant in ternary mixed solvent systems at various temperatures and compositions.

Very recently a correlative model for calculating dielectric constants of 1,2-dichloroethane + 2-methoxyethanol + 1,2-dimethoxyethane at temperatures from –10 to 80°C was proposed based on Redlich–Kister extension [3]. The MPD by this model is 3.05. Therefore MPD for the ANN model (0.8892) is very lower than the correlative model (3.05). The ANN and the correlative models are based on experimental values for building of the model. As a result, it was found that properly selected and trained neural network could fairly represent the dependence of dielectric constant on composition and temperature in ternary mixed solvent systems. Then the optimized neural network could simulate the complicated nonlinear relationship between dielectric constant of ternary mixed solvent systems and mole fractions and dielectric constants of constituents of mixture and temperature.

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