International Journal of Computational Intelligence Systems, Vol. 5, No. 3 (June, 2012), 460-471

Artificial Neural Network for Compositional Ionic Liquid Viscosity Prediction

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Received 13 February 2012
Accepted 1 March 2012

Abstract

Being a new generation of green solvents and high-tech reaction media of the future, ionic liquids have increasingly attracted much attention. Of particular interest in this context are room temperature ionic liquids (in short as ILs in this paper). Due to the relatively high viscosity, ILs is expected to be used in the form of solvent diluted mixture with reduced viscosity in industrial application, where predicting the viscosity of IL mixture has been an important research issue. Different IL mixture and many modelling approaches have been investigated. The objective of this study is to provide an alternative model approach using soft computing technique, i.e., artificial neural network (ANN) model, to predict the compositional viscosity of binary mixtures of ILs [C_n-mim][NTf_2] with n=4, 6, 8, 10 in methanol and ethanol over the entire range of molar fraction at a broad range of temperatures from T=293.0-328.0K. The results show that the proposed ANN model provides alternative way to predict compositional viscosity successfully with highly improved accuracy and also show its potential to be extensively utilized to predict compositional viscosity taking account of IL alkyl chain length, as well as temperature and compositions simultaneously, i.e., more complex intermolecular interactions between components in which it would be hard or impossible to establish the analytical model. This illustrates the potential application of ANN in the case that the physical and thermodynamic properties are highly non-linear or too complex.

Keywords: artificial neural network; room temperature ionic liquids; viscosity; viscosity compositions.

1. Introduction

Ionic liquids were originally developed with the aim of producing a salt which melts around room temperature, so it is generally defined as a salt consisting only of ions and existing in liquid state under room temperature,[1] such as organic nitrogen-containing heterocylic cations and inorganic anions.[2] Since the first dedicated work on ionic liquids, which was carried out between 1950 and 1990, an extensive number and range of ionic liquids have been prepared and reported. Numerous sub-categories have been defined. The most common sub-category is that of room temperature ionic liquids, salts with melting points of 25 ℃ or below. Room temperature ionic liquids (RTILs, in short as ILs in this paper), have enormous potential as alternative green solvents for a wide range of applications due to their important and unique properties, such as non-volatile and solvating properties. The rising scientific interest in ILs and their potential applications has triggered an explosive progress in the field of IL synthesis and fundamental research.[3, 4] The rapidly increasing research activity is reflected in the exponentially growing number of publications per year. It is remarkable that papers appear faster than 40 per week underlining the extreme growing interest in this field.[5]

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Although a wide range of research regarding ILs has been conducted, there are still a number of challenges on the way to apply ILs in large scale chemical processes. Among them, the separation, transportation and recycling of relatively highly viscous ILs have to be taken into consideration for process development. It should be noted that in most applications, ILs will be used in mixtures with other compounds. For instance, when used as a reaction solvent, the IL will contain both the reactants and the products. The presence of other compounds may significantly reduce the viscosity of the mixture, somewhat ameliorating the disadvantages of the intrinsically higher viscosities of ionic liquids. Consequently, viscosity of IL mixture is important in many future applications and it is imperative to develop knowledge of fluid and transport properties of ILs in mixtures with reactants, products or other co-solvents. Therefore, in addition to the study of fluid and transport properties of pure ionic liquids, studies of viscosity of mixtures of ionic liquids with different class of solvents in binary or tertiary systems are necessary and essential. However, reported studies of rheological behavior of binary mixture of ILs in aqueous, polar or non-polar phase are limited even for some well characterized ionic liquids.[6]

In industrial applications, such as in organic synthesis and extraction processes, an efficient ILs mixture viscosity estimation model can help to facilitate processing development prediction with less measurement work. Although various methods are developed for predicting pure compounds viscosities with varying thermodynamic variables,[7-12] when dealing with mixtures, the modelling to predict viscosity of IL is, by far, a much more complicated problem,[13] and is still on the way of investigation. In most of investigations, predictive compositional viscosity models are proposed to correlate viscosity of the binary mixtures with corresponding viscosity of the pure components. The models are kinds of semi-empirical models to predict the thermodynamic and the physical properties of the compositional viscosity based on theoretical relations and relying on data regression to obtain some empirical parameters, from the experimental data of the binary combinations of the components. The compositional viscosity models have shown worked well from different aspects. Parameters affecting viscosity may vary, many different components (e.g., more than two) can be found in mixtures of ILs and creating a model that accounts for all of them may be unrealistic. For a wide range of temperatures and viscosity compositions, i.e., more complex intermolecular interactions between components, it would be hard to establish analytical model. So in this paper, an ANN is utilized to predict compositional viscosity over a wide range of temperatures and viscosity compositions.

ANNs present significant advantages over conventional data regression models as there is no need to provide a model function, needs no previous knowledge of the data relationship before predicting the desired property. The learning capability of ANNs allows the discovery of more complex and subtle interactions between variables and ANNs are intrinsically more robust when it comes to handling noisy or inaccurate data.[14-15]

Neural networks have particularly proved their ability to solve complex problems with nonlinear relationships. This background makes ANN one of the most perspective techniques of nonlinear data analysis in almost all the fields of chemistry (from quantitative structure-property relationship studies[16-17] to petroleum chemistry.[18]

ANN has been widely applied to predict the physical and thermodynamic properties of chemical compounds. Recently a few researches have been performed by artificial neural networks for prediction of pure substances and petroleum fraction's properties[19]; activity coefficients of isobaric binary systems[20]; thermodynamic properties of refrigerants[21-24]; activity coefficient ratio of electrolytes in amino acid's solutions[25]; the phase stability problem[26]; and dew point pressure for retrograde gases.[27] Other ANN applications include density predication of ionic liquids[28]; modeling flow boiling heat transfer of pure fluids[29]; predicting slag viscosity over a broad range of temperatures and slag compositions[30]; ρ–T–P prediction for ionic liquids[31]; prediction of simple physical properties of mixed solvent systems,[32] etc. Those work demonstrated that neural networks can dramatically reduce the numerical errors and eliminate systematic deviation between predicted values and experimental values. Furthermore, industrial application of multivariate data

analysis methods is already observed in a number of fields.[33-35]

A complete list of properties has been presented that have been analyzed in the literature using different approaches to artificial neural networks.[36] Properties such as boiling point, critical temperature, critical pressure, vapor pressure, heat capacity, enthalpy of sublimation, heat of vaporization, density, surface tension, viscosity, thermal conductivity, and acentric factor, among others, were thoroughly reviewed. Applications of neural networks to mixture properties (PTV properties, vapor liquid equilibrium, activity coefficients) have been also presented in other publications.[22, 24, 37-38]

There are numerous viscosity measurements available in the literature. Unfortunately, the techniques used to obtain them vary greatly and the sources of potential errors are numerous. To the best of the author knowledge there is not much application for IL viscosity prediction; and on the prediction of these properties for IL's using ANN.

In this research work, the application of ANNs to the prediction of compositional viscosity of IL mixture is investigated. The work has been briefly outlined in Ref. 39. This paper aims at extending, refining, completing and systematizing the results in Ref. 39. The paper is organized as follows: ANN is briefly overviewed firstly in Section 2. Some fundamentals and modeling steps of ANN for this application are introduced in Section 3. Materials and experimental approaches are outlined in Section 4. Detailed results and discussion are reported in Section 5. The paper is concluded in Section 6.

2. Short Overview of ANN

The overview of fundamentals of ANN methodology was provided in this section. Additional specific information regarding the application of ANN in the IL predication is provided in Section 3.

ANN is a mathematical model or computational model that is inspired by the structure and/or functional aspects of biological neural networks. A neural network consists of an interconnected group of artificial neurons. It is a parallel distributed processing system and based on the principle that a highly interconnected system of simple processing elements (neruons) can learn complex interrelationships between independent and dependent variables. The reader is referred to Refs. 40-42 which all provide a good description and introduction of ANNs including their efficacies and limitations. Some brief introductions are given as follows.

In different ANNs model proposed, the most basic architecture normally involves a feed-forward backpropagation (BP) neural network consisting of three layers. A simple BP-ANN consists of an input layer, one or more hidden layers, and an output layer, and connected by neurons. Each neuron, receives one or more inputs and produces an output signal through an activation function, is linked to its neighbors with a varying weights that represents the connections' strength.

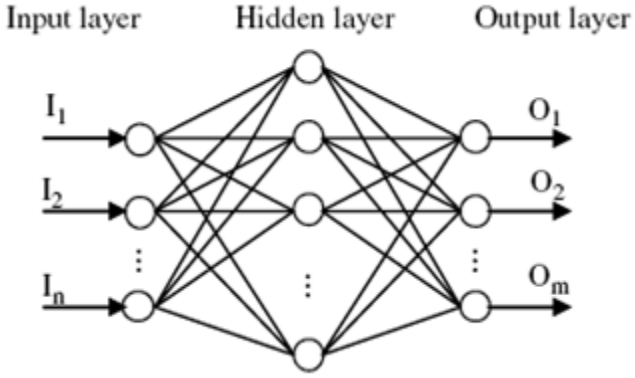


Fig. 2.1 Architecture of a three-layered neural network.

Fig. 2.1 illustrates a typical three-layered neural network structure with an input layer, a hidden layer and an output layer. Each neuron as a processing element in the hidden layer receives an activation signal, which is the weighted sum of all the input units from the external environment, i.e., each of the input units are multiplied by a connection weight:

$$x_j = \sum_i I_i W_{ij} \tag{2.1}$$

and generates an output through an activation function, here W_{ij} is the weight of the connection between the neurons *i* and *j* among the input neurons with the hidden layer, respectively. The output layer consists of neurons that communicate the system's output to the external environment. The process continues until a certain condition is satisfied and fires the output to the external

environment. There are several choices of activation functions in different form and may be linear or nonlinear, the sigmoid function is the most commonly used one, whose general form is given as:

$$h_j = f(x_j) = \frac{1}{1+e^{-x_j}} \tag{2.2}$$

such that

$$\frac{df}{dx_j} = f(x_j)[1-f(x_j)] \tag{2.3}$$

An activation function or also called a transfer function plays an important role to prevent the output value from being too large beyond the data range. The outputs of the hidden neurons are calculated using a transfer function associated with the neurons of this layer. The neurons in the output layer then receive the activation signals from the hidden neurons as follows:

$$y_j = \sum_j h_j W_{jk} \tag{2.4}$$

where W_{jk} is the weight of the connection between the neurons j and k in the hidden and output layers, respectively. Similar calculations are carried out to obtain the results of each neuron of the following layer until the output layer. These activation signals are transformed again to produce the outputs of the neural network by using a sigmoid function (2.5) or a liner transfer function:

$$o_k = f(x_k) = \frac{1}{1+e^{-y_k}} \tag{2.5}$$

which are the ANN system predicted values and then compared with their actual values to minimize the error. The error function at the output neurons is defined as

$$E(W) = \frac{1}{2}\sum_K (d_k - o_k)^2 \tag{2.6}$$

where d_k and ok are the desired and predicted values of the outputs, respectively. This process repeats for the ANN structure to be trained. For a successful process the objective of the algorithm is to train all the weights of the neural network minimizing the total mean squared error so that the neural network achieves the best performance.

Among others, ANN's most advantage is that no need of knowing the concrete functional relationship (i.e., mathematical modeling) between outputs and inputs. An ANN such as a three-layer BP-ANN can be used to learn and approximate any relationship, linear or nonlinear with sufficient large number of neurons in the hidden layer. With a specific approach to determine the number of neurons of the hidden layer not existing, many alternative combinations are possible. In the case that the mathematical modelling of functional relationship between outputs and inputs is unknown or rather difficult or even impossible to be determined, ANN could be more suitable than multiple regression analysis (MRA), which requires the relationship between output and inputs be known or specified.

Another remarkable advantage is that ANN has no restriction on the number of output. It is able to model the multiple inputs and multiple outputs data.

Apart from the fact that ANN has been successfully and widely used in a variety of applications and become very popular, there are also some obvious disadvantages, for example:

1) The subjectivity in designing an ANN and determining its parameters, e.g., the number of hidden layers, the number of neurons each hidden layer, the learning rate parameter determination, momentum factor and epoch, and the learning rule and transfer function determination are purely subjective rather than objective. Accordingly, different people may get different results for the same problem because they may design different networks and choose different parameters for training and testing.

2) ANN's connection weights (can either be positive or negative) are not easy to be explained in some special application context.

3) ANN is usually used for no constraint problem. If there are any constraint conditions on inputs and/or outputs, it will be difficult for an ANN to be trained to satisfy those constraints.

Although ANN has the above mentioned disadvantages, its advantages, especially the ability on learning and

approximate linear or nonlinear relationship far outweigh the disadvantages.

3. ANN Modeling for Viscosity Prediction of ILs Mixture

3.1. *Dataset and input variable selection*

In the work, we have done test for viscosities of binary [C_n-mim][NTf_2]-methanol and [C_n-mim][NTf_2]-ethanol mixtures measured at temperatures between 293.0K to 313.0K. Further analysis of the data reveals a compositional dependency of the viscosity, with a negative nonlinear departure from a linear compositional dependency based on viscosity of individual components.

The inputs selected for the ANN are elemental mole fractions and temperature, in Kelvin, normalized as follows:

$$\text{Temperature input} = \frac{\text{Temperature - minT}}{\max T - \min T} \tag{3.1}$$

Here minT and maxT are the minimal and maximal temperatures respectively. Molar fractions were normalized to have a sum of 1.

3.2. *Performance function*

The proper selection of the function which is minimized when adjusting the parameters of a model, the performance function, is important. In this study, we use the standard deviation of the correlation which is calculated using the following equation.

$$STD = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\eta_{cal,i} - \eta_{\exp,i}\right)^2} \tag{3.2}$$

for both IL-methanol and IL-ethanol mixtures, where N is the total number of experimental points, η_{cal} the value calculated using a given model, and η_{exp} the measured viscosity. STD represents the standard deviation of the correlation.

3.3. *Architecture and training*

There are many different types of neural networks. Each differs from the others in network topology and/or learning algorithm. In this work, a simple feed forward networks using back propagation (BP-ANN) learning algorithm is one of the commonly algorithm which is used for prediction, which is a multilayer feed-forward network with hidden layers between the input and output layer. The simplest implementation of BP learning updates the network weights and biases in the direction of the negative gradient which the performance function decreases most rapidly.

The topological structure of the ANN was shown in Fig. 2.1. The number of input neurons was based on the analysis purpose, which is equal to the number of parameters affecting viscosity. The output layer consisted of one neuron, i.e., viscosity.

The determination of the number of neurons in the hidden layer is more art than science. A very rough rule of thumb is given by Ref. 43:

$$h = \frac{\text{Number of training cases}}{5\times(m+n)} \tag{3.3}$$

where h is the number of neurons in the hidden layer, m the number of neurons in the output layer, and n the number of neurons in the input layer. In this study, a trial-and error method is performed to optimize the number of neurons in the hidden layer. Fig. 3.1 shows the STD of the viscosity prediction for [C_4-mim][NTf_2]-ethanol binary mixtures in correlating with the number of neurons in the hidden layer). It is observed that the number of neurons in hidden layer was systematically varied to obtain a good estimate of the data being trained. However, too many neurons in the hidden layer may cause over-fitting problem, which results in the network can learn and memorize the data very well (good at training), but lacks the ability to generalize (bad at testing). But no sufficient number of neurons in hidden layer will lead to the lack of learning ability for the network. Based on the experimental analysis, a BP-ANN with 4 or 5 neurons in the hidden layer seems to be appropriate for this application in most of cases. A BP-ANN with 4 neurons is the best for this case.

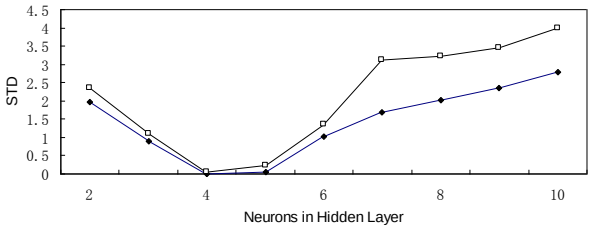


Fig. 3.1 SDT versus number of neurons in the hidden layer for: (♦) during the training, and (◊) during the prediction.

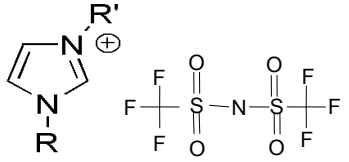
In addition, over-fitting is a problem sometimes appears in ANN application, there have been different approaches for preventing over-fitting, for example, training a network by supplying the validation data or early stopping, or training a neural network using regularization. In this application, due to the fact that the total number of sample data is not that big, to aovid over-fitting the data, we choose to use the regularization approach. Accordingly, the training function (`trainbr`) was used. This function applies the Levenberg–Marquardt algorithm with Bayesian regularization[44] (`trainbr` is a network training function that updates the weight and bias values according to Levenberg-Marquardt optimization. It minimizes a combination of squared errors and weights, and then determines the correct combination so as to produce a network which generalizes well. The process is called Bayesian regularization). The output values for training were the viscosity values in Pa s. All other settings were by default the newff function in Neural Network tool book[44] under MATLAB 7 (to create a feed-forward backpropagation network) which were used for ANN creation and training, respectively. By default the inputs are normalized to values between −1 and 1, the hidden neurons use tansigmoid transfer functions,[44] and the output neurons use a linear transfer function.

4. Materials and Experimental Methods

The work is focused specially on analysis of viscosities of IL series [C_n-mim][NTf_2] (*n*=4, 6, 8, 10) in polar solvents, methanol and ethanol, with concentration between 0M to 1M measured at temperatures ranged from 293.0 to 328.0K under atmospheric pressure.

The ionic liquids used in this work were synthesized by a metathesis reaction between halide (1-alkyl-3-methylimidazolium bromide) and lithium bis(trifluoromethylsulfonyl)imide.[45] The basic molecular and fluid properties of the synthesized ionic liquids are listed in Table 4.1. Synthesized ionic liquids were kept in a glove box after being dried at 70 °C under vacuum for two days, and the water contents of the samples were regularly checked by Karl–Fischer titration or Coulometry. Water content of the dried ionic liquids was 350±50 ppm. It has been reported [46] that water contents of 350ppm to 700ppm could result in viscosity values that are 3 % and 6 % lower than the absolute dry ILs, respectively. While 3% to 6% change in viscosity of pure ionic liquid is relatively significant, the trace water impact on the binary compositional viscosity is negligible after the addition of methanol or ethanol which results in exponential decrease of viscosity at even the lowest methanol/ethanol molar ratio examined in this study.

Table 4.1 Physical-chemical properties of pure ILs [C_n-mim][NTf_2] used in this work.

IL	C_4	C_6	C_8	C_{10}
Molecular weight (g/mol)	419.01	447.32	475.38	503.40
Molar volume ($cm^3\,mol^{-1}$)	291.10	326.20	359.40	391.52
Viscosity at 298.15 K (mPas)	56.2	86.3	115	146
Molecular structure	 imidazolium [C_n-mim]$^+$ bis-trifluoromeththylsulfonyl-imide NTf_2			

Analytical grade methanol and ethanol were used to make up the binary ionic liquid-solvent mixtures. These two polar solvents were chosen for their simplicity, widespread use as industrial solvents, and solvating ability for both hydrophobic and hydrophilic ionic liquids. They are also easily removable from the mixture by evaporation as the ionic liquids have near zero vapour pressure. The viscosities of pure methanol and ethanol at 298.15 K are 0.5514 mPas and 1.0784 mPas respectively.[47] Binary ionic liquid and methanol/ethanol mixtures were prepared by directly weighing constituent components according to predetermined compositional molar ratio. Measurements of viscosity or molar volume were carried out immediately after sample preparation. A cone and plate rheometer (Brookfield programmable DV-II+ Viscometer) was used for viscosity measurement. Digital density meter DMA 4500 (Anna ParrR) was used for the measurement of molar volume. Temperature control for the viscosity and density

measurement is within the precision ±0.1K. A minimum five sets of readings were taken for each sample, and the arithmetic mean, with standard deviation less than 3%, was used for further analysis and calculations.

5. Results and Discussions

The ANN was implemented using under MATLAB 7.0 environment. ANN has been trained and test for viscosity of [C_n-mim][NTf_2]-ethanol binary mixtures with *n*=4, 6, 8, and [C_n-mim][NTf_2]-Methanol binary mixtures with *n*=4, 6, 8, and 10, at the temperature range T=293-328K in terms of different molar ratios, respectively, where 1/2 of data set has been used for training and 1/2 of data have been used for test purpose to evaluate their accuracy and trend stability.

5.1. *ANN to predict compositional viscosity over a broad range of temperatures*

After training the ANN, the models become ready for testing and evaluation by unseen data with network. To examine the predictive ability of the ANNs, it is useful to look at plots of the predicted property value versus the measured value. A scatter plot of typically measured experimental data against the ANN model predictions for [C_4-mim][NTf_2]-ethanol binary mixtures was shown in Figure 5.1. 3-D plot of viscosity for [C_4-mim][NTf_2]-ethanol binary mixtures at the temperature range T=293-328K in terms of different molar ratios is shown in Fig. 5.2 (with training scheme) and Fig. 5.3 (standalone figure to be more clear).

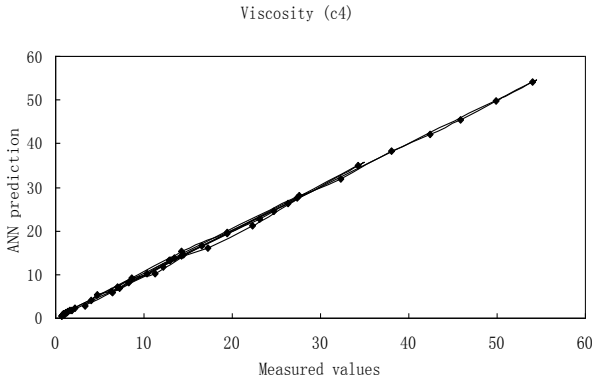


Fig. 5.1: Evaluation of ANN performance; A scatter plot of typically measured experimental viscosity data (mPas) against the ANN model for unseen viscosity data for [C_4-mim][NTf_2]-ethanol binary mixtures

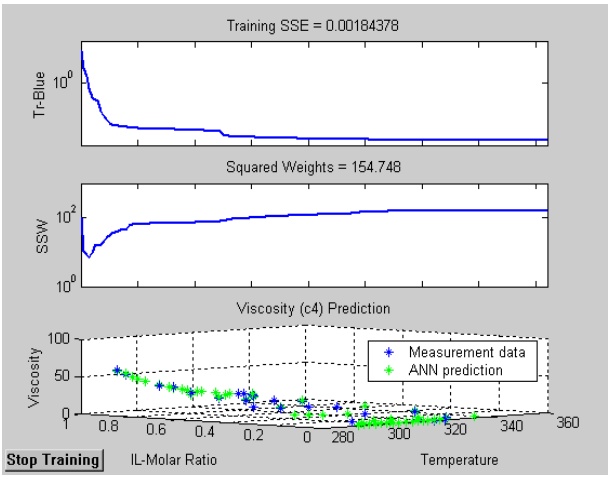


Fig. 5.2. Viscosity for [C_4-mim][NTf_2]-ethanol binary mixtures at the temperature range T=293-328K in terms of different molar ratios.

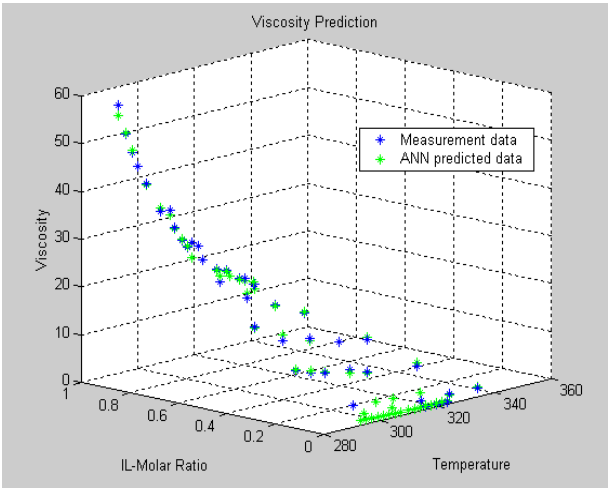


Fig. 5.3. Viscosity for [C_4-mim][NTf_2]-ethanol binary mixtures at the temperature range T=293-328K in terms of different molar ratios.

Results show a good agreement between experimental data and the predicted by ANN, while the artificial neural network has the overall agreement between experimental and prediction values in all of temperature ranges.

The standard deviation of ANN predictions are presented in Table 5.1 for the binary IL-methanol and IL-ethanol mixture respectively.

Table 5.1 Standard deviation of ANN prediction in compositional viscosity for each individual binary [C_n-mim][NTf_2]-ethanol and methanol system at temperature range T=293-328K

ethanol		methanol	
C_n	STD(ANN)	C_n	STD(ANN)
C4	0.0495	C4	0.0889
C6	0.0814	C6	0.1722
C8	0.1180	C8	0.1393
C10	0.1316	C10	0.2433

From Table 5.1, ANN achieves good performance. This is mainly attributed to the strong ability of BP neural network to learn nonlinear relationships among outputs and inputs.

In addition, the scatter plots for [C_n-mim][NTf_2]-ethanol binary mixtures with *n*=4, 6, 8, 10 were summarized in Fig. 5.4.

It is obvious from this figure that the ANN provides results very close to process measurements. The predictions which match measured values should fall on the diagonal line. Almost all data lay on this line, which confirms the accuracy of the ANN model. ANN's results showed acceptable estimation performance for prediction of the viscosity.

All results exhibit that neural networks can predict the viscosity satisfactory as a new method instead of approximate and complex analytic equations or thermodynamic models.

5.2. *The effects of various amounts of fluxing components at the wide range of temperatures*

Compositional viscosity predictions of liquid mixtures were evaluated to determine the effect of various amounts of fluxing components at the wide range of temperatures.

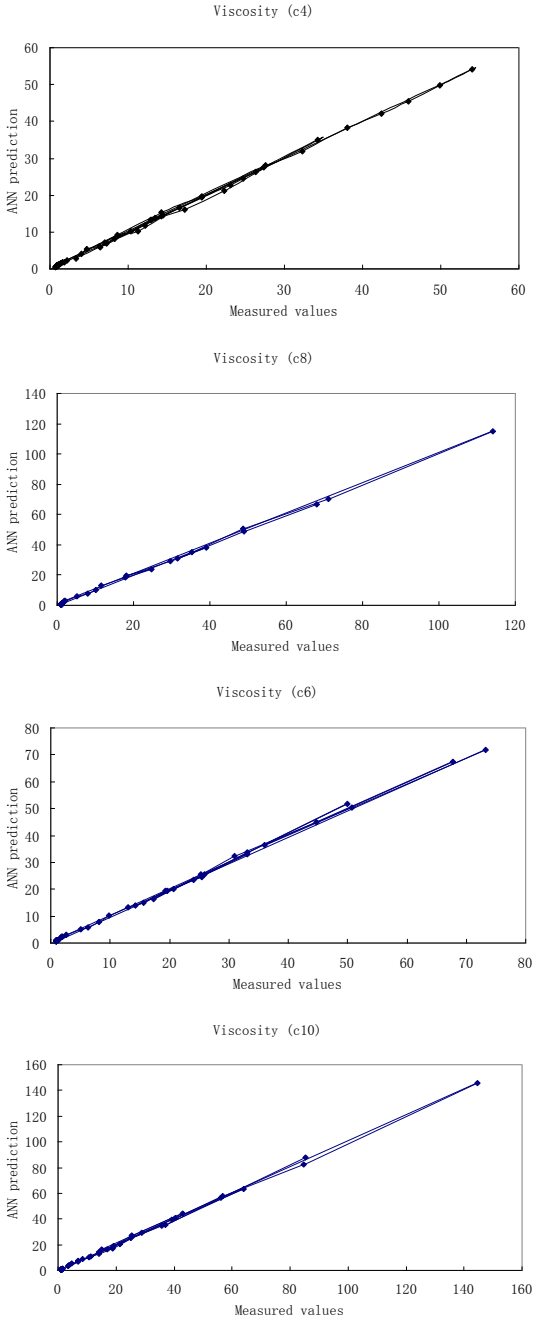


Fig. 5.4 A scatter plot as an evaluation of ANN performance for [C_n-mim][NTf_2]-ethanol mixture with *n*=4, 6, 8, 10.

Liquid viscosity strongly depends on temperature due to changes in thermal/kinetic energy at molecular level and changing activation energy of viscous flow. Temperature change may also significantly alter the nature of molecular interactions in binary mixtures, thereby increasing or decreasing the effect of molecular interactions on compositional viscosity. At elevated

temperatures, the compositional viscosity usually decreases logarithmically with increasing temperature. At lower temperatures, a dramatic viscosity will decrease and non-Newtonian behaviour may occur.

Viscosity predictions were made via ANN assuming that the viscosity composition is uniform. Fig. 5.5 showed the effect of adding polar solvent respectively under a broad range of temperatures T=293-328K.

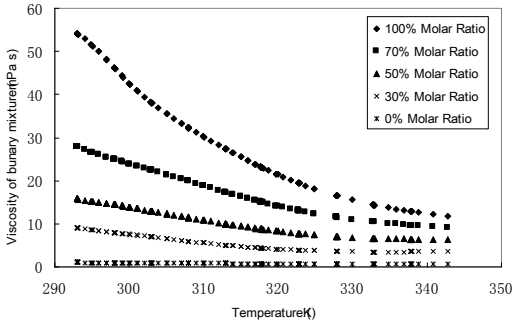


Fig. 5.5 Viscosity predictions with varying amounts of molar ratio for [C_4-mim][NTf_2]-ethanol mixture at temperature range T=293-328K.

Firstly, Fig. 5.5 shows dramatic decrease of compositional viscosity value with increasing temperatures for different fraction of component, suggesting the influence of molecular structure and chemical/physical interactions on compositional viscosity is much reduced at elevated temperature when molecules acquire large thermal and kinetic energy, becoming more mobile and less bound by chemical forces.

In addition, the effect of IL concentration on compositional viscosity also decreases with increasing temperature, as can be seen by the reduction in slope with increasing temperature in Fig. 5.5, the addition of polar solvent molar dose seems to reduce the viscosity sensitivity to temperature at higher temperatures. When the temperature is over 340K, the addition of molar has very little effect on the viscosity.

The results could also suggest that if different fluxing component is added, operation would have to be kept about how much temperature to have the viscosity below the recommended maximum.

For example, if we take 12 Pa s as the recommended maximum viscosity, if the molar ratio is 50%, operation would have to be kept above 300K to have the viscosity below the recommended minimum.

Addition of 70% molar increases the required temperature to 320K, while addition of 100% molar further increases the required temperature to 340K.

This kind of analysis is more useful to show the effect of adding each component under a broad range of temperatures when investigating more than two component mixtures. For the different components additions may yield different results about the required temperatures.

Furthermore, as can be seen by the reduction in slope with increasing temperature in Fig. 5.5, the addition of molar dose seems to reduce the viscosity sensitivity to temperature at higher temperatures. Consequently, if the viscosity threshold is set to a higher limit, addition of a fluxing agent may reduce the required operation temperature.

Viscosity predictions with varying amounts of molar ratio for [C_4-mim][NTf_2]-methanol mixture at temperature range T=293-328K yields similar results.

5.3. *ANN to predict compositional viscosity for different ILs over a broad range of temperatures*

In Section III-A, we discussed the ANN prediction for each individual [C_n-mim][NTf_2]-ethanol (also methanol) system when n=4, 6, 8, 10, in which the three input node are the temperature and the two molar ratio. The question would be that if we can predict viscosity of [C_4-mim][NTf_2] based on the measured data of [C_n-mim][NTf_2]-ethanol (also methanol) when n=6, 8, and 10. Now the input node increase into 4, i.e., the temperature, the two molar ratios, and also the number indicate the IL alkyl chain length.

The standard deviation of ANN predictions are presented in Table 5.2 for the binary IL-methanol and IL-ethanol mixture respectively. Again, the resulting ANN was tested statistically and found to be of quality predictive power. These results confirmed that the

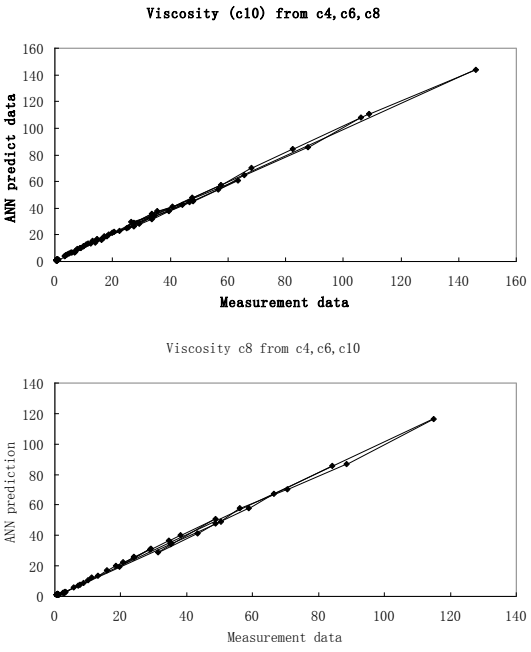
trained ANN could be effective in predicting the viscosity providing valuable tool.

Table 5.2 Standard deviation of ANN prediction in compositional viscosity for binary [C_n-mim][NTf_2]-ethanol and methanol system at temperature range T=293-328K

ethanol		methanol	
C_n	STD(ANN)	C_n	STD(ANN)
C_4 from C_6, C_8, C_{10}	0.0895	C_4 from C_6, C_8, C_{10}	0.2003
C_6 from C_4, C_8, C_{10}	0.1192	C_6 from C_4, C_8, C_{10}	0.1989
C_8 from C_4, C_6, C_{10}	0.1215	C_8 from C_4, C_6, C_{10}	0.1492
C_{10} from C_4, C_6, C_8	0.1288	C_{10} from C_4, C_6, C_8	0.2433

In addition, the scatter plots for [C_n-mim][NTf_2]-ethanol binary mixtures with *n*=4, 6, 8, 10 were summarized in Fig. 5.6.

The obtained results indicated that ANN can be very useful to predict IL mixture viscosity with varied alkyl chain length. As far as we know, there is no viscosity prediction methodology being able to take account of varied alkyl chain length and compositional temperatures at this same time.



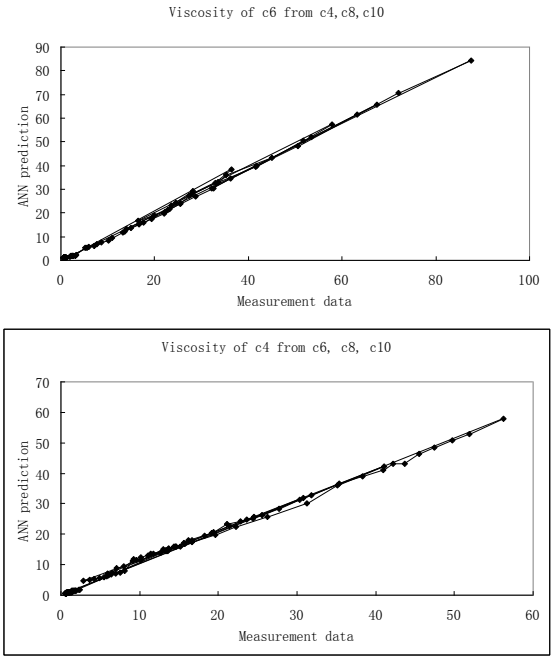


Fig. 5.6 A scatter plot as an evaluation of ANN performance for [C_n-mim][NTf_2]-ethanol mixture with *n*=4, 6, 8, 10.

6. Conclusions

In this work, the ability of ANN for modeling and prediction of viscosity prediction of ILs mixture has been investigated. The STD analysis based results are used for verification of the suggested approach. Results showed a good agreement between experimental data and the predicted by ANN. An important feature of the model is it doesn't require any theoretical knowledge during the training process. The results show that the presented new neural network models that provide better predictions and higher accuracy than the existing and proposed model. In each case, the ANN does not require a data relationship to predict the compositional viscosity but rather relies on the field data obtained for training. Since the ANN does not rely upon theoretical relations, it can easily be expanded to include other factors such as extra new components.

The work proposed only considered binary mixtures, but since the ANN does not rely upon theoretical relations, it can easily be expanded to the case for ternary and quaternary mixtures and even more new components. In addition, it can also be expanded to include other factors such as IL alkyl chain length, different type of IL or solvent, shear rate for non-Newtonian IL. For example, an attempt has been made to account for ionic liquid alkyl chain length. None of the conventional regression models mentioned previously directly account for both the carbon chain

length and measurement condition. With neural networks, the alkyl chain length can be accounted for by one or more additional inputs.

For this reason, although there are some obvious disadvantages of ANN as stated in literatures, it is still recommended that the ANN approach could be applied in ILs fields for reduction in error, computational time, and cost of overproduction and underproduction, because its advantages such as the ability to handle nonlinear data far outweigh the disadvantages.

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