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ρ–T–P prediction for ionic liquids using neural networks

Juan A. Lazzús *

Departamento de Física, Universidad de La Serena, Casilla 554, La Serena, Chile

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ABSTRACT

Densities of ionic liquids have been estimated using a combined method that includes an artificial neural network and a simple group contribution method. A total of 2410 data points of density at several temperatures and pressures (ρ–T–P), corresponding to 250 ionic liquids, have been used to train this network, developed using Matlab. To discriminate between the different substances, the molecular mass and the structure of the molecule, were given as input variables. Then, the ρ–T–P values of 72 other ionic liquids (773 data points) were predicted and results compared to experimental data from the literature. The study shows that the chosen artificial neural network and the group contribution method represent an excellent alternative for the estimation of densities of ionic liquids with acceptable accuracy.

1. Introduction

Ionic liquids (IL's) have been the object of increasing attention due to their unique physicochemical properties, such as high thermal stability, large liquidus range, high ionic conductivity, high solvating capacity, negligible vapor pressure, and nonflammability which make them ideal solvents for green chemistry and clean synthesis (Gardas *et al.*, 2007a).

Liquid density (ρ) of IL is a physical property required in several design problems and in liquid metering calculations (Gardas and Coutinho, 2008). The design of equipment such as condensers, reboilers, liquid/liquid two phase mixer–settler units, sizing of storage vessels, calculation of tower heights, material and energy balances involving liquids, vapor–liquid and liquid–liquid separation processes, all require accurate values of liquid density (Valderrama *et al.*, in press).

Density is probably the most measured property of IL's. One reason is that its determination is straightforward and can be very accurate if the appropriate equipment, usually a pycnometer or densimeter, is used (Esperança *et al.*, 2006a; Mantz and Trulove, 2002). Since many of the IL's have heavy anions, one should expect that their density would be relatively higher than common industrial solvents. The reported densities of IL's vary between 1.12 and 2.4 g/cm^3 (Mantz and Trulove, 2002).

There exist a great variety of analytical expressions that allow one to correlate and predict the density of liquid fluids. Such expressions are usually based on the use of adjustable parameters for each fluid (correlations), on the corresponding state principle, and on semi-empirical and predictive methods with the group contribution method (GCM).

Among the classical proposals presented in the literature, the approach developed by Lydersen (1955) is perhaps the most widely used GCM to estimate critical properties. Later, Joback and Reid (1987) developed a method that is frequently mentioned in the literature and used in several applications. In all these methods, the property of a compound is calculated by summing up the contributions of certain defined groups of atoms, at the same time considering the number frequency of each group occurring in the molecule.

Several authors use these concepts of GCM to calculate the density of diverse substances (Ammon and Mitchell, 1998; Ammon, 2001; Elbro *et al.*, 1991; Ihmels and Gmehling, 2003; Stefanis *et al.*, 2005; Tarver, 1979); however, in these works, the authors do not incorporate IL's. Recently, Ye and Shreeve (2007) proposed of group activity method for the estimation of densities of room-temperature ionic liquids and salts. They estimated the density of a small range of ionic liquids with a good accuracy, but the application of their method is restricted to 298.15 K and atmospheric pressure. Gardas and Coutinho (2008), proposed an extension of the Ye and Shreeve group contribution method (Ye and Shreeve, 2007) for the estimation of densities of IL's. The new version allows the estimation of densities in wide ranges of temperature and pressure, but for too small a range of IL's.

Another recent method for estimating the density of IL's is presented by Jacquemin *et al.* (2007), which uses a GCM to predict volumetric properties of ionic liquids as a function of temperature and pressure.

* Tel.: +56 51 204128; fax: +56 51 206658.
E-mail address: jlazzus@dfuls.cl.

Abbreviations: ANN, artificial neural network; GCM, group contribution method; IL's, ionic liquids; *PTV*, pressure–temperature–volume; ρ–T–P, liquid density–temperature–pressure.

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Nomenclature

b	bias of the neurons
$f(N)$	transfer function of the neural network
M	molecular weight
N	inputs of the neural network
P	pressure (kPa)
T	absolute temperature (K)
w	weight of the connection among the neurons with the hidden layers
y	output of the neural network
Greek symbols	
ρ	liquid density (g/cm^3)
ρ^{lit}	liquid density experimental
ρ^{calc}	liquid density calculated
Δ	deviations

The aforementioned group contribution methods use linear and nonlinear regression techniques to represent the relations among the variables of a given system. The relationship between the physical and thermodynamic properties is highly non-linear, and consequently an artificial neural network (ANN) can be a suitable alternative to model the underlying thermodynamic properties. ANN is an especially efficient algorithm to approximate any function with a finite number of discontinuities by learning the relationships between input and output vectors (Hagan *et al.*, 1996). Thus, an ANN is an appropriate technique to model the nonlinear behavior of chemical properties.

Taskinen and Yliruusi (2003) presented a complete list of properties that have been analyzed in the literature using different approaches to artificial neural networks. 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 (Ganguly, 2003; Laugier and Richon, 2003; Piotrowski *et al.*, 2003; Sözen *et al.*, 2004). To the best of the author knowledge there is no application for liquid density–temperature–pressure (ρ–T–P) prediction, such as the one presented here, and certainly there is no publication on the prediction of these properties for IL's using ANN.

2. The neural network used

Many models of neural networks have been used to estimate of thermodynamic properties (Espinosa *et al.*, 2001; Yaffe and Cohen, 2001). In this work a feedforward backpropagation neural network was used, which is one that is very effective in representing non-lineal relationships among variables. The network, programmed with the software Matlab, consists of a multilayer network, in which the flow of information spreads forward through the layers while the propagation of the error is back. In this process, the network uses some factors called "weights" (w_i) to quantify the influence of each fact and each variable. There are two main states in the operation of a neural network: learning and validation. The learning or training is the process by which a neural network modifies the weights in answer to initial information.

The most basic architecture normally used for this type of application involves a feed-forward backpropagation neural network consisting of three layers (Taskinen and Yliruusi, 2003). With a specific approach to determine the number of neurons of the hidden layer not existing, many alternative combinations are possible. In this research, the optimum number of neurons was determined by adding neurons in systematic form during the learning process.

This program considers the reading of the necessary data organized in an Excel file: ρ–T–P experimental data for each of the 272 IL's are used to train the network. To distinguish between the different physical and chemical properties of the substances considered in this study, so the network can discriminate and learn in the optimal form, the following properties are considered: the molecular mass M (size) and the structure of the molecules, represented by the number of well defined groups forming the molecule, are provided as variables.

The steps to calculate the output parameter (density), using the input parameters, are the following ones:

The net inputs are calculated (N) for the hidden neurons coming from the inputs neurons. For a hidden neuron:

$$N_j^h = \sum_i^n w_{ij}^h p_i + b_j^h \quad (1)$$

where p corresponds to the vector of the inputs of the training, j is the hidden neuron, w_{ij} is the weight of the connection among the input neurons with the hidden layer, and the term b_j corresponds to the bias of the neuron j of the hidden layer, reached in its activation. Starting from these inputs, the outputs of the hidden neurons are calculated (y) using a transfer function f^h associated with the neurons of this layer.

$$y_j^h = f_j^h\left(\sum_i^n w_{ij}^h p_i + b_j^h\right) \quad (2)$$

Similar calculations are carried out to obtain the results of each neuron of the following layer until the output layer.

To minimize the error, the transfer function f should be differentiable. In the net two types of transfer function were used: the lineal function $f(N_{jk}) = (N_{jk})$ and the hyperbolic tangent function (*tansig*) defined by the equation:

$$f(N_{jk}) = \frac{e^{N_{jk}} - e^{-N_{jk}}}{e^{N_{jk}} + e^{-N_{jk}}} \quad (3)$$

All the neurons of the network have an associate activation value for a given input pattern. The algorithm continues finding the error that is presented for each neuron, except those of the input layer. After finding the value of the gradient of the error, the weights of the network are actualized, for all layers.

This process repeats for the total number of patterns be trained. For a successful process the objective of the algorithm is to modernize all the weight and bias of the neural network minimizing the total mean squared error. Fig. 1 presents a block diagram of the program developed.

3. Data used and training

In this study, 2410 experimental data points of 250 IL's were used to train the ANN, introducing as entrance parameters: temperature (T), pressure (P), molecular mass (M), and the structural groups that form the molecules. The output parameter was ρ. Table 1 shows the 45 groups used as entrance variables. The value associated with the structural group was defined as 0 when the group does not appear in the substance and n, when the group appears n times in the substance. For instance, for 1-propyl-3-methylimidazolium hexafluorophosphate, besides the data points (T, P), the property data are: M = 270.2 (kg/kmol), and the structure of the molecule [–CH_3] = 2, [–CH_2–] = 2, [=CH–(ring)] = 3, [N– (ring)] = 1, [=N-(ring)] = 1, [–P] = 1 and [–F] = 6. Table 2 shows the properties for all IL's considered in the study.