World Wide Journal of Multidisciplinary Research and Development

WWJMRD 2016; 2(2): 1-6
www.wwjmrd.com
e-ISSN: 2454-6615

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Artificial neural network model to predict thermodynamic properties of low molar mass protic ionic liquid

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Abstract
This paper presents a model based on artificial neural networks (ANNs) to predict density and ultrasonic velocity of short aliphatic chain protic ionic liquids. An experimental database was used for developing the model, where the input variables in the network were temperature, number of carbon, hydrogen, nitrogen and oxygen atoms into each compound, as well as, the number of specific functional groups. The learning task was done through a nonlinear activation function of sigmoid and hyperbolic tangent nature. Correlation coefficients of 0.9783–0.9830 and mean squared error (MSE) of $1.2328 \cdot 10^{-4}$ and $2.5783 \cdot 10^{-6}$ were obtained for density and ultrasonic velocity, respectively, which suggests that the proposed ANNs model shows robust and accurate character for prediction of physical properties of these new promising chemicals.

Keywords: Artificial neural networks; protic ionic liquid; temperature; density; ultrasonic velocity

Introduction
Thermodynamic data play a key role in the understanding, design and optimization of chemical processes and they should be obtained by experimental procedures or non-experimental techniques. Experimental techniques belong to the most correct, accurate and reliable, but require expensive technical equipment, qualified researchers and long time necessary for experiment. If due to any of these items, the corresponding experiments cannot be realized, different theoretical estimation procedures should be applied. These methods include empirical relationships (correlations of the required property with different variables, geometrical molecular characteristics, different constants, etc), those based on theory (statistical thermodynamics) and several procedures based on an additive principle (mainly functional groups contribution methods).
A different approximation to this problem was derived from computational model for artificial neural networks (ANNs) based on mathematics and algorithms called threshold logic [1]. In modern software implementations of ANNs, the approach inspired by biology has been largely abandoned for a more practical based on statistics concepts and signal processing. There is no single formal definition of what a neural network is but usually it gathers two main characteristics, contains sets of adaptive weights (tuning parameters that should be modified by a learning algorithm), and capability of approximating non-linear functions of their data inputs. They are essentially simple mathematical models but sometimes they are also associated with a particular learning algorithm or rule. A common use of ANNs model is really referring to the interconnections between the neurons in the different layers of each system. An example system has three layers, the first layer has input neurons which send data via synapses to the second layer of neurons, and then via more synapses to the third layer of output neurons. More complex systems will have more layers of neurons, some having increased layers of input neurons and output neurons. The synapses store parameters called "weights" that manipulate the data in the computations.
This modern approach of computation has been applied in various disciplines which includes engineering, environmental science, business, chemical technology, computing or nanotechnology, being ANNs a very useful model for problem solving and machine learning. Recently, it has aroused great interest in academic and industrial areas related to neoteric substances as ionic liquids, due to their functionality on technology and their amazing properties, which probably it will result in a complete renovation of core chemical processes

in a next future [2]. A serious handicap that is delaying the widespread use of these compounds on an industrial level is the huge lack of thermodynamic information and the absence of reliable prediction methods for simulation studies.

With these facts in mind, continuing previous studies [3-6], in this work, we apply an artificial neural network (ANNs) model to predict density and ultrasonic velocities of a new group of protic ionic liquids (2-hydroxyethylammonium acetate (2-HEAA), 2-hydroxydiethylammonium acetate (2-HDEAA), 2-hydroxytriethylammonium acetate (2-HTEAA), 2-hydroxyethylammonium propionate (2-HEAPr), 2-hydroxydiethylammonium propionate (2-HDEAPr) and 2-hydroxytriethylammonium propionate (2-HTEAPr)) at different temperature.

These compounds gather an inverse dependence on the temperature for density and ultrasonic velocity, pointing out the particular form of packaging and the strong dependence of the kinetics of ions.

The main advantages of ANNs for thermodynamic properties estimation are that they should model without requiring any assumptions about the nature of phenomenological mechanisms, their ability to learn from the linear and nonlinear relationships between variables from a set of examples, their multiple modeling capability of simultaneously outputs and a reasonable application of the model to sparse data sets [7].

The obtained results for these new promising chemicals were of high accuracy, despite the strong interactions among ions and the high non-ideal trend of both physical properties.

Experimental

Preparation of the ionic liquids

The amine compounds (monoethanolamine, diethanolamine or triethanolamine, Merck Synthesis, better than 99%) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating is necessary for increasing miscibility between reactants and then allow reaction. The organic acid (acetic or propionic acid, Merck Synthesis, better than 99%) was added dropwise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Figure 1 shows the structures of the studied protic ionic liquids in this work.

Materials and equipment

During the course of the experiments, the purity of ionic liquids was monitored by density, ultrasonic velocity and ionic conductivity measurements. The pure ionic liquids were stored in sun light protected form, constant humidity and low temperature. Usual manipulation and purification in our experimental works was applied [5, 6]. The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} gcm^{-3} and 1 ms^{-1}. Apparatus calibration was performed periodically in accordance with vendor instructions. Accuracy in the measurement temperature was better than $\pm 10^{-2}$ K. The molar mass, experimental and literature data of the studied protic ionic liquids at 298.15 K are gathered in Table 1 [8-10].

Results and discussion

Neural Networks

Artificial Neural Networks (ANNs) are a powerful tool for modeling data with high-efficiency for physical properties of fluids and solutions. For the measured data of the studied protic ionic liquids [6], each database was randomized and partitioned into three groups: training (65%), cross validation (15%) and testing (20%). The cross-validation data set was used to test the performance of the network while training was in progress as an indicator of the level of generalization. Testing data set was used to examine the network generalization capability. To improve the behaviour of the ANN, input and output data were normalized according to Eq. 1 [11].

$$x_{i\,nom} = \left(\frac{ub - lb}{max_i - min_i} \right)(x_i - max_i) + ub \qquad (1)$$

where ub and lb are the limits normalized value and max_i and min_i, are the maximum and minimum values found within variable i.

Description of the ANN architecture

The ANN used in this work is a Multi-Layer Perceptron model (MLP) and supervised learning. It consists of the one input layer, one more hidden layer and one output layer. This is the most common flexible and general-purpose kind of ANN [11, 12]. The selection of the number of the hidden layers and the number of processing elements (neurons) in hidden layers, was performed using the method of trial and error until a good behavior of the networks is obtained. In this work, the number of hidden neurons varied from 2 to 6, with only one hidden layer. The information between layers is processed through a transfer or activation function. This function is typically a nonlinear activation function of sigmoid and hyperbolic tangent nature. In the most applications, hyperbolic tangent function behaves better as compared to sigmoid function [11, 13].

Figure 2 shows an ANN with two neuron in the input layer, three neurons in the hidden layer and two neurons in the output layer. Coefficients associated with the hidden layer (weights and biases) are grouped in the matrices P_1 and B_1 and coefficients associated with the output layer are grouped in the matrices P_2 and B_2. Using de matrix notation, the output of neural networks can be represented by the expression [11]:

$$Y = f_2\left(W_2 f_1\left(W_1 X + B_1\right) + B_2\right) \qquad (2)$$

The performance of the networks was measured by mean square error (MSE) and regression coefficient (r^2) between the predictive values of the network and the target or experimental values, as follows.

$$MSE = \frac{\sum_{k=1}^{k}\sum_{l=1}^{l}\left(z_{lk} - t_{lk}\right)^2}{KL} \qquad (3)$$

$$r^2 = 1 - \frac{\sum_{k=1}^{k}\sum_{l=1}^{l}(z_{lk} - t_{lk})^2}{\sum_{k=1}^{k}\sum_{l=1}^{l}(z_{lk} - t_{m})^2} \quad (4)$$

During the learning process, training and validating data sets were simultaneously used to avoid over-fitting. This was done by 4-fold-cross-validation and in each cross validation, three initial weights were randomly selected. The learning stopped after 3000 iterations. Then, average MSE and average r^2 from four cross validation were calculated to find the best network. The best network model was that of minimum MSE and maximum r^2 using the normalized predicted and target data, and this network was not over-fitting the data. This network was then used to predict outputs using the testing data set to further check if the network achieved good generalization. To predicted density and ultrasonic velocities values, the ANN model can be implemented using the algebraic system of equations, which is obtained by substitution of the corresponding weights and coefficient matrices in Eq. 2.

ANN Processing Elements or Neurons (PE) in hidden layer

The optimum number of hidden nodes was chosen upon minimized the difference between predicted ANN values and desired outputs, using r^2 and MSE during testing as performance indicators (Table 2). It may be important to point out that the optimal number of neurons in the hidden layer is four, and greater numbers of PE only to increase the structure complexity but do not improve the network behaviour.

ANN Performance

Prediction performance of ANN model (density and ultrasonic velocity) for training and testing data sets is shown in Figure 3a-3f.

The predicted values were very close to the desired values for both density and ultrasonic velocity. The mean of residuals was $1.15\ 10^{-5}$ and $2.24\ 10^{-4}$ for density and ultrasonic velocity, respectively. These results show a good approximation to a normal distribution around zero with 99% to find residuals below $6\ 10^{-3}$ gcm^{-3} for density and 3 ms^{-1} for ultrasonic velocities, which means a good generalization ability of ANN model for the range of values of these properties.

Conclusions

An ANN – based model was developed for prediction of density and ultrasonic velocity of the studied protic ionic liquids for wide range of temperatures. The model was able to predict successfully volumetric and acoustical properties of these compounds. The obtained results suggest that the proposed ANNs model shows robust and accurate character for prediction of physical properties of these new promising chemicals.

Table 1: Comparison of densities, ultrasonic velocities and ionic conductivities for the studied pure protic ionic liquids at 298.15 K and other relevant information.

	M/(gmol^{-1})*	**ρ/(gcm^{-3})**		**u/(ms^{-1})**		**□·10^3/(mScm^{-1})**	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
2-HEAA	121.1352± 0.0070	1.148360	1.146220[10] 1.149039[9]	1790.94	1790.73[9]	554.4	NA
2-HDEAA	165.1877± 0.0099	1.167483	1.170200[8]	1863.35		1051.38	NA
2-HTEAA	209.2402± 0.0128	1.188917		1833.25		236.61	NA
2-HEAPr	135.1617± 0.0083	1.092595		1636.90		462.33	NA
2-HDEAPr	179.2142± 0.0112	1.134793		1730.48		542.52	NA
2-HTEAPr	223.2667± 0.0141	1.141970		1663.73		252.45	NA

*Expressed in intervals of molar mass, NA: not available

Table 2: Effect of the number of hidden nodes on MSE and r^2 for density and ultrasonic velocity during testing.

Neurons in the Hidden Layer	**ρ (gcm^{-3})**		**u 10^{-3} (ms^{-1})**	
	MSE	**r²**	**MSE**	**r²**
1	$2.6788\ 10^{-4}$	0.9812	$1.7835\ 10^{-2}$	0.9770
2	$4.4035\ 10^{0}$	0.8901	$1.2112\ 10^{-3}$	0.8863
3	$1.2328\ 10^{-4}$	0.9830	$1.2749\ 10^{-3}$	0.9782
4	$1.1500\ 10^{-5}$	0.9825	$2.2400\ 10^{-5}$	0.9783
5	$1.0728\ 10^{-4}$	0.9820	$8.7143\ 10^{-5}$	0.9778
6	$5.3758\ 10^{-5}$	0.9823	$6.9088\ 10^{-5}$	0.9781
7	$3.6750\ 10^{-2}$	0.9122	$7.1583\ 10^{-1}$	0.9083
8	$1.3288\ 10^{-7}$	0.9825	$2.5883\ 10^{-6}$	0.9783
9	$1.6505\ 10^{-1}$	0.8901	$2.5783\ 10^{-6}$	0.9783
10	$8.5716\ 10^{-2}$	0.7249	$1.6696\ 10^{0}$	0.7218

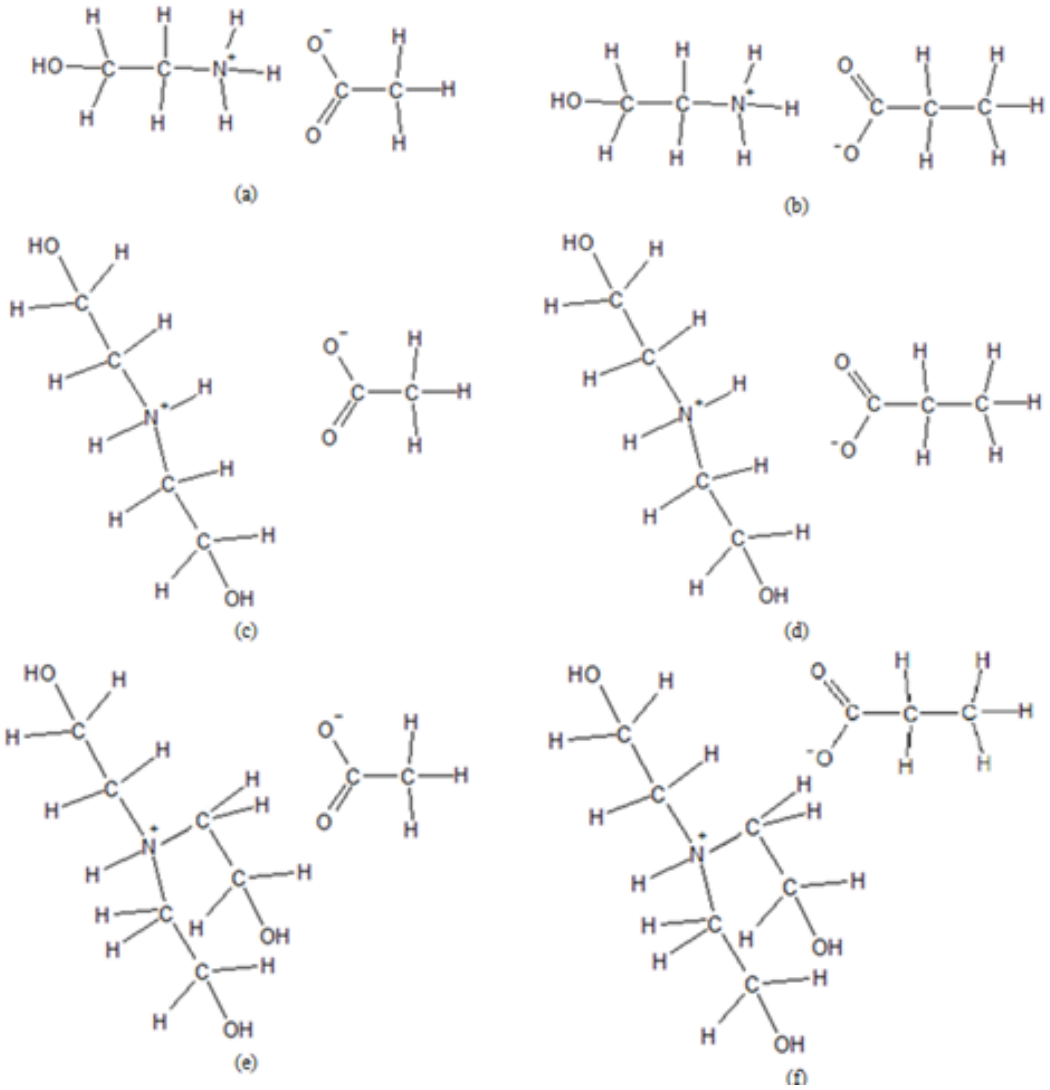

Fig 1: Chemical structures of the studied protic ionic liquids (a) 2-hydroxyethylammonium acetate (2-HEAA), (b) 2-hydroxyethylammonium propionate (2-HEAPr), (c) 2-hydroxydiethylammonium acetate (2-HDEAA), (d) 2-hydroxydiethylammonium propionate (2-HDEAPr), (e) 2-hydroxytriethylammonium acetate (2-HTEAA) and (f) 2-hydroxytriethylammonium propionate (2-HTEAPr)

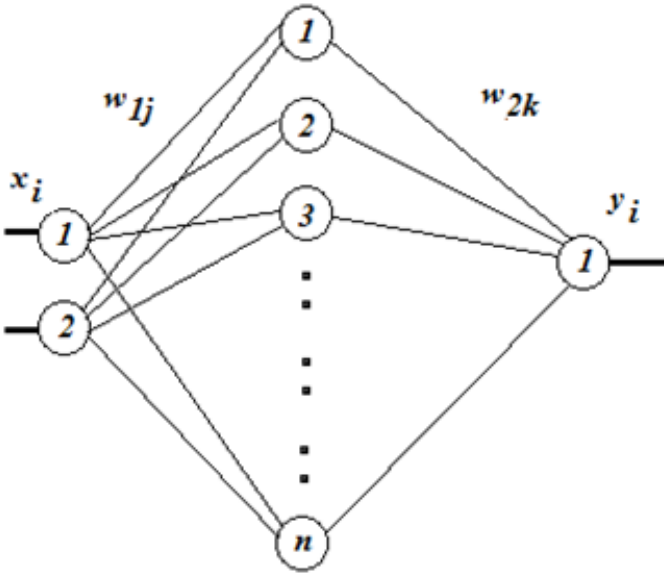

Fig 2: ANN architecture with two neuron in the input layer (x), three neurons in the hidden layer and two neurons in the output layer (y).

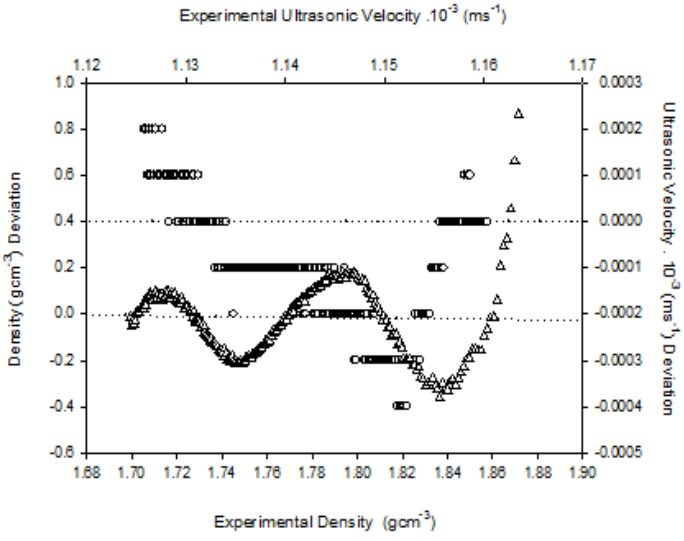

Fig 3a: Residual analysis of the estimated data ((○) density and (∆) ultrasonic velocity) from the network for 2-hydroxyethylammonium acetate (2-HEAA).

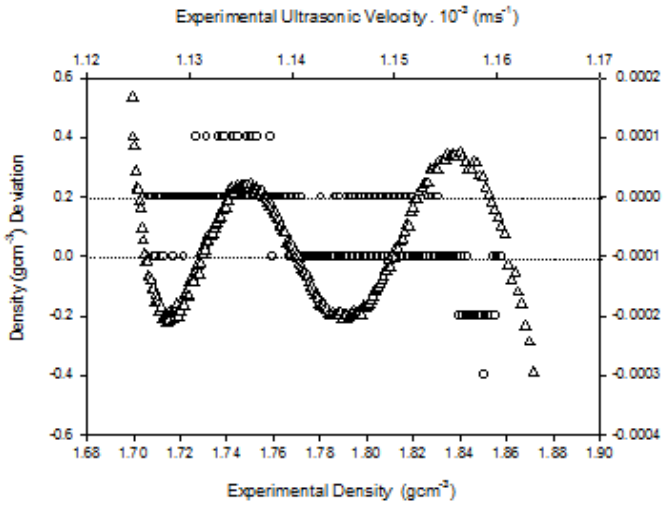

Fig 3b: Residual analysis of the estimated data ((○) density and (△) ultrasonic velocity) from the network for 2-hydroxydiethylammonium acetate (2-HDEAA).

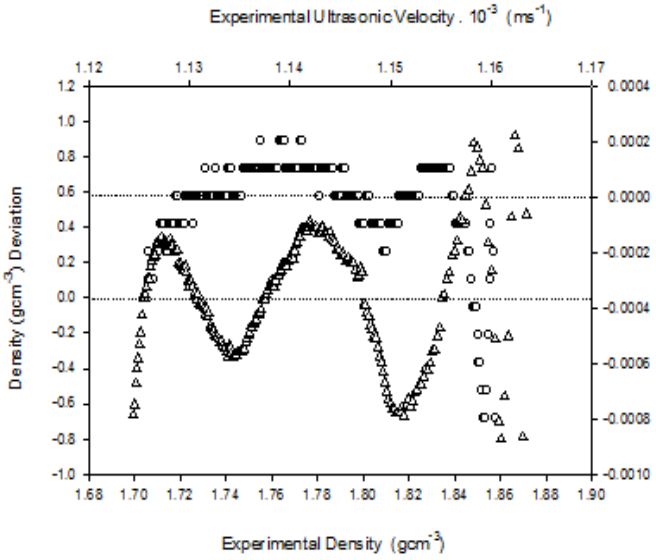

Fig 3c: Residual analysis of the estimated data ((○) density and (△) ultrasonic velocity) from the network for 2-hydroxytriethylammonium acetate (2-HTEAA).

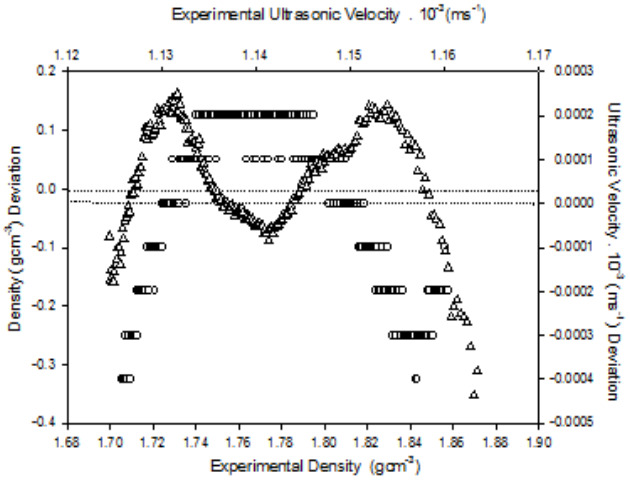

Fig 3d: Residual analysis of the estimated data ((○) density and (△)ultrasonic velocity) from the network for 2-hydroxyethylammonium propionate (2-HEAPr).

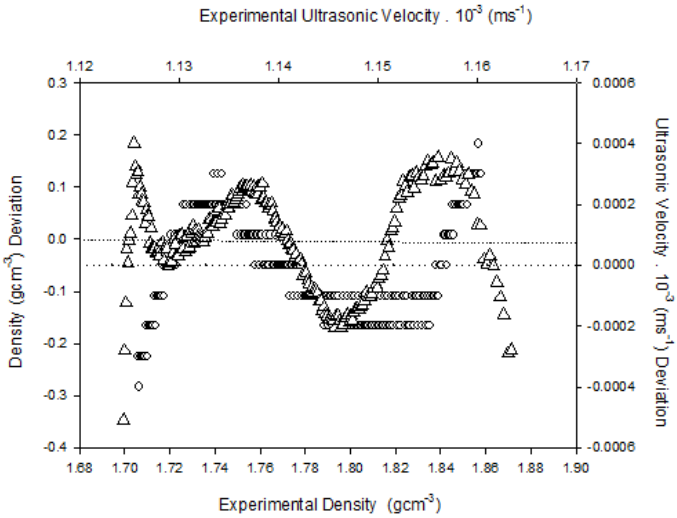

Fig 3e: Residual analysis of the estimated data ((○) density and (△) ultrasonic velocity) from the network for 2-hydroxydiethylammonium propionate (2-HDEAPr).

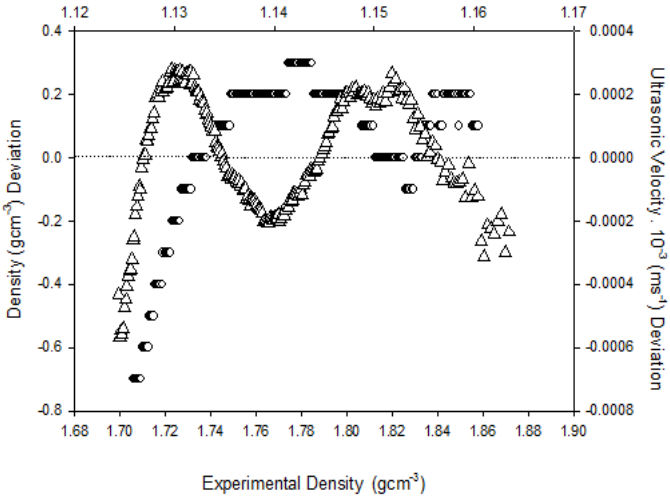

Fig 3f. Residual analysis of the estimated data ((○) density and (△) ultrasonic velocity) from the network for 2-hydroxytriethylammonium propionate (2-HTEAPr).

Acknowledgments

The authors would like to acknowledge FAPESB (Projeto Ação Referência, PET0071/2013) and CAPES (scientific grant R.S. Andrade) for their support in developing this research.

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