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Property Estimation of Water/Alcohol/Ionic Liquid Ternary System: Density

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ABSTRACT: One of the most highly important applications of ionic liquids is for separation of the components of water/alcohol azeotropic mixture. The use of ionic liquids for this purpose creates a ternary system for which the determination of thermodynamic behavior and physical properties is highly matter of interest in design and operation of effective separation plants. In this work, the density of the aqueous ionic liquid ternary system is modelled based on three intelligent connectionist approaches. For the modeling, 1663 experimental density data points for ternary systems including 17 different ionic liquids in four aqueous alcohols (methanol, ethanol, propanol, and pentanol) solution were analyzed and taken into account at temperature range [288 343] K and pressure ranges [100 3000] kPa. The Shuffled complex evolution (SCE) algorithm was employed for optimization of the model parameters and constants. Four statistical parameters of R^2, AARD, RMSE and STD were calculated for the connectionist models to compare their performance in the degree of comprehensiveness and accuracy. The highly matched results of the modelling with experimental demonstrates that the intelligent approach provides a suitable replacement for conventional thermodynamic models and equation of states which need too many fitting parameters.

Key words: Density, Alcohol water, Azeotropic mixture, Ternary system, LSSVM, SVM, ANN, SCE

1- Introduction

The purification of the alcohol is a major challenge in the industrial separation units such as distillation processes, because the components of aqueous alcohols have close boiling points, thereby forming azeotropic mixtures [1]. There are many methods available for doing separation a similar constituents of a mixture such as: distillation, extraction [2], membrane technology [3-5],

and etc. Extractive distillation is widely used in industry to separate these azeotropic mixtures. In this type of distillation, the separation of azeotropic mixture is obtained by adding a third component (the entertainer) as a mass agent for changing the relative volatility [6, 7]. There are many disadvantages of common entertainers (solid salts and organic compounds) used in extractive distillation such as corrosion, toxicity, volatility and high energy. Therefore, it is necessary to find another environmentally friendly entertainer for extractive distillation with easy regeneration and good performance in altering the relative volatility of the azeotropic mixtures.

Nowadays, the use of green renewable commodities is now beginning to enter into a wide range of applications in industry. Fuels [8-19], solvents [20-22], catalysts [23, 24] are now developing to ameliorate the quality of the human life one earth, whilst preserving the human resources for the future generations. The ionic liquids are considered as environmentally attractive alternatives for organic solvents [25]. They are type of salts with melting points below 100 °C. Ionic liquids are composed of two parts-an anion and a long chain cation. One of the strongest advantages of the use ionic liquid is that their properties can be easily manipulated by changing in cation or anion for a specific application. Negligible vapor pressure, non-flammability, high heat capacity, chemical and thermal stability are other main properties of ionic liquids [26] which makes them suitable as green solvents. There are a lot of studies that considered the ionic liquids as nonvolatile entertainers for separation processes of azeotropic mixtures.

The proper estimation of characteristics of ternary system is matter of thermodynamics. It is necessary to develop separation processes. There are many studies experimentally evaluating the physicochemical properties of the systems including water/alcohol/ionic liquid [27-42]. Therefore, it is highly matter of interest to have a simple and robust model to accurately predict the physiochemical properties such as density for water/alcohol/ionic liquid ternary systems. In the

recent years, intelligence methods are used as appropriate alternatives for the conceptual models, physically based models, and conventional statistical models. Artificial neural network (ANN), support vector machine (SVM) and least square support vector machine (LSSVM) are some examples of intelligent models. The models based on these intelligent approaches are now beginning to enter and solve variety of engineering problems [43-45]. ANN model, a computational system based on the operation of biological neural networks, has become popular as feasible tool in a variety of fields of study in recent years [46-50]. Lashkarbolooki et al. [51] evaluated the capability of ANNs for correlating the binary density of the ILs systems containing methanol for 426 data points. They concluded that their proposed ANN model was able to correlate the density of ionic liquid + methanol systems. Dopazo et al. [52] developed different ANNs to predict the density, viscosity and refractive index of binary and ternary mixtures of ionic liquids. SVM model is another intelligence model, proposed by Vapnik in 1995 [53], increasingly gained popularity to be employed in various engineering and science disciplines [54, 55]. The results of SVM model are obtained through quadratic programming (QP). Finally, the LSSVM method, introduced by Suykens and Vandewalle [56] as a modified version of conventional SVM, has the idea of the equality constraints which is the major advantage of LSSVM over the original SVM.

In this study, the density of water/alcohol/ionic liquid ternary systems has been predicted by intelligence methods including ANN, SVM and LSSVM models. These methods have been constructed by wide range of experimental data gathered from literature (1663 data points) for this ternary system with 17 different ionic liquids. The shuffled complex evolution (SCE) has been applied to obtain the adjustable parameters of SVM and LSSVM models. The accuracy of intelligent models was evaluated by common statistical parameters including average absolute

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relative deviation (AARD), root mean square error (RMSE), standard deviation error (SDE), and coefficient of determination (R^2). These developed models could be reliable tools for density estimation of water/alcohol/ionic liquid ternary system, even more efficient than thermodynamic models as they are generalized for several alcohols and ionic liquids and they offer a less prediction error compared to the thermodynamic models.

2. Model development

To develop a generalized model for density of alcohol/water/ionic liquid ternary system, a comprehensive repository of density data points for covering different ionic liquids and alcohol is required. For this purpose, data points available in the literature was collected and employed for the model development. In the next section, the data gathering is described with more detailed information about the materials and range of data points.

2-1. Data acquisition

The comprehensive experimental data covering wide range of material and operating points are required to have an accurate and precise model. Therefore, the experimental density data of water + alcohol + ionic liquid system at wide range of temperature and pressure were gathered from published studies in the literature over the years. Note that the data includes the density of both raffinate and extract phases. In this study, a data set consisting of 1663 data points for 17 different ionic liquids and four alcohols have been collected. Table 1 gives the characteristics of data points for the model development including the reference from which data was captured, type of alcohol and ionic liquid for each reference, number and range of density data points for each ternary system, ranges of temperatures and pressures, ranges of mass fractions of alcohol, water, and ionic in each ternary systems. The 17 ionic liquids were those widely implemented for the separation of

alcohol form the water. Table 2 shows the IUPAC names and chemical formulas of studied ionic liquids.

The density model development is also generalized for several types of ionic liquids and alcohols. To this end, the types ionic liquids and alcohol was taken into account of model development by assigning some input variables for them. The properties of ionic liquids including M_W, T_c, P_c and ω and molecular weight of alcohol was considered as input variable for model development. For those types of ionic liquids without the critical properties reported in the literature, the properties were estimated using Valderrama group contribution method [57, 58].

After gathering the required data, estimating the properties of ionic liquids and alcohols, data were classified into an input and output sets to develop the models. The input data are temperature, pressure, mole fraction of components (x_1, x_2 and x_3), molecular weight of alcohol and properties of ionic liquid, and the output parameter is density of water/alcohol/ionic liquid ternary system. The range of input and output parameters have been shown in Table 3.

2-2. Data normalization

For this study, data are scaled prior to the model development to remove the negative effects of the larger data on the smaller ones. For this purpose, all the inputs and output were normalized between 0 and 1. The normalization has been performed by the following equation:

$$x_n = \left(\frac{x}{1.5 \times x_{max}}\right) \times 0.8 + 0.1 \tag{1}$$

where x_n is normalized data, x_{max} is the maximum value of the data and x is the experimental data. The normalized values have been finally converted to their original values.

2-3. Mathematical model

To model the density of the alcohol/water/ionic liquid ternary systems including multilayer perceptron (MLP) neural network, support vector machines (SVM), least square support vector machine (LSSVM) were employed. The shuffled complex evolution was used for purpose of the optimization of SVM and LSSVM parameters. For ANN, trial and error strategy was utilized to obtain the optimized structure of a network for density estimation. The structure of the MLP neural networks is depicted in Figure 1. Input layer, hidden layer(s), and output layer are the main parts of MLP neural networks. Each layer is composed of some neurons defined as fully interconnected processing units. It should be mentioned that the number of neurons in the input and output layers are the same with number of input and output data, respectively. In constructing an optimized structure of networks, it is of interest to determine the minimum number of hidden layers and neuron therein which provides a reasonable accuracy for the density estimation. A trial and error method was used to obtain the number hidden layers and neurons in hidden layer. All input signals are received by input layer and transmitted to other neurons for processing in hidden layer. Then, the output layer received the information from hidden layers. The parameters of such network are synaptic weights and biases. These parameters are adjusted by using network error as a benchmark through receiving the input data within the training algorithm. An iterative optimization procedure starting with random guesses on synaptic weights and biases has been applied to train MLP neural network. This training process continues to reach a minimum value in squared weights and errors over several iterations.

SVM model is the second employed mathematical tool for density estimation. In this mathematical tool, a train sample of N data samples with input vector x and a dimension of $N \times n$ (n is the number of input parameters) is correlated to the relevant target samples y_k via a regression function. The regression function of SVM is defined based on the following equation:

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$$f(\mathrm{x}) = w^T \varphi(\mathrm{x}) + b \tag{2}$$

where $f(\mathrm{x})$ denotes the regression function. The w^T represents weight vector, $\varphi(\mathrm{x})$ indicates the kernel function, and b is a bias term. The parameters of this regression function (w^T and b) can be optimized from the following cost function [53]:

$$Cost\ function = \frac{1}{2}\ w^T + c \sum_{k=1}^{N}(\xi_k - \xi_k^*) \tag{3}$$

The abovementioned cost function should be satisfied the following condition:

$$\begin{cases} y_k - w^T \varphi(\mathrm{x}_k) - b \le \varepsilon + \xi_k & k = 1, 2, \dots, N \\ w^T \varphi(\mathrm{x}_k) + b - y_k \le \varepsilon + \xi_k & k = 1, 2, \dots, N \\ \xi_k . \xi_k^* \ge 0 & k = 1, 2, \dots, N \end{cases} \tag{4}$$

where x_k and y_k represent the input vector at the train sample k and the relevant target sample, respectively. The ε denotes a fixed precision of the approximation function and ξ_k (or ξ_k^*) is slack variable. The variable c is the deviation from the desired ε in Eq. (3) considered as the tuning parameter of the SVM model. The cost function is minimized by Lagrangian as follows:

$$L(a.a^*) = -\frac{1}{2} \sum_{k.I=1}^{N}(a_k - a_k^*)(a_I - a_I^*)K(\mathrm{x}_k, \mathrm{x}_I) - \varepsilon \sum_{k=1}^{N}(a_k - a_k^*) + \sum_{k=1}^{N} y_k(a_k - a_k^*) \tag{5}$$

$$\sum_{k=1}^{N}(a_k - a_k^*) = 0 \quad . \quad a_k . a_k^* \in [0, c] \tag{6}$$

$$K(\mathrm{x}_k . \mathrm{x}_I) = \varphi(\mathrm{x}_k)^T \varphi(\mathrm{x}_I) \quad k = 1, 2, \dots, N \tag{7}$$

where a_k and a_k^* are Lagrangian multipliers. The SVM regression function is obtained as:

$$f(\mathrm{x}) = \sum_{k.I=1}^{N}(a_k - a_k^*)\,K(\mathrm{x}, \mathrm{x}_k) + b \tag{8}$$

The unknown variables (a_k, a_k^*, and b) are obtained by solving a quadratic programming problem. The parameters ε, c and those in the kernel function are the adjustable parameters of SVM model.

The LSSVM is another mathematical approaches utilized for modelling of the density. The LSSVM is the least square modification of SVM through introducing a system of equations instead of a nonlinear quadratic programming in original SVM [56]. The LSSVM method represents a new optimization issue as:

$$\text{Cost function} = \frac{1}{2} w^T w + \frac{1}{2} \gamma \sum_{k=1}^{N} e_k^2 \tag{9}$$

where γ is the factor of regularization which is as an adjustable parameter .e_k represents the error of LSSVM in train data set. The equation (8) is optimized by the following equality constraint:

$$y_k = w^T \varphi(x_k) + b + e_k \tag{10}$$

The Lagrangian is utilized to find the solutions of the optimization in equation (9) along with its constraint introduced in Eq. (10) as follows:

$$L(w.b.e.a) = \frac{1}{2} w^T w + \frac{1}{2} \gamma \sum_{k=1}^{N} e_k^2 - \sum_{k=1}^{N} a_k (w^T \varphi(x_k) + b + e_k - y_k) \tag{11}$$

where a_k are support values or Lagrange multipliers. The derivatives of Eq. (10) should be equated to zero to acquire the solution as follows:

$$\begin{cases} \dfrac{\partial L}{\partial w} = 0 \Rightarrow w = \sum_{k=1}^{N} a_k \varphi(x_k) \\ \dfrac{\partial L}{\partial b} = 0 \Rightarrow \sum_{k=1}^{N} a_k = 0 \\ \dfrac{\partial L}{\partial e_k} = 0 \Rightarrow e_k = \gamma e_k \quad k = 1,2,\dots,N \\ \dfrac{\partial L}{\partial a_k} = 0 \Rightarrow w^T \varphi(x_k) + b + e_k - y_k = 0 \quad k = 1,2,\dots,N \end{cases} \tag{12}$$

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Eq. (12) shows 2N + 2 equations and 2N + 2 unknown parameters (a_k, e_k, w, and b). Thus, the parameters of LSSVM can be obtained by solving the system of equations defined in Eq. (12). The system of linear equations can be rewritten in matrix form as:

$$\begin{bmatrix} 0 & 1_v^T \\ 1_v & \Omega + \gamma^{-1}I \end{bmatrix} \begin{bmatrix} b \\ \alpha \end{bmatrix} = \begin{bmatrix} 0 \\ y \end{bmatrix} \tag{13}$$

where $y = [y_1 \dots y_N]^T$, $1_N = [1 \dots 1]^T$, $\alpha = [\alpha_1 \dots \alpha_N]^T$, I is an identity matrix, and $\Omega = \varphi(\mathrm{x}_k)^T$ in which $\varphi(\mathrm{x}_l) = K(\mathrm{x}_k, \mathrm{x}_l) \; \forall \, k, l = 1,2, \dots, N$. $K(\mathrm{x}_k. \mathrm{x}_l)$ is the kernel function considering the account the Mercer limitation [59]. The radial basis function (RBF) Kernel has been used in this study as follows:

$$K(\mathrm{x}. \mathrm{x}_k) = \exp(\frac{-|| \, \mathrm{x}_k - \mathrm{x}||^2}{\sigma^2}) \tag{14}$$

where σ^2 is squared bandwidth. The function estimation of LSSVM model is:

$$y(\mathrm{x}) = \sum_{k=1}^{N} \alpha_k K(\mathrm{x}, \mathrm{x}_k) + b \tag{15}$$

Finally, it should be mentioned that the parameters σ^2 and γ are the adjustable parameters of LSSVM model.

2-4. Computational procedure

The 1663 data points were randomly classified into two subsets, namely train and test data sets, to develop all three studied intelligent models. For this work, 75% of data points were used to train the intelligent models and increase their capability in prediction of density. The remaining 25 % of data points have been applied for test set to investigate the validity of models' prediction.

Temperature, pressure, mole fraction of components (x_1, x_2 and x_3), molecular weight of alcohol and properties of ionic liquid (M_W, T_c, P_c and ω) have been used to develop the intelligent models. The best structure of ANN model was determined through evaluating different networks. The adjustable parameters of SVM (c, ε, and σ^2) and LSSVM (γ and σ^2) have been obtained by SCE [60] through the experimental train data. SVM and LSSVM models have been constructed after finding the optimum parameters. The prediction data were obtained by replacing the test data sample into these models. The validity of models can be evaluated through these predictions.

2-5. Accuracy of intelligent models

The accuracy and reliability of studied intelligent models have been checked by several statistical and graphical error analyses such as coefficient of determination (R^2), average absolute relative deviation (AARD), root mean square error (RMSE), and standard deviation error (STD). The formulation of these statistical parameters are as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(\rho_{Pred}(i) - \rho_{Exp}(i)\right)^2}{\sum_{i=1}^{N}\left(\rho_{Pred}(i) - \bar{\rho}_{Exp}(i)\right)^2} \tag{16}$$

$$\% \, AARD = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|\rho_{Pred}(i) - \rho_{Exp}(i)\right|}{\rho_{Exp}(i)} \tag{17}$$

$$RMSE = \left(\frac{\sum_{i=1}^{N}\left(\rho_{Pred}(i) - \rho_{Exp}(i)\right)^2}{N}\right)^{0.5} \tag{18}$$

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$$STD = \sum_{i=1}^{N} \left(\frac{\left(\rho_{Pred}(i) - \bar{\rho}_{Exp}(i) \right)^2}{N} \right)^{0.5} \tag{19}$$

where ρ_{Exp} and ρ_{Pred} represent the experimental and predicted density, respectively. The $\bar{\rho}_{Exp}$ denotes the average of the experimental data values of density.

3- Results and discussion

The first intelligent approach verified to describe the density of the mixture of aqueous alcohol in ionic liquid was MLP ANN. The ANN is system of interconnected neurons that is able to predict the density of the desired ternary system based on the series of input variables. For analyzing the performance of MLP ANN, an optimum network for prediction of density was constructed. Our primary trial and error analysis reveals that the networks with one hidden layer and thirteen neurons have the less computational costs among other intricate structures while it maintains an acceptable accuracy with low error. Figure 1 depicts the constructed structure of MLP ANN model.

The SVM and LSSVM were also employed for density estimation according to the step-by-step numerical algorithm which is shown in fig. 2. The adjustable parameters of SVM and LSSVM were needed for construction of models based on these intelligent approaches. The SCE mathematical optimization tool was employed to obtain the c, ε, and σ^2 in SVM and γ and σ^2 in LSSVM for the extracted density data bank. The SCE estimated the optimized values $c = 766.421$, $\varepsilon = 0.0010$, and $\sigma^2 = 0.3226$ for the SVM. The optimized parameters $\sigma^2 = 0.4936$ and $\gamma = 9998.59$ were obtained by SCE optimization tools for LSSVM.

After finding the optimum structure of MLP ANN and parameters of the SVM and LSSVM, the efficacy of these initiatives in density estimation of the water/alcohol/ionic liquids was verified. In

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order to visualize the validity of studied intelligent models, crossplot and error distribution curves were sketched and interpreted. The predicted density values of intelligent models are shown versus the experimental density values in crossplot curve. The accumulation of data points around the 45° line (y=x) as the perfect model line confirms the high accuracy of model. The concentrations of data points around the y=x line for MLP ANN is more than the SVM and LSSVM algorithms. An overall same behavior for SVM and LSSVM numerical algorithm was observed - when the density of the alcohol/water/ionic ternary system is low, SVM and LSSVM density estimation deviates from the real density values.

In y=x graphs (crossplots in figure 3) where the predicted and experimental density values were brought in relation to each other, the error of the modelling can be discussed only in a qualitative term and no comment can be made regarding the absolute quantity of error. More comprehensive accuracy analysis can be made by reporting the accuracy of the models in quantitative prospects. To this end, the error distribution curves for MLP ANN, SVM, and LSSVM are given in the figs 4-5. The error trend can be well observed by showing error distribution around the zero error line. Two types of quantitative errors are discussed for the modelling purposes. Figure 4 represents the error of data bank in terms of error deviation:

$$(\text{Error deviation})_i = \rho_{Pred}(i) - \rho_{Exp}(i) \tag{20}$$

The error deviation gives the difference of absolute values of data predicted from its real experimental data. It shows how much the density of water/alcohol/ionic liquid was over-predicted or under-predicted by the current intelligent modelling. For MPL ANN, the error deviation varies from -30 to 50 kg/m^3 in the case of test data. However, this error type for SVM and LSSVM both are in the range [-70 70] kg/m^3. More precisely, the error deviation ranges of

density were almost $-30\ to\ 45$, $-65\ to\ 65$ and $-70\ to\ 65$ for ANN, SVM and LSSVM models, respectively.

Figure 5 represents the error of data bank in terms of relative deviation:

$$(\text{Relative deviation})_i = \frac{\rho_{Pred}(i) - \rho_{Exp}(i)}{\rho_{Exp}(i)} \tag{21}$$

The relative deviation is also reported for the density of the ternary system to provide the relative amount of error associated with each mathematical models. The relative deviation is the absolute quantity of error or error deviation divided by the real quantity of data for the density. The relative deviation for ANN model was almost in range of $-0.04\ to\ 0.05$ while these ranges for SVM and LSSVM models were almost $-0.08\ to\ 0.12$ and $-0.08\ to\ 0.10$, respectively. For the MLP ANN, the relative deviation remains low over all the predicted densities. However, the relative deviation for LSSVM and SVM approaches are high for low quantities of the densities. The number of data points for low density aqueous alcohol systems containing ionic liquids were not as many as the data for dense systems. Lack of enough information for light water/alcohol/ionic liquid systems results in the low accuracy of intelligent models in density estimation. The error analysis graphs can qualitatively approve that the ability of MLP ANN, SVM, LSSVM are in respective better in density estimation of mixture of ionic liquid and aqueous alcohols.

The statistical parameters were utilized to evaluate and compare the accuracy of the developed models quantitatively. They are tabulated in the table 4 for test and train datasets. A better comparison can be made by considering the statistical parameters of the test datasets. The obtained values for test set confirmed the effectiveness of studied models for globalization of results in presence of unseen data. Table 4 shows that the R^2 values were 0.9966, 0.9893 and

0.9916 for ANN, SVM and LSSVM models in train sets, respectively. These values for test sets were 0.9945, 0.9852 and 0.9798 for ANN, SVM and LSSVM models, respectively. The amount of statistical parameters RMSE, %AARD, and STD are also reported in the table 4, all confirms that the strength of the constructed MLP ANN is somewhat more than the SCE-SVM, and SCE-LSSVM in prediction of the density. It can be inferred from the values of four statistical parameters in Table 4 that the density has been successfully estimated with studied intelligent models.

4- Conclusion

The density of water/alcohol/ionic liquid ternary system was predicted by three mathematical intelligent models. The models include the multi-layer perception artificial neural networks (MPL ANN), support vector machine (SVM), and least square support vector machines (LSSVM). The models were generalized over 1663 experimental data for four alcohols and seventeen ionic liquids. Using trial and error, an optimum structure including 1 hidden layer with 13 neurons was obtained for MPL ANN. For this structure of artificial networks, a high possible accuracy is obtained while the network possesses an optimum computational costs in density prediction. To develop the SVM and LSSVM, design parameters of these models are obtained by shuffled complex evolution (SCE) over the datasets. The results in form of both graphical and statistical error parameters showed good consistency between experimental data and predicted values for the constructed networks. All three intelligent models provided an accurate prediction of the density against experimental data for studied ternary systems. The well choice of model parameters and input variables in the development of the studied models are main reasons for the good accuracyin density prediction. Finally, it can be concluded that all studied intelligent methods can be used as invaluable tools for the estimation of density instead of thermodynamic conventional approaches.

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Nomenclature

Abbreviations

AARD   Average absolute relative deviation

ANN   Artificial neural network

IL   Ionic liquid

LSSVM   Least square support vector machine

MLP   Multilayer perceptron

QP   Quadratic programming

RBF   Radial basis function

RMSE   Root mean square error

SCE   Shuffled complex evolution

STD   Standard deviation error

SVM   Support vector machine

Variables

a_k (a_k^*)   Lagrangian multiplier

C   Adjustable parameter of SVM model

e_k Error of LSSVM in training phase

P_c Critical pressure of ionic liquid

T_c Critical temperature of ionic liquid

w^T Weight vector

x_1 Composition of water

x_2 Composition of alcohol

x_3 Composition of ionic liquid

x_k Input vector at the train sample k

x_n Normalized data

y_k Target vector at the train sample k

Greek symbols

γ Regularization parameter

ε Adjustable parameter of SVM model

ξ_k (ξ_k^*)   Slack variable

ρ Density

σ^2 Squared bandwidth

$\varphi(\text{x})$ Kernel function

ω Acentric factor of ionic liquid

Subscripts

Exp   Experimental

Max   Maximum value

Pred   Predicted

Figure captions

Figure 1. Structure of studied MLP neural network.

Figure 2. Schematic presentation of SCE-SVM and SCE-LSSVM models.

Figure 3. Crossplot of density predictions versus experimental densities for studied models at both train and test sets.

Figure 4. The error distribution between experimental and predicted density data point for studied models.

Figure 5. The relative error distribution between experimental and predicted densities for studied models.

Figure 6. Comparison between the experimental data and the results of intelligent models for all data points: a) ANN model; b) SVM model and c) LSSVM model
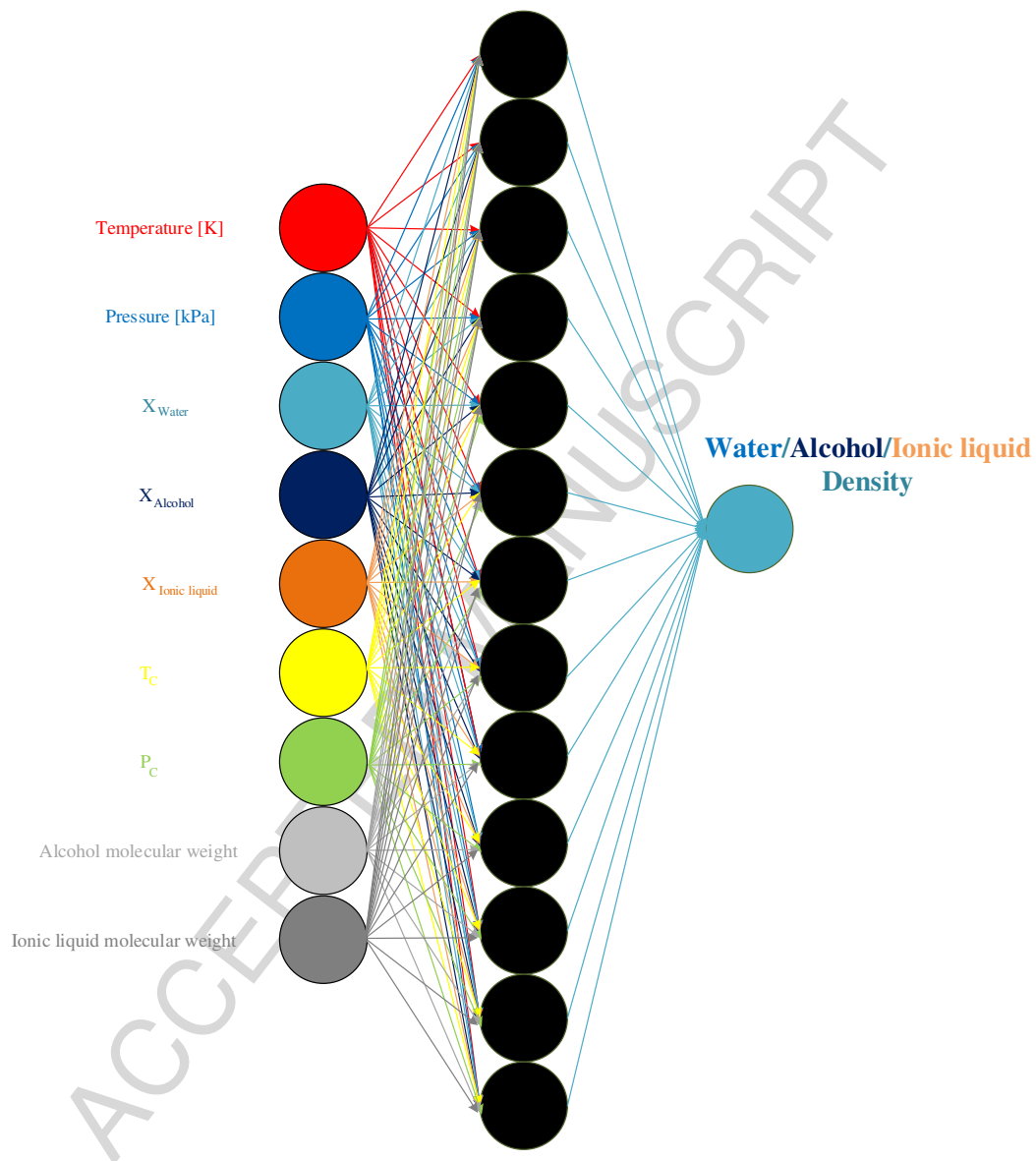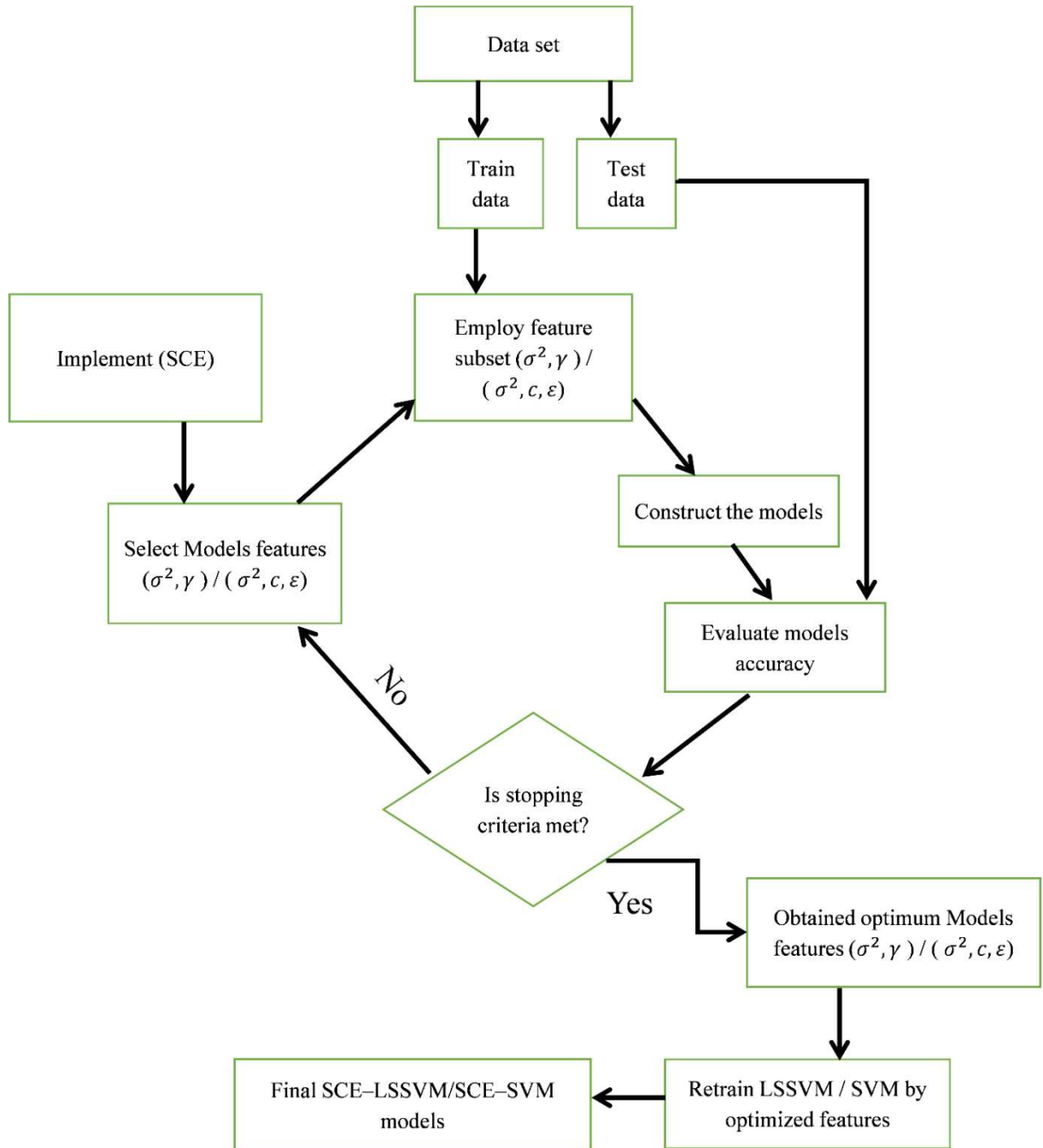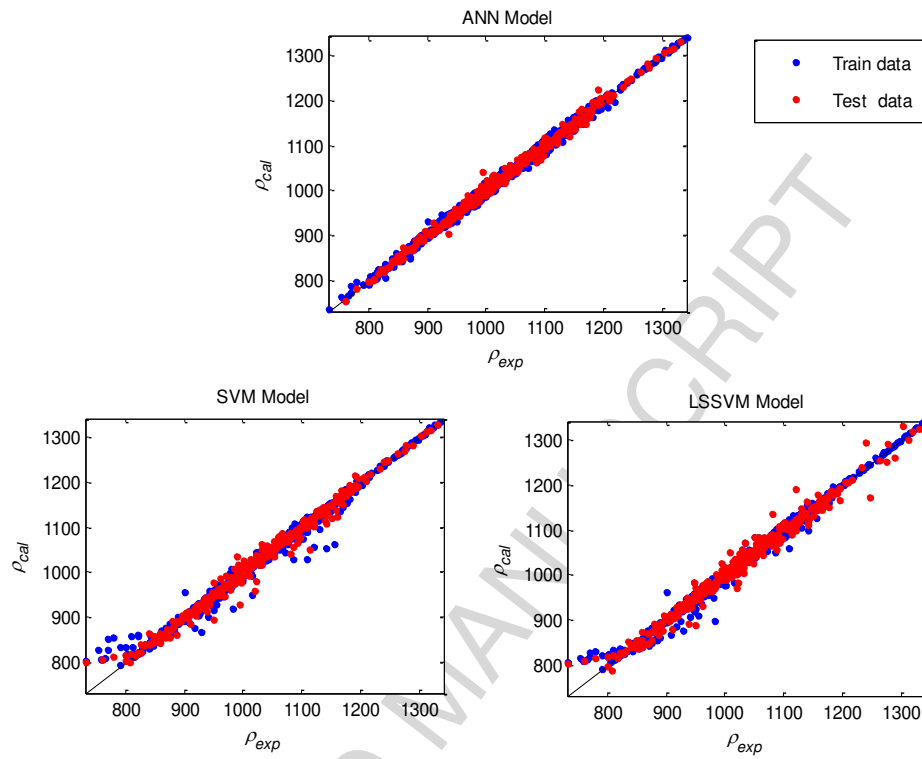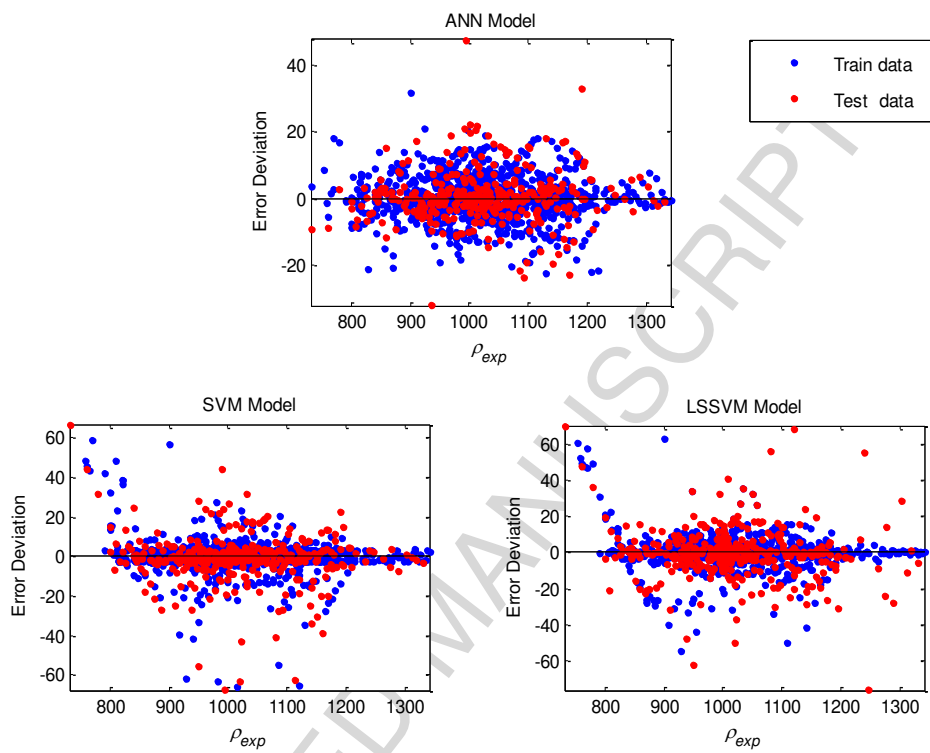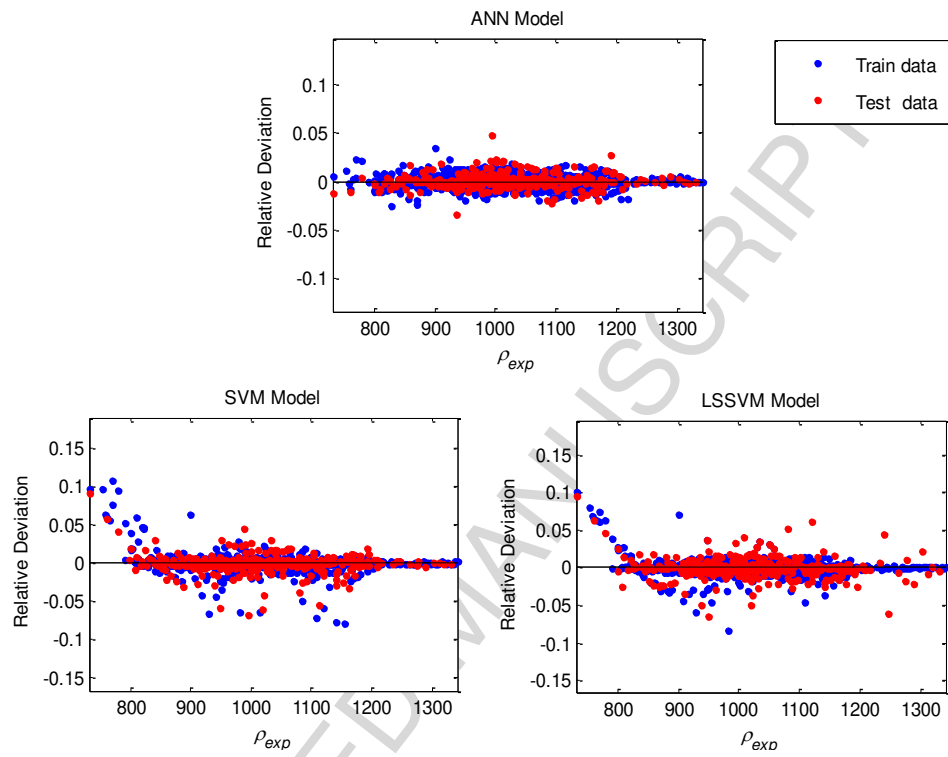
Figure 1-

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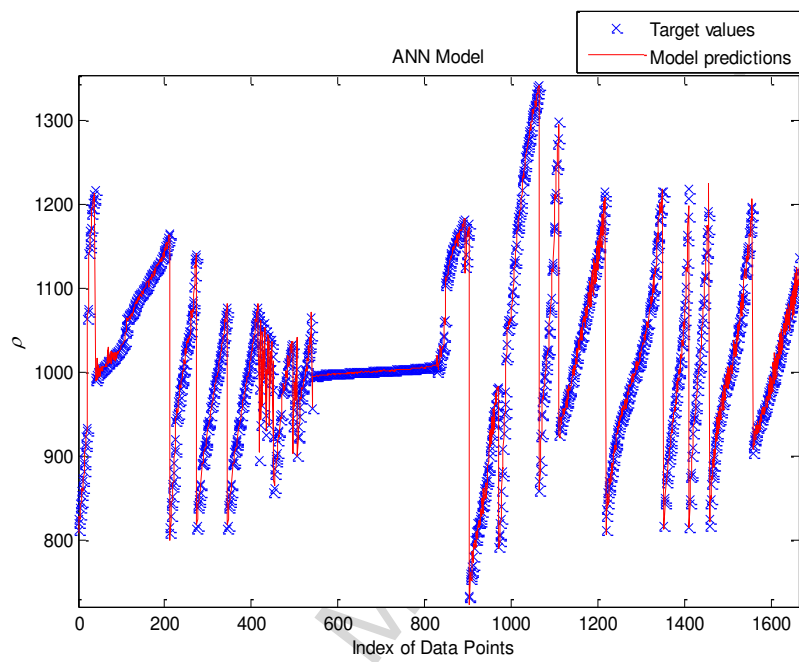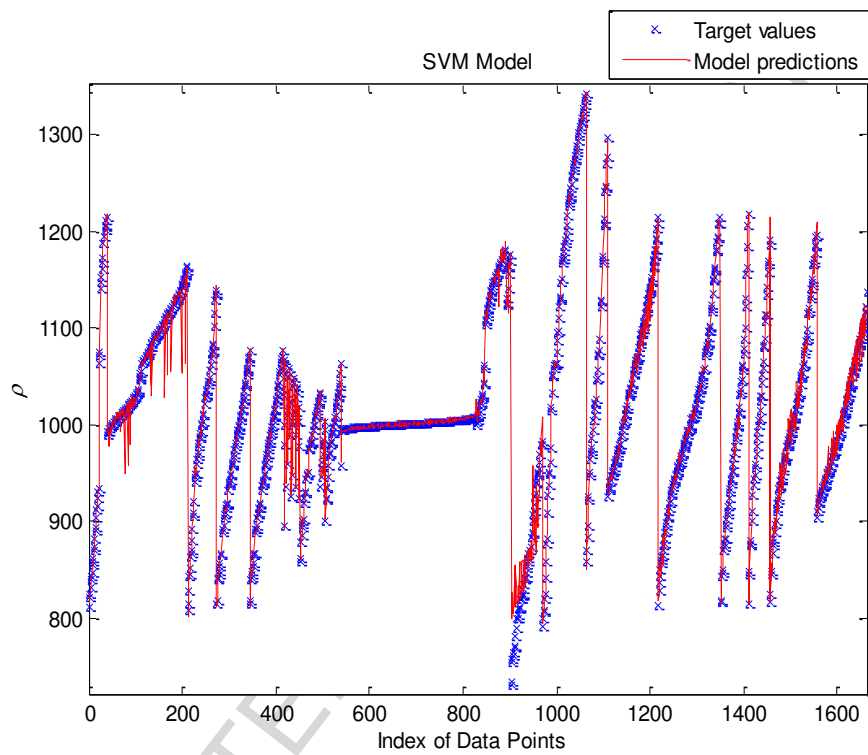
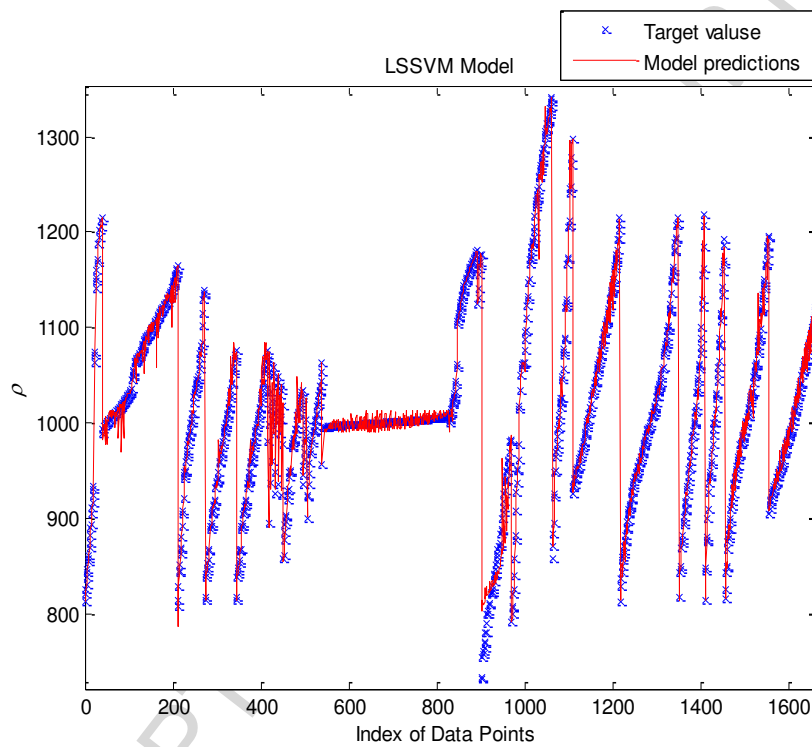Figure 6- a)

Figure 6- b)

Figure 6- c)

Table 1- List of experimental data points used in this study (density data covers both raffinate and extract phase of the ternary system alcohol/water/ionic liquid).

Ref.	Number of data points	Alcohol	Ionic liquid index	Temperature, K		Pressure, Kpa		Mole fraction H_2O		Mole fraction Alcohol		Mole fraction Ionic liquid		Density	
				min	max	min	Max	min	max	min	max	min	max	min	max
[27]	46	C_2H_6O	IL-9	298.15	298.15	100	100	0.0395	0.8266	0.099	0.9469	0.0069	0.747	857.86	1297.7
[28]	71	C_2H_6O	IL-14	298.15	298.15	101	101	0.0292	0.9357	0.0325	0.9459	0.0057	0.4802	814.04	1076.43
[29]	71	C_2H_6O	IL-14	298.15	298.15	101	101	0.0292	0.9357	0.0325	0.9459	0.0057	0.4802	814.04	1076.4
[30]	71	C_2H_6O	IL-11,12	298.15	343.15	101	101	0.0957	0.7052	0.1068	0.8465	0.0485	0.5323	894.4	1067.1
[31]	237	C_2H_6O	IL-13	298.15	323.15	100	30000	0.0239	0.7467	0	0.9416	0.0148	0.7556	989.5	1181.9
[32]	72	C_3H_8O	IL-13	298.15	298.15	101	101	0.0086	0.8908	0.0926	0.9817	0.0081	0.7864	807.7	1176.8
[33]	133	C_3H_8O	IL-15	298.15	298.15	101	101	0.0353	0.9011	0.0296	0.9565	0.0057	0.7651	812.4	1215.3
[34]	44	C_2H_6O	IL-2	298.15	298.15	101	101	0.0408	0.903	0	0.9476	0.003	0.4587	857.5	1033.7
[35]	46	C_2H_6O	IL-17	298.15	298.15	100	100	0.0475	0.825	0.0823	0.9409	0.005	0.7012	814.68	1192
[36]	100	$C_5H_{12}O$	IL-6,8	298.15	298.15	101	101	0.0391	0.8828	0.0463	0.9485	0.0047	0.7079	816.07	1195.9
[37]	93	C_2H_6O	IL-16	298.15	298.15	101	101	0	0.952	0	0.9541	0	0.9398	791.06	1342.1
[38]	70	C_2H_6O	IL-1,5,15	298.15	298.15	101	101	0.0425	0.9667	0.0134	0.9493	0.0043	0.7378	816.8	1218.1
[39]	216	C_3H_8O	IL-3,10	293.15	333.15	100	100	0.044	0.455	0.043	0.451	0.1	0.913	904	1215
[40]	39	CH_4O	IL-4	298.15	313.15	101	101	0.1101	0.7078	0.0532	0.8835	0.0019	0.5212	811.8	1215.6
[41]	287	$C_5H_{12}O$	IL-7	288	308	101	101	0.0004	0.0039	0.989	0.9993	0	0.0077	994.9	1008.7
[42]	67	$C_5H_{12}O$	IL-8	288.15	308.15	101	101	0.0009	0.0009	0.985	0.9987	0.0004	0.0141	731	982

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Table 2- Names and chemical formulas for ionic liquids of ternary systems used in this study.

IUPAC name	Index number	Chemical formula
1-ethyl-3-methylpyridinium ethylsulfate	IL-1	$C_{10}H_{17}NO_4S$
1-hexyl-3-methylimidazolium chloride	IL-2	$C_{10}H_{19}ClN_2$
1-ethyl-3-methylimidazolium diethylphosphate	IL-3	$C_{10}H_{21}N_2O_4P$
1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate	IL-4	$C_{11}H_{22}N_2O_6S$
1-octyl-3-methylimidazolium chloride	IL-5	$C_{12}H_{23}ClN_2$
N,N,N-trimethyl-1-decanaminium bromide	IL-6	$C_{13}H_{30}BrN$
N,N,N-trimethyl-1-dodecanaminium bromide	IL-7	$C_{15}H_{34}BrN$
N,N,N-trimethyl-1-tetradecanaminium bromide	IL-8	$C_{17}H_{38}BrN$
1,3-dimethylimidazolium methyl sulfate	IL-9	$C_6H_{12}N_2O_4S$
1,3-dimethylimidazolium dimethylphosphate	IL-10	$C_7H_{15}N_2O_4P$
1-ethyl-3-methylimizazolium dicyanamide	IL-11	$C_8H_{11}N_5$
1-ethyl-3-methylimizazolium acetate	IL-12	$C_8H_{14}N_2O_2$
1-butyl-3-methylimidazolium tetrafluoroborate	IL-13	$C_8H_{15}BF_4N_2$
1-butyl-3-methylimidazolium chloride	IL-14	$C_8H_{15}ClN_2$
1-ethyl-3-methylimidazolium ethylsulfate	IL-15	$C_8H_{16}N_2O_4S$
tris(2-hydroxyethyl) methylammonium methylsulfate	IL-16	$C_8H_{21}NO_7S$
1-butyl-3-methylimidazolium methylsulphate	IL-17	$C_9H_{18}N_2O_4S$

Table 3. Type and range of studied data points.

Type of data	Property	Minimum	Maximum
Inputs	Temperature, K	288	343.15
	Pressure, kPa	100	30000
	x_1	0	0.9667
	x_2	0	0.9992
	x_3	0	0.9398
	T_c ,K	643.18	1156.29
	P_c, bar	14.04	52.90
	W	0.2509	1.5198
	M_w of IL	170.21	336.39
	M_w of alcohol	32.04	88.15
Output	Density	731	1342.1

Table 4- Values of statistical parameters for intelligent models.

Model	Train				Test			
	R^2	RMSE	% AARD	STD	R^2	RMSE	% AARD	STD
ANN	0.9966	5.6754	0.3777	97.8059	0.9945	7.2242	0.4336	97.8379
LSSVM	0.9916	8.9148	0.4704	97.2675	0.9798	13.7381	0.8345	96.6767
SVM	0.9893	9.975	0.4462	96.5604	0.9852	11.765	0.6381	96.6246
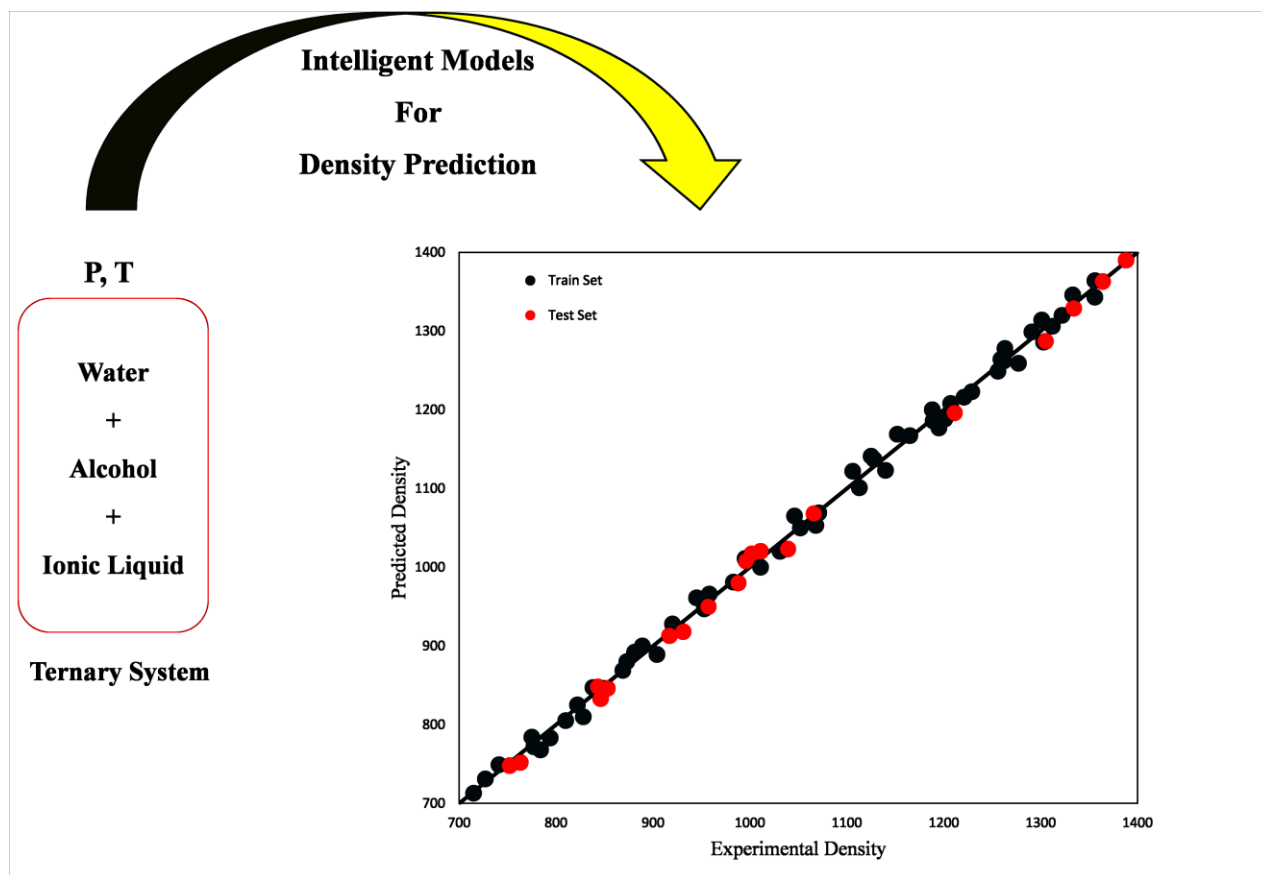
Graphical abstract

Highlights

➢ The density of water/alcohol/IL ternary systems are predicted.

➢ The ANN, SVM and LSSVM models have been applied as intelligent models.

➢ Total 1663 data points for 17 different ionic liquids are collected.