Predicting the heat capacities of ammonium- and phosphonium-based deep eutectic solvents using artificial neural network

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Abstract. Deep eutectic solvents (DESs) are more environment-friendly and sustainable solvents than ionic liquids (ILs). Determining their physical properties is vital prior to their application. However, it is not practical to experimentally determine the physical properties of all DESs. Therefore, developing models to estimate their physical properties is necessary. In this study, a generalized model using artificial neural network (ANN) was developed to predict the heat capacities of ammonium- and phosphonium-based DESs over the temperature range of 278.15 – 353.15 K at atmospheric pressure. The best ANN model developed from the training and optimization process has an architecture with two hidden layers of 7 and 6 neurons, respectively. The overall average absolute relative deviation of the proposed model from the data was 0.57%. Qualitative analyses suggest a promising predicting capability of the proposed model. The calculated values of the statistical descriptors are close to their ideal values. Therefore, the proposed model can be used to reliably predict the heat capacities of other ammonium- and phosphonium-based two-component DESs.

1. Introduction

For the past decade, deep eutectic solvents (DESs) have gained the interest of many researchers. So far, more than 200 research papers on the topic have been published. They are mostly compared with ionic liquids (ILs) due to the many characteristics and properties they share. However, there are advantages of using DESs over ILs. DESs have the potential to be less harmful to the environment and more sustainable than ILs because they are non-toxic, non-reactive with water, and biodegradable. They are usually formed by mixing a halide salt with a metal salt or hydrogen bond donor (HBD). The halide salt acts as a hydrogen bond acceptor (HBA) and forms a hydrogen bond with the HBD. The charge delocalized by the hydrogen bond is responsible for the low melting points of DESs compared to their constituting compounds. Their constituting compounds are commercially available, which makes DESs cheaper than ILs and more readily available for industrial and scale-up applications. DESs can also be customized to have specific functions to fit a particular application. Therefore, it is vital to determine the physical properties of DESs. Many DESs formulations with varying HBA and HBD are possible, where each has a different set of physical properties, such as viscosity, density, heat capacity, etc. Varying the molar ratio of HBA and HBD can also change the physical properties of the solvent. Due to this, it is not practical to investigate experimentally such numerous amounts of DESs. Therefore, developing generalized models that can estimate or predict the physical properties of DESs is necessary [1–4].
One of the methods to generate a model for the physical properties of DESs is through artificial neural networks (ANNs). In the past years, ANNs have been successfully used in a few studies to reliably predict the density [1,5] and conductivity [5,6]. Group contribution (GC) methods have also been used to reliably estimate density [1,5,7], viscosity [8], and heat capacity of DESs [3]. A new correlation was also introduced utilizing the concept of mass connectivity index (MCI) to estimate density [7,9].

Another method to generate generalized models is using empirical equations. Empirical equations such as the Vogel-Fulcher-Tammann equation or the Arrhenius equation has been used to estimate viscosity [10]. For the refractive index of DESs, the atomic contribution method is suitable for reliable estimations [7]. Most of the models developed using these methods, however, are DES-specific. Among the methods used for predicting some of the physical properties of DESs, the ANN method has shown increasing feasibility to generate a model with more reliable results as seen in different studies [1,5,6].

Artificial neural networks have been widely used in the prediction of properties (e.g. for ILs). They are suitable for applications, involving data sets and information that are incomplete or indistinct, and for problems that are very complex and inadequately explained [1]. The use of ANNs to predict the physical properties of DESs is vital since experimentally investigating all DESs, that can be formed, is practically impossible. However, this has only been applied by other researchers in their estimation of the density [1,5] and conductivity [5,6] of DESs. ANNs have yet to be used in the estimation of other physical properties of DESs. Up to the date of writing this research, only one study proposed a generalized model for the heat capacity of DESs [3], wherein, the critical properties and acentric factors were used to develop the correlation and Genetic Algorithm (GA) was used to optimize its fitting coefficients. This study chose ANN modeling to develop a generalized model capable of reliably predicting the heat capacity of DESs.

The main objective of this study was to propose a model for predicting the heat capacity of ammonium- and phosphonium-based two-component DESs using ANNs. Specifically, the best artificial neural network architecture along with its parameters was determined to predict the heat capacity of the considered DESs. The determination of the best ANN architecture was based on which produced the lowest average absolute relative deviation (AARD) for the training and test data. To assess the heat capacity predictions from the proposed neural network model, qualitative analyses, and quantitative analyses, by calculating several statistical descriptors, were done.

Heat capacity is one of the most important physical properties of DESs, especially in engineering application designs. Since it is not practical to experimentally measure the heat capacities of all DESs possible, a generalized model capable of reliable predictions is important. This study provides a generalized model that can reliably predict the heat capacities of ammonium- and phosphonium-based two-component DESs.

In this study, ammonium- and phosphonium-based two-component DESs were considered in the development of the generalized model. The DESs considered in the model commonly have either chlorine or bromine as an anion in their HBA, hence, they were the only considered anions as input in the input layer. Conventional ANN designing techniques were used such as selecting the appropriate input variables, dividing the data, determining the optimum number of neurons and layers, and choosing the appropriate training algorithm and hidden and output layer transfer function. The selection of the best ANN architecture along with its parameters was based on the AARD. The statistical assessment of the heat capacity predictions from the model was done by calculating several statistical descriptors. These are the index of agreement (IA), fractional bias (FB), normalized mean square error (NMSE), geometric variance (VG), geometric mean bias (MG), and regression coefficient ($R^2$).

2. Method

2.1. Data gathering

The isobaric heat capacities of DESs used in this study was taken from the data bank created by [3]. The heat capacities of ammonium- and phosphonium-based two-component DESs were the only considered data points in the bank. The uncertainty of measurement for all the experimental data
considered was also collected by [3] in their supporting information. The lowest uncertainty of measurement reported by the corresponding references for each DESs was ± 1%, and the highest was ± 2%, therefore, no further data trimming was done. A total of 439 data points from 20 different DESs, over the temperature range from 278.15 to 353.15 K and at atmospheric pressure was used to develop the model.

**Table 1.** List of the considered ammonium- and phosphonium-based binary mixtures of DESs.

| DES #  | HBA                          | HBD                          | Temperature Range (K) | Molar Ratio (HBA: HBD) | MW (g/mol) | NDP | Ref.          |
|--------|------------------------------|------------------------------|-----------------------|------------------------|------------|-----|---------------|
| DES1   | Choline Chloride             | Urea                         | 303.15–353.15         | 1:2                    | 86.58      | 23  | [11–13]       |
| DES2   | Choline Chloride             | Ethylene glycol              | 303.15–353.15         | 1:2                    | 87.92      | 14  | [11,12,14]    |
| DES3   | Choline Chloride             | Glycerol                     | 278.15–353.15         | 1:2                    | 107.94     | 39  | [11,12,14,15] |
| DES4   | Choline Chloride             | N,N-Diethylethanol ammonium chloride | 303.15–353.15   | 1:2                    | 112.61     | 11  | [16]          |
| DES5   | Choline Chloride             | Ethylene glycol              | 303.15–353.15         | 1:2                    | 92.6       | 11  | [16]          |
| DES6   | Choline Chloride             | Phenol                       | 298.15–353.15         | 1:3                    | 105.49     | 23  | [17]          |
| DES7   | Choline Chloride             | Glucose                      | 298.15–353.15         | 2:1                    | 153.13     | 23  | [17]          |
| DES8   | Choline Chloride             | Malonic Acid                 | 298.15–353.15         | 1:1                    | 121.84     | 23  | [17]          |
| DES9   | Choline Chloride             | Citric Acid                  | 298.15–353.15         | 1:2                    | 174.62     | 23  | [17]          |
| DES10  | Choline Chloride             | Oxalic Acid                  | 298.15–353.15         | 1:2                    | 106.56     | 23  | [17]          |
| DES11  | Choline Chloride             | Triethylene glycol           | 298.15–353.15         | 1:2                    | 145.65     | 23  | [17]          |
| DES12  | Choline Chloride             | Fructose                     | 298.15–353.15         | 2:1                    | 153.13     | 23  | [17]          |
| DES13  | Methyl triphenyl phosphonium bromide | Ethylene glycol            | 298.15–353.15         | 1:4                    | 121.1      | 23  | [17]          |
| DES14  | Methyl triphenyl phosphonium bromide | Malonic Acid                | 298.15–353.15         | 2:3                    | 205.32     | 23  | [17]          |
| DES15  | Methyl triphenyl phosphonium bromide | Glycerol                   | 298.15–353.15         | 1:3                    | 158.38     | 23  | [17]          |
| DES16  | Tetrabutyl ammonium chloride | Urea                        | 298.15–353.15         | 4:1                    | 234.34     | 19  | [17]          |
| DES17  | Tetrabutyl ammonium chloride | Malonic Acid                | 298.15–353.15         | 1:3                    | 147.52     | 23  | [17]          |
| DES18  | Tetrabutyl ammonium chloride | Triethylene glycol          | 298.15–353.15         | 1:1                    | 214.04     | 23  | [17]          |
| DES19  | Tetrabutyl ammonium chloride | Ethylene glycol             | 298.15–353.15         | 1:3                    | 116.03     | 23  | [17]          |
| DES20  | Tetrabutyl ammonium chloride | Glycerol                    | 298.15–353.15         | 1:5                    | 123.07     | 23  | [17]          |
Table 1 presents the HBA and HBD of the considered DESs, temperature range, molar ratio, molecular weight (MW), number of experimental data points (NDP), and the corresponding references. The structure of the HBAs and HBDs of the considered DESs are presented in table 2 and 3. The data gathered was randomly divided into training and test datasets. The ANN was trained using 70% of the considered data and the remaining 30% was used to test the generalization of the proposed model.

2.2. Artificial neural network

Figure 1 shows the architecture of the ANN model used in this study. An ANN mainly consists of three layers namely, the input, hidden, and output layer. If necessary, the network can have more than one hidden layer. Each layer contains neurons that imitates the neurons of a human brain. The neurons in each layer were linked by weights (w) and bias weights (b). The output layer was set to have only one expected output, that is, the heat capacity.

2.2.1. Artificial neural network parameters. The input parameters used to develop the model comprised of the temperature (T), molecular weight (MW), molar ratio of HBA: HBD, fed as mole HBA (nA) and mole HBD (nD), and structure-related parameters such as the cations and anions in HBAs, fed as ammonium cation (AC), phosphonium cation (PC), chlorine anion (CA), bromine anion (BA), and the reactive functional group/s present in HBDs, fed as amide (CN), carboxylic acid (COH), and alcohol (OH). A total of 11 inputs was fed to the input layer.

The relationship between the layers is described by weights, bias weights, and transfer functions as seen in equations (1-3) [18]:

$$H_l = f\left(\sum_{i=1}^{L} X_i w_{il} + b_i \right)$$

Figure 1. ANN architecture with two hidden layers.
\[ H^1_m = f\left( \sum_{l=1}^{M} H^1_l \times w_{ml} + b_m \right) \]
\[ O_n = f\left( \sum_{m=1}^{N} H^2_m \times w_{mn} + b_n \right) \]

where \( H^1_l \), \( H^2_m \), and \( O_n \), are the output vector of the neurons from the first hidden layer (l), second hidden layer (m), and output layer (n), respectively, and \( X_i \) is the input vector from the input layer (i).

**Table 2.** Structure of the hydrogen bond acceptors.

| Compound                  | Structure                                      |
|---------------------------|------------------------------------------------|
| Choline Chloride          | ![Choline Chloride](image1)                     |
| Methyl triphenyl phosphonium bromide | ![Methyl triphenyl phosphonium bromide](image2) |
| N,N-Diethylethanol ammonium chloride | ![N,N-Diethylethanol ammonium chloride](image3) |
| Tetrabutylammonium chloride | ![Tetrabutylammonium chloride](image4)         |

**Table 3.** Structure of the hydrogen bond donors.

| Compound                  | Structure                                      |
|---------------------------|------------------------------------------------|
| Urea                      | ![Urea](image5)                                |
| Citric acid               | ![Citric acid](image6)                         |
| Ethylene glycol           | ![Ethylene glycol](image7)                     |
| Oxalic acid               | ![Oxalic acid](image8)                         |
| Glycerol                  | ![Glycerol](image9)                            |
| Triethylene glycol        | ![Triethylene glycol](image10)                 |
| Phenol                    | ![Phenol](image11)                             |
| Fructose                  | ![Fructose](image12)                           |
| Glucose                   | ![Glucose](image13)                            |
| Malonic acid              | ![Malonic acid](image14)                       |
The transfer functions used in the hidden layers and output layer were the hyperbolic tangent sigmoid (tansig), equation (4), and linear (purelin), equation (5), respectively, as they provide the best predictions.

\[ f_{\text{tansig}} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \]  
\[ f_{\text{purelin}} = x \]  

2.2.2. Artificial neural network training and optimization. The ANN training was done in MATLAB® 2020a. The Levenberg-Marquardt Algorithm (trainlm) was used as the training function of the network. The training parameters such as the maximum number of epochs, training time, maximum and minimum mu (damping factor), and minimum performance gradient were set to their default values. The performance function was also set to default, where the mean square error is calculated by the network. These parameters were also the termination criteria for ANN training.

Generally, when the hidden layer has too few neurons, the model may not be capable enough of predicting the target output and cause underfitting. On the other hand, when the layer has too many neurons, it may negatively affect the model resulting to longer training time and overfitting. In this study, the training started with one hidden layer consisting of one neuron using the training dataset. The test dataset was then used to determine the generalization of the model developed from the training. New architectures were identified by gradually increasing the number of neurons and hidden layers until there was no more significant improvement in the AARD observed for both training and test dataset. The AARD of all the network architectures developed were collected and evaluated. The best network architecture was determined based on the one having the lowest AARD for both training and test dataset. Afterwards, the weights and bias weights of the model, with the best network architecture, was optimized by retraining the model using the same training dataset. The model with lowest AARD after retraining has the optimum weights and bias weights and was considered as the best ANN model. The AARD was calculated as follows:

\[ \text{AARD} = \frac{100\%}{N} \sum_{n=1}^{N} \frac{|E_{Cp,n} - P_{Cp,n}|}{E_{Cp,n}} \]  
where \( N \) is the number of data points, and \( E_{Cp} \) and \( P_{Cp} \) are the experimental heat capacity and the predicted heat capacity of the model, respectively.

2.3. Statistical assessment

The statistical assessment of the heat capacity predictions from the model was done by calculating several statistical descriptors. The overall accuracy of the model and the association between experimental and predicted heat capacities were showed by the IA and \( R^2 \). The tendency of the model to underpredict or overpredict was measured by the FB and MG. Systematic and random errors were indicated by the NMSE and VG. The expressions for these statistical descriptors are as follows:

\[ IA = 1 - \frac{\sum_{n=1}^{N} (P_{Cp,n} - E_{Cp,n})^2}{\sum_{n=1}^{N} (P_{Cp,n} - E_{Cp})^2} \]  
\[ FB = \frac{E_{Cp} - P_{Cp}}{0.5(E_{Cp} + P_{Cp})} \]  
\[ \text{NMSE} = \frac{(E_{Cp} - P_{Cp})^2}{E_{Cp}P_{Cp}} \]  
\[ MG = \exp \left( \ln E_{Cp} - \ln P_{Cp} \right) \]
\[ V_G = \exp \left[ \ln E_{Cp} - \ln \overline{P_{Cp}} \right] \]

\[ R^2 = 1 - \frac{\sum_{n=1}^{N} (E_{Cp,n} - \overline{P_{Cp,n}})^2}{\sum_{n=1}^{N} (E_{Cp,n} - \overline{E_{Cp}})^2} \]

where \( \overline{E_{Cp}} \) and \( \overline{P_{Cp}} \) are the average of the experimental heat capacity and average of the predicted heat capacity, respectively.

3. Results and discussion

The best ANN model determined from training and optimization has an architecture of 11-7-6-1. This means that the model has two hidden layers, between the input and output layer, that contains 7 and 6 neurons, respectively, as seen in figure 2. In this architecture, each weight from the input layer is being sent to 7 neurons of the first hidden layer. Then the 6 neurons of the second hidden layer receive each weight coming from the first hidden layer. Finally, each weight from the second hidden layer goes to the output layer. The optimum weights and bias weights of all the layers are summarized in table 4-6.

![Figure 2](image_url)

Figure 2. Architecture of the model generated by MATLAB®.

As presented in table 7, the calculated AARD for the overall dataset is 0.57%, indicating the high predictive capability and accuracy of the model. This is corroborated by the calculated AARD values for the training and test datasets which can be seen in the same table. A low AARD value for the training dataset indicates that the proposed ANN model correlated very well the input parameters and the model handled the complex nature of DESs. This also shows that it is important to appropriately select input parameters that suitably represent the systems [3]. This is the reason why structure-related parameters for the investigated DESs were considered, which are the cation and anion of the HBA and the reactive functional group/s of the HBD.

| Neuron (N) | \( b_{1,N} \) | \( w_{T,N} \) | \( w_{AC,N} \) | \( w_{PC,N} \) | \( w_{CA,N} \) | \( w_{BA,N} \) |
|-----------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1         | -2.3639       | 0.4611        | -0.5535       | 0.5737        | -2.0398       | 1.4857        |
| 2         | 0.5081        | -1.4343       | -0.0027       | -0.0398       | -0.0888       | 0.4209        |
| 3         | -3.5030       | -0.0425       | 0.8153        | -0.0200       | -0.5502       | -0.3051       |
| 4         | -0.4945       | 0.2289        | -2.3134       | 2.0362        | -1.2285       | 1.8057        |
| 5         | 0.0132        | 0.0538        | 0.9011        | -0.4739       | 0.2966        | 0.7688        |
| 6         | 1.3458        | 0.0565        | 0.5680        | -0.8212       | 0.5653        | -1.6508       |
| 7         | 3.4623        | -0.8417       | -0.2866       | 1.4705        | -1.0713       | 0.1068        |

Table 4(a). Weights and bias weights for the first hidden layer.

For the test dataset, the model achieved also a low AARD value. Test datasets are not used when an ANN model is being trained, therefore, they provide an unbiased evaluation of the model’s accuracy when they are used as input parameters. If the model can predict the test dataset accurately, that means there was only minimal overfitting occurred. Since the proposed model has a low AARD for the test dataset, this confirms the predictive capability and generalization of the model.
Underfitting since they cannot represent the variance in the real population. In underfitting, the model is not powerful enough to predict the experimental values of the training and test datasets, hence, resulting to high relative deviations. Therefore, the number of data points available for DESs having fructose or glucose as their HBD may not have been enough for the model to produce accurate predictions and resulted to them being underfitted. It is important to point out that this did not happen to DES 6, DES 9, and DES 10, which were the only solvents that contain phenol, citric acid, and oxalic acid, respectively.

However, the same cannot be said to DES 3, since glycerol as HBD is present in multiple DESs considered in the study. Comparing the DESs with glycerol as their HBD, there seems to be no particular explanation why the model underfitted DES 3 because majority of them have very low relative deviations. However, evaluating the available raw data for DES 3, its high percent errors could be attributed to the inconsistency of the experimental data. The data points of DES 3 came from multiple literature and their experimental method and sample purity were not the same. Comparing the values, a significant difference between their experimental heat capacities at multiple temperatures can

\[
\begin{array}{cccccccc}
\text{Neuron (N)} & \ \text{b}_0 & \text{b}_1 & \text{b}_2 & \text{b}_3 & \text{b}_4 & \text{b}_5 & \text{b}_6 \\
1 & -3.7601 & -0.5716 & -0.6450 & 0.5227 & -0.5313 & -1.4725 & -3.3495 \\
\end{array}
\]

Table 7. Calculated AARD (%) of the proposed model for each dataset.

| Dataset | NDP  | AARD (%) |
|---------|------|----------|
| Training | 307  | 0.52065  |
| Test    | 132  | 0.69964  |
| Overall | 439  | 0.57447  |

Table 8 presents the AARD values for the training, test, and overall datasets of each investigated DES. As seen in the table, three DESs achieved overall AARD greater than 1 namely DES 3, DES 7, and DES 12 (i.e. 2.74, 1.64, and 2.65%, respectively). For DES 7 and DES 12, their high percent errors could be attributed to the number of data points available for them. Unlike majority of other hydrogen-bond donors in this study, fructose is only present in DES 7 and glucose is only present in DES 12. Generally, the amount of training samples can affect the performance of the ANN model. Too few training samples can cause underfitting since they cannot represent the variance in the real population.
be observed, as seen in Table 9. The inconsistency in the collected data points could be the reason for the high percent errors of DES 3.

Up to the date of writing this study, there is only one literature model for predicting the heat capacities of DESs, which is by Taherzadeh et al. [3]. Their model considered critical properties and acentric factor they calculated as input parameters along with molar mass and temperature. Comparing the total AARD of the two models, our proposed model is significantly better than the model by Taherzadeh et al. (0.57% vs 4.70%, respectively). This is further corroborated by comparing their overall AARD values for each DES as seen in the same table. This also further confirms the feasibility of the ANN method to develop more accurate models for predicting the physical properties of DESs as compared to other methods, like the group contribution method done by the literature model. It is important to consider though that the literature model investigated more DESs than our proposed model (28 DESs vs 20 DESs, respectively) for a fair overview.

Table 8. The calculated AARD values of each dataset of the proposed model and the overall AARD values of Taherzadeh et al.’s model for each investigated DES.

| DES | Proposed model | Taherzadeh et al.’s model [3] |
|-----|----------------|-------------------------------|
|     | Training       | Test                          | Overall | Overall |
| 1   | 0.22           | 0.15                          | 0.20    | 1.70    |
| 2   | 0.08           | 0.08                          | 0.08    | 4.70    |
| 3   | 3.03           | 2.47                          | 2.74    | 4.90    |
| 4   | 0.49           | 0.57                          | 0.54    | 0.90    |
| 5   | 0.19           | 0.32                          | 0.21    | 4.10    |
| 6   | 0.28           | 0.26                          | 0.27    | 2.40    |
| 7   | 1.63           | 1.97                          | 1.64    | 6.30    |
| 8   | 0.08           | 0.07                          | 0.08    | 13.70   |
| 9   | 0.11           | 0.08                          | 0.10    | 0.20    |
| 10  | 0.10           | 0.09                          | 0.10    | 14.80   |
| 11  | 0.05           | 0.24                          | 0.12    | 1.10    |
| 12  | 2.49           | 2.95                          | 2.65    | 1.70    |
| 13  | 0.07           | 0.08                          | 0.08    | 6.70    |
| 14  | 0.06           | 0.06                          | 0.06    | 0.90    |
| 15  | 0.04           | 0.11                          | 0.07    | 1.70    |
| 16  | 0.07           | 0.37                          | 0.15    | 0.50    |
| 17  | 0.13           | 0.18                          | 0.14    | 8.10    |
| 18  | 0.08           | 0.12                          | 0.09    | 0.50    |
| 19  | 0.15           | 0.06                          | 0.13    | 14.90   |
| 20  | 0.06           | 0.05                          | 0.06    | 0.80    |
|     | 0.52           | 0.70                          | 0.57    | 4.70    |

Table 9. Experimental heat capacity of DES 3 (choline chloride + glycerol) at different temperatures of multiple literatures.

| Temperature (K) | Experimental Heat Capacity (J/mol-K) |
|-----------------|-------------------------------------|
|                 | [11] | [14] | [15] |
| 303.15          | 237.70 | 237.70 | 220.00 |
| 308.15          | 239.10 | -    | 221.50 |
| 313.15          | 240.80 | -    | 223.50 |
| 318.15          | 241.90 | -    | 225.00 |
| 323.15          | 243.50 | -    | 227.00 |
| 328.15          | 244.90 | -    | 228.50 |
| 333.15          | 246.90 | 246.90 | 230.00 |
| 338.15          | 248.40 | -    | 232.00 |
Figure 3. Behavior and trend of heat capacity versus temperature for five random DESs. The shapes are experimental values, and the dots are the predicted values of the model.

Figure 4. Behavior and trend of heat capacity versus temperature for DESs with constant HBA and molar ratio, but varying HBD. The HBA is choline chloride, and the HBD is either urea (DES 1), ethylene glycol (DES 2), glycerol (DES 3), citric acid (DES 9), oxalic acid (DES 10), or triethylene glycol (DES 11). The shapes are experimental values, and the dots are the predicted values of the model.
Qualitative analyses were done by determining the behaviors and trends of the predicted heat capacities and experimental heat capacities, to have a more comprehensive investigation on the capability of the model [3]. Figure 3 and 4 compares the behavior and trend of heat capacity vs. temperature for five random DESS and for DESS with fixed HBA and molar ratio but varying HBD, respectively. Comparing the slopes of the predicted values and experimental values in figure 3, it can be observed that their trends are nearly identical with each other. From this, the model’s capability to predict heat capacities at high temperatures is verified. Also, comparing the slopes in figure 4, the same trend is observed. From this, the model’s capability to adapt to the change in HBD is also verified. Both behaviors and trends were also observed by Taherzadeh et al. [3] in their proposed model.

Aside from qualitative analyses, quantitative analyses were also done by doing statistical assessment of the heat capacity predictions of the model. In table 10, the results of the statistical descriptors for the training dataset, test dataset, and the overall dataset are presented. The overall values for IA and R² indicate the overall great agreement between the predicted and experimental values, as seen also in figure 5. The overall values for NMSE and VG indicate that the model has minimal systematic errors and random scatter. The overall values for FB and MG indicate that the network with two hidden layers containing 7 and 6 neurons, respectively, has significantly low tendency to underfit due to systematic errors.

| Dataset     | IA (1.0000) | FB (1.0000) | NMSE (1.0000) | VG (1.0000) | MG (1.0000) | R² (1.0000) |
|-------------|-------------|-------------|---------------|-------------|-------------|-------------|
| Training    | 0.99974     | -0.000014   | 0.00010       | 1.00012     | 0.99994     | 0.99896     |
| Test        | 0.99956     | -0.002726   | 0.00016       | 1.00018     | 0.99709     | 0.99826     |
| Overall     | 0.99970     | -0.000784   | 0.00011       | 1.00014     | 0.99908     | 0.99879     |

*Ideal value of the statistical descriptor.

Table 10. Values of the statistical descriptors for the proposed ANN model.

Figure 5. Comparison between the predicted and experimental values.
4. Conclusion

This study proposed a model to predict the heat capacities of ammonium- and phosphonium-based two component DESs which was developed using artificial neural networks. A total of 439 data points was used for the training and optimization of the ANN model, where 70% was used as training dataset and the remaining 30% was used as test dataset. Temperature, molecular weight, mole ratio, and structure-related parameters (i.e. cation and anion of the HBA and the functional group/s of the HBD) were considered as input parameters in the input layer. The best ANN model developed from the training and optimization process has two hidden layers containing 7 and 6 neurons, respectively, for its architecture. The proposed model has an overall AARD value of 0.57%, which shows its overall accuracy. This indicates that the model handled the complex nature of the investigated DESs and has great predictive capability and generalization. The amount of training samples and consistency of the data could influence the performance of the model, which was observed on some of the investigated DESs. The feasibility of the ANN method to develop more accurate models for physical property predictions of DESs as compared to other methods was corroborated when the calculated overall AARD value of the proposed ANN model was lower than that of the literature model, where the GC method was used. Qualitative investigations of the predicted heat capacities showed that its behavior and trend follow that of the experimental heat capacities at high temperatures and varying HBA, confirming the proposed model's promising predicting capability. Quantitative investigations by statistical assessment of the predicted heat capacities showed that the calculated values of the statistical descriptors were close to their ideal values, indicating the overall great performance of the model.

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