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Electrical conductivity of ammonium and phosphonium based deep eutectic solvents: Measurements and artificial intelligence-based prediction

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ABSTRACT

The evaluation of deep eutectic solvents (DESs) as a new generation of solvents for various practical application requires an insight of the main physical, chemical, and thermodynamic properties. In this study, the experimental measurements of the electrical conductivity of two classes of DESs based on ammonium and phosphonium salts at different compositions and temperatures were reported. The results revealed that electrical conductivity of DESs has temperature-dependency. In addition, molar conductivities of ammonium and phosphonium salts in DESs were obtained using DESs experimental values of electrical conductivities. The feasibility of using an artificial neural network (ANN) model to predict the electrical conductivity of ammonium and phosphonium based DESs at different temperatures and compositions was also examined. A feed-forward back propagation neural network with 8 hidden neurons was successfully developed and trained with the measured electrical conductivity data. The results indicated that among the different networks tested, the network with 8 hidden neurons had the best prediction performance and gave the smallest value of Normalized Mean Square Error (NMSE) (0.0010) and acceptable values of Index of Agreement (IA) (0.9999) and Regression Coefficient (R^2) (0.9988). The comparison of the predicted electrical conductivity of DESs by the proposed model with those obtained by experiments confirmed the reliability of the ANN model with an average absolute relative deviation (AARD%) of 4.40%.

1. Introduction

Ionic liquids (ILs) are salts with weak ionic interaction which allows them to be liquid in ambient temperature (typically below 373.15 K). The scientific and significant importance of ILs have spanned a broad range of applications, owing to their tempting physicochemical properties, such as thermal and chemical stability, low melting point, negligible volatility, high ionic conductivity, moderate viscosity, high polarity, and solubility (affinity) with many compounds [1–5]. Their potential use in a variety of chemical and industrial applications as green solvents has been greatly explored [1,3]. Nevertheless, ILs are too expensive to be used in bulk applications since they cannot be well prepared at the laboratory with one step of synthesis. Due to the multi-stage purification processes required to purify the ILs after their synthesis, their production cost is quite high. Consequently, researchers prefer to buy them than to synthesize them locally. This imposes a constraint on using them as a viable and practical industrial chemical ingredient [6,7].

Fortunately, a low cost alternative for ILs is available. Deep eutectic solvents (DESs) belong to a class of ionic liquids which are mixtures of a quaternary salt with a metal halide (Lewis acid), a hydrated salt, or an ordinary hydrogen bond donor (HBD) such as alcohol, amide as well as carboxylic acid as complexing agent. This results in the formation of an eutectic mixture with a melting point that is considerably lower than its original precursors. For this reason, this mixture is called a DES. Moreover, DESs overcome some principal disadvantages from ILs, they are easy to prepare in pure state, non-reactive with water, fairly safe (when carefully designed from benign components) and biodegradable [8–12].

Recently, few research groups reported the synthesis and use of DESs in different applications. Abbott research group was the first to report the synthesis and use of ammonium-based DESs in different promising applications [9]. They described for the first time the electrodeposition of composite materials using DESs [13]. Kareem et al. [14] reported some important physical properties of

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phosphonium-based DESs and used them for the potential use in the separation of aromatics from naphtha feed streams [15]. Shahbaz et al. [16] used phosphonium-based DESs to remove glycerol from palm oil-based biodiesel. They also revealed that DESs were successful for the removal of residual catalyst and water from palm oil-based biodiesel [17]. A recent review by Zhang et al. [8] gives a comprehensive overview of the recent applications of DESs.

The evaluation of DESs as new generation of solvents for various practical applications requires enough knowledge of some of the main physical, chemical, and thermodynamic properties. Few research articles were recently added to the literature dealing with this topic [18–25], yet, the door is still wide-open for more research in this area.

The electrical conductivity is one of fundamental physical properties that represent how well a material can conduct electrical current. It is also an indication for how much a material is resistive for the motion of electrons within its molecules (resistivity). In addition, it is a useful measurement in a variety of industries [14,26]. The electrical conductivity is also one of the important electrical properties of electrolytes, such as carrier concentration, carrier mobility, and the longevity of excess carriers. In engineering applications, it is crucial to measure the electrical conductivity of an electrolyte in order to design, control and optimize the electrolysis processes and the production of electrochemical power sources. For corrosion protection, electrical conductivity provides practical information for assessing the corrosivity of aqueous media and for cathodic protection system. It is also used to gain insight into the properties of electrolyte solutions and to evaluate the characteristic quantities such as dissociation constants [27–30]. Therefore, there is a significant need to measure the DESs' electrical conductivity and develop a reliable technique to predict it in order to properly manage their future applications.

It was found that using predictive tools such as artificial neural network (ANN) can be practical for the prediction of physical properties of DESs. The application of ANNs in predicting physical and chemical properties of materials is growing quickly. Several studies have been accomplished to predict physical properties of particular DESs and ILs using ANNs [22,31–35].

As the literature does not show any research article on the application ANN for the prediction of electrical conductivity of DESs, it is proposed here that such ANN is built for this purpose. In this work, we report experimental data of electrical conductivities of two classes of DESs based on ammonium and phosphonium salts at different conditions of composition and temperature. In addition, the applicability of artificial neural network model to predict the electrical conductivities of the above mentioned DESs at different temperatures is examined.

2. Methodology

2.1. Synthesis of DESs

In this work, choline chloride ($C_5H_{14}ClNO$), N,N-diethyl ethanol ammonium chloride ($C_6H_{16}ClNO$) and methyl triphenyl phosphonium bromide ($C_{19}H_{18}PBr$) as salts and glycerol ($C_3H_8O_3$) and ethylene glycol ($C_2H_6O_2$) as hydrogen bond donors were selected for the synthesis of DESs. All the above-mentioned chemicals were supplied by Merck (Darmstadt, Germany) and were of high purity (>98%). The chemicals specifications are described in Table 1. The eutectic mixtures were formed by mixing the salt and HBD together at a specific temperature and atmospheric pressure in a jacketed vessel until a homogenous and colorless liquid formed. All the experimental work of this study was conducted inside a glove box whereby the humidity was less than 0.4 ppm. The synthesized DESs were placed in tight and humidity-safe screw-capped bottles and stored in a dehumidifier chamber to prevent any contamination with atmospheric water vapor. For each DES, the mole fractions of salt and HBD around the eutectic points were chosen. All of the DESs were easily synthesized at temperatures less than 363.15 K. The freezing point and water content of all synthesized DESs were measured using the methods described in our previous works [22]. In this work, the uncertainty in freezing point measurement was ±0.01 K. For the sake of simplicity, the DESs were given abbreviated names. The abbreviations together with the freezing temperatures are summarized in Table 2.

Table 1
Material description.

Chemical names	Source	Mass fraction purity
Choline chloride	Merck	≥0.98
Methyl triphenyl phosphonium bromide	Merck	≥0.98
N,N-diethyl ethanol ammonium chloride	Merck	≥0.98
Glycerol	Merck	≥0.99
Ethylene glycol	Merck	≥0.99

2.2. Electrical conductivity measurement

The electrical conductivity of the synthesized DESs was measured by a multi parameter analyzer (DZS-708, Cheetah) with a resolution of 0.001 ($\mu S\,cm^{-1}$). The cell constant was calibrated by measuring the conductivities of aqueous solutions of KCl at different concentrations according to the IUPAC recommendation [36]. The accuracy of the cell constant was found to be 0.2%. The DESs' electrical conductivity in this study was measured at a temperature range of 298.15-353.15 K at 5 K intervals. The variation of the temperature was achieved by using a water bath with temperature control. For each measurement three replicates were carried out and the uncertainties of the electrical conductivity and temperature values were within the range of ±0.003 $mS\,cm^{-1}$ and ±0.1 K, respectively.

2.3. Neural network modeling

An artificial neural network (ANN) consists of an interrelated set of artificial neurons, and it processes information using a connectionist approach to computation. ANNs are computing systems which can be trained to learn a complex relationship between two or more variables or datasets [37]. Amongst the available ANNs, the feed-forward neural network is one of the most important historical developments in neurocomputing [22]. In this study, a feed-forward back propagation neural network with hyperbolic tangent sigmoidal activation functions was developed for the prediction of DESs' electrical conductivity. It consists of three layers namely, the input, hidden and the output. Normally, designing a neural network for a particular task involves the selection of the optimum network architecture and parameters. The designed network will be then trained with experimental input–output data. Subsequently, this is followed by a validation step of the network model. This is achieved by testing a dataset which was not considered in the training stage. This is needed to check the interpolative capability of the obtained optimum network. In order to train and validate the neural network built here, experimentally measured electrical conductivities of the studied DESs were used as testing data. The electrical conductivity datasets for the DESs of this study are shown in Tables 3, 4 and 5. In the first step, the input and output parameters of the model were defined. As can be seen from Fig. 1, the input parameters to the developed network comprise mole fractions of choline chloride ($x_{C_5H_{14}ClNO}$), N,N-diethyl ethanol ammonium chloride ($x_{C_6H_{16}ClNO}$) and methyl triphenyl phosphonium bromide ($x_{C_{19}H_{18}PBr}$) as sources of salt, mole fractions