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Non-linear models applied to experimental spectroscopical quantitative analysis of aqueous ternary mixtures of imidazolium and pyridinium-based ionic liquids

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ABSTRACT

The study of a ternary system formed by two ionic liquids (ILs) (N-butyl-pyridinium chloride ([bpy][Cl]) and 3-butyl-1-methylimidazolium chloride ([bmim][Cl])) and water has been carried out using UV–vis absorption measurements. The results were employed to design non-linear mathematical models based on artificial neural networks. The models provided accurate results for the estimation of the concentration of [bpy][Cl] and [bmim][Cl] (the best model offered the following mean prediction errors (MPEs): $MPE_{[bpy][Cl]} = 3.81\%$ and $MPE_{[bmim][Cl]} = 5.78\%$). Different methodologies have been considered to describe the system, which has led to discussions regarding the relevance of number, type, and quality of independent variables used in the models. This study allowed improving the estimations achieved by different models and decreasing the error attained seven- and twelve-fold for the concentration estimation of [bpy][Cl] and [bmim][Cl], respectively, from the worst to the best model.

1. Introduction

Since their first synthesis decades ago, ionic liquids (ILs) have attracted the attention of the scientific community due to the surprising and compelling properties that some of them possess, such as non-volatility, non-flammability, high electrochemical and thermal stability, and being relatively environmental-friendly [1–3]. These compounds are formed solely by ions: large organic cations (imidazolium, phosphonium, pyridinium, and more) and anions (such as borates, phosphates, sulphates, succinates, and so on). As the properties of ILs depend on their conforming molecules, the wide variety of existing ions and counter ions provides the chance to synthesize ILs "à la carte", turning them into "designers' solvents" [4].

Even though the number of potential ILs is immense (millions of feasible simple ILs can be designed), the possibility of creating mixtures vastly increases this number, reaching around 10^{18} plausible ternary mixtures [5]. The mixtures of ILs show properties that differ from the ones offered by pure compounds, making them an attractive and promising alternative to traditional solvents for industrial processes due to the fact that these can be optimized to fulfil specific tasks. An example can be seen in the work of Taige et al. [6], where a binary mixture of an imidazolium- and pyridinium-based ILs showed a decrease in its viscosity and an enhanced conductivity. These property variations highly depend on the composition of the mixture, that is, on the concentration of the ILs involved [4]. Additionally, this concentration ought to be carefully determined and monitored due to a series of intrinsic characteristics that these compounds present, such as being toxic for both *in vitro* cells and mammals [7–9].

One way to determine the composition of mixtures is employing spectroscopic techniques, such as UV–vis absorption, which permit defining a direct relation between the concentration of a given compound and the absorption of light in a specific range of wavelengths. Therefore, the analysis of the measured spectra could give information about the composition when the studies are carried out at the correct wavelengths.

Unfortunately, the applications of binary and ternary mixtures of ILs are scarce due to the lack of data regarding significant properties, environmental effects, and, consequently, models that describe them [10,11]. Therefore, designing mathematical models that are able to process these systems must be a priority in order to establish their implementation in industrial processes, which would lead to an improvement in yield and solvent economy [8].

Regarding this point, artificial neural networks (ANNs) have proven to be an appealing option to design models that achieve this task, as an alternative to other used methods [12]. ANNs are mathematical tools that are known for finding non-linear

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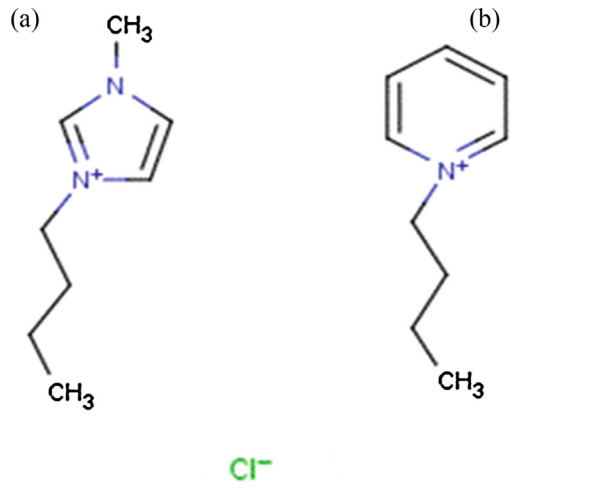

Fig. 1. Molecular structure of (a) [bmim][Cl] and (b) [bpy][Cl].

relationships between independent and dependent variables in huge databases. They estimate results through non-linear interpolation. This is the reason why they are restricted to the database range, which must contain enough data points with an acceptable experimental and statistical quality, as well as an adequate distribution in the whole range studied to maximize the statistical performance [13,14]. ANNs are also heavily influenced by their topology and the information which is provided initially. In other words, the quality and accuracy of the model will highly depend on the independent variables selected and their relation with the estimated dependent ones [15]. Therefore, modifying the number of independent variables, or the particular information provided by them, will affect the final efficiency of the mathematical tool.

In this work, the estimation of the composition of ternary mixtures of two ILs (N-butyl-pyridinium chloride ([bpy][Cl]) and 3-butyl-1-methylimidazolium chloride ([bmim][Cl])) (Fig. 1) and water is achieved through ANNs. Additionally, a study regarding the importance of the adequate selection of the number and nature of the independent variables has been performed, and their influence on the accuracy of the final estimations of the different models evaluated.

2. Materials and methods

2.1. Reagents and solutions

Both ILs were purchased from Iolitec with a purity degree greater than 99%. They were mixed with milli-Q quality water in order to prepare 68 different aqueous solutions with concentrations varying from 0 to 300 mM for [bpy][Cl] and from 0 to 500 mM for [bmim][Cl]. The final concentrations for each IL were chosen after initial experimental studies, as the absorption measurements reached values higher than 1.0 when these compounds were concentrated any further. Due to the great increase of the error after this point, these absorption readings are not reliable enough for accurate quantitative measurements and were discarded prior to the design of the different models.

2.2. Absorption measurements

The absorption spectra of the solutions prepared (*vide supra*) were measured between 300 and 600 nm using a UV-Vis spectrophotometer (JASCO Model V-530). The samples were introduced in a UV–vis quartz cuvette of 1 cm length path. Each mathematically analyzed spectrum was the result of the average of three independent measurements of the specific mixture.

The analysis of the attained spectra was carried out using the OriginPro v8.0724 (B724) software package.

2.3. Artificial neural networks

In order to achieve an accurate estimation of the composition of ternary mixtures of ILs and water, ANNs were applied. These algorithmic tools have been used to determine non-linear relations between dependent and independent variables within the database [16], which is formed by 68 data points that cover the composition of the mixtures and information from their respective absorption spectrum. One of the most commonly used ANN during scientific research is the supervised multilayer perceptron (MLP), and it has been selected to perform the desired estimation. Supervised MLPs require target data in order to be trained and optimized properly [17]. It is worth noting that these systems will be much more effective when interpolating within the range considered by the data employed during their training, as the error increases significantly when they are forced to extrapolate or perform the estimation outside this range [18].

The units that form a MLP are arranged in a characteristic layered topology. There are three different types of layers: the input, the hidden, and the output layer. The first one is formed by nodes, which simply introduce the information given by the independent variables into the network. The other two layers contain neurons, which are the true calculation centers of the system. The number of neurons that exist in the output layer are fixed according to the dependent variables to be estimated, whereas the ones from the hidden layer ought to be optimized for the correct design of the model [19].

Although the nodes do not perform any calculation, the number of inputs is vital for the model, as they represent the independent variables of the system [20]. This means that the accuracy of a MLP highly depends on the variables selected as input information. Each unit (node or neuron) is connected with all other units contained in neighboring layers, and these connections are controlled by weighted parameters known as weights. They play an essential role in ANNs as their correct optimization is crucial for accurate estimations [21].

2.4. ANN optimization

The optimization process of an ANN consists of two different phases: training and verification phase. In order to achieve a useful estimative tool, a good number of high quality data points (in terms of accuracy, repeatability, and reproducibility) are required. To correctly perform the training phase, the gathered database must be divided at least into two different datasets, known as training and verification datasets. The first one usually contains around 85% of the data and it is responsible of the optimization of the weights, which are modified in order to reach a better statistical performance (more accurate estimations). The second one is formed by the remaining 15% and it is employed for testing the generalization capability attained and avoiding any possible over-fitting effects by stopping the training cycles of the model earlier than it would when only a training dataset is employed [22].

Both defined datasets are involved in every training cycle or epoch that takes place, but these cease to continue when errors during verification start to increase. When the verification dataset comes into play, the values of the weights are fixed and the accuracy of the model is simply evaluated with it. The estimation is then