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Development of a group contribution method for estimating the thermal decomposition temperature of ionic liquids

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ABSTRACT

In this communication, a reliable group contribution (GC) method is presented for the estimation of the thermal decomposition temperature (T_d) of ionic liquids. A dataset comprising experimental T_d data for 613 ionic liquids (ILs) that covers a temperature range from 374 to 740 K was collated from various literature sources. Approximately 80% of the dataset (T_d data for 489 ILs) was used to develop the model and the remaining 20% (T_d data for 124 ILs) was implemented to evaluate the predictive capability of the obtained model. The method uses a total of 30 substructures or structural functional groups to estimate the T_d. In order to distinguish the effects of the anion and cation on the T_d, 10 sub-structures related to the chemical structure of the anion, and 20 substructures related to the chemical structure of the cation were implemented. The results of this method show an average relative deviation (AARD%) of about 4.4% from dataset values.

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1. Introduction

Ionic liquids (ILs) are special salts, which are typically liquid below the normal boiling point of water or in case of room temperature ILs, below room temperature. These ILs which are entirely composed of ions generally consist of a combination of a large organic cation with smaller sized and more symmetrical anion. Their most important characteristic is that their properties can be significantly manipulated for any particular application by changing their combination of anion and cation. This latter attribute makes them "designable materials" [1,2].

In order to design a new IL, one of the first steps requires the estimation of the elementary physico-chemical properties of the substance. One of the most significant properties of ILs, which determines their processing temperature range, is their liquidus range which is bounded by their normal melting temperature (T_m) as the lower limit and their thermal decomposition temperature (T_d) as the upper limit of temperature. Although the T_m of ILs has been carefully studied and numerous models have been suggested to date for its prediction [3–16], T_d has not been appropriately investigated and only two models have been recently proposed for its estimation [17,18].

One of the estimation methods mentioned above, which was developed by Lazuss [17], is a group contribution method (GC). The model is based on a dataset containing 198 experimental T_d data for correlation and prediction (120 data points for developing the model and tuning the model parameters, and the remaining 78 for its validation). Using a combination of a genetic algorithm as an optimizer method and least square error as an objective function, the method introduced a collection of 58 sub-structures (27 cation-based and 31 anion-based) to estimate the T_d. The average absolute relative deviations of the model results from experimental data for the correlation set and the prediction set were calculated as 4.3% and 4.2%, respectively.

The second estimation method which was proposed by Yan et al. [18] is a quantitative structure–property relationship (QSPR) model using a dataset of 158 experimental T_d data (126 data points for developing the model and tuning the model parameters, and the remaining 32 values for its validation). The average absolute relative deviations of this 25-parameter model from experimental data for the training set and the test set were approximated as 3.1% and 3.5%, respectively.

In addition to reviewing the estimation methods available for T_d, an extensive literature survey undertaken during this study

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revealed that the available experimental T_d data in the literature was considerably more than those used in the aforementioned studies. Consequently, as part of this study an extensive data collection exercise was conducted to collate a comprehensive experimental T_d database which would aid in the development of a more general model for the prediction of T_d of ILs. Since, GC methods have proved their capability in accurate estimation of various physical properties [16,19], this method was employed in this estimation study.

2. Methodology

2.1. Data preparation

A database of experimental T_d data for 613 ILs was collected from open literature. In order to assess the quality of the data when comparing them in case of multiple reported data, their experimental reported uncertainties were considered. The ILs within the dataset were categorized into 20 groups containing 1,3-dialkyl imidazolium, 1-alkyl imidazolium, amino acids, ammonium, double imidazolium, guanidinium, morpholinium, oxazolidinium, phosphonium, piperidinium, pyridazinium, pyridinium, pyrrolidinium, quinary alkyl imidazolium, sulfonium, tetra-alkyl imidazolium, tetrazolium, tri-alkyl imidazolium, triazolium, and uronium.

The information about the names, abbreviations, and the original reference for each data point are presented as supplementary materials. It should be noted that the ILs within the gathered database comprise 58 anions and 313 cations. The chemical structures of the anions and cations are also presented as supplementary materials.

Before moving to the next step, namely, developing the model, the dataset should be divided into two sub-datasets; one for developing the model (training set), and the other one for its testing (test set). The division of the data can be performed randomly; however, this may lead to an inappropriate allocation of compounds to each sub-dataset. In other words, all of the larger T_d values might end up in the test set. As a result, it would be of great interest if we could split the main dataset so that both the training set and the test set are uniform and have almost the same ranges and means. In order to take the aforementioned points into account, the K-means clustering technique was used to split the dataset into two sub-datasets [20,21]. This technique is used to partition a dataset into k sub-datasets in which each data belongs to the cluster with the nearest mean. As a result, nearly 20% of the data (124 data points) were kept out to test the model [22]. The remaining data (489 data points) were implemented for the model development.

2.2. Development of a new group contribution model

To develop a reliable GC model, the chemical structures of all the ILs were examined thoroughly to find out the most efficient sub-structures for the estimation of the T_d. In order to improve the understanding of the effects of anions and cations on the T_d, the contributions of anions and cations were independently investigated. Therefore, in total 30 chemical sub-structures (10 for anions and 20 for cations) were found to be most efficient for the prediction of the T_d of ILs. The sub-structures were used, in addition to their number of occurrences in chemical structures of anions and cations for each IL, as the model parameters. They are presented as supplementary materials.

To ensure the diversity of ILs present in both the training and test sets, a diversity test was conducted in this study [23]. There are many approaches to measure diversity, owing to its many definitions. In this study, the Euclidean distance approach was applied to measure the diversity of the ILs studied. In this approach, each IL

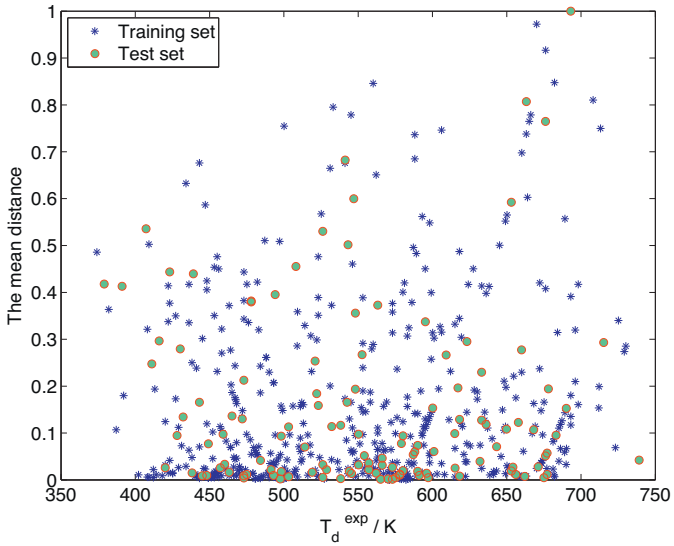

Fig. 1. Diversity of training and test sets.

(X_i) is described by a vector of corresponding sub-structures incorporating both anion and cation (x_{im}) as its elements where m is number of all total substructures:

$$X_i = (x_{i1}, x_{i2}, x_{i3}, \ldots, x_{im}) \tag{1}$$

The distance between two different ILs (d_{ij}) is defined as follows:

$$d_{ij} = \left\| X_i - X_j \right\| = \sqrt{\sum_{k=1}^{m} (x_{ik} - x_{jk})^2} \tag{2}$$

Next, the mean distance of one sample to the remaining ones (d_i) is calculated as follows:

$$\overline{d_i} = \frac{\sum_{j=1}^{n} d_{i,j}}{n-1} \tag{3}$$

where n refers to number of all ILs. Then, the calculated mean distances are normalized according to following definition:

$$\overline{d_i^{Norm}} = \frac{\overline{d_i} - \overline{d_{\min}}}{\overline{d_{\max}} - \overline{d_{\min}}} \tag{4}$$

d_i^{Norm} indicates the structural diversity of ILs (i) in comparison to others. Fig. 1 presents the values of the diversity test for both the test and training sets.

2.3. Optimization of group contributions

In order to generate the GC model, the T_d of ILs should be correlated using the aforementioned parameters. The conventional method for this purpose is the assumption of an existence of a multi-linear relationship between these groups and the desired property (here the T_d of ILs). This technique is conventionally used to develop most of the GC methods [16,24]. As a result, the collection of 30 sub-structures is introduced to develop the model (input parameters). To calculate the contribution of these parameters, the well-known least square method is employed.

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