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# Determination of the speed of sound in ionic liquids using a least squares support vector machine group contribution method

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ABSTRACT

A group contribution method (GCM) combined with least squares support vector machine (LSSVM) algorithm was used to correlate and predict the speed of sound (SS) of ionic liquids at atmospheric pressure. The NIST Standard Reference Database was used to compile a dataset comprised 41 ionic liquids and consisted of 446 experimental data values. Instead of modelling using a pre-selected and fixed number of functional groups, Forward Feature Selection was combined with the LSSVM algorithm to select the most effective variables, while keeping the number of model parameters as low as possible. The result is an 8-parameter model which has the capability of prediction as well as correlation of the speed of sounds of ionic liquids. The proposed model has an average absolute relative deviation (AARD%) of 0.36%, a coefficient of determination ($R^2$) of 0.997, and a root mean square error (RSME) of 8.47 $ms^{-1}$.

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## 1. Introduction

In recent years there has been a great deal of attention paid by researchers in investigating ionic liquids (ILs). This has mainly been due to the tremendous potential that ILs have in reaction and separation technology. Ionic liquids belong to the class of liquids which are entirely composed of ions and are fluids at temperatures below 100 °C [1].

Interesting features of ILs are their physical, chemical, and biological properties. These properties vary in a wide range and can be altered by changing the constituent anions and cations of the IL molecule. The high thermal stability, very low vapor pressure, large fluidity range, non-flammability, and high ionic conductivity, to name a few properties, of ILs make them suitable for many applications. As mentioned, altering the combination of constituent anions and cations of the ILs varies their properties and hence it is possible to design and tune the molecule for a specific application [2]. Therefore theoretically if one had a model that could predict the properties of ILs, it could be used to determine the most optimal chemical structure for a desired set of physicochemical properties. In this study, the relationship between the speed of sound and chemical structure is determined and an appropriate group contribution (GC) model is developed.

The speed of sound (SS) is an important property in chemistry and physics which is usually used in the development of an equation of state that describes the fluid and consequently can be used to derive several thermophysical properties, such as the reduced isobaric thermal expansion coefficient, isentropic and isothermal compressibility, bulk modulus, thermal pressure coefficient, isobaric and isochoric heat capacities, and the Joule–Thomson coefficient [3–6]. Unfortunately, the SS has not been fully and extensively utilized for thermodynamic property derivation for ILs due to limited experimental data being available.

There are surprisingly very few publications in literature regarding SS model development for ILs. The first study was conducted by Gardas and Coutinho [4] in 2008 in which 133 experimental data for 14 imidazolium-based ILs was used which related the SS to surface tension and density of ILs. They applied some modifications to the relationship proposed by Auerbach [7] and developed following equation:

$$\log SS = 0.6199 \ \log\left(\frac{\sigma}{\rho}\right) + 5.9447 \quad (1)$$

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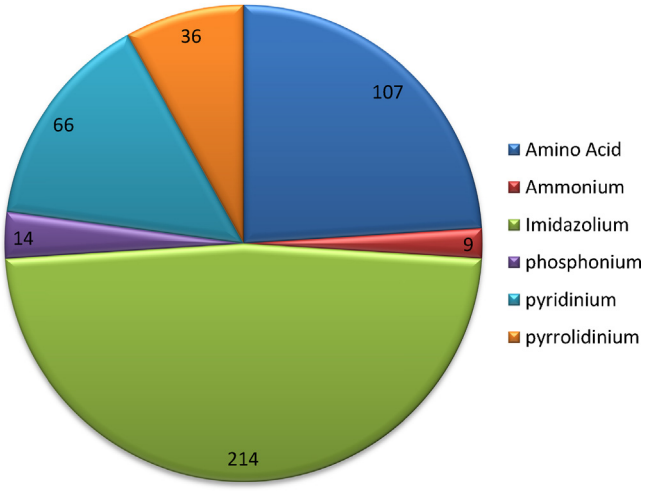


**Fig. 1.** Number of experimental data points for speed of sound according to different families of ILs.

where $\sigma$ and $\rho$ are the surface tension in $N\,m^{-1}$ and density in $kg\,m^{-3}$, respectively. The overall relative deviation of their model results was 1.96%. A disadvantage of the proposed model was the lack of experimental data for both the surface tension and density for each of the ILs. As a result, they developed two correlations to predict $\sigma$ and $\rho$. This meant that a relatively large number of computations were required to use this model to predict SS. The next and only other study in literature was undertaken by Singh and Singh [8]. They used the same approach as Gardas and Coutinho and developed a model for 3 additional imidazolium-based ILs.

The aim of this study was to develop of a model to correlate/predict the speed of sound of ionic liquids directly from chemical substructures without the need of other thermodynamic properties as input parameters.

## 2. Model development methodology

### 2.1. Data preparation

The NIST Standard Reference Database #103b [9] was used as the source of speed of sound data for the model development. Data for a total of 41 ILs for which there consisted 446 experimental values was extracted. The ILs belonged to the ammonium, imidazolium, pyrrolidinium, pyridinium, phosphonium, and amino acid class of compounds. All the ILs could be constituted from pairing of 29 cations and 11 anions. The diversity of the ILs with regard to the compound families is shown in Fig. 1. The names and structures of cations and anions are available in Tables S1 and S2 as supplementary materials.

The extracted dataset covered a wide range of temperatures (278.15–343.15 K) and values (1128.4–1885.4 $m\,s^{-1}$). Table 1 lists the ILs studied and the range of temperatures and SS. The complete dataset, including the original source of experimental data are available as supplementary materials.

The dataset was divided into three subsets: a *training set* used to develop and train the model, a *validation set* for optimizing the model parameters (internal validation), and a *test set* which was used to determine the prediction capability of the model for new compounds which have not been used in model development (external validation). In this study, *k*-means clustering is applied to choose the components of the subsets. *k*-means clustering is a method of cluster analysis which aims to partition *n* observations into *k* clusters in which each observation belongs to the cluster with the nearest mean. As a result, 20% of the ILs were used in the validation set and the test (10% each for both subsets) and the remaining 80% used in the training set to develop the model.

### 2.2. Model development

In the group contribution approach, it is assumed that each functional group in the molecule has a contribution to the value of the physical property. This approach is most widely used in the form of linear multivariate models because it is relatively easy to use [10,11], but in case of complex and nonlinear relationships between input parameters and desired property, linear modelling fails. In such cases, nonlinear modelling such as Artificial Neural Networks (ANN) and support vector machine (SVM) are used [12,13]. In recent years, ANNs have been used extensively for modelling in various fields of science; however they may suffer from some disadvantages such as converging at local minima instead of global minima, overfitting if training goes on for too long, and non-reproducibility of results, partly as a result of random initialization of the networks and variation of the stopping criteria during optimization [14,15].

The support vector machine is a highly accepted algorithm developed from the machine-learning community. SVM methods have significant advantages over ANNs which are [15,16]:

1. Unlike ANN which has a heuristic development path, SVM has a strong theoretical background which provides a high generalization capability so it can avoid local minima.
2. SVM always has a solution that can be quickly obtained by a standard algorithm (quadratic programming).
3. SVMs are less prone to overfitting or underfitting because fewer parameters are required for its development in comparison with ANNs.
4. The SVM does not need to determine the network topology and complexity in advance, which can be automatically obtained when the training process ends.
5. SVMs use structural risk minimization whilst ANNs use empirical risk minimization. Thus, SVM is usually less vulnerable to the overfitting problem.

As a result of its advantages, the SVM shows outstanding performance and can be used for both linear and nonlinear regression.

Suykens and Vandewalle [17] applied some modifications to the traditional SVM algorithm to simplify the process of finding a model by solving a set of linear equations (linear programming) instead of nonlinear equations (quadratic programming) and named it as least square support vector machine (LSSVM). As a result, LSSVM includes similar advantages of traditional SVM, but it performs faster computationally. The basic concept of SVM is to transform the signal to a higher dimensional feature space and find the optimal hyper-plane in the space that maximizes the margin between the classes [13]. In LSSVM, the target is: fitting a linear relation ($y = wx + b$) between the independent variables ($x$) and the dependent variable ($y$). To find the best relation, the cost function (penalized cost function) should be minimized.

$$Q_{\mathrm{LSSVM}} = \frac{1}{2} w^T w + \gamma \sum_{k=1}^{N} e_k^2 \tag{2}$$

where

$$e_k = y_k - (w^T \phi(x_k) + b) \quad k = 1, 2, \ldots, N \tag{3}$$

The first term of Eq. (2) is the $L_2$ norm on regression weights which is penalized quadratically. The second term is the summation of regression errors ($e_k$) for all of the $N$ training objects weighted by parameter $\gamma$, which has to be optimized by the user. Eq. (3) is the definition of the regression error which is the difference between the true and the predicted values and can be seen as a constraint

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