



# A simple group contribution correlation for the prediction of ionic liquid heat capacities at different temperatures



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## ABSTRACT

The heat capacities of pure ionic liquids (ILs) are among the thermophysical properties that are required for certain engineering calculations and designs. In this study, a simple correlation is presented for the prediction of the heat capacities of pure ionic liquids. This correlation is a temperature-dependent relation that uses temperature, molecular weight and the number of atoms (such as carbon, hydrogen, oxygen, nitrogen, etc.) in the structure of the IL as input parameters. A dataset of approximately 128 different ILs, consisting of 4822 data points, was used to develop and validate this general correlation, covering a temperature range from 190 to 663 K. Nearly three-quarters of the data were used for optimization and a quarter for validation. The resulting correlation gives good estimations for heat capacities, while having a number of advantages over previous literatures methods. These advantages include (a) being very simple; (b) not requiring any experimental data as input parameters; (c) being more global than previous literature models by having been constructed over a larger databank of ionic liquids; (d) being accurate. The average absolute relative deviation (AARD%) was calculated to be 5.8% for the optimization dataset, and 5.6% for the validation dataset. This is smaller than what is obtained for the literature atomic-contribution methods proposed by Farahani et al. and Sattari et al., with AARD% values of 14.2% and 6.6%, respectively, based on the validation dataset of this study.

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## 1. Introduction

Ionic liquids (ILs) are organic salts that consist completely of ions but are liquid at, or below, room temperature [1]. Because of their very unique properties, they have the potential to be used in a variety of industrial and chemical processes [2,3]. However, highly accurate data regarding the physicochemical properties of ionic liquids are necessary for the design and operation of such processes [2,4]. Heat capacity is among the important pure component properties in its own right, furthermore, the temperature-dependency of various thermodynamic properties, such as enthalpy, entropy, and Gibbs energy, can be calculated from the heat capacity of a compound [5]. For example, from a thermodynamic point of view, the heat capacity at constant pressure is the first derivative of enthalpy with respect to temperature. This further highlights the significance of accurate knowledge of heat capacity for many theoretical and engineering calculations.

Some reports have now become available in literature on experimental measurements or the estimation and prediction

techniques for determination of pure ionic liquid physicochemical properties. The most common experimental methods for measuring heat capacity, as reported in the literature, are differential scanning calorimetry and adiabatic calorimetry [6]. The heat capacities of some ionic liquids have also been measured with these methods [6–8]. However, such information is still lacking for many ionic liquids which have either not been measured yet, or are available at only limited temperatures.

Only a limited number of publications are available on estimation methods of ionic liquid heat capacities at different temperatures and constant pressure. Valderrama et al. [9] presented a correlation for heat capacities of ionic liquids using the concept of mass connectivity index, which had recently been defined by the authors to estimate the critical properties of ionic liquids. This correlation also requires molar volume and the ratio of mass of the cation to that of the anion, as input data. Despite the high accuracy, the experimental molar volume at 298 K is unknown for yet-unsynthesized ionic liquids (as ionic liquids are considered to be designer solvents, and so, some research tasks are involved with feasibility predictions of yet-unsynthesised ILs). Soriano et al. [1] applied a second-order group additive method to propose a model for the predication of heat capacities of ionic liquids. The database that they used consisted of 3149 data points

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### Nomenclature

AARD%	Average absolute relative deviation
B	Boron
Br	Bromine
C	Carbon
$C_p$	Heat capacity ( $\text{J mol}^{-1} \text{K}^{-1}$ )
F	Fluorine
ILs	Ionic liquids
MW	Molecular weight
N	Nitrogen
$n$	Number of data in Eq.id=6#(1)
O	Oxygen
P	Phosphorous
S	Sulfur
$T$	temperature (K)

### Subscripts and superscripts

A	Anion
C	Cation
cal	Calculated
exp	Experimental

from 32 ionic liquids, within a wide range of temperatures (188–663 K). Since they used only large sub-structures as the groups in their derivation (consisting of the whole cation and anion segments), their model is not able to estimate the heat capacities of ionic liquids for which either the specific cation or anion are not present in their own data set, for example the family of ammonium-based ionic liquids. Recently, Farahani et al. [10] proposed a structural method for the prediction of heat capacities of ionic liquids. Their databank contained 2940 data points from 56 ionic liquids, covering a temperature range of 188–663 K. Since they used only five input parameters, consisting of temperature, the atom count in both the anion and cation structures, the number of hydrogen atoms in the anion, and the number of methyl groups in the cation of the ionic liquids, they actually ignored the other elements such as oxygen, nitrogen, etc., which are often present in the structure of ionic liquids. Sattari et al. [11] proposed a new approach which combines a group-contribution method with the genetic function approximation (GFA) for the prediction of atmospheric pressure liquid heat capacities for ionic liquids. The simplicity of their model was the advantage of their work. The dataset used comprised of 3726 experimental data points from 82 ionic liquids. An overall average absolute relative deviation of 1.68% was achieved in their work. In a different work, but with the same experimental database, Sattari et al. [12] developed a quantitative structure–property relationship (QSPR) to predict atmospheric pressure liquid heat capacities of ionic liquids. Instead of using non-linear modeling, such as artificial neural network (ANN) or support vector machine (SVM), the GFA method was applied to determine the model by a binary combination of descriptors rather than using single ones. Valderrama et al. [13] presented a simple and accurate group contribution method to estimate the heat capacities of ionic liquids. They considered a structural parameter known as the mass connectivity index. They used 469 heat capacity data points from 32 ionic liquids. In another work presented by Valderrama et al. [14], artificial neural networks were used with the concept of mass connectivity index to correlate and predict constant-pressure heat capacities of ionic liquids. They used 477 heat-capacity data at several temperatures from 31 ILs to train their network. In order to discriminate among the different substances, they considered the molecular masses of the anion and

of the cation and the mass connectivity index as the independent variables. Gardas and Coutinho [15] developed a second-order group contribution method for the estimation of the liquid heat capacities of imidazolium-, pyridinium-, and pyrrolidinium-based ionic liquids containing either the hexafluorophosphate ( $\text{PF}_6$ ), tetrafluoroborate ( $\text{BF}_4$ ), bis(trifluoromethanesulfonyl) amide ( $\text{Tf}_2\text{N}$ ), bromide (Br), ethyl sulfate ( $\text{EtSO}_4$ ), or trifluoromethane sulfonate ( $\text{CF}_3\text{SO}_3$ ) anions, within the temperature range of 196.36–663.10 K, having liquid heat capacities ranging between 264.8 and 825.0  $\text{J mol}^{-1} \text{K}^{-1}$ . Albert and Müller [16] used first order group contributions to describe the structure of the ions. They used 2419 experimental heat capacity data points from 106 ILs, divided into two separate subsets for parameter fitting and testing to allow for a reliable external validation. The testing group heat capacities were calculated by their model with the mean absolute error of 5.4%. In another study, Müller and Albert [17] proposed temperature-dependent contributions to the heat capacity of ILs. They developed their model using 39 cations and 32 anions, from a database containing 2443 data points from 104 ILs. They reported that the experimental data in their test dataset could be reproduced with a mean relative error of 4.4%.

In this study, we have attempted to introduce a simple correlation to cover a wider range of ionic liquids, for more extensive applications than already available in literature. A temperature-dependent correlation based on the basic molecular parameters, including molecular weight and the number of elements such as carbon, hydrogen, oxygen, nitrogen, etc. in the structure of the ionic liquid, is presented to predict the heat capacities of ionic liquids.

## 2. Method

Since the objective of this study was to present a very simple, yet general, correlation to predict the heat capacities of numerous ionic liquids, as the first step, the input parameters of the temperature-dependent correlation were chosen to be basic structural parameters such as molecular weight and the number of the various elements in the structure of the ionic liquid. These input parameters were chosen because they are readily known parameters and very simple to find.

The proposal of any empirical correlation requires an adequate database of trustworthy experimental data. In this work, the physical property data of ionic liquids were obtained from various literature references [2,6,18–61]. A total of 4822 experimental heat capacity data points from a total of 128 different ILs, with a temperature range of (190–663.10 K) were considered. In this manner, the data covered a wide range of liquid heat capacities (93–1764  $\text{J mol}^{-1} \text{K}^{-1}$ ). The investigated ILs covered 53 different cations and 34 different anions. The names and structures of the cations and anions are presented in Tables S.1 and S.2 of the Supplementary section, respectively. Of the total of 128 ionic liquids investigated in this study, 100 were randomly considered for obtaining the correlation and the remaining 28 were set aside for validation of the suggested correlation. A complete list of all the 100 ILs used for optimizing the correlation is reported in Table 1, and the relevant information about the data is also provided, including the reference, the number of data for each IL, the molecular weight (MW), temperature range, and heat capacity range.

The optimization technique of genetic algorithm (GA) was used to obtain the constants of the correlation. GA is among the family of evolutionary algorithms (EA). It is a direct, parallel, stochastic method for global search and optimization, which imitates the evolution of living beings [62]. Genetic algorithm works with a set of individuals, representing possible solutions of the task at hand. The selection principle is applied by using a criterion, giving an

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