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Predictive model for the heat capacity of ionic liquids using the mass connectivity index

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ABSTRACT

A simple and accurate model to predict the heat capacity of ionic liquids is presented. The proposed model considers variables readily available for ionic liquids and that have important effect on heat capacity, according to the literature information. Additionally a recently defined structural parameter known as mass connectivity index is incorporated into the model. A set of 602 heat capacity data for 146 ionic liquids have been used in the study. The results were compared with experimental data and with values reported by other available estimation methods. Results show that the new simple correlation gives low deviations and can be used with confidence in thermodynamic and engineering calculations.

1. Introduction

The heat capacity of liquids is of special importance in engineering applications being required in calculations of energy transfer and thermodynamics. This property is involved in processes such as distillation, evaporation, extraction and heating, found in the petrochemical, pharmaceutical and food industry, among others [1]. There is abundant information in the literature on the heat capacity of organic and inorganic compounds; experimental data, generalized correlations, empirical equations, and group contribution methods. For ionic liquids, however, studies and models for estimating the heat capacity of ionic liquid properties are more limited but a reasonable amount of data is available, although data from one source or another are in some cases considerably different [2]. Several problems arise when measuring properties for ionic liquid, being the presence of impurities one of the main sources of discrepancies in the reported data [3–6]. Due to these problems and mainly because of the need of ionic liquid properties to make a faster progress on modeling, simulation and design of processes involving these special fluids, estimation methods are an attractive way of obtaining the necessary data.

The estimation of physical and physico-chemical properties of fluids, and in particular of ionic liquids (ILs), requires the knowledge of some basic properties not always available. For instance, generalized equations to predict the heat capacity of fluids, among others, require the critical properties, the normal boiling temperature or the acentric factor, properties not readily available in many cases [7,8]. Equations of state applications for pure compounds and mixtures also require critical properties, besides other properties [9,10]. Part of the problem has been solved with the availability of estimation methods for the critical properties, group contribution methods and neural networks modeling [11–13].

Gardas and Coutinho [14] used a group contribution method to estimate the heat capacity of ILs. Models and correlations for the heat capacity of ILs have been proposed for some limited cases. Strechan et al. [15] correlated the heat capacity of two ILs in terms of the temperature and the molecular mass of the ILs. Waliszewski et al. [16] used a group contribution method to estimate the heat capacity of four ILs. Gardas and Coutinho [14] proposed a group contribution method for heat capacity estimation of ILs based on experimental liquid heat capacity data collected from the literature. Also neural networks have been used to estimate properties of ionic liquids [8,11]. What is common in all these proposals is the use of some sort of parameters related to the structure of the molecule. This is a reasonable approach for ILs since the values of the properties are highly dependent not only on the type of anion and cation forming the ILs but also on the structure and the branching of the molecule [6,17,18].

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Nomenclature

List of symbols

A, B, C	parameters for the heat capacity equation (Eq. (1))
a, b, c, d, e, f	universal constants for any ionic liquids (Eq. (4))
C_P	heat capacity
C_{P0}	reference heat capacity at $\mathbf{T_0}$
M^+	mass of the cation
M^-	mass of the anion
T	temperature
T_0	reference temperature (298.15 K)
p, q	constants for the proposed heat capacity model (Eq. (2))
V	molar volume (Eq. (3))

Greek letters

α_0, α_1	parameters in density correlation (Eq. (1))
λ	mass connectivity index (MCI)

Abbreviations

Av.	average
ILs	ionic liquids
Max.	maximum
MCI	mass connectivity index

2. Property correlations and modeling

Researchers in the past have proposed different parameters to discriminate between one substance and another in generalized correlations for the estimation of fluid properties [7]. For hydrocarbons, for instance, the acentric factor is a good parameter for correlating several properties and has been widely employed in many applications [7]. This is not the case for ILs and acentric factors can be roughly estimated with the properties available for ILs at present. In a recent work the authors proposed a molecular parameter that appropriately involves some characteristics of the molecular structure of the ionic liquid as a discriminating parameter for generalized correlations or neural network models [2].

Also, at present there are more than 15,000 heat capacity data for about 60 ionic liquids. Most of the open access data are compiled by the Standard Reference Database of the National Institute of Standards and Technology in its Ionic Liquids Database [19]. The data provided by NIST, however, cannot be directly used because NIST only compile the data without a profound analysis and cross-checking of the data, although estimated uncertainties of the data are provided. Therefore, before using the data these need to be analyzing from an analytical, statistical and physical meaning point of view. As an example of this, Fig. 1 presents experimental data listed in the NIST data base for [emim][BF_4] in Fig. 1a and for [bmim][BF_4] in Fig. 1b. Differences such as those shown in the figure cause numerical conflicts when obtaining correlating and predicting models.

Recently, Valderrama and Rojas [2] analyzed the NIST database on heat capacity of ionic liquids, eliminated repeated data, studied the tendency of published data by common anion and cation, eliminated data that according to other sources could be solid at the given temperatures, and constructed a data base with selected 538 data for 33 ionic liquids. The authors proposed a model for estimating the temperature dependency of the heat capacity for ionic liquids. The correlation requires the knowledge of a reference heat capacity, defined by the authors at 298.15 K. Therefore the model cannot be used when this reference heat capacity value is not available or if the ionic liquid is not a liquid at that temperature. Some ionic liquids such as [bmpyr][bti], [hdmapy][bti], [bmim][C_8S] or [6,6,6,14-P][bti] for which liquid heat capacity data have melting temperatures higher than 298.15 K [19]. Therefore these substances are solids at the reference temperature of the previous model of Valderrama and Rojas [2].

In this work, a simple and accurate model to predict the heat capacity of ionic liquids from basic data, without any reference value, and with the use of a recently defined structural parameter named mass connectivity index is presented. The proposed model considers variables readily available for ionic liquids and that have important effect on heat capacity, according to the literature information. The results are compared with experimental data and with values reported by other available estimation methods.

3. Heat capacity models

In the ranges for which heat capacity data for ILs are available, the behavior of these properties with temperature is relatively simple and well known. The dependency of the heat capacity (C_P) follows a quadratic dependency (second order polynomial). Some authors have proposed to generalize the slopes of these linear or quadratic expressions in terms of some specific structural parameters or specific properties. Gardas and Coutinho [14] developed a group contribution method in which the classical quadratic temperature dependency of C_P on temperature was used:

$$C_P = A + B \cdot T + C \cdot T^2 \tag{1}$$

In this equation, the parameters A, B and C are determined by group contribution, and the groups are divided into three anion groups, six cation groups and three neutral groups. Heat capacity data for 19 ILs were used in determining the values of the contributions for calculating the parameters A, B and C.

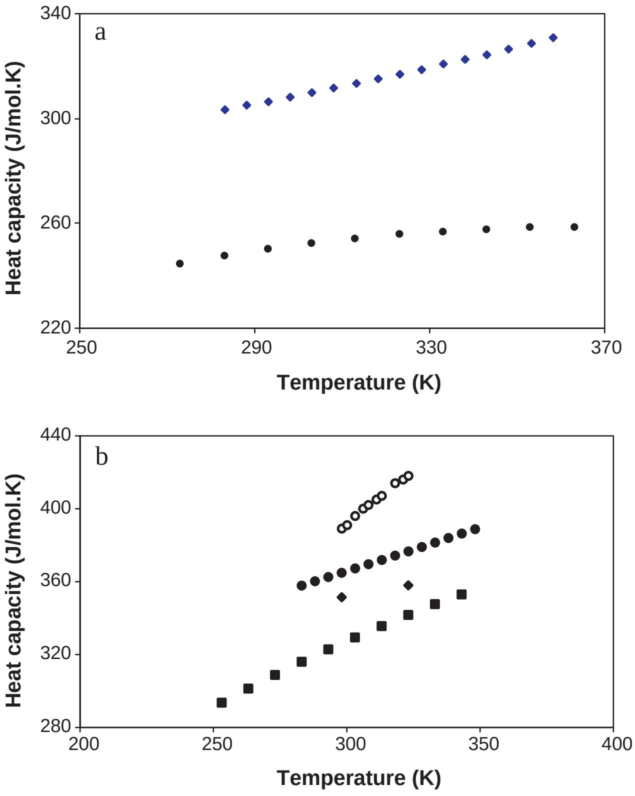

Fig. 1. Experimental data for the heat capacity of two ionic liquids as reported by NIST [19]: (a) [emim][BF_4]: (◆) Waliszewski et al. [16], (●) Van Valkenburg et al. [20]; (b) [bmim][BF_4]: (○) Kim et al. [21], (◆) Fredlake et al. [22], (●) Waliszewski et al. [16], (■) Van Valkenburg et al. [20].

Table 1
Basic properties of the 33 ionic liquids used in this study [2].

No.	Ionic liquid	Global formula	IUPAC names	M	λ
1	[6,6,6,14-P][bti]	$C_{34}H_{68}NPF_6S_2O_4$	Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide	764.0	5.53
2	[bdmapy][bti]	$C_{13}H_{19}N_3F_6S_2O_4$	1-Butyl-4-(dimethylamino)pyridinium bis[(trifluoromethyl)sulfonyl]imide	459.4	3.13
3	[bmim][Ac]	$C_{10}H_{18}N_2O_2$	1-Butyl-3-methylimidazolium acetate	198.3	1.61
4	[bmim][TfO]	$C_9H_{15}N_2F_3SO_3$	1-Butyl-3-methylimidazolium trifluoromethanesulfonate	288.3	2.11
5	[bmim][bti]	$C_{10}H_{15}N_3F_6S_2O_4$	1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	419.4	2.66
6	[bmim][C_8S]	$C_{16}H_{32}N_2SO_4$	1-Butyl-3-methylimidazolium octylsulfate	348.5	2.83
7	[bmim][dca]	$C_{10}H_{15}N_5$	1-Butyl-3-methylimidazolium dicyanamide	205.3	1.80
8	[bmim][MSO_4]	$C_9H_{18}N_2SO_4$	1-Butyl-1-methylimidazolium methylsulfate	250.3	1.84
9	[bmim][ta]	$C_{10}H_{15}N_2F_3O_2$	1-Butyl-3-methylimidazolium trifluoroacetate	252.2	2.01
10	[bmim][Br]	$C_8H_{15}N_2Br$	1-Butyl-3-methylimidazolium bromide	219.1	1.51
11	[bmim][BF_4]	$C_8H_{15}N_2BF_4$	1-Butyl-3-methylimidazolium tetrafluoroborate	226.0	2.17
12	[bmim][NO_3]	$C_8H_{15}N_3O_3$	1-Butyl-3-methylimidazolium nitrate	201.2	1.66
13	[bmim][tos]	$C_{15}H_{22}N_2SO_3$	1-Butyl-3-methylimidazolium tosylate	310.4	2.81
14	[bmim][PF_6]	$C_8H_{15}N_2PF_6$	1-Butyl-3-methylimidazolium hexafluorophosphate	284.2	2.04
15	[bmpyr][bti]	$C_{11}H_{20}N_2F_6S_2O_4$	1-Butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide	422.4	2.63
16	[bpy][BF_4]	$C_9H_{14}NBF_4$	1-Butylpyridinium tetrafluoroborate	223.0	2.20
17	[bpy][bti]	$C_{11}H_{14}F_6N_2O_4S_2$	1-Butylpyridinium bis[(trifluoromethyl)sulfonyl]imide	416.4	2.69
18	[dmprim][bti]	$C_{10}H_{15}N_3F_6S_2O_4$	1,2-Dimethyl-3-propylimidazolium bis[(trifluoromethyl)sulfonyl]imide	419.4	2.68
19	[edmapy][bti]	$C_{11}H_{15}N_3F_6S_2O_4$	n-Ethyl-4-(n′,n′-dimethylammonium)pyridinium bis[(trifluoromethyl)sulfonyl]imide	431.4	2.85
20	[emim][ESO_4]	$C_8H_{16}N_2SO_4$	1-Ethyl-3-methylimidazolium ethylsulfate	236.3	1.69
21	[emim][bti]	$C_8H_{11}N_3F_6S_2O_4$	1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	391.8	2.38
22	[emim][BF_4]	$C_6H_{11}N_2BF_4$	1-Ethyl-3-methylimidazolium tetrafluoroborate	198.0	1.88
23	[emim][TfO]	$C_7H_{11}N_2F_3SO_3$	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	260.2	1.83
24	[hdmapy][bti]	$C_{15}H_{23}N_3F_6S_2O_4$	4-(Dimethylamino)-1-hexylpyridinium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methanesulfonamide	487.5	3.42
25	[hmim][BF_4]	$C_{10}H_{19}N_2BF_4$	1-Hexyl-3-methylimidazolium tetrafluoroborate	254.1	2.46
26	[hmim][bti]	$C_{12}H_{19}N_3F_6S_2O_4$	1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	447.4	2.95
27	[hmim][TfO]	$C_{12}H_{21}N_2F_3SO_3$	1-Hexyl-3-methylimidazolium trifluoromethanesulfonate	316.3	2.40
28	[moim][BF_4]	$C_{12}H_{23}N_2BF_4$	1-Methyl-3-octylimidazolium tetrafluoroborate; 1-octyl-3-methylimidazolium tetrafluoroborate	282.1	2.74
29	[omim][bti]	$C_{14}H_{23}N_3F_6S_2O_4$	1-Octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	475.5	3.23
30	[omim][TfO]	$C_{13}H_{23}N_2F_3SO_3$	1-Octyl-3-methylimidazolium trifluoromethanesulfonate	344.4	2.69
31	[prmpyr][bti]	$C_{10}H_{18}N_2F_6S_2O_4$	1-Methyl-1-propylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide	408.4	2.49
32	[bdmim][PF_6]	$C_9H_{17}F_6N_2P$	1-Butyl-2,3-dimethylimidazolium hexafluorophosphate	298.2	2.20
33	[N4444][doc]	$C_{36}H_{73}NSO_7$	Tetrabutylammonium docusate	664.1	5.35

Recently the authors developed a generalized correlation with the inclusion of a new molecular parameter based on the concept of molecular connectivity [2]. This concept of molecular connectivity was first introduced by Randić [23], later developed and expanded by Kier and Hall [24,25], and used by several authors for several applications [24,26–29]. Randić proposed an algorithm to encode bond contributions to a molecular branching index that is known today as molecular connectivity. This concept has allows in some way to at least partially quantify the extent of branching in a molecule, an aspect of especial importance to correlate and predict properties of ionic liquids. In a recent paper the authors provided details on this concept and on the index that they named mass connectivity index (MCI). The MCI, designated by λ, considers both the type of connections between groups and the mass of such groups.

Following the concepts developed by Randić [23], the *mass connectivity index* is defined as the sum of the inverse of the mass connectivity interactions, calculated as the square root of the product of the mass of groups immediately connected in a molecule:

$$\lambda = \sum \left(\frac{1}{\sqrt{m_i m_j}} \right)_i \tag{2}$$

In this equation, m_i and m_j are the mass of neighboring groups i and j, respectively, in a molecule. In summing up the connections, $m_i m_j$ is different from $m_j m_i$. The advantage of the defined mass connectivity index, besides the simplicity of its calculation, is that not only it encodes the degree of skeletal branching but also the mass of the groups being connected.

The authors also showed that the MCI can accurately represent the variation of heat capacity on temperature for many ionic liquids. The deficiency of that heat capacity model, however, is that it requires a reference value C_{P0} for the heat capacity:

$$C_P = C_{P0} + \lambda[p(T - T_0) + q(T - T_0)^2] \tag{3}$$

The constants "p" and "q" are universal constants for any ionic liquids and were determined from experimental heat capacity data taken from the literature. In the equation, C_{P0} is the heat capacity at a reference temperature T_0, usually 298.15 K. The authors explained that the main purpose of the models they presented was to demon-

Table 2
Results for the heat capacity (Eq. (4)) using the general model including the mass connectivity index.

Heat capacity results	
$C_P =$	$a = 15.80$
$a + bV + c\lambda + d\eta + \lambda[e(T - T_0) + f(T^2 - T_0^2)]$	$b = 1.663$
	$c = 28.01$
	$d = -7.350$
	$e = 0.2530$
	$f = -1.372 \times 10^{-05}$
Range of temperature (K)	250–425
Range of property (J/K mol)	306–1413
Range of connectivity (λ)	1.509–5.525
Range of volume (cm^3/mol)	159–716
Range of cation mass/anion mass (η)	0.40–2.36
Results for data used in correlation	
Number of data	473
Av. deviation	0.1%
Av. absolute deviation	2.3%
Max. Av. absolute deviation	8.8%
Results for other temperatures and other ionic liquids	
Number of data	65
Av. deviation	0.7%
Av. absolute deviation	2.1%
Max. Av. absolute deviation	8.2%

Table 3
Overall deviations in calculated heat capacity using the proposed correlation and other methods from the literature.

	Waliszewski et al. [16]	Ge et al. [31]	Gardas and Coutinho [14]	Valderrama and Rojas [2]	This work	
					Correl.	Predic.
Number of ionic liquids	4	53	19	33	31	9
Number of data	64	961	2396	528	473	65
Av. % deviation	–	−0.8	0.4	0.9	0.1	0.7
Av. % absolute deviation	2.5	2.9	2.4	2.2	2.3	2.1
Max. Av. % absolute deviation	12.0	19.3	9.0	5.6	8.8	8.2

strate the capabilities of the defined mass connectivity index for distinguishing between different ionic liquids.

In this work a general correlation that considers the most important factors that according to present knowledge affects the heat capacity is proposed to determine C_{P0}. Once C_{P0} is modeled as proposed here a totally predictive and reasonable accurate equation for the heat capacity of ionic liquids at any temperature is derived.

One way of determining the variables that affect heat capacity is by analyzing empirical and semi-empirical models available for correlating and predicting heat capacity. Such models are usually based on the use of adjustable parameters for each fluid (correlations), on the corresponding state principle (semi-empirical and predictive), and on group contribution methods (semi-empirical and predictive). Poling et al. [7] present a good discussion of several of these methods. However, these generalized correlations and models were not developed for ionic liquids and have not been thoroughly tested for appropriateness and accuracy with these special fluids.

Gardas and Coutinho [14] showed that heat capacity depends on molar volume for a series of imidazolium-, pyridinium-, and pyrrolidinium-based ionic liquids. Also known is the strong dependency of ionic liquids properties on the type of anion and cation are also used to consider the important influence of the type of anion and cation as suggested in the literature [14]. The structure is also an important factor for determining the properties of an ionic liquid [30], and in this work this factor is considered by including the mass connectivity index, a molecular parameter recently defined by the authors [2].

In this work a general correlation valid for any ionic liquid, in function of the molar volume (V), the mass connectivity index (λ) and the ratio between the mass of the cation and that of the anion $\eta = M^+/M^-$, is proposed. Thus in Eq. (3) C_{P0} is expressed as:

$$C_{P0} = a + bV + c\lambda + d\eta \tag{4}$$

The general model which is an extension and generalization of the previous model is:

$$C_P = a + bV + c\lambda + d\eta + \lambda[e(T - T_0) + f(T^2 - T_0^2)] \tag{5}$$

Here, a, b, c, d, e and f are the universal constants valid for any ionic liquid, T_0 is a reference temperature defined as 298.15 K, and T is the temperature in kelvin.

4. Results and discussion

The parameters in Eq. (4) were determined by regression analysis of available experimental data obtained from the literature. As explained above, all data were selected from the NIST Database [19] using the 538 data points previously used by the authors for 33 ionic liquids. Part of the data (473 data points) was used for determining the model parameters and part of the data (65 data points) was used to check the predictive capabilities of the proposed model. The ionic liquids and the basic properties of them are presented in Table 1.

Table 2 summarizes the results, showing the values of the parameters for each property and some parameters that describe the accuracy of the proposed models, for both correlation and prediction. It should be emphasized that the cases considered for prediction were not used for determining the parameters of the models. Therefore this type of calculation represents a good test to check the predictive capabilities of the models. Table 3 shows the overall deviations in calculated heat capacities using the proposed correlation compared with predictions by group contribution methods of Waliszewski et al. [16], of Ge et al. [31], and of Gardas and Coutinho [14], and with a recent correlations by the authors [2]. However, care must be taken when comparing one method to another. For instance, Waliszewski et al. [16] estimated values for four ionic liquids using a group contribution method developed for organic liquids. Ge et al. [31] determined the contributions of 17 groups using the literature heat capacity data and correlated values for 53 ionic liquids. Gardas and Coutinho [14] presented correlated values only and no predictions were reported and they used only three types of ionic liquids. Additionally, as explained above, the equation recently proposed by Valderrama and Rojas [2] needs a reference value for the heat capacity, which is not always available.

As seen in Table 2, average absolute deviations are 2.3% in correlation and 2.1% in prediction. Maximum deviations are lower than 9% for both correlation and prediction. Considering the fully predictive capabilities of the proposed correlation this deviations are acceptable for engineering calculations and are below the deviations given by other methods available in the literature [2,14,16,31]. All these results guarantee the robustness of the proposed models and the appropriateness of the variables chosen for representing the heat capacity.

5. Conclusions

As stated in the literature and demonstrated in this paper the variables that affect heat capacity of ionic liquids are the volume, the type of cation and anion represented here by their masses, and the structure and branching of the molecule, represented in a simple way by the mass connectivity index. Also this index demonstrated to be a good parameter functionality of the heat capacity of ionic liquids. The proposed model can be considered to be predictive in the sense that the value heat capacity can be estimated with good accuracy at a given temperature using only basic data that is readily available: the molar volume at 298.15 K, the mass of the cation and of the anion, and the mass connectivity index.

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