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Wu, K-J orcid.org/0000-0001-8658-5449, Chen, Q-L and He, C-H (2014) Speed of sound of ionic liquids: Database, estimation, and its application for thermal conductivity prediction. AIChE Journal, 60 (3). 3. pp. 1120-1131. ISSN 0001-1541

https://doi.org/10.1002/aic.14346

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Speed of sound of ionic liquids: database, estimation, and its application for thermal conductivity prediction

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Abstract: Speed of sound is an important thermodynamic property of ionic liquids (ILs) and always chosen as a source to determine other properties. In this paper, a database for the speed of sound of pure ILs is created by collecting experimental data from literature covering the period from 2005 to 2013. The effects of temperature and the alkyl chain length on the speed of sound are discussed and a second-order corresponding states group contribution (CSGC) method is developed to estimate the speed of sound. An average absolute deviation (AAD) of 2.34% has been obtained. This method offers a simple but reliable approach to estimate the speed of sound of new ILs. Finally, the speed of sound is used to determine the thermal conductivity of ILs based on the Bridgman theory. The calculated values of thermal conductivity show a good agreement with the experimental ones with an AAD of 3.91%.

Keywords: speed of sound, ionic liquids, database, second-order CSGC method, thermal conductivity

Introduction

Ionic liquids (ILs), as possible replacements for volatile organic solvents, have been widely investigated due to their distinctive properties such as negligible vapor pressure, large liquidus range, high thermal stability, high ionic conductivity, and large electrochemical window. Knowledge of the physical and chemical properties of ionic liquids is essentially important to optimize the use of ILs and design the desirable ILs. The speed of sound, u, is an important thermodynamic property that can be experimentally determined with great precision over a broad range of temperature and pressure, and it can be related with other thermodynamic properties such as density, heat capacity, thermal conductivity, and isentropic and isothermal compressibilities[1], which are essential for the accurate design and optimization of several industrial processes. The speed of sound is related to density, ρ and isentropic compressibility, κ_S through Newton-Laplace's equation:

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

It is therefore related to the isothermal compressibility, κ_T,

$$\kappa_T = \kappa_S + \frac{T\alpha_P^2}{\rho C_P} \tag{2}$$

and to the change of density with pressure,

$$\rho(T,p) = \rho(p_{\mathrm{atm}},T) + \int_{p_{\mathrm{atm}}}^{p} \frac{1}{u^2}dp + T\int_{p_{\mathrm{atm}}}^{p} \frac{\alpha_p^2}{C_p}dp \tag{3}$$

where T is the temperature in K, α_p is the cubic expansion coefficient in 1/K, C_p is the isobaric heat capacity in J kg^{-1} K^{-1}, and subscript atm stands for atmospheric condition. Due to the high measurement accuracy, several authors also used speed of sound to determine the virial coefficients, the Van der Waals constants, the Lennard-Jones potential parameters and other equation of state constants for many compounds in which accurate critical properties are not available[2,3]. The reliable speed of sound data seem to be even more important for the development of equations of state of ILs, given the difficulty of measuring ILs critical properties or vapour pressures commonly used for this purpose[4].

However, the speed of sound for ILs seems to be a forgotten property compared with other properties. The IL Thermo database[5] only records the speed of sound for 22 ILs, most of which are imidazolium, and there is no update since 2009. Therefore, a database for speed of sound for ILs is valuable and desired. In this paper, a database of speed of sound for pure ILs is established. A wealth of important information is provided including ILs names, abbreviation, CAS registry number, molecular formula, molecular structure, molar mass, references, measurement apparatus of the speed of sound, uncertainty, samples sources, purity (the purity of ILs and water, halide content), purification method of samples, and experimental data of the speed of sound at different temperatures. Totally 96 ILs, 4478 data points in the temperature 273.14-343.15 K are covered in this database.

Given the huge potentials of ILs, experimental data of the speed of sound for all ILs of interest are still very insufficient. Therefore, it is of great importance to develop a method for estimating the speed of sound of ILs with a wide range of applicability and favorable accuracy. The reports on the prediction of the speed of sound are scarce still. Several papers[6-8] tried to obtain calculated values of speed of sound for ILs by theoretical and empirical formulas, such as Auerbach's equation. Auerbach's equation[9] is a well-known empirical relation between the speed of sound, surface tension, and density of liquids:

$$u = \left(\frac{\sigma}{6.33 \cdot 10^{-10} \rho} \right)^{a} \tag{4}$$

where a is equal to 2/3, u is the speed of sound in m s^{-1}, σ is the surface tension in N m^{-1}, and ρ is the density in kg m^{-3}. But Gardas and Coutinho[10] showed the original version of Auerbach's equation can't be used to predict the speed of sound for ILs directly, they proposed a modified version of Auerbach's relation with $a = 0.6714 \pm 0.0002$ in eq. 4. The density and surface tension data required in eq. 4 can be obtained using their previous models[11,12]. Using this new equation, the experimental speed of sound data can be described with success. For 133 data points of 14 imidazolium-based ILs, an overall relative deviation of 1.96% and a maximum deviation inferior to 5% were achieved. Undeniably, it is a good method to predict the speed of sound for ILs at that time, however, due to the lack of experimental speed of sound data, some issues are still needed to discuss: (1) a was obtained based on imidazolium-based ILs, its applicability for other kinds ILs is still questionable. (2) The accuracies of surface tension and density calculated may have a significant effect on the estimating results of speed of sound.

We already succeeded in developing simple but reliable predictive methods for surface tension[13], thermal conductivity[14] and static dielectric constant[15] of ILs in a wide range of temperature. In continuation of our previous work, here we propose a second-order CSGC method for estimating the speed of sound of ILs based on the database established in this paper. It will be a good addition for the research on the speed of sound for ILs.

The thermal conductivity is another important thermophysical property for the rational design of ILs as heat transfer fluids. However, only limited information on the thermal conductivity of ILs is available in the literature. The high viscosity and conductivity make them be not easy to measure, thus, quantitative calculation methods with a reasonable uncertainty for thermal conductivity must be developed. The aim of this paper is to find out the relation between thermal conductivity and other accessible properties (e.g. speed of sound and density), and establish a generalized model for the thermal conductivity of ILs.

Database

The speed of sound data of ILs are collected through the following steps. (1) A search of publications on the speed of sound of ILs is performed using SciFinder Scholar, the search topic is “speed of sound, ionic liquid ”, and there is no limit to publication year, document type or language. (2) The initial search results are further screened to exclude publications in which no speed of sound data are reported or only calculated values of speed of sound are available. (3) Based on the initial search results, the database is expanded by the inclusion of new publications and references contained in the selected publications. Finally, the speed of sound data are collected and tabulated from the publication pool which including totally 96 ILs, containing 51 cations and 23 anions (see Supplementary material for more detail)[16-76]. In Supplementary material Table S1, the abbreviation of ionic liquids, full name of ionic liquids, CAS registry number, molecular formula, molecular structure, and molar mass were listed. In Supplementary material Table S2, the experimental data of speed of sound (1128.40-2052.40 m s^{-1}), measurement temperatures (278.14-343.15 K), measurement apparatus, uncertainty, samples source (synthesized by the authors or commercially obtained), purity (the purity of IL, water content, and halide content), purification method, and references (from 2005 to 2013) were listed.

Development of second-order corresponding states group contribution method

In this paper, we develop a second-order corresponding states group contribution method to estimate the speed of sound of ILs. In this new method, the molecular structure of an ionic liquid is considered to be a combination of two types of groups: first-order groups and second-order groups. The first-order groups are used to describe the basic structure of ILs, while the role of the second-orders groups is to provide supplementary information for molecular structure of ILs whose description is insufficient through the first-order groups. As we know, the combination of a broad variety of cations and anions leads to a theoretically possible number of 10^{18} ILs, thus, a multi-order group division is required to describe the structure of ILs perfectly. At the present stage, a second-order group division is highly qualified to describe the structure of ILs due to the limited ILs available with experimental data of speed of sound.

First-order groups

The first level of estimation has a large set of simple groups that allow describing a wide variety of ILs. At present, most ILs with experimental data of speed of sound can be described with only first-order groups.

The first-order groups were mainly determined based on the Joback and Reid method[77], but with the inclusion of -CH$_2$- (with ammonium-, with phosphonium- and with others) which were defined as our previous work[13,14]. We selected 27 molecular groups as first-order groups to allow one to treat diverse types of ionic liquids as shown in Table 1.

(Table 1 about here)

Two points should be noted:

(1) The groups in the level should be as small as possible to improve the universality of this method. For example, ethylsulfate (EtSO$_4$) can be describe as the sum of -CH$_3$-, -CH$_2$-, -SO$_2$- and two -O- groups, so that, this method can be expanded to describe propylsulfate (PrSO$_4$), butylsulfate (BuSO$_4$), octylsulfate (OcSO$_4$) by simply adding -CH$_2$- group.

(2) In Joback and Reid method, the charged groups are not involved. In our method, we considered that the value of the group contribution of >N- (without rings) is equal to $>N<^+$ (without rings) and $-N-^-$ (without rings), and the value of the group contribution of >N- (with rings) is equal to $>N<^+$ (with rings) which were also adopted by Valderrama et al.[78] to predict the critical properties of ILs.

Second-order groups

The second-order groups which were also listed in Table 1 provide more structural information about molecular structure of ILs whose description is insufficient through the first order groups, such as the differentiation among isomers for ILs. At the moment, only experimental data for isomeric pyridinium-based ionic liquids are available. Thus, there are only three groups included in the set of second-order groups, namely, PYs^2 (2-substituted pyridinium cation), PYs^3 (3-substituted pyridinium cation), and PYs^4 (4-substituted pyridinium cation).

Corresponding states group contribution method

The variation of the speed of sound in liquids with changes in temperature has been studied by various researchers. For most liquids studied, with the exception of water below a certain temperature, the speed of sound decreases with increasing temperature. Over short ranges of temperature, the speed of sound-temperature curves appear essentially linear. Rao[79] proposed the relation to describe the variation of u with temperature T,

$$u = u_0 \left(1 - T/T_\mathrm{c}\right)^{0.9} \tag{5}$$

where u_0 is the speed of sound at absolute zero, T_c is the critical temperature in K. It is interesting to note that this relation is similar to that proposed by Guggenheim[80] for the dependence of surface tension on temperature. In our previous work[13], a CSGC model based on Guggenheim equation was proposed to predict the surface tension of ILs with success, thus, here we proposed a second-order CSGC model based on Rao's equation to calculate the speed of sound for ILs,

$$u = u_0^{'} \left(1 - T/T_\mathrm{c}\right)^{m} \tag{6}$$

where u'_0 is a temperature independent constant which only depends on the molecular structure of ILs, m is the coefficient. The critical temperature T_c is rather easy to obtain by Valderrama group contribution method[78],

$$T_{\mathrm{c}} = \frac{T_{\mathrm{b}}}{\left(\left[A + B\sum_{j=1}^{k} n_j \Delta T_{\mathrm{c}} - \left(\sum_{j=1}^{k} n_j \Delta T_{\mathrm{c}}\right)^2\right]\right)} \tag{7}$$

where A = 0.5703 and B = 1.0121, n_j is the number of occurrences of a group j in the molecular, ΔT_{c} is the contribution to the critical temperature, and the boiling temperature T_{b} is calculated as,

$$T_{\mathrm{b}} = 198.2 + \sum_{j=1}^{k} n_j \Delta T_{\mathrm{b}} \tag{8}$$

where n_j is the number of occurrences of a group j in the molecule, and ΔT_{b} is the contribution to the boiling temperature. Their contributions to the boiling temperature T_{b} and the critical temperature T_{c} were determined in the same way that explained by Alvarez and Valderrama[81]. The reliability of this method has been tested by using literature values of ILs densities and compared with calculated values using a generalized correlation that makes use of those estimated critical properties[78]. The critical properties obtained by this method have been widely used to calculate other chemical and physical properties, such as density[82], heat capacity[83], surface tension[13], and thermal conductivity[14].

The u'_0 in eq. 6 is obtained by the second-order CSGC method according to the following equation,

$$u'_0 = \sum_{i=0}^{3} a_i \left(\sum_{j=1}^{k} n_j \Delta u_{0,j}\right)^i \tag{9}$$

where n_{j} is the number of groups of type j, k is the total number of different groups in the molecule, and the parameters a_{i} and $\Delta u_{0,\mathrm{j}}$ were estimated as presented in Table 1 by minimizing the objective function O.F. in eq. 10,

$$O.F. = \sum_{i=1}^{N_p} \left[\left(u_{\mathrm{calc}} - u_{\mathrm{exp}}\right)^2\right]_i \tag{10}$$

where N_{p} represents the number of data points. Eq. 9 is similar in form to Ma and Li equations[84] which can be used to determine the assumed-critical temperature and assumed-critical pressure based on the group-contribution method.

Finally, a new equation based on the second-order CSGC method can be obtained for the estimation of the speed of sound,

$$u = \sum_{i=0}^{3} a_i \left(\sum_{j=1}^{k} n_j \Delta u_{0,j} \right)^i \left(1 - T/T_\mathrm{c}\right)^m \tag{11}$$

and the AAD result is defined to evaluate the accuracy of our method,

$$\mathrm{AAD}(\%) = \frac{\sum_{i=1}^{Np} \left| \left(u_\mathrm{cacl} - u_\mathrm{exp}\right) / u_\mathrm{exp} \right|_i}{Np} \times 100 \tag{12}$$

Results and Discussion

Effect of temperature

The temperature dependence of speed of sound for six ILs, namely 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6mim][PF_6]$[19], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_4mpyrr][NTf_2]$[36], 1-butyl-3-methylpyridinium tetrafluoroborate, $[B_3mpy][BF_4]$[55], tributyl methyl phosphonium methylsulfate, $[P_{4441}][MeSO_4]$[64], 2-hydroxyethyltrimethylammonium L-(+)-lactate, [HE3MA][LAC][69], diethylammonium acetate, DEAA[63] is shown in Figure 1 as example.

(Figure 1 about here)

(1) For most of ILs, such as $[C_6mim][PF_6]$, $[C_4mpyrr][NTf_2]$, $[B_3mpy][BF_4]$, and $[P_{4441}][MeSO_4]$, the speed of sound decreases linearly with increasing temperature for the whole temperature range studied. The assumption that the speed of sound is a linear function of the temperature is applicable over the range studied.

(2) For few ionic liquids, such as [HE3MA][LAC] and [3HEMA]MS, the speed of sound

decreases non-linearly with increasing temperature in the low-temperature region ($T < 298$ K). Aparicio et al.[69] assumed that some fluid rearrangements appear for this low-temperature region leading to the nonlinear behavior.

(3) For only one ionic liquid, diethylammonium acetate (DEAA), a striking phenomenon was observed that the speed of sound increases linearly with increasing temperature[63]. DEAA was synthesized in the lab by the authors, and the mass fraction purity is 0.99 which was confirmed through ^{1}H NMR spectroscopy. But the speed of sound of DEAA was measured by a single crystal ultrasonic interferometer (model F-05) only at 298.15, 303.15, 308.15, and 313.15 K. More experiments are needed to confirm this result, and the future progress in the mechanism of the special trend with temperature is prospected.

Effect of the alkyl chain length of the cation

The effect of the alkyl chain length was studied comparing the pyridinium-based ILs [Empy][NTf$_2$]/[Pmpy][NTf$_2$]/[Bmpy][NTf$_2$], the ammonium-based ILs TMAH/TEAH/TPAH /TBAH, and the imidazolium-based ILs [C$_2$mim][BF$_4$]/ [C$_4$mim][BF$_4$]/[C$_6$mim][BF$_4$]/ [C$_8$mim][BF$_4$], and [C$_2$mim][NTf$_2$]/[C$_3$mim][NTf$_2$]/[C$_4$mim][NTf$_2$]/[C$_5$mim][NTf$_2$]/[C$_6$mim][NTf$_2$] /[C$_8$mim][NTf$_2$]. From Figure 2, it was observed that speed of sound changes irregularly with elongation of the alkyl chain length. For [C$_n$mim][NTf$_2$] at 293.15 K, the order for the speed of sound is [C$_2$mim][NTf$_2$] > [C$_8$mim][NTf$_2$] > [C$_3$mim][NTf$_2$] > [C$_6$mim][NTf$_2$] > [C$_4$mim][NTf$_2$] > [C$_5$mim][NTf$_2$]. For [(C$_n$)$_4$N][OH] at 298.15 K, [C$_n$mim][BF$_4$] and [C$_n$mpy][NTf$_2$] at 293.15 K, the value of the speed of sound decreases as the alkyl chain length increases, but the speed of sound in [C$_3$mpy][NTf$_2$] is comparable with that in [C$_4$mpy][NTf$_2$]. Therefore, when it comes to the effect of the alkyl chain length, both the types of anions and cations should be taken into account.

(Figure 2 about here)

Second-order CSGC method

In this paper, the database for the speed of sound was divided into two sets: the training set (86 ionic liquids, 3875 data points) and the test set (10 ionic liquids, 603 data points). The training set was used to obtain the parameters for the second-order CSGC method, and the testing set was used to test the validity of this method. The AAD results were listed in Table 2 for both the training and test sets.

(Table 2 about here)

From Table 2, it is observed that 23.62% of the calculated speed of sounds were within absolute deviation of 0.00-1.00%, 67.66% were within 1.00-5.00%, 7.99% were within 5.00-10.00%, and only 0.71% were superior to 10%. It's worth noting that the speed of sound for DEAA increases linearly with increasing temperature, but our method was established based on the assumption that the speed of sound decreases with increasing temperature, thus this method can't provide a correct information on speed of sound-temperature relation for diethylammonium acetate (DEAA), although the calculated values agreed well with the experimental ones (AAD = 3.31%). More detail about calculated values and calculation method can be found in the Supplementary material Table S3.

The calculated values of the speed of sound (Y) display a good agreement with the experimental ones (X) for both the training and test sets: $Y = (1.00120 \pm 0.0004713)X$ (the training set) and $Y = (0.98684 \pm 0.0009705)X$ (the test set), as shown in Figure 3.

(Figure 3 about here)

Relative deviations between the calculated and experimental speed of sound data were shown in Figure 4, in which hollow stars stand for the training set and the hollow squares stand for the test set. The overall AAD is 2.34% and the maximum deviations equal to 19.72% and 13.20%, for the training and test sets, respectively. These results show clearly that this second-order CSGC method could be applicable to other ILs with 27 first-order groups and 3 second-order groups we defined before.

(Figure 4 about here)

This method has an advantage over simple group contribution method in that it can distinguish among isomeric pyridinium-based ionic liquids. It is also practical because it is simple to use and requires only a compound's structure. However, it still faces some problems which may limit its accuracy and scope. First of all, this second-order CSGC method was established based on a large database. The accuracy of experimental data has a significant effect on the reliability of this model. At present stage, although the amount of data points exceeds 4400, for many kinds of ILs, either only 1 literature is available or the experimental values form different authors show large discrepancies, which make it difficult for us to identify the reliability of the experimental data. In addition, this method cannot provide satisfactory results for some kinds of protic ionic liquids (PILs). Due to the presence of proton-donor and -acceptor sites, some PILs possess a number of particular properties compared to other ILs. However, in this paper, we have no special treatment of PILs for the sake of simplicity. It can be found that all the ILs with an AAD larger than 10% are PILs systems, such as DEAS (17.20%), TEAS (13.22%), and TEAS (11.11%). Finally, the critical temperature T_c obtained by Valderrama group contribution method is required in this method and the accuracy of this method depends partly on the accuracy of T_c.

Prediction of thermal conductivity

For ionic liquids, measurements and experiments on thermal conductivity are not always easy and cheap. Thus, it is a good choice to determine thermal conductivity from other easily obtained properties, such as density and speed of sound.

For most pure liquids, the thermal conductivity can be estimated by using the Bridgman equation[85],

$$\lambda = \rho c_V v_y a \tag{13}$$

where λ is the thermal conductivity in W m^{-1} K^{-1}, ρ is the density in g m^{-3}, c_v is the heat capacity at constant volume (per unit mass) in J K^{-1} g^{-1}, v_y is the mean molecular speed in the y direction, which can be replaced by the speed of sound, u. The distance a, that the energy travels between two successive collisions is taken to be the lattice spacing $\left(V/N\right)^{1/3}$. Making these substitutions in eq. 13 gives,

$$\lambda = \rho c_V u\left(V/N\right)^{1/3} = k\rho c_V u\left(\frac{M}{\rho}\right)^{1/3} = k\rho^{2/3}M^{1/3}uc_V \tag{14}$$

where k is a constant.

Paulechka et al.[86] analyzed the linear correlations of the molar heat capacity at constant pressure (C_p) with the molar volume (V) of 18 ILs at 298.15 K and the temperature modification for the whole temperature range was proposed. But, based on the database of heat capacities from Farahani et al.[87], we found that when more ILs and temperatures were taken into account, the C_p-V relation deviates from linear law. Thus, a better fit is needed for the function C_p=$f(V,T)$. The difference between C_P and C_v is very small for solids and liquids, therefore, in this paper, we considered that the heat capacity at constant volume (per unit mass) (c_v) can also be described as a function of molar volume (V) at 298.15 K,

$$c_V = \frac{C_V}{M} = \frac{k_0 V^{\alpha}}{M} \tag{15}$$

where α is the power which is equal to 1 in Paulechka' work to describe C_p-V relation.

For the whole temperature range, a temperature modification is needed,

$$c_V = \frac{k_0 V^{\alpha}}{M} + \left(k_1 T + k_2\right) = \frac{k_0 \left(\frac{M}{\rho}\right)^{\alpha}}{M} + \left(k_1 T + k_2\right) \tag{16}$$

Based on eqs. 14 and 16, the following equation can be obtained,

$$\lambda = \rho^{2/3} M^{1/3} u \left(k_0 \frac{M^{\alpha-1}}{\rho^{\alpha}} + \left(k_1 T + k_2\right) \right) \tag{17}$$

In eq. 17, k_0, k_1, k_2 and α are constants for all ionic liquids studied. Values of the density, ρ and speed of sound, u can be obtained by experiments or estimation models. In this paper, the density for ionic liquids was calculated by Valderrama method[88],

$$\rho = \left(\frac{A}{B}\right) + \left(\frac{2}{7}\right) \cdot \left\{\frac{A \cdot LnB}{B}\right\} \frac{\left(T - T_b\right)}{\left(T_c - T_b\right)} \tag{18}$$

$$A = a + b \cdot \frac{M}{V_c} \tag{19}$$

$$B = \left(\frac{c}{V_c} + \frac{d}{M}\right) \cdot V_c^{\delta} \tag{20}$$

the values of the constants, valid for any ionic liquid, are: $a = 0.3411$, $b = 2.0443$, $c = 0.5386$, $d = 0.0393$, $\delta = 1.0476$, and the speed of sound was calculated by the method developed in the previous section.

A database of thermal conductivity for ionic liquids was established by collecting data from literature published in 2007-2012[89-95]. 276 data points for 34 ILs, based on 13 cations with 17 anions (see Supplementary material Table S4 for more detail on the structure of each ionic liquid) were used in this work to obtain the parameters in eq. 17. Table 3 gives the values of parameter needed in eq. 17 and the deviations between the experimental and calculated values of thermal conductivity were summarized in Table 4. From Table 4, it can be seen that the model guarantees with 92.0% probability that the deviation will be lower than 10% and with 68.1% probability that the deviation will be below 5%. The model also guarantees that the deviation will not be greater than 15%. The deviation of each data points was shown in Figure 5. Other details on the accuracy of the model and the calculation of density, speed of sound, and thermal conductivity in eq. 17 can be found in Supplementary material Table S5.

(Table 3 about here)

(Table 4 about here)

(Figure 5 about here)

In our previous work, a group contribution method was developed to estimate the thermal conductivity of ionic liquids[14]. An average absolute deviation of 1.66% was achieved for total 286 data points of 36 ionic liquids. Compared with the method described here, we found that each has both advantages and disadvantages. The GC method is easy to follow, don't require other properties, and has a better accuracy, but the GC method is a structure-based method which requires large amounts of data to ensure the accuracy of the parameters and the applicability of the model. Unfortunately, a lack of reliable thermal conductivity data still exists at present. Compared with previous empirical methods[14,96,97], eq. 17 is a generalized equation which can be considered as a modification of Bridgman equation for ILs. Although density and speed of sound data are needed to determine thermal conductivity, the measurements of density and speed of sound are much easier and with higher accuracy. Sometimes, they can even be carried out simultaneously in a commercial sound analyzer (e.g. Anton Paar model DSA5000). The large database of density and speed of sound of ILs also ensures the applicability of predictive model. When the experimental values are not available, the calculated ones form predictive model are also good choices. But due to the propagation of error, the accuracy of the models for density and speed of sound estimation has a significant impact on the model for thermal conductivity estimation. The AAD result of this method is 3.91%, which is a little larger than previous empirical methods, but is still comparable with the experimental uncertainties (3-5%) [89,92].

Conclusions

In this work, a database for the speed of sound of pure ILs was established covering the period from 2005 to 2013. A wealth of important information for 96 ionic liquids which have 51 cations and 23 anions was provided. Based on the database, a second-order CSGC method was developed to estimate the speed of sound of ionic liquids with good accuracy. An overall relative deviation of 2.34% and a maximum deviation inferior to 20% were achieved. The correlation allows us to calculate the speed of sound of different ILs in a wide temperature range. Whilst with the calculated speed of sound data, the thermal conductivities of ionic liquids were determined based on a modified Bridgman equation in which only density and speed of sound data are needed. For a database of 276 data points 34 ionic liquids, the calculated thermal conductivities agree well with the experimental data from literature with an AAD of 3.91%.

Acknowledgment

Financial support from the National Natural Science Foundation of People's Republic of China (project-nos: 21176206 and 21306167) is gratefully acknowledged.

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Caption

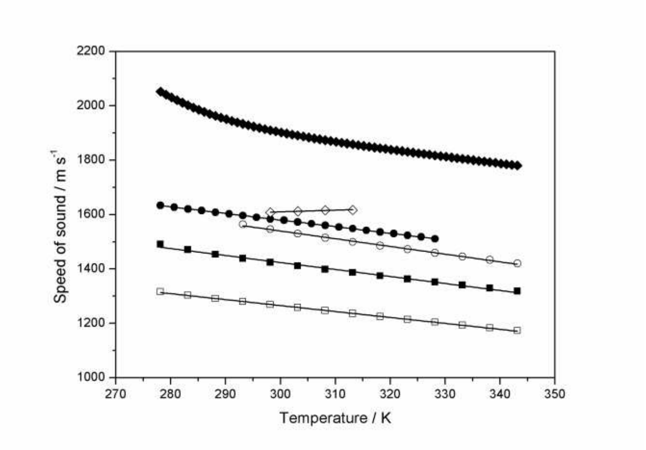

Figure 1. Speed of sound, *u*, of six ionic liquids as a function of temperature: ■, $[C_6mim][PF_6]$; □, $[C_4mpyrr][NTf_2]$; ●, $[B_3mpy][BF_4]$; ○, $[P_{4,4,4,1}][MeSO_4]$; ◆, [HE3MA][LAC]; ◇, DEAA.

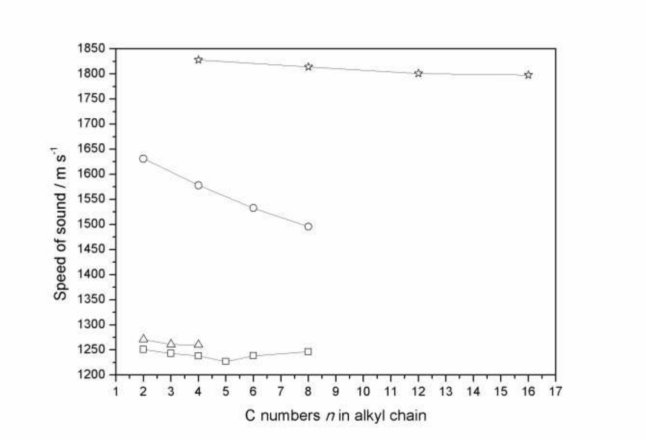

Figure 2. The variation trend of speed of sound for □, $[C_nmim][NTf_2]$, ○, $[C_nmim][BF_4]$, and △, $[C_nmpy][NTf_2]$ at 293.15 K and ☆, $[(C_n)_4N][OH]$ at 298.15 K with different C numbers in alkyl chain.

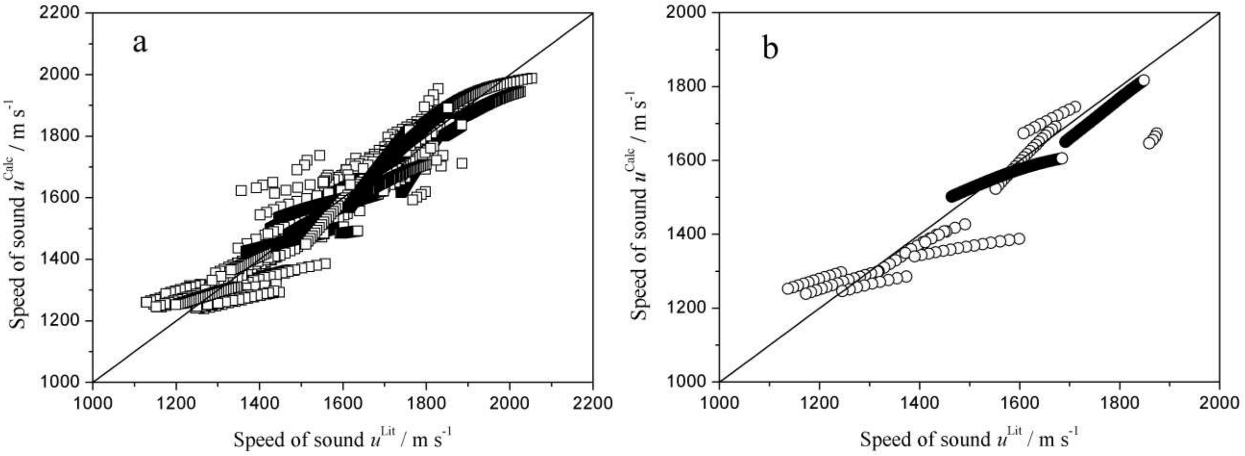

Figure 3. Linear relationship between experimental and calculated speed of sounds for ionic liquids: (a) □, the training set; (b) ○, the test set.

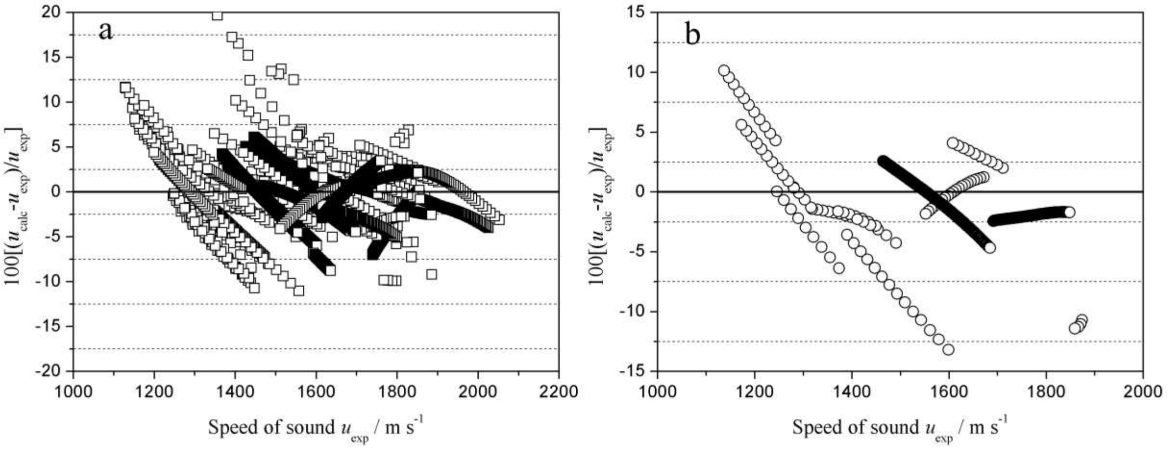

Figure 4. Relative deviations between the calculated and experimental speed of sound data as a function of experimental speed of sound for all data points used in the current study: (a) □, the training set; (b) ○, the test set.

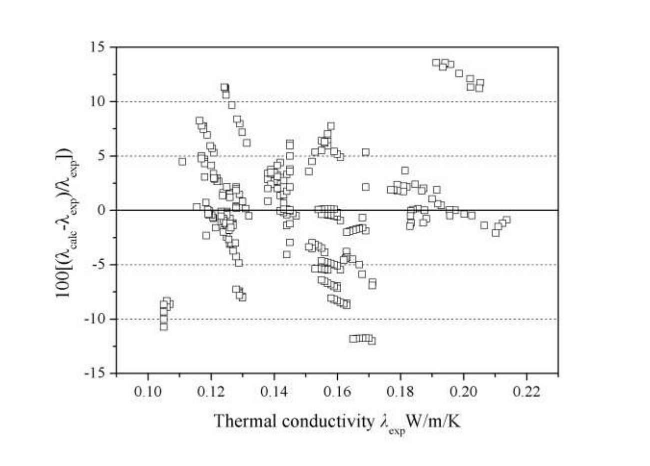

Figure 5. Relative deviations between the calculated and experimental thermal conductivity data.

as a function of experimental thermal conductivity for all data points used in the current study.

Table 1. The coefficients and values of the group contribution.

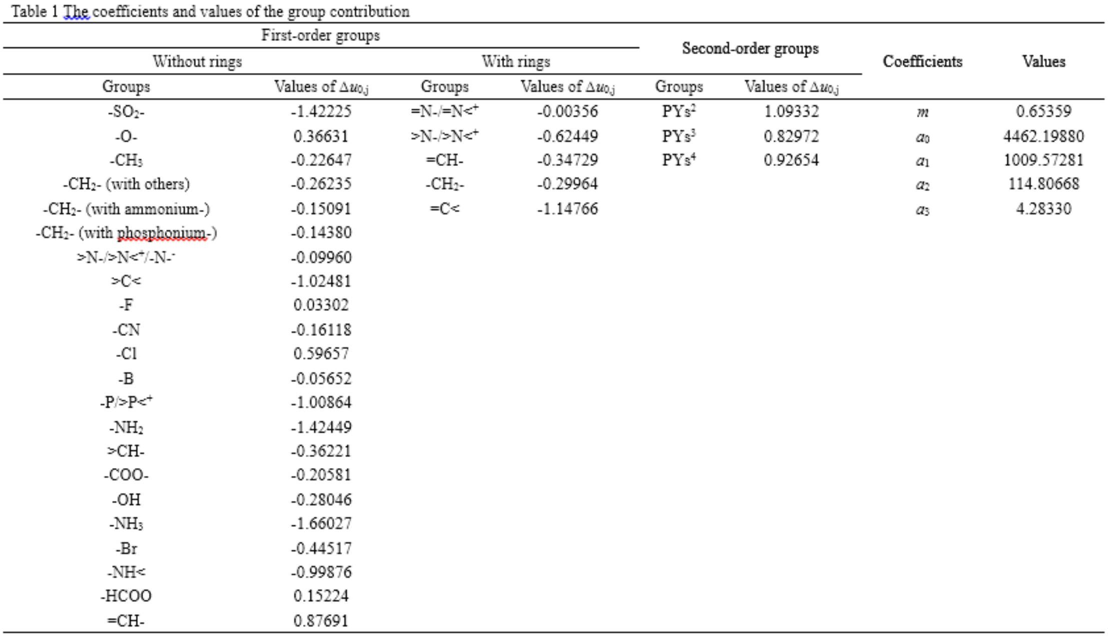

Table 1 The coefficients and values of the group contribution

First-order groups				Second-order groups		Coefficients	Values
Without rings		With rings					
Groups	Values of $\Delta u_{0,j}$	Groups	Values of $\Delta u_{0,j}$	Groups	Values of $\Delta u_{0,j}$		
-SO$_2$-	-1.42225	=N-/=N<$^+$	-0.00356	PYs^2	1.09332	m	0.65359
-O-	0.36631	>N-/>N<$^+$	-0.62449	PYs^3	0.82972	a_0	4462.19880
-CH$_3$	-0.22647	=CH-	-0.34729	PYs^4	0.92654	a_1	1009.57281
-CH$_2$- (with others)	-0.26235	-CH$_2$-	-0.29964			a_2	114.80668
-CH$_2$- (with ammonium-)	-0.15091	=C<	-1.14766			a_3	4.28330
-CH$_2$- (with phosphonium-)	-0.14380						
>N-/>N<$^+$/-N-$^-$	-0.09960						
>C<	-1.02481						
-F	0.03302						
-CN	-0.16118						
-Cl	0.59657						
-B	-0.05652						
-P/>P<$^+$	-1.00864						
-NH$_2$	-1.42449						
>CH-	-0.36221						
-COO-	-0.20581						
-OH	-0.28046						
-NH$_3$	-1.66027						
-Br	-0.44517						
-NH<	-0.99876						
-HCOO	0.15224						
=CH-	0.87691						

Table 2. Estimation of the speed of sound of pure ionic liquids under atmospheric pressure.

Training set						
No.	Ionic liquid	Temperature range (K)	T_c (K) calculated by eq. 7	Data points	AAD (%)	Reference
1	[C$_4$mim][PF$_6$]	298.15	719.39	1	1.38	16
		283.15-338.15		13	1.65	17
		293.15		1	2.26	18
		278.15-343.15		14	1.39	19
		293.15-303.15		3	1.34	20
		298.15-318.15		5	1.43	21
		298.15		1	1.30	22
		293.15-323.15		7	1.40	23
2	[C$_8$mim][PF$_6$]	278.15-343.15	810.85	14	5.03	19
		293.15-303.15		3	5.60	20
		293.15-303.15		3	5.60	26
3	[C$_2$mim][BF$_4$]	293.15-308.15	596.23	4	5.38	27
4	[C$_4$mim][BF$_4$]	298.15-318.15	643.18	5	2.44	16
		283.15-343.15		13	2.42	17
		293.15		1	4.20	18
5	[C$_6$mim][BF$_4$]	293.15-318.15	689.98	6	0.16	28

		293.15-318.15		6	0.16	[29]
		288.15-318.15		7	0.05	[24]
6	[C$_8$mim][BF$_4$]	283.15-343.15	736.99	13	2.30	[17]
		298.15		1	3.36	[30]
7	[C$_2$mim][NTf$_2$]	293.15	1249.10	1	4.72	[18]
		293.15-343.15		11	6.61	[31]
		293.12-323.22		7	5.49	[32]
8	[C$_4$mim][NTf$_2$]	283.15-323.15	1269.73	5	5.87	[34]
		293.15		1	5.71	[18]
				7	6.51	[32]
9	[C$_5$mim][NTf$_2$]	293.15	1280.88	1	5.91	[18]
10	[C$_6$mim][NTf$_2$]	283.15-343.15	1292.58	16	7.55	[35]
		293.15		1	5.79	[18]
		293.15-343.15		11	8.44	[31]
11	[C$_8$mim][NTf$_2$]	293.15	1317.63	1	6.66	[18]
		288.22-323.28		9	6.91	[32]
12	[C$_2$mim][TfO]	278.15-338.15	992.24	7	4.63	[37]
13	[C$_4$mim][TfO]	293.15-318.15	1023.44	6	2.03	[28]
		288.15-308.15		3	1.54	[38]
		293.15-343.15		11	2.97	[31]
		298.15-318.15		6	2.03	[29]
14	[C$_8$mim][Cl]	298.15	869.41	1	2.74	[39]
		298.15-328.15		3	2.54	[40]
		278.15-343.15		14	3.98	[41]
15	[C$_4$mim] [OcSO$_4$]	298.15-343.15	1189.84	46	4.57	[42]
		278.15-343.15		14	6.67	[41]
16	[C$_4$mim][MeSO$_4$]	278.15-343.15	1081.64	14	1.25	[43]
		293.15-303.15		3	0.35	[20]
		278.15-343.15		14	1.17	[41]
		298.15-313.15		4	0.43	[44]
17	[C$_2$mim][EtSO$_4$]	298.15-328.15	1067.49	3	3.35	[45]
		288.15-343.15		12	3.54	[46]
		298.15		1	2.10	[47]
18	[C$_1$mim][MeSO$_4$]	293.15-303.15	1040.00	3	3.22	[20]
		283.15-343.15		13	3.90	[48]
19	[C$_1$py][MeSO$_4$]	288.15-308.15	995.18	3	1.49	[38]
		293.15-343.15		11	2.11	[49]
20	[C$_2$mim][CH$_3$COO]	283.15-343.15	807.14	13	3.78	[51]
21	[C$_4$mim][CH$_3$COO]	283.15-343.15	847.31	13	1.53	[51]
22	[C$_4$mim][DCA]	288.15-308.15	1035.84	3	2.04	[38]
		293.15-343.15		11	3.21	[31]
23	[C$_6$mim][DCA]	288.15-308.15	1073.82	3	2.73	[38]
		293.15-343.15		11	1.47	[31]
24	[C$_4$mpyrr][DCA]	288.15-308.15	988.28	3	0.43	[38]

		293.15-343.15		11	0.85	[52]
25	[C$_4$mpyrr][TfO]	288.15-308.15	967.87	3	2.77	[38]
		293.15-343.15		11	1.61	[31]
26	[C$_4$mpy][TfO]	288.15-308.15	997.71	3	1.11	[38]
27	[C$_2$epy][EtSO$_4$]	288.15-308.15	1054.38	3	2.53	[38]
		293.15-343.15		11	1.30	[49]
28	[B3mpy][BF$_4$]	293.15-323.15	625.79	4	1.13	[54]
		278.15-328.15		21	0.84	[55]
		293.15-318.15		6	1.03	[28]
		293.15-318.15		6	1.03	[29]
29	[B4mpy][BF4]	293.15-323.15	625.79	4	0.53	[54]
		278.15-328.15		21	0.67	[55]
30	AlaC3LS	288.15-343.15	1183.54	12	6.11	[56]
31	GluC3LS	288.15-343.15	1353.64	12	3.39	[56]
32	ValC3LS	288.15-343.15	1225.57	12	5.52	[56]
33	AlaC4LS	288.15-343.15	1203.57	12	5.24	[56]
34	GlyC4LS	303.15-343.15	1181.76	9	3.23	[56]
35	GluC4LS	323.15-343.15	1376.94	5	1.22	[56]
36	ValC4LS	288.15-343.15	1246.41	12	5.84	[56]
37	[Empy][NTf$_2$]	293.15-343.15	1217.56	11	4.25	[31]
38	[Pmpy][NTf$_2$]	293.15-343.15	1228.67	11	5.06	[31]
39	[Bmpy][NTf$_2$]	293.15-343.15	1240.28	11	5.34	[31]
40	[Hmim][TFO]	303.15-343.15	1055.50	9	1.10	[31]
41	[B3mpy][N(CN)$_2$]	278.15-328.15	1014.92	21	0.64	[57]
42	[Mmpy][MeSO$_4$]	293.15-343.15	1010.09	11	1.99	[49]
43	[Empy][MeSO$_4$]	293.15-343.15	1024.63	11	0.73	[49]
44	[EM$_2$N(CH$_2$)$_2$OH][BSO$_3$]	298.15	923.74	1	1.55	[58]
45	[BEM$_2$N][EtSO$_4$]	298.15	872.02	1	5.45	[58]
46	[EM$_2$N(CH$_2$)$_2$OH][EtSO$_4$]	298.15	1100.38	1	0.62	[58]
47	[C$_6$mim][Br]	298.15-318.15	873.47	7	2.60	[24]
48	[E2mpy][NTf$_2$]	278.15-338.15	1217.56	25	1.62	[59]
49	[P2mpy][NTf$_2$]	278.15-338.15	1228.67	25	1.89	[59]
50	[Ppy][BF$_4$]	278.15-338.15	573.81	25	1.99	[60]
51	m-2-HEAF	278.15-338.15	589.88	241	3.22	[61]
52	m-2-HEAPr	278.15-338.15	738.08	241	0.81	[61]
53	m-2-HEAB	278.15-338.15	760.26	241	2.10	[61]
54	m-2-HEAiB	278.15-338.15	761.66	241	1.05	[61]
55	m-2-HEAP	278.15-338.15	782.49	241	3.00	[61]
56	[C$_3$mim][Br]	288.15-308.15	815.60	5	2.62	[62]
57	DEAS	298.15-313.15	901.32	4	17.20	[63]
58	TEAA	298.15-313.15	668.03	4	4.94	[63]
59	[P$_{4,4,4,8}$][Cl]	293.15-343.15	904.14	11	6.04	[64]
60	[P$_{4,4,4,1}$][MeSO$_4$]	293.15-343.15	1001.26	11	2.23	[64]
61	TMAA	298.15-313.15	668.03	4	13.22	[65]

62	TMAS	298.15-313.15	917.40	4	6.55	65
63	[Beim][TfO]	278.15-338.15	1039.35	7	1.67	66
64	[Empyrr][EtSO$_4$]	308.15-343.15	1008.1	8	4.05	67
65	[Bepyrr][EtSO$_4$]	328.15-343.15	1055.67	4	3.13	67
66	[Bmpyrr][MeSO$_4$]	298.15-343.15	1023.74	10	2.31	67
67	[E$_3$MN][MeSO$_4$]	308.15-343.15	926.27	8	0.36	67
68	TMAH	298.15-313.15	625.07	4	6.25	68
69	TEAH	298.15-313.15	715.38	4	1.78	68
70	TPAH	298.15-313.15	805.63	4	3.88	68
71	TBAH	298.15-313.15	898.53	4	9.87	68
72	[HE3MA][LAC]	293.15-343.14	806.00	66	1.96	69
73	[3HEMA][MS]	293.15-343.14	1093.44	66	2.06	69
74	2-HEAA	290.65-323.15	699.22	15	3.20	70
75	2-HEAO	278.14-343.15	1073.14	237	2.35	71
76	2-HE2AO	278.16-343.15	1244.61	261	2.87	71
77	2-HEAPE	278.15-338.15	765.05	241	1.27	72
78	2-HTEAPE	278.15-338.15	1019.45	241	2.95	72
79	[Emin][LAC]	278.15-343.15	912.67	66	2.90	73
80	[Bpy][BF$_4$]	278.15-338.15	597.61	25	1.60	74
81	[Bpy][TfO]	298.15-338.15	979.70	17	1.47	74
82	2-HEAF	278.15-338.15	571.30	240	1.66	75
83	2-HDEAF	278.15-338.15	707.50	241	1.65	75
84	2-HTEAF	323.15-338.15	825.09	60	2.40	75
85	Ecoeng 500	303.15-343.15	1489.87	5	9.46	76
86	DEAA	298.15-313.15	646.51	4	3.31	63

Test set

No.	Ionic liquid	Temperature range (K)	T_c (K) calculated by eq. 7	Data points	AAD (%)	Reference
87	[C$_6$mim][PF$_6$]	278.15-343.15	764.89	14	2.31	19
		293.15-303.15		3	2.51	20
		288.15-318.15		7	2.11	24
		293.15-303.15		3	2.51	25
88	[C$_3$mim][NTf$_2$]	293.15-343.15	1259.13	11	7.24	33
89	[C$_4$mpyrr][NTf$_2$]	278.15-343.15	1208.96	14	2.52	36
		293.15-343.15		11	3.02	31
90	[P$_{6,6,6,14}$][DCA]	278.15-343.15	1525.46	14	8.23	36
91	[C$_2$py][EtSO$_4$]	298.15-343.15	1023.78	10	3.08	50
92	[B2mpy][BF$_4$]	288.15-338.15	625.79	21	0.82	53
93	GlyC3LS	303.15-343.15	1162.01	9	3.06	56
94	m-2-HEAA	278.15-338.15	715.92	241	1.98	61
95	TEAS	298.15-313.15	917.40	4	11.11	63
96	2-HDEAPE	278.15-338.15	897.69	241	1.66	72
	Total	***278.14-343.15***		***4478***	***2.34***	

Table 3. The values of parameters for eq. 17.

Parameters	Values
k_0	1.1407E-4
k_1	5.3458E-9
k_2	-9.7345E-6
α	0.7380

Table 4. Estimation of thermal conductivity of pure ionic liquids under atmospheric pressure.

No.	Ionic liquid	Temperature range (K)	M	Data points	AAD(%)	Reference
(1)	[C_2mim][NTf_2]	293.00-353.00	391.32	7	7.68	89
		273.15-353.15	391.32	9	0.57	90
(2)	[C_4mim][NTf_2]	293.00-353.00	419.37	7	3.01	89
		296.00-332.00	419.37	3	2.26	91
(3)	[C_6mim][NTf_2]	293.00-353.00	447.42	7	0.77	89
		273.15-353.15	447.42	9	2.73	90
(4)	[C_8mim][NTf_2]	293.00-353.00	475.48	7	1.04	89
(5)	[C_{10}mim][NTf_2]	293.00-353.00	503.53	7	1.26	89
(6)	[C_4mim][OTf]	293.00-353.00	288.29	7	0.24	89
		293.00-353.00	288.29	7	3.27	92
(7)	[C_2mim][$EtSO_4$]	293.00-353.00	236.29	7	1.99	89
		273.15-353.15	236.29	9	0.60	90
(8)	[C_2mim][$OcSO_4$]	273.15-353.15	320.46	9	5.12	90
(9)	[C_4mpyrr][NTf_2]	293.00-323.00	422.41	4	1.06	89
		293.00-333.00	422.41	5	4.64	92
		296.00-332.00	422.41	3	2.27	91
(10)	[$P_{6,6,6,14}$][NTf_2]	293.00-353.00	764.02	7	1.73	89
(11)	[$P_{6,6,6,14}$][Cl]	293.00-353.00	519.32	7	5.76	89
(12)	[C_4mim][BF_4]	294.70-334.90	226.03	3	2.72	93
(13)	[C_6mim][BF_4]	293.00-353.00	254.08	7	5.71	92
(14)	[C_4mim][PF_6]	293.00-353.00	284.18	7	3.21	92
		294.90-335.10	284.18	3	3.75	94
(15)	[C_6mim][PF_6]	293.00-353.00	312.24	7	2.90	92
		294.10-335.20	312.24	3	1.18	94
(16)	[C_8mim][PF_6]	295.10-335.20	340.29	3	2.76	94
(17)	[C_2mim][CH_3COO]	273.17-353.15	170.21	9	1.09	90
(18)	[C_2mim][DCA]	273.17-353.15	177.21	9	12.52	90
(19)	[C_2mim][$C(CN)_3$]	273.17-353.15	201.23	9	1.38	90
(20)	[C_4bim][NTf_2]	273.17-353.15	461.45	9	6.96	90
(21)	[$N_{8,8,8,1}$][NTf_2]	273.17-353.15	648.86	9	9.31	90
(22)	[$N_{4,4,4,1}$][Ser]	298.15-353.15	304.48	7	1.82	95

(23)	[N$_{4,4,4,1}$][Tau]	298.15-353.15	324.53	7	0.53	[95]
(24)	[N$_{4,4,4,1}$][Lys]	298.15-353.15	345.57	7	11.83	[95]
(25)	[N$_{4,4,4,1}$][Thr]	298.15-353.15	318.50	7	0.11	[95]
(26)	[P$_{4,4,4,4}$][Ser]	298.15-353.15	363.52	7	4.96	[95]
(27)	[P$_{4,4,4,4}$][Tau]	298.15-353.15	383.58	7	6.82	[95]
(28)	[P$_{4,4,4,4}$][Lys]	298.15-353.15	404.62	7	8.43	[95]
(29)	[P$_{4,4,4,4}$][Thr]	298.15-353.15	377.55	7	3.39	[95]
(30)	[P$_{4,4,4,4}$][Val]	313.15-353.15	375.58	5	5.43	[95]
(31)	[N$_{4,1,1,1}$][NTf$_2$]	296.00-332.00	396.38	3	1.60	[91]
(32)	[C$_4$mmim][NTf$_2$]	296.18-333.16	433.40	3	1.95	[91]
(33)	[C$_4$mpyrr][FAP]	293.00-353.00	587.27	7	9.24	[89]
(34)	[C$_4$mim][NPf$_2$]	296.14-332.36	519.38	3	2.36	[91]
	Total	***273.15-353.15***		***276***	***3.91***	

Supplementary Material Table S1-S5.