Predictive Group Contribution Models for the Thermophysical Properties of Ionic Liquids

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Ionic liquids have been the object of intense interest from both academic and industrial research groups aiming at a wide range of applications in novel processes and products. The knowledge of their thermophysical properties, or the ability to estimate them, is often required for the design of these processes and products. However, experimental data for many properties are in short supply and often contradictory among various sources available. Based on experimental data collected from the literature, predictive group contribution models were developed after a critical analysis of the data for various thermophysical properties, *viz.* density, viscosity, surface tension, speed of sound, refractive index, heat capacity, electrical conductivity, thermal conductivity, isobaric expansivity, and isothermal compressibility, of various families of ionic liquids. The results of the proposed models show average absolute relative deviations generally of the same order as the experimental accuracy of the data itself. These rapid and facile predictive models are very easy to use, can provide predictions of property values for the new ionic liquids, and also allow them to be extended to new groups of cations and anions as further data become available.

Introduction

Ionic liquids, due to their unique properties, are expected to replace volatile organic compounds (VOCs) in several applications and to produce important developments in the chemical industry *(1)*. They result from the combination of large organic cations with inorganic or organic anions; the possible number of ionic liquids is estimated to be more than a trillion. Changes in the cation, anion, or the moieties attached to each ion of ionic liquid, will allow the thermophysical properties to be modified to meet the design criteria for a given application.

The study of thermophysical and transport properties and structure-property relationships of ionic liquids is lagging behind when compared with the investigations of their potential applications. Thermophysical properties are required for the design of processes and products involving these compounds. Yet the experimental data available are currently scarce for most properties, and often data from various sources are contradictory.

Given the huge number of potential ionic liquids, the experimental measurement of the thermophysical and transport properties for all ionic liquids of interest is infeasible. The alternative is to develop predictive models, based on some experimental data, from which the required properties with the desired accuracy can be obtained. The development of group contribution methods for the properties of ionic liquids is particularly apt for this purpose as (i) from a restricted amount of data, it will be possible to expand the information available to a large number of compounds, and (ii) it will also allow for a critical evaluation of the accuracy of available data.

The possibility of tailoring the properties of an ionic liquid to meet the requirements of some specific application makes ionic liquids designer solvents par excellence. Given the large number of potential ionic liquids, designing an ionic liquid by experimental trial an error or based on some empirical heuristics is not the most promising approach *(2)*. The design of ionic liquids will certainly require the development of methods for Computer Aided Molecular Design (CAMD) of these compounds. Besides their obvious interest for the prediction of thermophysical and transport properties, group contribution methods are also at the basis of the development of CAMD methods *(3,4)*.

In this work, we present a number of group-contribution methods for the estimation of thermophysical and transport properties of ionic liquids. Our goal is to show that these methods can be used for fast and easy prediction of physical properties, with acceptable deviations, for a wide range of ionic liquids.

In a previous series of articles, a number of predictive methods for density *(5),* surface tension *(6),* viscosity *(7),* speed of sound *(8),* liquid heat capacity *(9),* electrical conductivity, thermal conductivity, refractive index, isobaric expansivity, and isothermal compressibility *(10)* of ionic liquids have been proposed. Moreover, a correlation for the self diffusion coefficients of ionic liquids based on the Stokes-Einstein relation will also be proposed. It will be shown that the proposed models allow a good description of the respective experimental data available, usually within the agreement of the experimental data of different authors, as described in the report of the IUPAC task group for the development of standard systems for the measurement of thermodynamic

properties of ionic liquids (http://www.iupac.org/web/ins/2002-005-1-100). The effect of the cation, anion and alkyl chain length on the studied properties is discussed briefly.

Collection of Physical Properties of Ionic Liquids

The experimental density, surface tension, viscosity, speed of sound, liquid heat capacity, electrical conductivity, self-diffusion coefficients, thermal conductivity, refractive index, isobaric expansivity and isothermal compressibility data of ionic liquids, collected from open literature, measured in our laboratory, and from the International Union of Pure and Applied Chemistry (IUPAC) database *(11)* have been used to develop predictive methods for the estimation of the these properties of ionic liquids. The following ionic liquid ions were considered in this study: cations, 1,3-dialkylimidazolium, $[C_n mim]^+$; 1-alkylpyridinium, $[C_n py]^+$; 1,1-dialkylpyrrolidinium, $[C_n mpyrr]^+$; 1,1-dialkylpiperidinium, $[C_n mpip]^+$; tetraalkylphosphonium, $[P_{wxyz}]^+$; and tetraalkylammonium, $[N_{wxyz}]^+$: anions, hexafluorophosphate, $[PF_6]^-$; tetrafluoroborate, $[BF_4]^-$; bis{(trifluoromethyl)sulfonyl}amide, $[NTf_2]^-$; chloride, Cl^-; ethanoate, $[CH_3COO]^-$; methyl sulfate, $[MeSO_4]^-$; ethyl sulfate, $[EtSO_4]^-$; trifluoromethanesulfonate, $[CF_3SO_3]^-$; bis{(perfluoroethyl)sulfonyl}amide, $[NPf_2]^-$; trifluoroethanoate, $[CF_3COO]^-$; dimethylphosphate, $[(CH_3)_2PO_4]^-$; methoxyethyl sulfate, $[CH_3OC_2H_4SO_4]^-$; dicyanamide, $[N(CN)_2]^-$; tricyanomethanide, $[C(CN)_3]^-$; tetrachloroferrate(III), $[FeCl_4]^-$; tetrachloroaluminate(III), $[AlCl_4]^-$; tetrachlorogallate(III), $[GaCl_4]^-$; tetrachloroindate(III), $[InCl_4]^-$; and trichlorozincate(II), $[ZnCl_3]^-$.

After collection of physical property data, a critical analysis was carried out before using it for parameter estimation. Group contribution parameters were obtained using at least two different ionic liquids. Single available ionic liquids with a new cation and/or anion were discarded in this study with the exception of a cation with three methyl groups attached to the imidazolium ring that was used to estimate the methyl group.

Group Contribution Parameters Calculation

For each property, initially, available data for each individual ionic liquid were fitted to the appropriate predictive equations to obtain parameters. Then, by comparison of the parameter values of ionic liquids containing similar cations and anions, it was possible to make an initial estimation for the values of parameters for each cation and anion. Then the cation was split into the parent cation (heterocyclic ring, or alkylammonium, or alkylphosphonium), methylene, and methyl group. Using these initial estimates, the objective function (square of the difference of experimental and predicted property data) is minimised for all the data points available, to obtain optimum values of the group parameter.

Results and Discussion

Density

We proposed a predictive method for the estimation of ionic liquids densities *(5)* over a wide range of temperatures (273.15-393.15) K and pressures (0.10-100) MPa, according to Equation (1).

$$\rho = \frac{Mw}{NV(a + bT + cP)} \qquad (1)$$

where ρ is the density in kg m^{-3}, Mw is molecular weight in kg mol^{-1}, N is the Avogadro constant, V is the molecular volume in Å^3, T is the temperature in K and P is the pressure in MPa. The coefficients a, b and c were estimated by fitting Equation (1) to our previously published experimental data *(12,13)*. About 800 density data points were used. The values of coefficient a, b and c obtained were $8.005 \times 10^{-1} \pm 2.333 \times 10^{-4}$, $(6.652 \times 10^{-4} \pm 6.907 \times 10^{-7})$ K^{-1} and $(-5.919 \times 10^{-4} \pm 2.410 \times 10^{-6})$ MPa^{-1} respectively, at a 95% confidence level. The average percentage deviation of the calculated densities from the experimental densities is 0.29%. The experimental density (ρ_{exp}) for the ionic liquids used to derive coefficients a, b and c of Equation (1) are in very good agreement with the corresponding calculated density (ρ_{cal}): $\rho_{exp} = (0.9998 \pm 0.0003)\rho_{cal}$ (correlation coefficient: $R^2 = 0.9989$, at a 95% level of confidence). For the density calculation, volume parameters (V) of ions and groups were either directly taken from literature *(14)* or calculated following the Jenkins' procedure *(15)*. Experimental densities available in the literature for imidazolium, pyridinium, pyrrolidinium and alkylphosphonium derived ionic liquids were predicted by using Equation (1). Predicted densities (ρ_{cal}) are in good agreement with experimental literature densities (ρ_{exp}) over a wide range of temperatures (273.15–393.15 K) and pressures (0.10–100 MPa) *(4)*; $\rho_{exp} = (0.9968 \pm 0.0004)\rho_{cal}$ for imidazolium-based ionic liquids and $\rho_{exp} = (1.0133 \pm 0.0010)\rho_{cal}$ for phosphonium-based ionic liquids. The mean percent deviation (MPD) of 0.45% is observed for 1086 data points of imidazolium-based ionic liquids, while that is 1.49% for 404 data points of phosphonium-based ionic liquids. A low MPD ranging from 0.41% to 1.57% was also observed for 31 data points of pyridinium and pyrrolidinium-based ionic liquids. Recently *(16,17)*, it was shown that Equation (1) can be applied with confidence to the ionic liquids from families other than those used in the development of the correlation *(5)*.

Isobaric Expansivity

Isobaric expansivity data of ionic liquids are required for their development as heat transfer fluids or for heat storage applications or, as recently suggested, for ionic liquid based liquid-in-glass thermometers *(18)*. The isobaric expansivity (α_P) is defined by Equation (2).

$$\alpha_P = \frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P \qquad (2)$$

where V_m is molar volume, ρ is density, and T is temperature at constant pressure P.

A total of 109 data points for experimental isobaric expansivity of 49 ionic liquids (based on imidazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, and ammonium cations with 19 different anions, at 298.15 K and 0.1 MPa) were collected from the literature or calculated using experimental density data using Equation (2). In spite of the wide range of ionic liquids investigated, the isobaric expansivities observed fall in a narrow range of values: 4.48×10^{-4} to 7.44×10^{-4} K^{-1} at 298.15 K. As discussed previously *(5)*, the precision to which this property is currently known precludes any study of its temperature dependency, as this is inferior to the experimental uncertainty. For this reason the isobaric expansivity will be here correlated at the temperature of 298.15 K and atmospheric pressure by a group contribution approach:

$$\alpha_P = A_{\alpha_P} = \sum_{i=1}^{k} n_i a_{i,\alpha_P} \qquad (3)$$

where n_i is the number of groups of type i, and k is the total number of different groups in the molecule, and the estimated parameters $a_{i,\alpha P}$ are presented in reference *(10)*.

For the studied ionic liquids, the calculated isobaric expansivity values ($\alpha_{P,cal}$), using Equation (3) and group contribution parameters $a_{i,\alpha P}$ *(10)*, are in good agreement with the corresponding experimental isobaric expansivity ($\alpha_{P,exp}$) data; where $\alpha_{P,cal} = (1.0007 \pm 0.0027)\alpha_{P,exp}$. For 109 data points of 49 ionic liquids available in literature, the overall MPD is 1.98 %, with a maximum deviation of the order of 7 %. It was noticed that the isobaric expansivity of the studied ionic liquids is weakly dependent on the anion and increases slightly with the alkyl chain length of the cation *(10)*.

Isothermal Compressibility

Isothermal compressibility of ionic liquids is relevant for the design of industrial fluids to be used in pumps or compressors *(19)*. The isothermal compressibility (κ_T) can be expressed by Equation (4).

$$k_T = -\frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_T \qquad (4)$$

A total of 26 data points for experimental isothermal compressibility directly available in the literature, or calculated using experimental density data using Equation (4) for 22 ionic liquids based on imidazolium, pyridinium, pyrrolidinium, piperidinium, and phosphonium cations with different anions, at

298.15 K and 0.1 MPa, were collected. As discussed previously (5,16), the precision to which this property is known precludes any study of its temperature or pressure dependency, as this is inferior to the experimental uncertainty. For this reason, the isothermal compressibility was correlated at 298.15 K and atmospheric pressure by a group contribution approach in the studied range 0.33 to 0.73 GPa^{-1} of experimental isothermal compressibility data

$$\kappa_T = A_{\kappa_T} = \sum_{i=1}^{k} n_i a_{i,\kappa_T} \tag{5}$$

where n_i is the number of groups of type i, and k is the total number of different groups in the molecule, and the parameters a_{i,κ_T} are reported in reference (10).

For the studied ionic liquids, the isothermal compressibility ($\kappa_{T,cal}$), calculated using Equation (5) and group contribution parameters $a_i\kappa_T$ (10), are in good agreement with the corresponding experimental isothermal compressibility ($\kappa_{T,exp}$) data; where $\kappa_{T,cal} = (1.0055 \pm 0.0064)\kappa_{T,exp}$. For 26 data points of 22 ionic liquids available in literature, the overall MPD is 2.53 % with a maximum deviation of the order of 6.7 %, and from these about 46.2 % of the estimated isothermal compressibility data having less than 1 % relative deviation. However, with the limited amount of experimental data, it is not possible to provide any definitive conclusion on the effect of cation, anion and alkyl chain length on isothermal compressibility of ionic liquids.

Surface tension

Experimental data for the surface tension of ionic liquids is very scarce and essentially restricted to imidazolium-based ionic liquids. Using surface tension data of ionic liquids measured in our laboratory along with a database obtained from the literature, a correlation was developed for the surface tensions of ionic liquids (6) showing that it is possible to use the parachor to obtain good predictions for surface tension.

The surface tensions of ionic liquids can be obtained using Equation (6),

$$\sigma = (P_{ch}\rho/Mw)^4 \tag{6}$$

where P_{ch} is the parachor which is calculated from Knotts et al. (20) parachor QSPR correlation, using the parameter table estimated from the second training set containing experimental surface tension values with an uncertainty less than 1%, and ρ is the density obtained using Equation (1). Predicted surface tensions (σ_{cal}), from Equation (6), of imidazolium-based ionic liquids display a good agreement with the corresponding experimental surface tensions (σ_{exp}): $\sigma_{cal} = (0.987 \pm 0.004)\sigma_{exp}$. For the 361 data points for 38 imidazolium based ionic liquids studied, the overall MPD is 5.75 %, and a maximum deviation inferior to 16% observed.

The predictive capability of Equation (6) for ionic liquid surface tension was further checked below through its potential to correlate the speed of sound of ionic liquids through Auerbach's relation, as discussed in the next Section.

Speed of sound

Experimental data for speed of sound in ionic liquids is scarce and limited to imidazolium-based ionic liquids. The speed of sound (u) in units of m s^{-1} can be estimated, using the surface tension (σ) in N m^{-1} units and density (ρ) in kg m^{-3} units, through the theoretical Auerbach's relation [21]

$$u = (\sigma / 6.33 \times 10^{-10} \rho)^a \qquad (7)$$

where $a = 2/3$.

To examine the functional dependence of u and σ/ρ, a double logarithmic plot was drawn using speed of sound data from the literature and density and surface tension obtained using Equations (1) and (6) respectively, and the resulting linear correlation was:

$$\log_{10} u_{exp} = (0.6199 \pm 0.0092)\log_{10} (\sigma / \rho) + (5.9447 \pm 0.0414) \qquad (8)$$

with a correlation coefficient $R^2 = 0.9717$ at 95% confidence level.

Although Equation (7) directly (with $a=2/3$) is not capable of predicting sound velocities of ionic liquids, a modified version of it, following the approach of Oswal et al. [22,23], could be used to correlate the speed of sound in ionic liquids [8].

The experimental speed of sound (u_{exp}) of imidazolium-based ionic liquids displays a good agreement with the corresponding calculated speed of sound (u_{cal}) using Equation (8) where $u_{exp} = (0.9952 \pm 0.0022)$ u_{cal}. For the 133 data points of 14 imidazolium-based ionic liquids, the overall MPD is 1.96 % with a maximum deviation inferior to 5 %.

Viscosity

Experimental viscosity data for ionic liquids are still in short supply and restricted to a few families of well-studied ionic liquids. In a previous work [7], the viscosity of ionic liquids was correlated using an Orrick–Erbar-type approach [24] by estimating parameters A and B in Equation (9):

$$\ln \frac{\eta}{\rho.Mw} = A + \frac{B}{T} \qquad (9)$$

where η and ρ are the viscosity in cP and density in g cm^{-3}, respectively. Mw is the molecular weight and T is the absolute temperature. A and B can be obtained by a group contribution method and the group contribution parameters for them are presented in [7]. Equation (9) was used for about 500 data points for 29 ionic liquids, providing a relative average deviation of 8 % and a maximum deviation of 28 %.

The Orrick–Erbar method requires knowledge of the density for the prediction of viscosity. To overcome this limitation, and to attempt the development of an improved viscosity model with lower deviations in estimated viscosities, a new correlation based on the Vogel-Tammann-Fulcher (VTF) equation, Equation (10), was proposed *(10)*.

$$\ln \eta = A_\eta + \frac{B_\eta}{(T - T_{0\eta})} \tag{10}$$

where η is viscosity in Pa s, T is temperature in K, and A_η, B_η, and $T_{0\eta}$ are adjustable parameters. The ratio of parameters B_η, and $T_{0\eta}$, $B_\eta/T_{0\eta}$, is also known as Angell strength parameter. It was found that the optimum value of $T_{0\eta}$ is 165.06 K. A_η and B_η, can be obtained by a group contribution method according to Equations (11).

$$A_\eta = \sum_{i=1}^{k} n_i a_{i,\eta} \qquad\qquad B_\eta = \sum_{i=1}^{k} n_i b_{i,\eta} \tag{11}$$

where n_i is the number of groups of type i, and k is the total number of different groups in the molecule, and the parameters $a_{i,\eta}$ and $b_{i,\eta}$ are presented in *(10)*. Close to 500 data points for 25 ionic liquids based on imidazolium, pyridinium, and pyrrolidinium cations with different anions, covering wide ranges of temperature, 293.15-393.15 K and viscosity, 0.004-1.065 Pa s, were used in this study.

A remarkable agreement was observed between the calculated and the experimental viscosity data, using the Vogel-Tammann-Fulcher (VTF) equation with $T_{0\eta}$=165.06 K and the group contribution parameters $a_{i,\eta}$ and $b_{i,\eta}$ for imidazolium, pyridinium, and pyrrolidinium based ionic liquids containing $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, $[CH_3COO]^-$, $[MeSO_4]^-$, $[EtSO_4]^-$, and $[CF_3SO_3]^-$ anions over a wide range of temperature and viscosity. Viscosities of ionic liquids having imidazolium-based cations increas according to the series: $[NTf_2]^-$ < $[CF_3SO_3]^-$ < $[BF_4]^-$ < $[EtSO_4]^-$ < $[MeSO_4]^-$ < $[PF_6]^-$ < $[CH_3COO]^-$ *(7)*. For ionic liquids having a common anion and a similar alkyl chain length on the cation, the viscosity increases with cation following the order: $[C_n mim]^+$ < $[C_n py]^+$ < $[C_n mpyrr]^+$ *(7)*.

The calculated viscosity (η_{cal}) of the ionic liquids studied displays a good agreement with the corresponding experimental viscosity (η_{exp}), where $\ln \eta_{cal} = (0.9647 \pm 0.0043)\ln \eta_{exp}$ (R^2=0.9907 at 95% level of confidence). For 482 data points for 25 ionic liquids available in literature, the overall MPD is 7.50 % with a maximum deviation inferior to 23 %. Rejection of doubtful experimental data was not possible due to the limited amount of experimental data currently available and the large discrepancies in experimental viscosity values reported in literature among authors, which may be due to impurities like water and halogen ions present in ionic liquid samples, or the experimental method adopted.

The predictive capability of the group contribution method here developed for ionic liquid viscosity was further checked by its potential to correlate with equivalent conductivity and the self-diffusion coefficient using fractional forms

of the Walden rule *(25)* and the Stokes-Einstein relation *(26)*, respectively, as discussed in subsequent Sections.

Electrical Conductivity

A database of experimental electrical conductivity (λ) available from the open literature was collected. A global number of 300 data points for 15 ionic liquids based on imidazolium, pyridinium, pyrrolidinium, and tetraalkylammonium cations with [PF$_6$]$^-$, [BF$_4$]$^-$, [NTf$_2$]$^-$, [EtSO$_4$]$^-$, [CF$_3$SO$_3$]$^-$, [NPf$_2$]$^-$, or [CF$_3$COO]$^-$ as anions, covering wide ranges of temperature, 258.15-433.15 K and electrical conductivity, 0.01-12.68 S m^{-1}, were used in this study.

A Vogel-Tammann-Fulcher (VTF) type equation, Equation (12), similar to that used for viscosity, was used to correlate the electrical conductivity of ionic liquids.

$$\ln \lambda = \ln A_\lambda + \frac{B_\lambda}{(T - T_{0\lambda})} \tag{12}$$

where A_λ, B_λ, and $T_{0\lambda}$ are adjustable parameters, from which A_λ and B_λ can be obtained with a group contribution method.

$$A_\lambda = \sum_{i=1}^{k} n_i a_{i,\lambda} \qquad\qquad B_\lambda = \sum_{i=1}^{k} n_i b_{i,\lambda} \tag{13}$$

where n_i is the number of groups of type i, and k is the total number of different of groups in the molecule, and the parameters $a_{i,\lambda}$, and $b_{i,\lambda}$ estimated for the ionic liquids studied are presented in *(10)*. It was found that $T_{0\lambda}$ presents a value for all studied ionic liquids close to 165 K, surprisingly similar to $T_{0\eta}$, which clearly indicates that these values have a physical meaning. The $T_{0\lambda}$ value was thus fixed to a value identical to $T_{0\eta}$ ($T_{0\lambda} = T_{0\eta} = 165.06$ K). About 300 experimental electrical conductivity data points for 15 ionic liquids available were then used to estimate the values of the group contribution parameters $a_{i,\lambda}$, and $b_{i,\lambda}$.

The calculated electrical conductivity (λ_{cal}), using the Vogel-Tammann-Fulcher (VTF) equation, Equation (12), with $T_{0\lambda} = 165.06$ K and using group contribution parameters $a_{i,\lambda}$, and $b_{i,\lambda}$ for imidazolium, pyridinium, pyrrolidinium, and ammonium-based ionic liquids having [PF$_6$]$^-$, [BF$_4$]$^-$, [NTf$_2$]$^-$, [EtSO$_4$]$^-$, [CF$_3$SO$_3$]$^-$, [NPf$_2$]$^-$, or [CF$_3$COO]$^-$ as anions, are in good agreement with the corresponding experimental electrical conductivity (λ_{exp}), where $\lambda_{cal} = (0.9974 \pm 0.0022)\lambda_{exp}$ ($R^2 = 0.9985$ at 95% level of confidence). For 307 data points for 15 ionic liquids available in literature, the overall MPD is 4.57 % with a maximum deviation of the order of 16 %. Water content present in ionic liquid samples may increase its electrical conductivity significantly *(27)*, which may be a possible reason for some of the larger deviations observed in the calculated electrical conductivity.

For ionic liquids containing the [C$_4$mim]$^+$ (1-butyl-3-methylimidazolium) cation, electrical conductivity increases the anion following the order [NPf$_2$]$^-$ ≤ [PF$_6$]$^-$ < [CF$_3$SO$_3$]$^-$ < [NTf$_2$]$^-$ ≤ [CH$_3$COO]$^-$ < [BF$_4$]$^-$ *(10)*. Electrical conductivity

decreases with the increase of alkyl chain length in the imidazolium cation, and this decrease is more pronounced at higher temperatures. For ionic liquids having a common anion and a similar alkyl chain length on the cation, the electrical conductivity, behaving in the opposite manner to viscosity, decreases with cation nature following the order: $[C_n\text{mim}]^+ > [C_n\text{py}]^+ > [C_n\text{mpyrr}]^+$. However, more experimental data and theoretical studies are required to fully understand the influence of cation and anion on the electrical conductivity of ionic liquids.

The relationship between viscosity and conductance in terms of the fractional Walden rule *(25)* can be written as:

$$\Lambda\eta^\alpha = \text{constant} \tag{14}$$

where Λ is equivalent conductivity and α is a constant between zero and unity. To evaluate if Equation (14) can provide an adequate relation between the electrical conductivities and viscosities of ionic liquids, experimental electrical conductivity data collected from the literature were converted into equivalent conductivity using density calculated from Equation (1), and fluidity is obtained as the reciprocal of viscosity from Equation (10). In a log-log plot; the slope (α) of the Walden line is obtained as 0.935 ± 0.008. This indicates that equivalent conductances (Λ) can be predicted from a correlation with viscosities (η), using the linear relation:

$$\log_{10}(\Lambda\ /\ \text{S cm}^2\ \text{mol}^{-1}) = (0.935 \pm 0.008)\log_{10}(\eta^{-1}/\text{Poise}^{-1}) - (0.226 \pm 0.005) \tag{15}$$

and also indicates that the conductivity decreases with the increase in viscosity.

Self-Diffusion Coefficient

The self-diffusion coefficient (D) is related to viscosity in terms of the fractional form of the Stokes-Einstein relation *(26)*, according to which the self-diffusion coefficient is proportional to the ratio of temperature and viscosity and can be written as:

$$D(\eta/T)^\beta = \text{constant} \tag{16}$$

where β is a constant.

Experimental self-diffusion coefficient (D) data of ionic liquids available in the literature were collected to evaluate the relation between the self-diffusion coefficients (D) and the viscosities (η). For this purpose, the viscosity was calculated using Equation (10). For 45 data points for five ionic liquids based on the imidazolium cation with $[BF_4]^-$ or $[Tf_2N]^-$ as anion, covering wide ranges of temperature, 263.15-353.15 K and self-diffusion coefficient, 2.43×10^{-12}-3.71×10^{-10} m^2 s^{-1}, a very good linear correlation is observed with T/η *(10)*, where

$$10^{12}D\ /\ \text{m}^2\ \text{s}^{-1} = (6.995 \pm 0.061)(T/\eta)\ /\ \text{K mPa}^{-1}\ \text{s}^{-1} \tag{17}$$

It would be interesting to correlate the ionic diffusivity with conductivity through the Nernst-Einstein equation, but the limited amount of experimental data available restricts such a development at this point. We are confident that such correlation for ionic liquids will be possible when an adequate amount of experimental data become available.

Thermal Conductivity

The knowledge of thermal conductivity is important to obtain the heat transfer coefficient of fluids, which is essential for the design of heat transfer fluid and equipments. Among the different transport properties, thermal conductivity is one of the most difficult to estimate using predictive methods.

The data base of experimental thermal conductivity (κ) available in the literature contains 107 data points for sixteen ionic liquids based on imidazolium, pyrrolidinium, and phosphonium cations with $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, $[EtSO_4]^-$, $[CF_3SO_3]^-$, or Cl^- as anions, covering a wide range of temperatures, 293-390 K, and thermal conductivities, 0.124-0.199 W m^{-1} K^{-1}. The experimental thermal conductivities suggest that they are weakly dependent on temperature, and could be fitted with a linear correlation of the form:

$$\kappa = A_\kappa - B_\kappa T \tag{18}$$

where T is temperature in K, and A_κ and B_κ are fitting parameters that can be obtained from a group contribution approach as:

$$A_\kappa = \sum_{i=1}^{k} n_i a_{i,\kappa} \qquad\qquad B_\kappa = \sum_{i=1}^{k} n_i b_{i,\kappa} \tag{19}$$

where n_i is the number of groups of type i, and k is the total number of different groups in the molecule, and the parameters $a_{i,\kappa}$ and $b_{i,\kappa}$ are presented in (10).

The calculated thermal conductivity (κ_{cal}) using the group contribution parameters $a_{i,\kappa}$ and $b_{i,\kappa}$ for imidazolium, pyrrolidinium, and phosphonium based ionic liquids having $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, $[EtSO_4]^-$, $[CF_3SO_3]^-$, or Cl^- as anions, are in very good agreement with the corresponding experimental thermal conductivity (κ_{exp}); where $\kappa_{cal} = (0.9991 \pm 0.0017)\kappa_{exp}$. For 107 data points for sixteen ionic liquids available in literature, the overall MPD is 1.06 % with a maximum deviation of 3.5 %. The thermal conductivity of the ionic liquids is similar to that observed for organic molecular liquids and much lower than that for pure water. Small amounts of impurities, such as water and chloride, in the ionic liquid sample do not seem to have a significant effect on the thermal conductivity; however, the thermal conductivity seems to increase with the amount of impurities (28). For ionic liquids having an imidazolium based cation, the thermal conductivity increases with the anion following the trend: $[NTf_2]^- < [CF_3SO_3]^- \leq [PF_6]^- < [EtSO_4]^- < [BF_4]^-$ (10). The thermal conductivity also increases somewhat with the increase of alkyl chain length on the imidazolium cation.

Refractive Index

Refractive index (n_D) is a fundamental physical property and it is used to test a material, confirm its purity, or for analytical purposes such as the assessment of the concentration of a mixture. It is also related to other properties such as dielectric constant, density, and surface tension through thermodynamic equations.

Experimental refractive index data available in the open literature, with 245 data points for 24 imidazolium-based ionic liquids having [PF$_6$]$^-$, [BF$_4$]$^-$, [NTf$_2$]$^-$, [MeSO$_4$]$^-$, [EtSO$_4$]$^-$, [CF$_3$SO$_3$]$^-$, or Cl$^-$ as anions, covering a wide range of temperature, 283.15-363.15 K, were used in the study. For the studied ionic liquids, in the temperature range available, it was observed that the experimental refractive index decreases linearly with temperature, and could be fitted with a linear correlation of the form:

$$n_D = A_n - B_n T \tag{20}$$

where A_n and B_n can be obtained from a group contribution approach as:

$$A_{n_D} = \sum_{i=1}^{k} n_i a_{i,n_D} \quad B_{n_D} = \sum_{i=1}^{k} n_i b_{i,n_D} \tag{21}$$

where n_i is the number of groups of type i, and k is the total number of different of groups in the molecule, and the parameters $a_{i,n}$, and $b_{i,n}$ here estimated are reported in (10).

The calculated refractive indices ($n_{D,cal}$) were in excellent agreement with the corresponding experimental refractive index ($n_{D,exp}$); where $n_{D,cal} = (0.9999 \pm 0.0002) n_{D,exp}$. For 245 data points of 24 ionic liquids available in the literature, the overall MPD is 0.18 % with a maximum deviation of the order of 0.6 %. The results indicate that the refractive index of the studied ionic liquids is weakly dependent on temperature and slightly decreases with temperature. The refractive index of all studied ionic liquids is higher that observed for pure water. Water present in the ionic liquid sample as an impurity has little effect on the refractive index; however, from the refractive index data of aqueous solutions of ionic liquids (21,29,30), it is clear that the refractive index decreases with increasing amount of water. For ionic liquids having imidazolium based cations, the refractive index increases with the anion following the trend: [PF$_6$]$^-$ < [BF$_4$]$^-$ < [NTf$_2$]$^-$ < [CF$_3$SO$_3$]$^-$ < [MeSO$_4$]$^-$ < [EtSO$_4$]$^-$ < Cl$^-$ (10); and it increases slightly with the increase of alkyl chain length on the imidazolium cation. The low deviations observed in calculated refractive indices for a wide range of imidazolium based ionic liquids shows that the group contribution method here developed can predict refractive index of new ionic liquids over wide ranges of temperatures and, as data for new groups of cations and anions become available, can be easily extended to a larger range of ionic liquids.

Heat Capacity

Heat capacity is one of the basic thermodynamic properties that characterises a compound. Variations in heat capacities provide information of phase transitions and are important for understanding changes in the structure of a compound. Experimental data for the heat capacity of ionic liquids are scarce and limited to a few classes of well-studied ionic liquids. A database of experimental liquid heat capacities (C_{pL}) of ionic liquids available in the open literature, a global number of 2396 data points for 19 ionic liquids based on imidazolium cations with $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, Br^-, $[EtSO_4]^-$, or $[CF_3SO_3]^-$ as anions, and pyridinium and pyrrolidinium cations with $[NTf_2]^-$, covering wide ranges of temperature, 196.36-663.10 K and liquid heat capacity, 264.8-825.0 J mol^{-1} K^{-1}, were used in the study.

The approach proposed by Ruzicka and Domalski *(31,32)* was adopted and a second-order group additivity method used for the estimation of the liquid heat capacity of (C_{pL}) of ionic liquids. It employs a group contribution technique to estimate the A_{Cp}, B_{Cp} and D_{Cp} parameters in Equation (22):

$$C_{pL} = R \cdot \left[A_{Cp} + B_{Cp} \cdot \left(\frac{T}{100}\right) + D_{Cp} \cdot \left(\frac{T}{100}\right)^2 \right] \tag{22}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is temperature in K. The group contributions to calculate A_{Cp}, B_{Cp} and D_{Cp} parameters are obtained from:

$$A_{Cp} = \sum_{i=1}^{k} n_i a_{iCp} \qquad B_{Cp} = \sum_{i=1}^{k} n_i b_{iCp} \qquad D_{Cp} = \sum_{i=1}^{k} n_i d_{iCp} \tag{23}$$

where n_i is the number of groups of type i, k is the total number of different kinds of groups, and the parameters a_{iCp}, b_{iCp}, and d_{iCp} are presented in *(9)*.

The method proposed here allows the estimation of heat capacities of ionic liquids as a function of temperature over wide ranges of temperature, 196.36-663.10 K, and can be extrapolated to temperatures outside the temperature range recommended. However, the predictive accuracy decreases with extrapolation and the user must also be aware of the possible degradation of the ionic liquids at high temperatures. Due to the low vapour pressures of ionic liquids, no distinction is made between the isobaric heat capacity and the saturation heat capacity.

The calculated heat capacity, C_{pL}^{cal}, of the ionic liquids studied displays a very good agreement with the corresponding experimental heat capacity, C_{pL}^{exp}, where $C_{pL}^{cal} = (0.9994 \pm 0.0002)C_{pL}^{exp}$. For 2396 data points for 19 ionic liquids available in literature, 90.2 % estimated heat capacities data present deviations of the experimental values smaller than 1 % and the overall MPD is 0.36 % with a maximum deviation smaller than 2.5 %. In almost all cases where the experimental uncertainty is provided in the original reference, the deviations in predicted heat capacities are inferior to the assigned experimental uncertainties. The proposed method for the estimation of the heat capacities of ionic liquids is not only a powerful and accurate tool for the estimation of heat capacities when

no experimental information is available, but also to evaluate the quality of the available or new data as it can check the coherence between the data from various data sets for different ionic liquids.

For ionic liquids containing the imidazolium cation, heat capacity increases with the anion mass in the order $Br^- < [BF_4]^- < [PF_6]^- < [EtSO_4]^- \approx [CF_3SO_3]^- <$ $[NTf_2]^-$ *(9)*. For ionic liquids having a common anion and a similar alkyl chain length on the cation, it is observed that the heat capacity increases with cation following the order: $[C_n py]^+ < [C_n mim]^+ < [C_n mpyrr]^+$ *(9)*.

Summary and Future Work

The total number of ionic liquids and data points used for the correlation of all studied thermophysical properties are summarised in Table 1, along with the mean percent deviation (MPD) and maximum deviation (MD) observed. By using the predictive models developed, we have started working for the Computer Aided Molecular Design (CAMD) of ionic liquids. As a part of that, a free online thermophysical property calculator, THERMOPHIL, which can be accessed at http://path.web.ua.pt/thermophil.asp, was developed for the estimation of thermophysical properties of ionic liquids.

Table 1. Thermophysical Property Prediction for Ionic Liquids

Property	MPD / %	Maximum deviation %	Number of data points	Number of Ils
Density	0.73	1.57	1521	21
Isobaric Expansivity	1.98	7.10	109	49
Isothermal Compressibility	2.53	6.67	26	22
Surface Tension	5.75	15.58	361	38
Speed of Sound	1.96	4.93	133	14
Viscosity	7.78	27.75	498	29
Electrical Conductivity	4.57	16.01	307	15
Thermal Conductivity	1.08	3.51	107	16
Refractive Index	0.18	0.61	221	24
Heat Capacity	0.36	2.43	2396	19

Conclusions

Group contribution methods for the estimation of the thermophysical and transport properties of ionic liquids were developed for density, viscosity, surface tension, speed of sound, electrical conductivity, thermal conductivity, heat capacity, refractive index, isobaric expansivity, and isothermal compressibility. A further correlation for the self diffusion coefficients based on the Stokes Einstein relation is also proposed. The parameters of the group contribution methods were determined for imidazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, and ammonium based ionic liquids containing several different anions, and *ca.* 5680 experimental data points were used for this purpose. A comparison between the experimental and correlated values shows that the proposed models describe the experimental data available with absolute relative deviations generally of the same order as the agreement of experimental data between different authors as described in the report of the IUPAC task group for the development of standard systems for the measurement of thermodynamic properties of ionic liquids (http://www.iupac.org/web/ins/2002-005-1-100). Care is recommended when comparing or using physical properties of ionic liquids, as differences among the results of several authors may be important since the presence of small amounts of water or other impurities such as chloride seem to have a remarkable effect on most of the these properties.

The proposed methods can be useful for predicting the studied properties for the design of processes or products involving ionic liquids, as the procedures involved are rapid and facile. They can also be used for the development of Computer Aided Molecular Design (CAMD) methods for ionic liquids that could help identify a compound, or range of compounds to fit a set of requirements for a particular application.

The group contribution methods proposed here can, in the future, be extended to a larger range of ionic liquids, as data for these become available.

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