

Group Contribution Methods for the Prediction of Thermophysical and Transport Properties of Ionic Liquids

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Thermophysical and transport properties of ionic liquids are required for the design of processes and products. Yet the experimental data available are scarce and often contradictory. Based on experimental data collected from the literature, group contribution methods were developed for the estimation of viscosity, electrical conductivity, thermal conductivity, refractive index, isobaric expansivity, and isothermal compressibility, of various families of ionic liquids. Using the Stokes–Einstein relation a correlation for the self-diffusion coefficients with the viscosity is also proposed. The results of the proposed models show average absolute relative deviations generally of the same order of the experimental accuracy of the data. They are easy to use and can provide predictions of property values for ionic liquids never previously studied. The group contribution basis of these models will allow them to be extended to new groups of cations and anions as further data became available. © 2009 American Institute of Chemical Engineers AICHE J, 55: 1274–1290, 2009

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Introduction

Ionic liquids (ILs) are novel solvents belonging to the class of molten salts liquid at room temperature that are expected to produce important developments in the industrial chemistry and chemical technology, and are spurring several research fields. They are, usually, the combination of large organic cations with various alkyl substituents and inorganic or organic anions; so the feasible number of ILs (from chemical combinations) is estimated to be more than a trillion. One of the major goals of the chemical industry today is to search for safer alternatives of volatile organic compounds (VOCs) that will minimize air pollution, climatic changes, and human health-related problems. ILs exhibit cer-

tain desirable physical properties, such as negligible vapor pressure, wide liquidus range, wide electrochemical window, wide thermal window, nonflammability, large range of densities, and viscosities, high potential for recycling, and highly solvating capacity for organic, inorganic and organometallic compounds, which merit the consideration of ILs to the replacement of VOCs in current processes or in the design of new processes and products based on the unique properties of these compounds. An interesting feature of ILs is that simple changes in the cation and anion combinations or the nature of the moieties attached to each ion allow the physical properties to be tailored for specific applications.

Although most effort in ILs has been focused on the investigation of their potential applications, the characterization of ILs properties and structure-property relationships of ILs is of equivalent importance but has lagged behind. The thermophysical and transport properties of ionic liquids are required for the design of processes and products involving these compounds. Yet the experimental data available is

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currently scarce for most properties and often data from various sources are contradictory.

Given the huge number of potential ILs, the experimental measurement of the thermophysical and transport properties for all ionic liquids of interest is unfeasible. The alternative is to develop predictive models, based on some experimental data, from which the required properties with the desired accuracy could be obtained. The development of group contribution methods for the properties of ionic liquids is particularly apt for this purpose as from a restricted amount of data it will help to expand the information available for a large number of compounds and 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 ILs designer solvents per 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.¹ 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.^{2,3}

In this work, we intend to present group contribution methods that are employed to estimate thermophysical and transport properties of ILs. Our goal is to show that group contribution methods may be applied for rapid and facile prediction of physical properties with acceptable deviations for a wide range of ILs.

In a previous series of articles a number of predictive methods for density,⁴ surface tension,⁵ viscosity,⁶ speed of sound,⁷ and liquid heat capacity⁸ of ILs have been proposed. The development of group contribution methods for the transport and thermophysical properties of ionic liquids will be here completed with the presentation of new group contribution methods for the prediction of viscosity, electrical conductivity, thermal conductivity, refractive index, isobaric expansivity, and isothermal compressibility of ionic liquids. 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 experimental data by different authors as described on 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>). A brief discussion on the effect of the cation, anion and alkyl chain lengths on the property values will be done for each property investigated.

Collection of physical properties of ILs

The experimental viscosity, electrical conductivity, self-diffusion coefficients, thermal conductivity, refractive index, isobaric expansivity, and isothermal compressibility data of the ILs, here used to estimate the group contribution parameters for the various correlations proposed, were taken from open literature concerning the physical properties of ILs,^{9–11} and from the International Union of Pure and

Applied Chemistry (IUPAC) database.¹¹² The following IL ions were considered in this study: cations imidazolium [Im], pyridinium [Py], pyrrolidinium [Pyr], piperidinium [Pip], alkyl phosphonium [Ph], and alkyl ammonium [Am]; anions, hexafluorophosphate [PF₆], tetrafluoroborate [BF₄], bis(trifluoromethanesulfonyl) amide [Tf₂N], chloride [Cl], acetate [CH₃COO], methyl sulfate [MeSO₄], ethyl sulfate [EtSO₄], trifluoromethanesulfonate [CF₃SO₃], bis(perfluoroethylsulfonyl)imide [Pf₂N], trifluoroacetate [CF₃COO], dimethylphosphate [(CH₃)₂PO₄], methoxyethylsulfate [CH₃OC₂H₄SO₄], dicyanamide [N(CN)₂], tricyanomethanide [C(CN)₃], tetrachloroaluminate [AlCl₄], tetrachloroironate [FeCl₄], tetrachlorogallate [GaCl₄], tetrachloroindate [InCl₄], and trichlorozincate [ZnCl₃]. The combinations of cations and anions and the data points of the individual properties of the ILs studied in this work are presented in tables in next section.

Results and Discussion

Viscosity

The viscosities of ILs are relatively high compared to those of common organic solvents. Experimental viscosity data of ILs are still in short supply and restricted to a few families of well-studied ILs. More data and a better understanding of the viscosity of ILs are required for task-specific development. In the absence of experimental data, theoretical or empirical methods must be used to obtain acceptable estimation of viscosities as defined by the design specifications.

In a previous work,⁶ the viscosity of ILs was correlated using an Orrick–Erbar-type approach¹¹³ by estimating parameters A and B in Eq. 1:

$$\ln \frac{\eta}{\rho \cdot M} = A + \frac{B}{T} \quad (1)$$

where η and ρ are the viscosity in cP units and density in g cm⁻³ units respectively. M is the molecular weight and T is the absolute temperature. Eq. 1 was used for circa 500 data points of 29 ILs providing a relative average deviation of 8% and a maximum deviation of 28%. The Orrick–Erbar method requires density data 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 (Eq. 2) is here proposed. The data base of experimental viscosities of ILs used is reported in Table 1.

$$\ln \eta = A_{\eta} + \frac{B_{\eta}}{(T - T_{0\eta})} \quad (2)$$

where η is viscosity in Pa s units, 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. As it will be shown below, $T_{0\eta}$ is similar for all the ILs studied. A_{η} and B_{η} can be obtained by a group contribution method according to

$$A_{\eta} = \sum_{i=1}^k n_i a_{i,\eta} \quad B_{\eta} = \sum_{i=1}^k n_i b_{i,\eta} \quad (3)$$

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 parameters

Table 1. Prediction of Viscosity of Imidazolium-, Pyridinium-, and Pyrrolidinium-Based Ionic Liquids

Ionic Liquid	Temperature Range (K)	Data Points	Relative Deviation (range) (%)	Average Absolute Relative Deviation (%)	Reference
[C ₄ mIm][PF ₆]	293.15–353.15	16	–3.49; 2.56	1.57	19
	293.15–353.15	4	–4.21; 0.01	2.05	29
	293.1–353.1	8	3.70; 12.90	10.59	28
[C ₆ mIm][PF ₆]	293.15–323.15	7	7.47; 9.58	8.76	36
	293.15–323.15	7	–11.90; –2.76	7.29	36
	293.15–353.15	11	–15.43; –1.83	7.84	33
[C ₈ mIm][PF ₆]	293.15–303.15	2	–14.17; –12.31	13.24	11
	298.1	1	–0.32	0.32	12
	293.15–323.15	7	–2.73; 4.32	2.00	36
[C ₄ mIm][BF ₄]	293.15–343.15	11	–8.75; 2.92	4.58	25
	293.15–353.15	4	–7.63; 7.60	5.31	39
	293.15–303.15	2	7.25; 12.21	9.73	11
[C ₆ mIm][BF ₄]	293.15–303.15	2	13.34; 14.01	13.68	14
	298.1	1	4.26	4.26	41
	293.15–353.15	31	–3.45; 1.50	1.58	34
[C ₈ mIm][BF ₄]	293.15–323.15	7	0.63; 1.34	1.00	38
	293.15–323.15	6	–14.34; 22.77	10.57	16
	293.67–388.04	11	–0.64; 22.31	5.91	26
[C ₂ mIm][Tf ₂ N]	293.15–353.15	4	3.08; 5.02	4.26	29
	293.1–353.1	8	1.24; 10.05	5.98	28
	293.1–303.1	2	–10.46; –10.42	10.44	11
[C ₄ mIm][Tf ₂ N]	293.15–323.15	7	–5.94; –3.74	4.57	38
	293.15–353.15	15	–12.59; –22.79	18.47	25
	293.15–323.15	7	9.72; 21.36	15.28	38
[C ₆ mIm][Tf ₂ N]	293.15	1	–4.25	4.25	9
	293.15–353.15	7	–9.95; –15.63	14.03	13
	303.15	1	–13.08	13.08	20
[C ₈ mIm][Tf ₂ N]	298.15	1	–3.79	3.79	10
	293–343	7	–9.03; –17.96	13.72	18
	293.15–353.15	7	–16.72; –15.00	15.72	21
[C ₄ mIm][Tf ₂ N]	293.1–353.1	8	–19.20; –15.23	17.19	28
	293.39–388.19	11	–7.23; –22.13	18.81	26
	293.15	1	2.02	2.02	9
[C ₆ mIm][Tf ₂ N]	293.40–387.51	11	–12.66; 13.55	9.11	26
	293.15–353.15	7	–15.31; –6.20	9.35	21
	293.1–353.1	8	–15.60; –5.69	10.20	28
[C ₈ mIm][Tf ₂ N]	293.15–353.15	13	–16.85; –9.05	12.24	33
	303.15	1	–12.53	12.53	17
	293.15–363.15	15	–4.67; 6.86	3.38	42
[C ₂ mIm][CF ₃ SO ₃]	293.1–353.1	8	–4.23; 6.79	2.89	28
	293–343	7	–1.83; 1.61	0.95	18
	293.15–373.15	12	–3.44; 2.08	1.88	40
[C ₄ mIm][CH ₃ COO]	293.15–353.15	7	–0.82; 7.77	4.73	21
	293.15–393.15	14	–4.01; 8.34	2.85	35
	293.15–353.15	7	18.55; 20.14	19.54	21
[C ₆ mIm][MeSO ₄]	293.1–353.1	8	18.54; 22.74	19.94	28
	293–343	7	–3.05; 2.77	1.60	18
	293.15–343.15	9	6.05; 18.05	12.89	14
[C ₈ mIm][EtSO ₄]	293.15–343.15	9	–10.01; –21.17	15.71	37
	298.15	1	–1.39	1.39	22
	298.15	1	–1.39	1.39	30
[C ₄ mIm][EtSO ₄]	298.15–348.15	6	–0.75; 4.21	2.56	27
	298.15–328.15	3	1.46; 2.16	1.88	32
	298.15–343.15	10	1.46; 2.26	1.88	23
[C ₂ mPy][EtSO ₄]	296.80–388.19	11	–3.55; –0.72	1.77	26
	298.15–348.15	6	–0.80; 18.64	10.65	27
	293.15–323.15	6	–10.45; 9.05	4.54	16
[C ₄ mPy][Tf ₂ N]	293.15	1	9.05	9.05	9
	293.1–353.1	8	–12.31; 0.48	4.54	28
	293.1–353.1	8	–3.03; 0.76	1.44	28
[C ₆ Py][Tf ₂ N]	293–343	7	8.39; 17.05	13.12	18
	293–343	7	–5.03; –0.98	2.08	18
	293–343	7	11.08; 17.45	14.71	18
[C ₄ Py][BF ₄]	293–343	7	11.08; 17.45	14.71	18
	298–343	6	–13.56; –1.95	7.42	18
	293–343	7	–2.28; 2.50	1.15	18
[C ₂ Py][EtSO ₄]	293–343	7	–6.37; 2.90	2.72	18
	293.1–353.1	8	–15.44; –8.82	11.12	28
	301.0–343.0	6	–12.52; 21.33	9.53	31
TOTAL	293.15–393.15	482	–22.79; 22.77	7.50	

Table 2. Group Contributions Parameters $a_{i,\eta}$ and $b_{i,\eta}$ in Eq. 3 for Temperature Range 293.15–393.15 K

Species	$a_{i,\eta}$	$b_{i,\eta}$ (K)
Cations		
1,3-dimethylimidazolium (+)	-7.271	510.51
1-methylpyridinium (+)	-7.541	587.66
1,1-dimethylpyrrolidinium (+)	-7.512	601.77
Anions		
PF ₆ ⁻	-1.834	433.14
BF ₄ ⁻	-1.680	288.05
Tf ₂ N ⁻	-1.119	94.20
CH ₃ COO ⁻	-2.739	618.50
MeSO ₄ ⁻	-1.580	339.90
EtSO ₄ ⁻	-1.498	317.87
CF ₃ SO ₃ ⁻	-1.150	176.97
Groups		
CH ₂	-7.528×10^{-2}	40.92
CH ₃	-1.450×10^{-3}	8.02

$a_{i,\eta}$, and $b_{i,\eta}$ here estimated are presented in Table 2. Close to 500 data points for 25 ILs based on imidazolium-, pyridinium-, and pyrrolidinium cations with PF₆, BF₄, Tf₂N, CH₃COO, MeSO₄, EtSO₄, or CF₃SO₃ as anions, covering wide ranges of temperature, 293.15–393.15 K and viscosity, 0.004–1.065 Pa s,^{9–42} were used in this study.

The VTF equation was fitted to the experimental data available for each IL studied. From these initial estimates, it was, surprisingly, found that $T_{0\eta}$ was similar for all the ILs studied, with a value close to 165 K. From a simultaneous optimization of the entire database using the objective function described in Eq. 4 it was found that the optimum value of $T_{0\eta}$ is 165.06 K.

$$\text{O.F.} = \sum_{i=1}^{N_p} \left[\left(\exp \left(\ln A_{\eta} + \frac{B_{\eta}}{(T - T_{0\eta})} \right) - \eta_{\text{exp}} \right)^2 \right]_i \quad (4)$$

With the relative average deviation (RD) defined as,

$$\text{RD (\%)} = \frac{100 \times \sum_{i=1}^{N_p} |(\eta_{\text{cal}} - \eta_{\text{exp}}) / \eta_{\text{exp}}|}{N_p} \quad (5)$$

where subscripts cal and exp denote calculated and experimental property respectively, N_p represents the number of available data points for each system reported in Table 1.

Taking $T_{0\eta}$ as a constant valid for all ILs estimates of the values of $a_{i,\eta}$ and $b_{i,\eta}$ for each group are then obtained using Eqs. 3 and 4.

As shown in Figure 1a, a remarkable agreement is observed between the calculated and the experimental viscosity data, by using VTF equation (Eq. 2) with $T_{0\eta} = 165.06$ K and using group contribution parameters $a_{i,\eta}$ and $b_{i,\eta}$ (Table 2) for imidazolium-, pyridinium-, and pyrrolidinium-based ILs containing PF₆, BF₄, Tf₂N, CH₃COO, MeSO₄, EtSO₄, and CF₃SO₃ anions in a wide range of temperature and viscosity. Viscosities of ILs having imidazolium based cations increases in the series: [Tf₂N] < [CF₃SO₃] < [BF₄] < [EtSO₄] < [MeSO₄] < [PF₆] < [CH₃COO].⁶ For ILs having a common anion and a similar alkyl chain length on the cation, the viscosity increases with cation following the order: [Im] < [py] < [pyr].⁶

The calculated viscosity (η_{cal}) of the ILs studied displays a good agreement with the corresponding experimental vis-

cosity (η_{exp}), where $\ln \eta_{\text{cal}} = (0.9647 \pm 0.0043) \cdot \ln \eta_{\text{exp}}$ ($R^2 = 0.9907$ at 95% level of confidence). Relative deviations between the calculated and experimental viscosity data as a function of experimental viscosity for all data points used in the current study are shown in Figure 1b. For 482 data points of 25 ILs available in literature, the overall RD is 7.50% with a maximum deviation smaller than 23%. From these 49.8% of the estimated viscosities were within relative deviation of 0.00–5.00%, 16.2% within 5.001–10.00%, 16.8% within 10.001–15.00%, 12.4% within 15.001–20.00%, and only 4.8% of the estimated viscosities having larger than 20.0% deviation. The maximum relative deviation is 22.79% observed for [C₈mim][BF₄] (1-octyl-3-methylimidazolium tetrafluoroborate) at 293.15 K.³⁸ At present stage, rejection of doubtful experimental data is not possible due to the

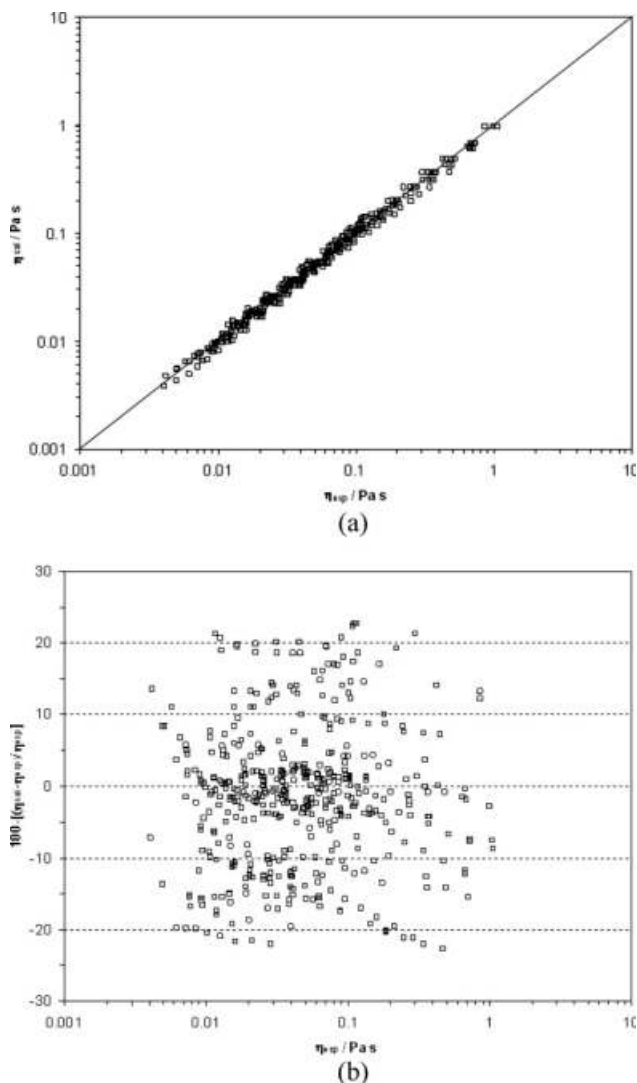


Figure 1. (a) Linear relationship between experimental and calculated viscosity using Eq. 2 and (b) relative deviations between the calculated and experimental viscosity data as a function of experimental viscosity for imidazolium-, pyridinium-, and pyrrolidinium-based ionic liquids in the current study.

Table 3. Prediction of Electrical Conductivities of Imidazolium-, Pyridinium-, Pyrrolidinium-, and Ammonium-Based Ionic Liquids

Ionic Liquid	Temperature Range (K)	Data Points	Relative Deviation (range) (%)	Average Absolute Relative Deviation (%)	Reference
[C ₄ mIm][PF ₆]	288.15–323.15	5	–5.82; 1.04	2.62	46
	263.1–373.1	10	–4.61; 8.68	3.58	28
	298.14–353.12	17	–2.20; 4.28	2.31	47
[C ₂ mIm][BF ₄]	298.1	1	1.38	1.38	15
	258.1–433.1	36	–15.93; 1.89	3.27	48
[C ₄ mIm][BF ₄]	298.1	1	5.27	5.27	15
[C ₁ mIm][Tf ₂ N]	263.1–373.1	10	–0.30; 16.01	4.67	28
	263.15–373.15	12	–11.86; 3.89	4.75	21
[C ₂ mIm][Tf ₂ N]	293.1–373.1	7	–10.33; 4.00	5.07	28
	288.15–323.15	5	–9.89; 1.77	4.12	46
[C ₄ mIm][Tf ₂ N]	263.15–373.15	12	–14.86; 13.33	8.57	21
	263.1–373.1	10	–15.92; 15.98	8.08	28
	288.15–323.15	5	–10.21; –4.55	7.95	46
[C ₆ mIm][Tf ₂ N]	263.15–373.15	12	–7.17; 12.26	5.98	21
	263.1–373.1	10	–7.97; 15.92	5.38	28
	288.15–323.15	5	–1.74; 2.54	1.39	46
[C ₈ mIm][Tf ₂ N]	263.15–373.15	12	–10.07; 9.33	5.34	21
	263.1–373.1	10	–6.76; 11.09	5.34	28
	278.15–323.15	9	–3.08; 3.68	1.52	35
[C ₂ mIm][EtSO ₄]	263.15–373.15	12	–16.01; 10.13	6.93	21
[C ₄ mIm][CF ₃ SO ₃]	263.1–373.1	10	–13.71; 7.03	6.39	28
[C ₄ mIm][PF ₂ N]	258.1–433.1	36	–15.31; 14.93	8.28	48
[C ₄ mIm][CF ₃ COO]	263.1–373.1	10	–3.48; 1.64	1.21	28
[C ₄ mIm][PF ₂ N]	263.1–373.1	10	–4.76; 0.58	1.87	28
[C ₄ mIm][CF ₃ COO]	263.1–373.1	10	–2.82; 5.16	1.87	28
[C ₄ Py][Tf ₂ N]	263.1–373.1	10	–4.07; 5.05	2.36	28
[C ₄ mPyr][Tf ₂ N]	263.1–373.1	10	–2.32; 3.46	1.41	28
[Am(4)111][Tf ₂ N]	263.1–373.1	10	–3.59; 5.39	2.66	28
TOTAL	258.1–433.1	307	–16.01; 16.01	4.57	

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 IL samples, or the experimental method adapted.

The predictive capability of the group contribution method here developed for IL viscosity will be further checked below by its potential to correlate with equivalent conductivity and the self-diffusion coefficient using fractional forms of Walden rule¹¹⁴ and Stokes–Einstein relation,¹¹⁵ respectively, as will be discussed in subsequent sections of this work.

Electrical conductivity

Electrical conductivity (λ) or specific conductivity measures the ability of a material to conduct an electric current. It is defined as the ratio of the current density to the electric field strength. Electrical conductivity is the most important property for chemists and engineers to understand the structure of ionic chemical systems, to control and to design industrial processes, and in the development of electrochemical devices such as high energy batteries. As applications of ILs are rising exponentially in several scientific fields including electro chemistry, it is important to develop a predictive method for the electrical conductivity of ILs which will be used, when experimentally measured electrical conductivity of ILs are not available, to establish if the electrical conductivities are within acceptable limiting values defined in design specifications.

A database of experimental electrical conductivity (λ) available from the open literature was collected and is

reported in Table 3. A global number of 300 data points for 15 ILs based on imidazolium-, pyridinium-, pyrrolidinium-, and ammonium-based cations with PF₆, BF₄, Tf₂N, EtSO₄, CF₃SO₃, PF₂N, or CF₃COO as anions, covering wide ranges of temperature, 258.1–433.15 K and electrical conductivity, 0.01–12.68 S m⁻¹,^{15,21,28,35,46–48} were used in this study.

A VTF type equation (Eq. 6), similar to what was used for the viscosity, will be here applied to the correlation of the electrical conductivity of ILs.

$$\ln \lambda = \ln A_{\lambda} + \frac{B_{\lambda}}{(T - T_{0\lambda})} \quad (6)$$

where A_{λ} , B_{λ} , and $T_{0\lambda}$ are adjustable parameters, from which A_{λ} and B_{λ} can be obtain by a group contribution method.

$$A_{\lambda} = \sum_{i=1}^k n_i a_{i,\lambda} \quad B_{\lambda} = \sum_{i=1}^k n_i b_{i,\lambda} \quad (7)$$

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 $b_{i,\lambda}$ here estimated for the ILs studied are presented in Table 4. The estimation of the parameters followed an approach similar to what was described above for the viscosities. Again, from the correlation of the individual IL electrical conductivities, it was found that $T_{0\lambda}$ presented a value for all studied ILs 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 $T_{0\eta}$ ($T_{0\eta} = T_{0\lambda} = 165.06$ K). The circa 300 experimental electrical conductivity data points of 15 ILs

Table 4. Group Contributions Parameters $a_{i,\lambda}$ and $b_{i,\lambda}$ in Eq. 7 for Temperature Range 258.15–433.15 K

Species	$a_{i,\lambda}$	$b_{i,\lambda}$ (K)
Cations		
1,3-dimethylimidazolium (+)	78.0	-573.7
1-ethyl-3-methylimidazolium (+)	28.1	-454.0
1-methylpyridinium (+)	69.7	-581.0
1,1-dimethylpyrrolidinium (+)	62.5	-588.4
Tetramethyl ammonium (+)	89.4	-670.2
Anions		
PF ₆ ⁻	117.3	-278.6
BF ₄ ⁻	85.8	-129.4
Tf ₂ N ⁻	10.1	-46.4
CF ₃ SO ₃ ⁻	9.0	-76.7
EtSO ₄ ⁻	120.2	-356.5
Pf ₂ N ⁻	3.0	-161.1
CF ₃ COO ⁻	51.6	-123.9
Group		
CH ₂	0.1	-36.1

available was then used to obtain the values of the group parameter $a_{i,\lambda}$, and $b_{i,\lambda}$ reported in Table 4, by minimization of the objective function

$$\text{O.F.} = \sum_{i=1}^{N_p} \left[\left(\exp \left(\ln A_i + \frac{B_i}{(T - T_{0i})} \right) - \lambda_{\text{exp}} \right)^2 \right] \quad (8)$$

The calculated electrical conductivity (λ_{cal}), by using VTF equation (Eq. 6) with $T_{0i} = 165.06$ K and using group contribution parameters $a_{i,\lambda}$, and $b_{i,\lambda}$ (Table 4) for imidazolium-, pyridinium-, pyrrolidinium-, and ammonium based ILs having PF₆, BF₄, Tf₂N, EtSO₄, CF₃SO₃, Pf₂N, or CF₃COO as anions, are in good agreement with the corresponding experimental electrical conductivity (λ_{exp}), as shown in Figure 2a; where $\lambda_{\text{cal}} = (0.9974 \pm 0.0022) \cdot \lambda_{\text{exp}}$ ($R^2 = 0.9985$ at 95% level of confidence). Relative deviations between the calculated and experimental electrical conductivity data as a function of experimental electrical conductivity for all data points used in the current study are shown in Figure 2b. For 307 data points of 15 ILs available in literature, the overall RD is 4.57% with a maximum deviation of the order of 16%. From these 38.1% of the estimated electrical conductivities were within relative deviation of 0.00–2.00%, 25.7% within 2.001–5.00%, 22.8% within 5.001–10.00%, and only 13.4% of the estimated electrical conductivities having larger than 10.0% deviation. The maximum relative deviation of 16.01% is observed for [C₄mim][BF₄] (1-butyl-3-methylimidazolium tetrafluoroborate) at 263.1 K²⁸ and for [C₈mim][Tf₂N] (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide) at 263.15 K.²¹ Water content present in IL sample may increase its electrical conductivity significantly¹¹⁶ which may be a possible reason for some of the larger deviations observed in the calculated electrical conductivity.

For ILs having [C₄mim]⁺ (1-butyl-3-methylimidazolium cation), electrical conductivity is increased with anion following the order [Pf₂N] ≤ [PF₆] < [CF₃SO₃] < [Tf₂N] ≤ [CH₃COO] < [BF₄]. Electrical conductivity decreases with the increase of alkyl chain length on imidazolium cation and this decrease is more pronounced at higher temperatures. For ILs having a common anion and a similar alkyl chain length on the cation, the electrical conductivity, behaving opposite

to viscosity, decreases with cation following the order: [Im] > [Py] > [Pyr]. However more experimental data and theoretical studies are required to fully understand the influence of cation and anion on the electrical conductivity of ILs.

Generally, high conductive liquids have high fluidity, as would be expected from the Walden rule¹¹⁴ connecting the ionic mobility to the frictional resistance of ion to its movement offered by the liquid viscosity, under the electrochemical force. The relationship between viscosity and conductance in terms of the fractional Walden rule can be written as:

$$\Lambda \cdot \eta^\alpha = \text{constant} \quad (9)$$

where Λ is equivalent conductivity and α is a constant between zero and unity. The log Λ versus log η^{-1} plot is shown in Figure³ using reciprocal poise (P⁻¹) and S cm² mol⁻¹ as the units for fluidity and equivalent conductivity, respectively. For

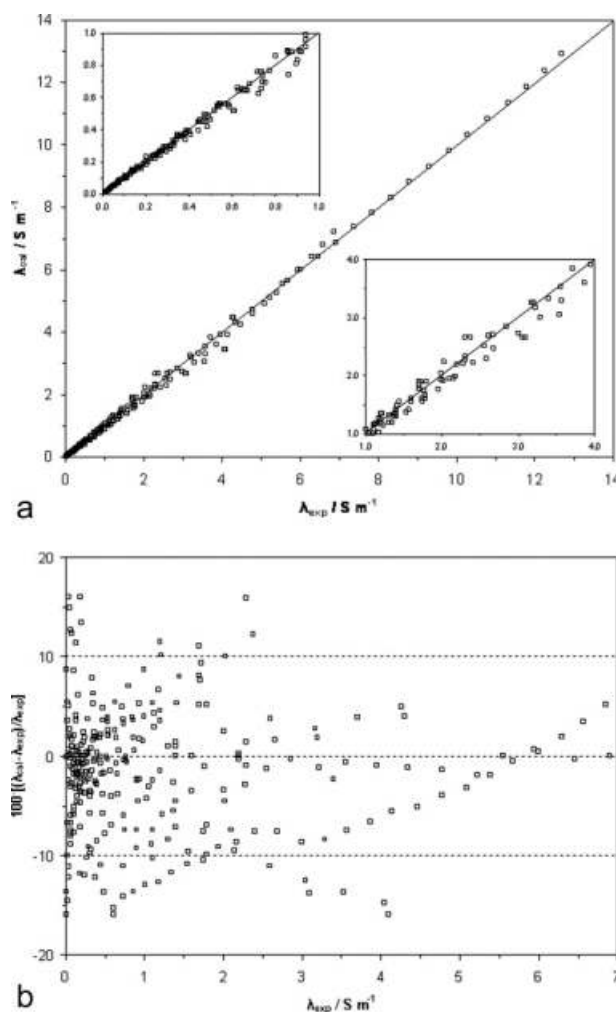


Figure 2. (a) Linear relationship between experimental and calculated electrical conductivity using Eq. 6 and (b) relative deviations between the calculated and experimental electrical conductivity as a function of experimental electrical conductivity for imidazolium-, pyridinium-, pyrrolidinium-, and ammonium-based ionic liquids in the current study.

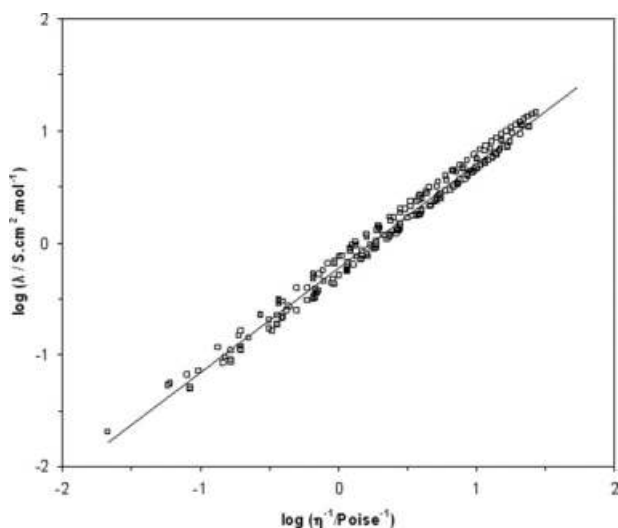


Figure 3. Walden plot showing the behavior of equivalent conductivity of ionic liquids expected from precise correlation with their viscosity.

Experimental electrical conductivity data collected from literature are converted into equivalent conductivity using density calculated from our previous model (Ref. 4), and fluidity is obtained as the reciprocal of viscosity from group contribution method developed in this work.

the chosen units, the “ideal” Walden line runs from corner to corner of a square diagram. The Walden plot can also be useful to understand the relationship between electrical conductivity and vapor pressure.¹¹⁷ For the purpose of Figure 3, experimental electrical conductivity data collected from literature^{15,21,28,35,46–48} are converted into equivalent conductivity using density calculated from our previous model,⁴ and fluidity is obtained as the reciprocal of viscosity from group contribution method developed in this work. In the log-log plot (Figure 3); the slope (α) of the Walden line is obtained as 0.935 ± 0.008 . From the plot it is clear that equivalent conductance (Λ) can be predicted from precise correlation with viscosity (η), using linear relation: $\log \Lambda = (0.935 \pm 0.008) \cdot \log \eta^{-1} - (0.226 \pm 0.005)$ and, as usual, the conductivity decreases with viscosity increase. This correlation also supports the predictive ability of the model for density previously proposed⁴ and the group contribution method here developed for viscosity.

Self-diffusion coefficient

Self-diffusion coefficient (D) is one of the most important transport properties of fluids, which is required in the framework of chemical reaction kinetics and process design. It is related to viscosity in terms of the fractional form of the Stokes–Einstein relation¹¹⁵ according to which the self-diffusion coefficient is proportional to the ratio of temperature and viscosity and can be written as:

$$D \cdot (\eta/T)^\beta = \text{constant} \quad (10)$$

where β is a constant.

Experimental self-diffusion coefficient (D) data of ILs are still scarce in the open literature. The data available were

collected to evaluate the relation between self-diffusion coefficient (D) and viscosity (η) as shown in Figure 4. For this purpose the viscosity was calculated using the group contribution method proposed above. For 45 data points for 5 ILs based on imidazolium cation with BF_4 or Tf_2N as anion, covering wide ranges of temperature, 263.15–353.15 K and self-diffusion coefficient, $2.43 \times 10^{-12} - 3.71 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$,^{21,118} a very good linear correlation is observed with T/η , as shown in Figure 4; where

$$D \cdot 10^{12} = (6.995 \pm 0.061) \cdot (T/\eta) \quad (R^2 = 0.997 \text{ at } 95\% \text{ level of confidence}) \quad (11)$$

This correlation further supports the predictive ability of group contribution method here proposed for the viscosity of ILs and allows an estimation of the self-diffusion coefficient of ILs based on viscosity data.

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

Thermal conductivity

Thermal conductivity measures the ability of a material to conduct heat. It depends on many properties of a material, particularly on its structure and temperature. The knowledge of the thermal conductivity is important to obtain the heat transfer coefficient of fluids which is essential for the design of heat transfer fluid and equipments.¹¹⁹ Among the different transport properties, thermal conductivity is one of the most difficult to estimate using predictive methods.

The database of experimental thermal conductivity (κ) available in the open literature, reported in Table 5, is limited. The 107 data points available, for 16 ILs based on

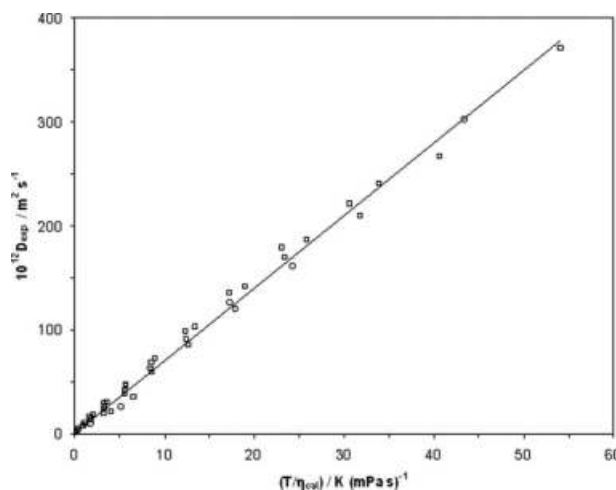


Figure 4. Plot showing the validity of the fractional form of the Stokes–Einstein relation for the studied ionic liquids.

Experimental self-diffusion coefficient data collected from literature and viscosity obtained from group contribution method developed in this work.

Table 5. Prediction of Thermal Conductivities of Imidazolium-, Pyrrolidinium-, and Phosphonium-Based Ionic Liquids

Ionic Liquid	Temperature Range (K)	Data Points	Average Absolute Relative Deviation (%)	Reference
[C ₄ mIm][PF ₆]	294.9–335.1	3	0.15	44
[C ₆ mIm][PF ₆]	294.9–335.2	3	0.22	44
[C ₈ mIm][PF ₆]	294.9–335.1	3	0.26	44
[C ₂ mIm][BF ₄]	300–390	10	3.07	43
[C ₄ mIm][BF ₄]	300–390	10	2.49	43
[C ₂ mIm][Tf ₂ N]	293–353	7	1.58	45
[C ₄ mIm][Tf ₂ N]	293–353	7	1.26	45
	298.15	1	2.06	42
[C ₆ mIm][Tf ₂ N]	293–353	7	1.40	45
[C ₈ mIm][Tf ₂ N]	293–353	7	1.09	45
[C ₁₀ mIm][Tf ₂ N]	293–353	7	0.78	45
[C ₃ mmIm][Tf ₂ N]	300–390	10	0.20	43
[C ₂ mIm][EtSO ₄]	293–353	7	0.15	45
[C ₄ mIm][CF ₃ SO ₃]	293–353	7	0.15	45
[THTDPh][Tf ₂ N]	293–353	7	0.66	45
[THTDPh][Cl]	293–353	7	0.24	45
[C ₄ mPyr][Tf ₂ N]	293–353	7	0.19	45
TOTAL	293–390	107	1.06	

imidazolium-, pyrrolidinium-, and phosphonium based cations with PF₆, BF₄, Tf₂N, EtSO₄, CF₃SO₃, or Cl as anions, covering wide range of temperature, 293–390 K and thermal conductivity, 0.124–0.199 W m⁻¹ K⁻¹,^{42–45} were used in this study. From the experimental thermal conductivity, it was observed that the thermal conductivity is weakly dependent on temperature, and could be fitted with a linear correlation of the form:

$$\kappa = A_{\kappa} - B_{\kappa}T \quad (12)$$

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

$$A_{\kappa} = \sum_{i=1}^k n_i a_{i,\kappa} \quad B_{\kappa} = \sum_{i=1}^k n_i b_{i,\kappa} \quad (13)$$

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 $b_{i,\kappa}$ here estimated for ILs studied are given in Table

Table 6. Group Contributions Parameters $a_{i,\kappa}$ and $b_{i,\kappa}$ in Eq. 13 for Temperature Range 293–390 K

Species	$a_{i,\kappa}$	$b_{i,\kappa}$ (K ⁻¹)
Cations		
1,3-dimethylimidazolium (+)	0.1356	1.564×10^{-5}
1,1-dimethylpyrrolidinium (+)	0.1325	1.668×10^{-5}
Tetramethyl phosphonium (+)	0.1503	3.230×10^{-5}
Anions		
PF ₆ ⁻	0.0173	9.088×10^{-6}
BF ₄ ⁻	0.0874	8.828×10^{-5}
Tf ₂ N ⁻	0.0039	2.325×10^{-5}
CF ₃ SO ₃ ⁻	0.0305	5.284×10^{-5}
EtSO ₄ ⁻	0.0700	6.552×10^{-5}
Cl ⁻	0.0166	1.000×10^{-5}
Groups		
CH ₂	0.0010	2.586×10^{-6}
CH ₃	0.0042	7.768×10^{-6}

6. According to Eq. 12, a plot of κ versus T gives the values of B_{κ} as slope and A_{κ} as intercept. After an initial correlation of each individual IL using Eq. 12 an approach similar to what was used previously for the other properties discussed above was followed to obtain the optimum values of the group contribution parameters $a_{i,\kappa}$ and $b_{i,\kappa}$ reported in Table 6 by minimization of the objective function below

$$\text{O.F.} = \sum_{i=1}^{N_p} [((A_{\kappa} - B_{\kappa}T) - \kappa_{\text{exp}})^2]_i \quad (14)$$

The calculated thermal conductivity (κ_{cal}) using the group contribution parameters $a_{i,\kappa}$, and $b_{i,\kappa}$ reported in Table 6 for imidazolium-, pyrrolidinium-, and phosphonium based ILs

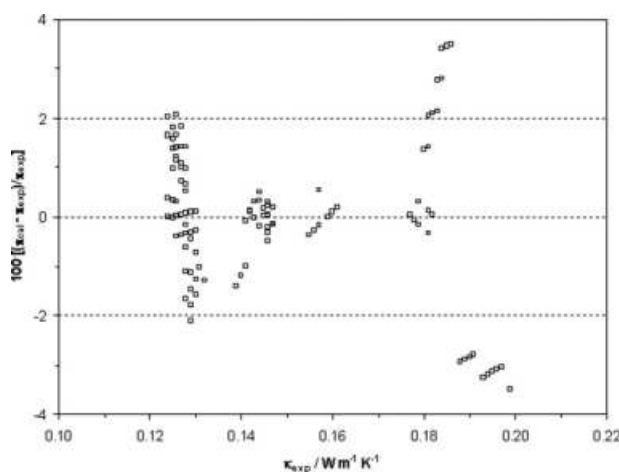


Figure 5. Relative deviations between the calculated and experimental thermal conductivity as a function of experimental thermal conductivity for imidazolium-, pyrrolidinium-, and phosphonium-based ionic liquids in the current study.

Table 8. Group Contributions Parameters a_i, n_D and b_i, n_D in Eq. 16 for Temperature Range 283.15–363.15 K

Species	a_i, n_D	b_i, n_D (K^{-1})
Cations		
1,3-dimethylimidazolium (+)	1.4436	2.268×10^{-4}
Anions		
PF_6^-	0.0330	2.821×10^{-5}
BF_4^-	0.0427	2.835×10^{-5}
Tf_2N^-	0.0628	7.506×10^{-5}
$CF_3SO_3^-$	0.0783	8.653×10^{-5}
$MeSO_4^-$	0.1314	1.016×10^{-4}
$EtSO_4^-$	0.1667	1.749×10^{-4}
Cl^-	0.1247	2.836×10^{-5}
Groups		
CH_2	0.0045	4.587×10^{-6}
CH_3	0.0353	7.330×10^{-5}

The thermal conductivity also increases somewhat with the increase of alkyl chain length on imidazolium cation.

Refractive index

Refractive index (n_D) is a fundamental physical property and it is used to testing a material, confirm its purity, or to calculate the concentration of a mixture. It is important for optics related research fields. 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 are reported in Table 7. It was possible to find 245 data points for 24 imidazolium based ILs having PF_6^- , BF_4^- , Tf_2N^- , $MeSO_4^-$, $EtSO_4^-$, $CF_3SO_3^-$, or Cl^- as anions, covering a wide range of temperature, 283.15–363.15 K,^{12,19,22,23,24,30,32,36,37,41,49–74} that were used in this study. For the studied ILs in the temperature range available, it was observed that the experimental refractive index of IL linearly decreases with temperature, and could be fitted with a linear correlation of the form:

$$n_D = A_{n_D} - B_{n_D}T \quad (15)$$

where A_{n_D} and B_{n_D} can be obtained from a group contribution approach as

$$A_{n_D} = \sum_{i=1}^k n_i a_{i,n_D} \quad B_{n_D} = \sum_{i=1}^k n_i b_{i,n_D} \quad (16)$$

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_D} , and b_{i,n_D} here estimated are reported in Table 8.

The parameter estimation followed the approach previously described for the other properties by minimization of the objective function below

$$O.F. = \sum_{i=1}^{N_p} [(A_{n_D} - B_{n_D}T) - n_{D,exp}]_i^2 \quad (17)$$

The calculated refractive index ($n_{D,cal}$) from Eqs. 15 and 16 using with group contribution parameters A_i , n_D and b_i from Table 8 for imidazolium based ILs having PF_6^- , BF_4^- , Tf_2N^- , $MeSO_4^-$, $EtSO_4^-$, $CF_3SO_3^-$, or Cl^- as anions, are in excellent agreement with the corresponding experimental refractive index

($n_{D,exp}$); where $n_{D,cal} = (0.9999 \pm 0.0002) \cdot n_{D,exp}$ ($R^2 = 0.9977$ at 95% level of confidence). Relative deviations between the calculated and experimental refractive index data as a function of experimental refractive index for all data points used in the current study are shown in Figure 6. For 245 data points of 24 ILs available in literature, the overall RD is 0.18% with a maximum deviation of the order of 0.6%. From these about 47.8% of the estimated refractive indices were within a relative deviation of 0.00–0.10%, 45.7% within 0.101–0.50%, and only 6.5% of the estimated refractive indices having larger than 0.5% deviation. The maximum relative deviation is 0.61% observed for $[C_6mim][Cl]$ (1-hexyl-3-methylimidazolium chloride).²⁴ The results indicate that the refractive index of studied ILs is weakly dependent on temperature and it slightly decreases with temperature. The refractive index of all studied ILs is higher than what is observed for pure water. Water present in IL sample as an impurity has no significant effect on the refractive index; however, from the refractive index data of aqueous solutions of ILs,^{23,41,120} it is clear that the refractive index decreases with increasing amount of water. For ILs having imidazolium based cation, refractive index is increased with anion follows the trend: $[PF_6^-] < [BF_4^-] < [Tf_2N^-] < [CF_3SO_3^-] < [MeSO_4^-] < [EtSO_4^-] < [Cl^-]$; and it increases a little 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 ILs shows that the group contribution method here developed can predict refractive index of new ionic liquids in wide ranges of temperatures and, as data for new groups of cations and anions became available, can be easily extended to a larger range of ionic liquids.

Isobaric expansivity

Thermal expansion of a material must be considered in engineering applications where changes in dimension or density due to temperature are expected. It is an important property to be considered while developing the ILs as heat transfer fluids or for heat storage applications^{42,43,121} or, as recently suggested, for IL based liquid-in-glass thermometers.¹²²

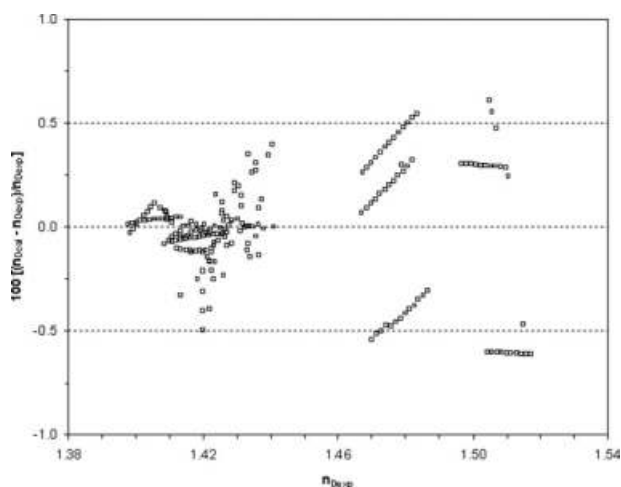


Figure 6. Relative deviations between the calculated and experimental refractive index as function of experimental refractive index for imidazolium-based ionic liquids in the current study.

Table 9. Prediction of Isobaric Expansivity of Imidazolium-, Pyridinium-, Pyrrolidinium-, Piperidinium-, Phosphonium-, and Ammonium-Based Ionic Liquids at 298.15 K and 0.1 MPa

$10^4 \alpha_{\text{Pexp}} (\text{K}^{-1})$	Relative Deviation (%)	Reference	$10^4 \alpha_{\text{Pexp}} (\text{K}^{-1})$	Relative Deviation (%)	Reference
	[C ₄ mIm][PF ₆]			[C ₄ mIm][C(CN) ₃]	
6.00	2.83	29	7.41	0.00	94
6.06	1.79	75		[C ₆ mIm][Cl]	
6.11	1.01	76	5.50	-1.24	24
6.16	0.20	77		[C ₈ mIm][Cl]	
6.16	0.18	81	5.72	-3.67	24
6.17	0.01	78	5.72	-3.67	73
6.20	-0.40	79		[C ₁ mIm][MeSO ₄]	
6.23	-0.91	36	5.42	0.89	54
6.24	-1.15	56	5.44	0.67	70
6.31	-2.13	82	5.76	-4.95	95
6.10	1.19	34		[C ₄ mIm][MeSO ₄]	
	[C ₆ mIm][PF ₆]		5.48	2.00	84
6.18	1.19	33	5.61	-0.22	37
6.36	-1.74	58	5.61	-0.27	51
6.20	0.87	34	5.61	-0.34	96
	[C ₈ mIm][PF ₆]			[C ₂ mIm][EtSO ₄]	
6.20	2.11	25	5.42	0.97	98
6.33	0.04	36	5.47	0.00	23
6.20	2.17	34	5.49	-0.36	27
	[C ₄ mmIm][PF ₆]		5.61	-2.44	89
7.11	-0.43	81		[C ₄ mIm][CF ₃ COO]	
	[C ₂ mIm][BF ₄]		6.32	-0.20	28
5.76	1.56	82		[C ₄ mIm][PF ₂ N]	
5.64	3.77	83	6.68	-0.23	28
6.18	-5.23	84		[C ₁ mIm][(CH ₃) ₂ PO ₄]	
	[C ₄ mIm][BF ₄]		5.16	0.83	95
5.68	4.44	84		[C ₁ mIm][CH ₃ OC ₂ H ₄ SO ₄]	
5.90	0.63	85	5.27	-0.53	95
5.91	0.49	86		[C ₄ mIm][AlCl ₄]	
5.94	-0.02	60	4.48	-0.12	98
5.94	-0.09	75		[C ₄ mIm][FeCl ₄]	
5.96	-0.36	34	4.74	0.01	99
5.96	-0.48	38		[C ₄ mIm][ZnCl ₃]	
5.99	-0.91	87	5.36	-0.04	100
6.02	-1.42	77		[C ₂ mIm][GaCl ₄]	
6.01	-1.22	28	5.82	-0.01	101
6.05	-1.91	56		[C ₄ mIm][GaCl ₄]	
6.18	-4.00	29	5.98	-1.33	102
5.90	0.59	34		[C ₂ mIm][InCl ₄]	
	[C ₆ mIm][BF ₄]		6.53	-0.76	103
6.13	-1.79	38		[C ₄ mIm][InCl ₄]	
6.30	-4.44	84	6.50	-0.95	104
	[C ₈ mIm][BF ₄]			[C ₂ Py][Tf ₂ N]	
6.20	-1.60	38	6.55	-6.77	95
6.23	-2.21	25		[C ₄ Py][Tf ₂ N]	
6.28	-2.93	56	6.36	-2.79	28
6.20	-1.66	34		[C ₃ mPy][Tf ₂ N]	
	[C ₁ mIm][Tf ₂ N]		7.22	-2.38	105
6.67	-0.31	88		[C ₄ Py][BF ₄]	
6.57	1.18	28	5.01	6.77	106
	[C ₂ mIm][Tf ₂ N]			[C ₄ mPy][BF ₄]	
6.44	3.81	28	5.91	5.84	107
6.57	1.78	21	6.37	-1.79	108
6.62	1.02	89		[C ₃ mPyr][Tf ₂ N]	
6.61	1.25	77	7.03	-6.49	105
6.70	-0.23	88		[C ₄ mPyr][Tf ₂ N]	
	[C ₄ mIm][Tf ₂ N]		6.21	6.50	109
6.53	3.67	21	6.51	1.53	28
6.60	2.55	77	7.04	-6.05	105
6.64	1.92	77		[C ₃ mPip][Tf ₂ N]	
6.66	1.68	58	7.17	2.03	105
6.70	1.02	34		[THTDPh][Tf ₂ N]	
6.68	1.38	80	7.44	3.91	110
6.73	0.56	88		[THTDPh][Cl]	
	[C ₆ mIm][Tf ₂ N]		6.63	-4.79	112
6.53	4.92	40	5.96	5.97	110

Table 9. (Continued)

$10^4 \alpha_{\text{Pexp}} (\text{K}^{-1})$	Relative Deviation (%)	Reference	$10^4 \alpha_{\text{Pexp}} (\text{K}^{-1})$	Relative Deviation (%)	Reference
6.54	4.71	90		[THTDPh][CH ₃ COO]	
6.60	3.72	91	6.77	-0.31	110
6.65	2.97	35		[THTDPh][N(CN) ₂]	
	[C ₈ mIm][Tf ₂ N]		5.69	-0.62	111
6.73	2.97	92		[Am(4)111][Tf ₂ N]	
	[C ₂ mIm][CF ₃ SO ₃]		6.05	-7.10	111
6.08	-0.07	93		[Am(6)111][Tf ₂ N]	
6.08	0.06	27	5.92	-3.69	111
	[C ₄ mIm][CF ₃ SO ₃]			[Am(10)111][Tf ₂ N]	
6.16	-0.04	28	6.03	-2.76	111
	[Am(6)222][Tf ₂ N]			[Am(1)888][Tf ₂ N]	
5.79	0.58	111	5.93	7.09	111

The isobaric expansivity (α_{P}) is defined as

$$\alpha_{\text{P}} = \frac{1}{V_{\text{m}}} \left(\frac{\partial V_{\text{m}}}{\partial T} \right)_{\text{P}} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{\text{P}} = - \left(\frac{\partial \ln \rho}{\partial T} \right)_{\text{P}} \quad (18)$$

where V_{m} is molar volume, ρ is density and T is temperature at constant pressure P .

Experimental isobaric expansivity data directly available in literature or calculated using experimental density data using Eq. 18 at 298.15 K are reported in Table 9. 109 data points for 49 ILs based on imidazolium-, pyridinium-, pyrrolidinium, piperidinium-, phosphonium-, and ammonium cations with 19 different anions, at 298.15 K and 0.1 MPa,^{21,23–25,27–29,33–38,40,51,54,56,58,60,70,74,76–107,106–111} were used in this study. In spite of the wide range of ILs investigated, the isobaric expansivities observed fall in a narrow range of values (4.48×10^{-4} to $7.44 \times 10^{-4} \text{ K}^{-1}$) at 298.15 K. As discussed previously⁴ 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.

$$\alpha_{\text{P}} = A_{\alpha_{\text{P}}} = \sum_{i=1}^k n_i a_{i,\alpha_{\text{P}}} \quad (19)$$

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 $a_{i,\alpha_{\text{P}}}$ here estimated for are presented in Table 10.

The parameter estimation was carried by the minimization of the objective function below

$$\text{O.F.} = \sum_{i=1}^{N_{\text{p}}} [(A_{\alpha_{\text{P}}} - \alpha_{\text{Pexp}})^2]_i \quad (20)$$

For the studied ILs, the calculated isobaric expansivity ($\alpha_{\text{P,cal}}$), using Eq. 19 and group contribution parameters $a_{i,\alpha_{\text{P}}}$ reported in Table 10, are in good agreement with the corresponding experimental isobaric expansivity ($\alpha_{\text{P,exp}}$) data; where $\alpha_{\text{P,cal}} = (1.0007 \pm 0.0027) \cdot \alpha_{\text{P,exp}}$ ($R^2 = 0.9992$ at 95% level of confidence). Relative deviations between the calculated and experimental isobaric expansivity data as a function of experimental isobaric expansivity for all data points used in the current study are shown in Figure 7. For 109 data points of 49 ILs available in literature, the overall RD is 1.98% with a maximum deviation of the order of 7%. From these about 40.4% of the estimated refractive indices were within relative deviation of 0.00–1.00%, 36.7% within 1.001–3.00%, 13.8% within 3.001–5.00%, and only 9.2% of the estimated isobaric expansivities having larger than 5% deviation. The maximum relative deviation is 7.10% observed for [THTDPh][N(CN)₂] (triethyl(tetradecyl)phosphonium dicyanamide).¹¹¹ The re-

Table 10. Group Contributions Parameters $a_{i,\alpha_{\text{P}}}$ in Eq. 19 at 298.15 K and 0.1 MPa

Species	$a_{i,\alpha_{\text{P}}} (\text{K}^{-1})$	Species	$a_{i,\alpha_{\text{P}}} (\text{K}^{-1})$
Cations		Anions	
1,3-dimethylimidazolium (+)	3.498×10^{-4}	Cl ⁻	1.733×10^{-4}
1-methylpyridinium (+)	2.916×10^{-4}	CH ₃ COO ⁻	2.170×10^{-4}
1,1-dimethylpyrrolidinium (+)	3.342×10^{-4}	CF ₃ COO ⁻	2.683×10^{-4}
1,1-dimethylpiperidinium (+)	4.085×10^{-4}	MeSO ₄ ⁻	1.975×10^{-4}
Trihexylteradecyl phosphonium (+)	4.583×10^{-4}	EtSO ₄ ⁻	1.935×10^{-4}
Tetramethyl ammonium (+)	2.350×10^{-4}	(CH ₃) ₂ PO ₄ ⁻	1.701×10^{-4}
Groups		CH ₃ OC ₂ H ₄ SO ₄ ⁻	1.748×10^{-4}
CH ₂	4.054×10^{-6}	Pf ₂ N ⁻	3.041×10^{-4}
CH ₃	9.024×10^{-5}	N(CN) ₂ ⁻	1.072×10^{-4}
Anions		AlCl ₄ ⁻	8.551×10^{-5}
PF ₆ ⁻	2.553×10^{-4}	FeCl ₄ ⁻	1.120×10^{-4}
BF ₄ ⁻	2.315×10^{-4}	ZnCl ₃ ⁻	1.738×10^{-4}
Tf ₂ N ⁻	3.149×10^{-4}	GaCl ₄ ⁻	2.281×10^{-4}
CF ₃ SO ₃ ⁻	2.541×10^{-4}	InCl ₄ ⁻	2.942×10^{-4}
C(CN) ₃	3.795×10^{-4}		

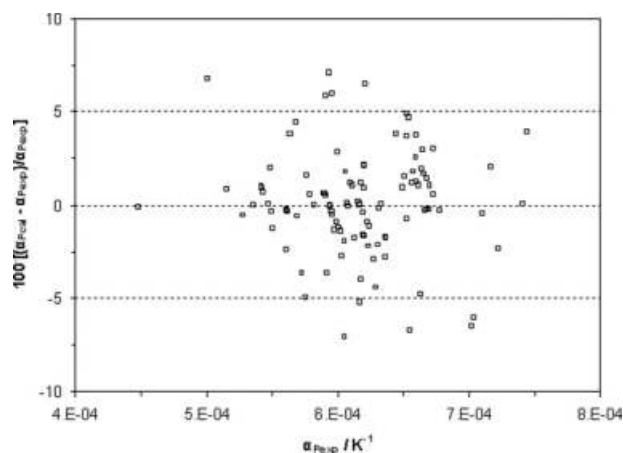


Figure 7. Relative deviations between the calculated and experimental isobaric expansivity as a function of experimental isobaric expansivity for imidazolium-, pyridinium-, pyrrolidinium-, piperidinium-, phosphonium-, and ammonium-based ionic liquids in the current study.

sults indicate that the isobaric expansivity of studied ILs is weakly dependent on anion and it increases poorly with the alkyl chain length on cation.

Isothermal compressibility

Compressibility is an important factor in thermodynamics, aerodynamics, earth sciences, geotechnical engineering and industrial chemistry. In ionic liquids it is relevant for the design of industrial fluids to be used in pumps or compressors.¹²³ The isothermal compressibility (κ_T), is a measure of the relative volume change of a fluid as a response to a pressure change at constant temperature, is directly or indirectly related to several thermodynamic properties, and can be expressed as

$$\kappa_T = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = \left(\frac{\partial \ln \rho}{\partial P} \right)_T \quad (21)$$

Experimental isothermal compressibility data directly available in literature or calculated using experimental density data using Eq. 21 at 298.15 K are reported in Table 11. In this study 26 data points for 22 ILs based on imidazolium-, pyridinium-, pyrrolidinium, piperidinium-, and phosphonium cations with PF₆, BF₄, Tf₂N, EtSO₄, CF₃SO₃, CH₃COO, Cl or C(CN)₃ as anions, at 298.15 K and 0.1 MPa,^{75,77,81,86,90,94,105,106,110,124} were used. As discussed previously^{4,81} the precision to which this property is known preclude any study of its temperature or pressure dependency as this is inferior to the experimental uncertainty. For this reason the isothermal compressibility will be here correlated at the temperature of 298.15 K and atmospheric pressure by a group contribution approach in the studied range (0.33–0.73 GPa⁻¹) of experimental isothermal compressibility data.

$$\kappa_T = A_{\kappa_T} = \sum_{i=1}^k n_i a_{i,\kappa_T} \quad (22)$$

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 , here estimated are given in Table 12.

The parameter estimation was carried by the minimization of the objective function below

$$\text{O.F.} = \sum_{i=1}^{N_p} [(A_{\kappa_T} - \kappa_{T,\text{exp}})^2]_i \quad (23)$$

For the studied ILs, the calculated isothermal compressibility ($\kappa_{T,\text{cal}}$), using Eq. 22 and group contribution parameters a_i , κ_T (Table 12), are in good agreement with the corresponding experimental isothermal compressibility ($\kappa_{T,\text{exp}}$) data; where $\kappa_{T,\text{cal}} = (1.0055 \pm 0.0064) \cdot \kappa_{T,\text{exp}}$ ($R^2 = 0.9990$ at 95% level of confidence). Relative deviations between the calculated and experimental isothermal compressibility data as a function of experimental isothermal compressibility for all data points used in the current study are shown in Figure 8. For 26 data points of 22 ILs available in literature, the overall RD 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. The maximum relative deviation is 6.67% observed for [C₈mim][BF₄] (1-octyl-3-methylimidazolium tetrafluoroborate).⁸¹ Imidazolium based ILs are less compressible compare to phosphonium based ILs. 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 ILs.

Table 11. Prediction of Isothermal Compressibility of Imidazolium-, Pyridinium-, Pyrrolidinium-, Piperidinium-, and Phosphonium-Based Ionic Liquids at 298.15 K and 0.1 MPa

Ionic Liquid	$\kappa_{T,\text{exp}}$ (GPa)	Relative Deviation (%)	Reference
[C ₄ mIm][PF ₆]	0.348	5.75	77
[C ₆ mIm][PF ₆]	0.420	-0.05	81
[C ₈ mIm][PF ₆]	0.473	-0.22	81
	0.469	0.58	106
[C ₂ mIm][BF ₄]	0.331	-6.47	94
[C ₄ mIm][BF ₄]	0.386	-6.24	75
	0.386	-6.25	86
	0.360	0.56	77
[C ₈ mIm][BF ₄]	0.437	6.67	81
[C ₂ mIm][Tf ₂ N]	0.469	0.00	94
[C ₃ mIm][Tf ₂ N]	0.517	-4.22	124
[C ₄ mIm][Tf ₂ N]	0.530	-1.63	90
	0.498	4.62	76
[C ₅ mIm][Tf ₂ N]	0.544	0.46	124
[C ₆ mIm][Tf ₂ N]	0.549	4.31	90
[C ₂ mIm][CF ₃ SO ₃]	0.435	-3.24	105
[C ₄ mIm][CF ₃ SO ₃]	0.457	3.43	81
[C ₄ mIm][C(CN) ₃]	0.405	-0.05	94
[C ₂ mIm][EtSO ₄]	0.733	0.00	77
[C ₂ Py][BF ₄]	0.396	-1.76	106
[C ₃ mPyr][Tf ₂ N]	0.516	-0.05	105
[C ₄ mPyr][Tf ₂ N]	0.524	3.36	105
[C ₃ mPip][Tf ₂ N]	0.507	-0.01	105
[THTDPh][Tf ₂ N]	0.601	5.71	110
[THTDPh][Cl]	0.573	0.10	110
[THTDPh][CH ₃ COO]	0.573	0.05	110

Table 12. Group Contributions Parameters a_i, κ_T in Eq. 22 at 298.15 K and 0.1 MPa

Species	a_i, κ_T (GPa ⁻¹)
Cations	
1,3-dimethylimidazolium (+)	0.196
1-methylpyridinium (+)	0.223
1,1-dimethylpyrrolidinium (+)	0.217
1,1-dimethylpiperidinium (+)	0.208
Trihexyltetradecyl phosphonium (+)	0.388
Group	
CH ₂	0.026
Anions	
PF ₆ ⁻	0.094
BF ₄ ⁻	0.088
Tf ₂ N ⁻	0.247
CF ₃ SO ₃ ⁻	0.199
C(CN) ₃ ⁻	0.131
Cl ⁻	0.186
CH ₃ COO ⁻	0.185
EtSO ₄ ⁻	0.511

Conclusions

Group contribution methods for estimating the thermo-physical and transport properties of ILs were developed for viscosity, electrical conductivity, thermal conductivity, 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 circa 1250 experimental data points were used for this purpose. A comparison between the experimental and correlated values showed that the proposed models describe the experimental data available with absolute relative deviations generally of the same order of the agreement of experimental data by dif-

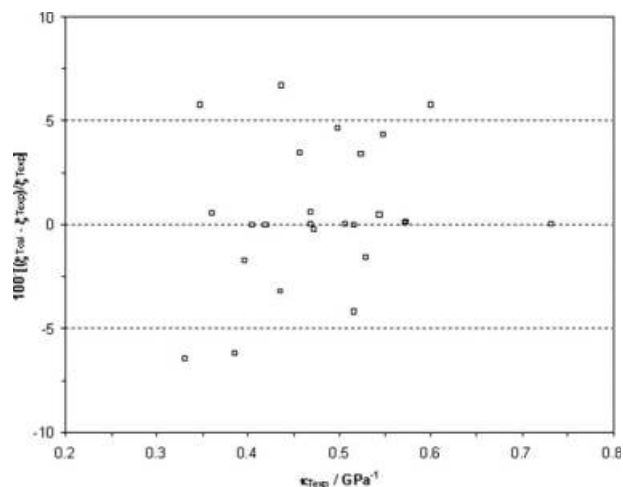


Figure 8. Relative deviations between the calculated and experimental isothermal compressibility as a function of experimental isothermal compressibility for imidazolium-, pyridinium-, pyrrolidinium-, piperidinium-, and phosphonium ionic liquids in the current study.

ferent authors as described on 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 ILs 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 these properties.

The proposed methods can be useful for predicting the studied properties for design of processes or products involving ionic liquids as the procedure involved are rapid and facile. They can also be used for the development of 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 here proposed can, in the future, be extended to a larger range of ionic liquids as data for these become available.

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Notation

- [C_nmIm]⁺ = *n*-alkyl-3-methylimidazolium cation
- [C_neIm]⁺ = *n*-alkyl-3-ethylimidazolium cation
- [C_nmPy]⁺ = *n*-alkyl-3-methylpyridinium cation
- [C_nmPyr]⁺ = *n*-alkyl-1-methylpyrrolidinium cation
- [C_nmPip]⁺ = *n*-alkyl-1-methylpiperidinium cation
- [THTDPh]⁺ = trihexyl(tetradecyl)phosphonium cation
- [Am(*n*)nnn]⁺ = *n,n,n*-tetraalkylammonium cation

Subscripts

- exp = experimental property
- cal = calculated property

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