The Residual Volume Approach II: Simple Prediction of Ionic Conductivity of Ionic Liquids

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Dedicated to Professor Dr. Gerhard Maas on the occasion of his 60th birthday

The Residual Volume Approach (RVA), a recently developed method for the prediction of fundamental physical properties of ionic liquids (ILs) is extended and now allows the estimation of ionic conductivity of unknown ILs, using a simple linear correlation between the ionic conductivity and previously defined substituent parameters – β^X. The proposed method is applied to the conductivity correlations of 61 *n*-alkyl substituted imidazolium, tetraalkylammonium, pyrrolidinium, piperidinium, sulfonium and phosphonium homologous ILs, containing $[BF_4]^-$, $[Tf_2N]^-$, $[C_2F_5PF]^-$, $[CF_3BF_3]^-$, $[C_2H_5BF_3]^-$, $[F(HF)_{2.3}]^-$, $[Br]^-$, $[I]^-$, and $[formate]^-$ as anions. The influence of the ion type – both anion and cation – on the property changes is discussed. Moreover, it is shown that relatively rigid cations with C_2 symmetry decrease the expected conductivity in the same manner as they increase the viscosity of the ILs.

Key words: Ionic Liquids, Predictive Methods, Ionic Conductivity, Viscosity, Structure-Property Relationships

Introduction

Ionic liquids (ILs) or molten salts, as they were called in the past, are organic compounds with ionic structure that have per definition a melting point below 100 °C. The great interest in some of them in the past few years is mainly due to their physicochemical properties and application in different industrial fields. The good solvating properties, high conductivity, non-volatility, low toxicity, large electrochemical window (*i. e.* the electrochemical potential range over which the electrolyte is neither reduced nor oxidized on electrodes) and good electrochemical stability, insolubility in water and/or common organic solvents make ILs suitable for many applications. These properties have led to their use in photovoltaics [1] and Li ion batteries [2] and as membranes [3], solvents and catalysts [4] *etc*. Therefore the amount of publications on ionic liquids has increased considerably in the recent few years [5]. In response to the need to synthesize ILs with predefined, task-specific properties, a number of papers appeared describing different predictive methods which allow the prediction of some of their fundamental physical properties – density [6a – h], viscosity [7a – f], surface tension [8a, b], conductivity [7b, e, 9a – e], melting points [6a, 10a – d] *etc*. Although most of these methods have good predictive ability, they require complicated models, extended data sets and considerable computer time. In order to reduce the expensive computer time, simple predictive methods are desirable. To overcome this problem, we have recently developed a method – The Residual Volume Approach (RVA) [11] – which is based on simple linear correlations between volume-dependent physical properties of ILs (density and viscosity) and the differences between the molecular volumes of the members of a given homologous series. The basic idea is that for a given series of ionic liquids, the members of which differ only by the substituent X in a certain position in the cation structure, the differences in the studied property of the X- and the methyl-substituted compounds are proportional to

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Table 1. Values of the residual volume substituent constants (β^X), for more details see Ref. [11].

Substituent	β^X (nm^3)	Substituent	β^X (nm^3)
Methyl, (-CH_3)	0	Heptyl, (-C_7H_{15})	0.149
Ethyl, (-C_2H_5)	0.029	Octyl, (-C_8H_{17})	0.169
Propyl, (-C_3H_7)	0.056	Nonyl, (-C_9H_{19})	0.189
Butyl, (-C_4H_9)	0.081	Decyl, (-$C_{10}H_{21}$)	0.208
Pentyl, (-C_5H_{11})	0.105	Undecyl, (-$C_{11}H_{23}$)	0.223
Hexyl, (-C_6H_{13})	0.127	Dodecyl, (-$C_{12}H_{25}$)	0.235

the differences in their molecular volumes. Since for each series of ILs this difference in molecular volume is constant, a new constant describing that difference – β^X – can be defined. Its values for unbranched alkyl chains are given in Table 1. Therefore, one of the greatest advantages of the RVA is that it is cation- and anion-independent, since it takes into account the difference in molecular volumes of two homologs only and not the type of ions they are composed of.

We have already demonstrated [11] the predictive power of RVA for the viscosity and density of a large number of imidazolium- and tetraalkylammonium-based ILs. Nevertheless, an important issue for the successful application of both our and other predictive methods should be stressed. The lack of experimental data in the literature and the significant deviations between the values reported by different authors restrict the development of more adequate property-predictive methods. It seems that most of the measurements were carried out using compounds of not clearly established purity, and since the properties of ILs vary considerably in the presence of even small amounts of impurities (usually water or halide ions) [12a, b] the need for accurate experimental data of ILs with proven high purity is essential.

As we mentioned above, the high ionic conductivity (IC) and electrochemical and thermal stability of ILs make them ideal electrolytes in electrochemical devices [13]. In their application as electrolytes for batteries, the value of IC should be more than 6 mS cm^{-1}, and hence ILs with higher ionic conductivities are required. Therefore, reliable methods for predicting the IC of task-specific ILs are of great value. As we already noted, there are some IC-predictive methods available [7b, e, 9a – e], but just as in the cases of the other properties their use is complicated and requires considerable computer time. Encouraged by the successful application of RVA for the prediction of density and viscosity of ILs [11], here we report its application for the prediction of IC by using simple correlations between the experimentally measured IC and the corresponding β^X constants.

Results and Discussion

Recently, Slattery *et al.* [7e] showed that the molecular volumes (V_m) of a series of ILs hold a strong exponential correlation with their IC (σ), following an equation of the type

$$\ln\sigma = -aV_m + C \qquad (1)$$

and they defined the empirically obtained constants a and C, which are anion-dependent. It is obvious that this equation is applicable for any member of the series, and this allows us to make the assumption, as we did for density and viscosity [11], that the differences in the IC should be proportional to the differences in the molecular volumes for a given homologous series. The latter may be expressed by Eq. 2,

$$\ln\sigma^X = a\beta^X + \ln\sigma^0 \qquad (2)$$

where σ^X is the IC of the X-substituted member, a is the slope of the line, the intercept $\ln\sigma^0$ is the IC of the methyl-substituted member, and β^X is the corresponding substituent constant (see Table 1). Eq. 2 quantifies the effect of substituents on property changes and allows us to set up a hypothesis that in the case of any ILs series for which data on a reasonable number of n-alkyl substituted compounds are available, a plot of $\ln\sigma^X$ against β^X will give a straight line with a slope of the best fit a and an intercept – the conductivity of the first member of the series (the methyl-substituted compound). Subsequently, if data for at least three members of a given group are available, it will be possible to predict the values of σ^X using the corresponding β^X constants and the empirically obtained parameters a and σ^0.

Based on the above reasoning, the application of the current approach has been generalized by correlating the experimental IC of a vast number of representative ILs and substituent constants β^X.

Collection of IC of ILs and RVA correlations

A database of experimental IC (mentioned in the captions of Figs. 1 – 3) was collected from the literature (see Table 3). The imidazolium-based ILs are the most frequently investigated molten salts, and thus the applicability of the RVA correlations was tested mainly on them (Fig. 1A). Series of ILs based on the quaternary

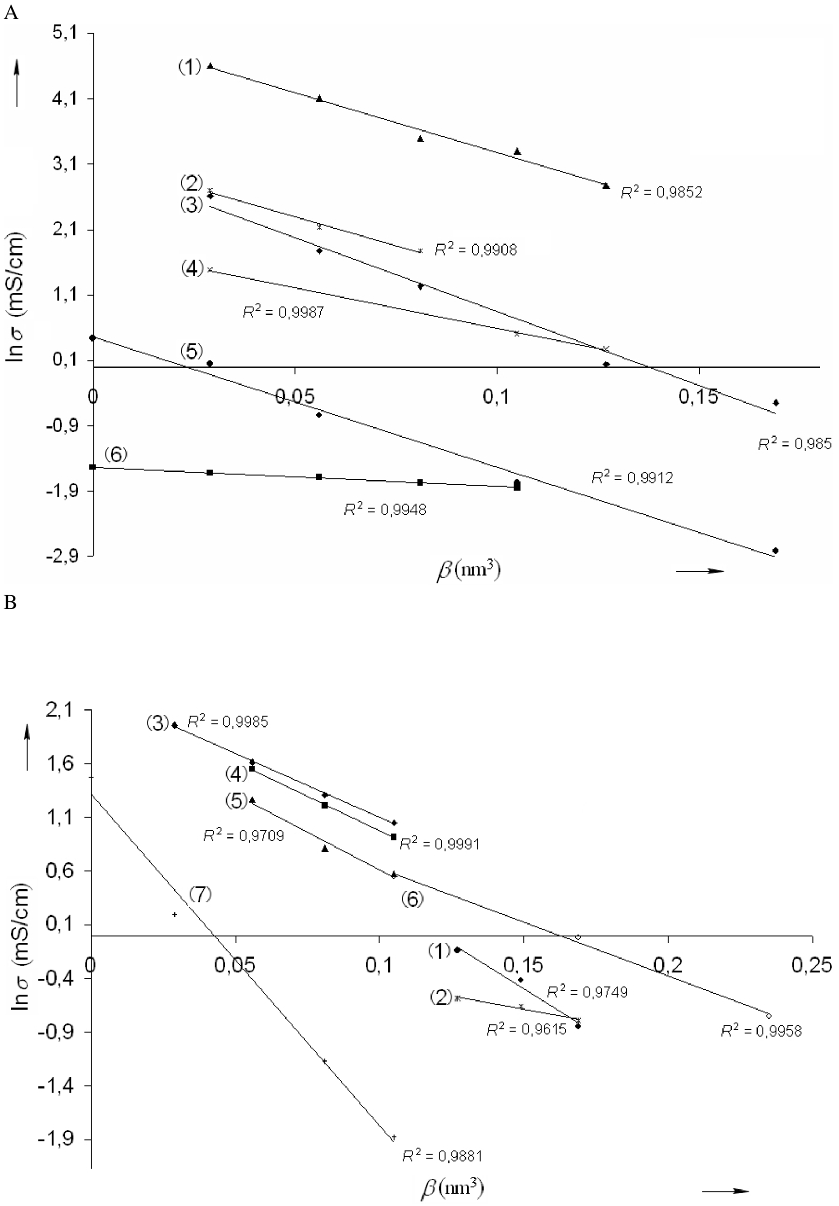


Fig. 1. Correlation between β constants and experimental ionic conductivity for A) imidazolium- and B) alkylammonium-, sulfonium- and phosphonium-based ILs at 25 °C: A) (1) [C_n-mim][$F(HF)_{2.3}$], $n = 1-6$ [14a]; (2) [C_n-mim][CF_3BF_3], $n = 1-4$ [9c]; (3) [C_n-mim][BF_4], n = 2, 3, 4, 6, 8 [9c]; (4) [C_n-mim]-[$(C_2H_5)_3PF_3$], n = 2, 5, 6 [14b]; (5) [C_n-allyl-im][Br], n = 1, 2, 3, 5, 8 [14c]; (6) [C_n-vinyl-im][I], $n = 1-5$ [14d]; (B) (1) [C_n-N_{222}][Tf_2N], $n = 6-8$ [14e]; (2) [C_n-N_{111}][Tf_2N], $n = 6-8$ [14e]; (3) [C_n-S_{22}][Tf_2N], $n = 2-5$ [14f]; (4) [C_n-S_{12}][Tf_2N], $n = 3-5$ [14f]; (5) [C_n-S_{11}]-[Tf_2N], $n = 3-5$ [14f]; (6) [C_n-P_{222}][Tf_2N], n = 5, 8, 12 [14g]; (7) [C_n-N_{HHH}][formate], n = 1, 2, 4, 5 [14h].

ammonium, sulfonium, phosphonium (Fig. 1B), pyrrolidinium, and piperidinium cations were also tested. Thus, a total number of 61 suitably substituted imidazolium (8 series), ammonium (3 series), sulfonium (3 series), phosphonium, pyrrolidinium and piperidinium (1 series each) based ILs, containing $[BF_4]^-$, $[Tf_2N]^-$, $[C_2F_5PF]^-$, $[CF_3BF_3]^-$, $[C_2H_5BF_3]^-$, $[F(HF)_{2.3}]^-$, $[Br]^-$, $[I]^-$, and $[formate]^-$ as anions were used in this study. Plots of $\sigma = f(\beta)$ for 49 RTILs are shown in Fig. 1. For the sake of clarity, the imidazolium series are presented in a separate chart (Fig. 1A), and the alkylammonium-, sulfonium- and phosphonium-based series are in Fig. 1B.

[C_n-mpyr][$F(HF)_{2.3}$] (n = 2, 3, 4, 6 at 25 °C) [14a], [C_n-mpip][$F(HF)_{2.3}$] (n = 2, 3, 4 at 25 °C) [14a], [C_n-mim][$C_2H_5BF_3$] (n = 1, 2, 3, 4 at 25 °C) [9c] and [C_n-mim][Tf_2N] (n = 1, 2, 4, 6, 8 at 30 °C) [17a] series have not been included in Fig. 1 because of overlapping, but the corresponding plots $\sigma = f(\beta)$ in these cases give straight lines with R^2 = 0.977, 0.981, 0.989, and 0.992,

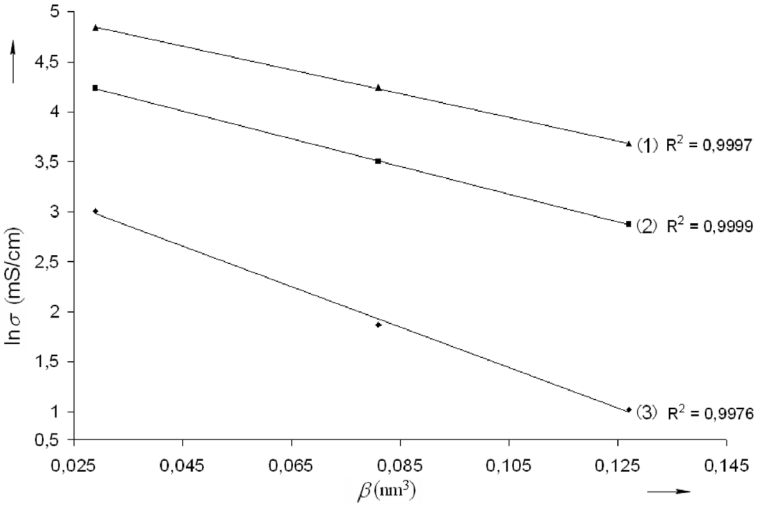


Fig. 2. Correlation between β constants and experimental ionic conductivity for [C_n-mim][BF_4], n = 2, 4, 6 at different temperatures [15]: (1) 433 K; (2) 373 K; (3) 308 K.

respectively. It should be mentioned here that the relatively rigid compounds possessing C_2 symmetry (see Fig. 3) have been omitted from Fig. 1 due to significant deviations form the corresponding correlations, but the latter phenomena are discussed in detail below.

As can be seen from Fig. 1, each homologous series follows a very good linear relationship (correlation coefficient: $R^2 = 0.9615-0.9987$). Thus, Fig. 1 supports the hypothesis defined above, that the difference in the conductivities of the X- and methyl-substituted compounds ($\ln\sigma^X - \ln\sigma^0$) are proportional to the difference in their molecular volumes ($V^X - V^0$), and that the residual volume substituent constants β^X may be correlated with the experimentally measured IC giving a linear relationship according to Eq. 2. Therefore, the application of RVA gives us the opportunity not only to predict the IC values in a given ILs homologous series, but is also a powerful tool for calculating the maximum IC ($\ln\sigma^0$) which is achievable for a given cation-anion combination.

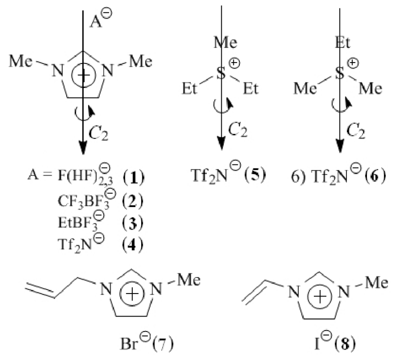
Let us demonstrate how the proposed approach works by implementing it on the [C_n-vinyl-im] [I] series ($n = 1-5$) at 25 °C (Fig. 1A, series 6). The plot of IC of methyl-, propyl- and pentyl-substituted members [14d] against the corresponding β^X gives a straight line (correlation coefficient: $R^2 = 0.995$) with slope $a = -2.9255$ and intercept $\ln\sigma^0 = -1.5311$. The latter is, in fact, the predicted value of σ^{Me} at 25 °C {exp. $\ln\sigma^{Me} = -1.5371$ [14d]}. Knowing the empirical equation $\sigma^X = -2.9255\beta^X - 1.5311$ and the corresponding β^X constants (Table 1), the IC of the remaining members of the group can be easily calculated. The predicted and experimental values {in parentheses [14d]}, expressed in mS/cm, are as follows: $\sigma^{Et} = 0.199$ (0.197); $\sigma^{Bu} = 0.171$ (0.170). It is noteworthy that for a better prediction it is necessary for the reference members under study not to be immediate neighbors, especially in the case of more extended homologous series. Furthermore, the fact that IC changes linearly with temperature allows the application of the RVA for prediction of IC at different conditions. Fig. 2 presents the plots of $\sigma = f(\beta)$ for [C_n-mim][BF_4] (n = 2, 4, 6) ILs [15]. It is clear that the selected representative temperatures hold a linear relationship (correlation coefficient: $R^2 = 0.998-0.999$), even for the wide range of temperature ($308 < T < 433$ K). Unfortunately, the data for the remaining members of the series at these temperatures is missing, and thus, the predictive ability of RVA can not be tested in this case. However, since the RVA works well in the case of density and viscosity predictions at different temperatures, we can assume that it will also work in the case of IC.

Ionic conductivity

In the description of classical electrolyte solutions, the mobile charge carrier is related to its diffusion coefficient D through the Nernst-Einstein equation (Eq. 3) [9d],

$$\Lambda = \frac{z^2 e_0 F D}{k_B T} = \frac{z^2 e_0^2 N_A D}{k_B T} \qquad (3)$$

where z represents the valence of the charge carrier, e_0 the elementary charge, N_A the Avogadro number, T the temperature, k_B the Boltzmann constant and F the Faraday constant. On the other hand, the diffusion co-



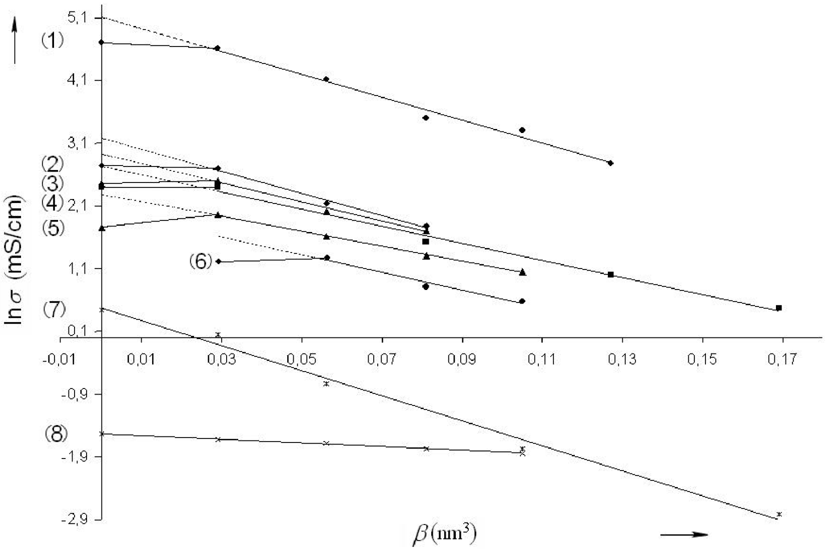


Fig. 3. Correlation between β constants and experimental ionic conductivity for imidazolium- and sulfonium-based ILs at 25 °C, including the rigid C_2-symmetrical compounds omitted in Fig. 1: (1) [C_n-mim][F(HF)$_{2.3}$], n = 1 – 6; (2) [C_n-mim][CF$_3$BF$_3$], n = 1 – 4; (3) [C_n-mim][(C$_2$H$_5$)$_3$PF$_3$], n = 2, 5, 6; (4) [C_n-mim][Tf$_2$N], n = 1, 2, 4; (5) [C_n-SEt$_2$][Tf$_2$N], n = 1 – 5; (6) [C_n-SMe$_2$][Tf$_2$N], n = 2 – 5; (7) [C_n-allyl-im][Br], n = 1, 2, 3, 5, 8; (8) [C_n-vinyl-im][I], n = 1 – 5.

efficient of a spherical model species of an effective radius r depends on the medium viscosity, η, according to the Stokes-Einstein equation (Eq. 4) [9d].

$$D = \frac{k_B T}{6\pi r \eta} \qquad (4)$$

Combining Eq. 3 and Eq. 4, and taking into account that $\sigma = \Lambda c = \Lambda n/V$ (n is the number of moles of the charge carrier) and $N = nN_A$ is the number of charge carriers present in the volume V, leads to the following equation for the ionic conductivity σ (Eq. 5) [9d].

$$\sigma = \frac{z^2 e_0}{6\pi r V}\frac{N}{\eta} \qquad (5)$$

Finally, the specific interactions between the mobile ions in the melts can be described by including the anion and cation microviscosity factors (ζ_a and ζ_c, respectively) in Eq. 5, leading to Eq. 6 [16].

$$\sigma = \frac{z^2 e_0 N}{6\pi V \eta (\zeta_a r_a + \zeta_c r_c)} \qquad (6)$$

Thus, the conductivities of liquid salts can be related with a reasonable degree of approximation to the medium viscosity (η), to the volume (V, or the density and molecular weight, respectively) and to the radii of their ions (r_a and r_c), following Eq. 6. Taking into account the plots in Fig. 1, the latter equation appears to be verified qualitatively. The conductivity decrease of a given homologous series with β^X for all the examined ILs is in agreement with the trend for viscosity to increase with the increase of the number of carbon atoms in the alkyl group n. Beside the obvious influence of the viscosity, Bonhôte *et al.* [16] stressed that the effect of the ion size and molecular weight must also be considered during the search of new highly conductive ILs.

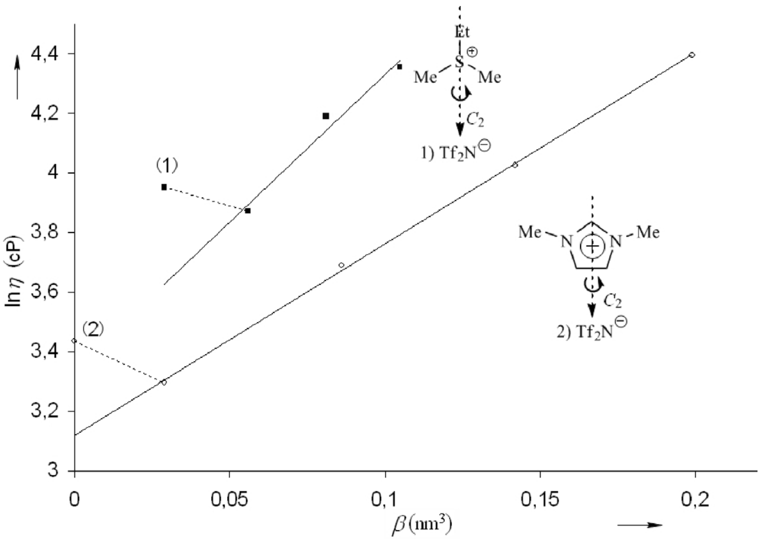


Fig. 4. Correlation between β constants and experimental viscosities for: (**1**) [C$_n$-SMe$_2$][Tf$_2$N], n = 2, 3, 4, 5 at 25 °C [14f] and (**2**) [C$_n$-mim][Tf$_2$N], n = 1, 2, 4, 6, 8 at 30 °C [17].

To summarize: combination of small ions will lower the viscosity and thus will lead to ILs with higher conductivity. These effects can be rationalized by comparing Me,Et-disubstituted pyrrolidine, piperidinium and imidazolium cations with combination with [F(HF)$_{2.3}$] anions [14a]. The decrease of IC (in mS cm^{-1}) in this case, 100 for [Me,Et-im]$^+$ > 74.6 for [Me,Et-pyr]$^+$ > 37.2 for [Me,Et-pip]$^+$, is in agreement with the increase of the viscosity (in cP) of 4.9 for [Me,Et-im]$^+$ > 9.9 for [Me,Et-pyr]$^+$ > 24.2 for [Me,Et-pip]$^+$. Furthermore, the trend for IC to decrease with the increase of the anion volume can be seen from Fig. 3 (series 1–4). The data for the ILs with common 1,3-dimethylimidazolium cations decrease in the range [F(HF)$_{2.3}$]$^-$ > [CF$_3$BF$_3$]$^-$ > [C$_2$H$_5$BF$_3$]$^-$ > [Tf$_2$N]$^-$, according to the anion volume.

Considering the cation type, the opposite is valid in the case of the sulfonium-based [Tf$_2$N]$^-$ series (Fig. 3, series 5 and 6). It seems somehow confusing that the higher mass cation [SMeEt$_2$]$^+$ shows higher IC than [SMe$_2$Et]$^+$. This observation suggests that the specific interactions between the ions in a given combination play an important role and should be considered in the future.

Table 2. Experimental and calculated IC of C_2-symmetrical ILs **1**–**6**.

	Compound	σ^{exp} (mS cm^{-1})	σ^{calcd} (mS cm^{-1})	$\sigma^{\text{exp}}/\sigma^{\text{calcd}}$
1	[dmim][F(HF)$_{2.3}$]	110	166.2	0.662
2	[dmim][CF$_3$BF$_3$]	15.5	24.1	0.643
3	[dmim][C$_2$H$_5$BF$_3$]	11.7	18.6	0.629
4	[dmim][Tf$_2$N]	9	15.3	0.59
5	[SMe$_2$Et][Tf$_2$N]	3.35	7.6	0.44
6	[SMeEt$_2$][Tf$_2$N]	5.8	9.9	0.586

Another interesting result appears from the analysis in Fig. 3. As we mentioned above, the relatively rigid compounds with methyl-substituted cations possessing C_2 symmetry (Fig. 3, compds. **1**–**6**) show significant deviations form the corresponding RVA correlations and have therefore been omitted from Fig. 1. Such a deviation can also be found in other articles published before [17], but no explanation has been offered. It is noteworthy that the predicted IC values (σ^0) of all C_2-symmetrical first members examined here (Fig. 3, compds. **1**–**6**) deviate from the experimentally measured ones nearly in the same manner, showing lower values for the experimental IC (σ^{exp}) than for the predicted IC σ^{calcd}. The values of σ^{exp}, σ^{calcd}, and $\sigma^{\text{exp}}/\sigma^{\text{calcd}}$ for compounds **1**–**6** (Fig. 3) are presented in Table 2. The plot of experimental conductivities (Y) in this case linearly correlates with the corresponding predicted conductivities (X) following the equation: $Y = 0.6687\,X - 1.0429$ (correlation coefficient: $R^2 = 0.9999$). The factor 0.6687 seems to be very close to $\ln 2 = 0.693$, which is in fact the entropy of the system with symmetry number $\sigma_{\text{S}} = 2$. The entropy and symmetry are simply correlated [18] by a logarithmic expression: $S = -\ln \sigma_{\text{S}}$, where σ_S is the apparent symmetry number, the apparent number of the symmetric or indistinguishable microstates, for which the symmetric transformations can leave the macroscopic state of the system unchanged. According to this equa-

Table 3. Experimental IC data (at 25 °C) used in this study[a].

Compound	σ (mS cm^{-1})	Compound	σ (mS cm^{-1})	Compound	σ (mS cm^{-1})
[C_1-mim][$F(HF)_{2.3}$]	110 [14a]	[C_6-N_{222}][Tf_2N]	0.67 [14e]	[C_2-mpyr][$F(HF)_{2.3}$]	74.6 [14a]
[C_2-mim][$F(HF)_{2.3}$]	100 [14a]	[C_7-N_{222}][Tf_2N]	0.51 [14e]	[C_3-mpyr][$F(HF)_{2.3}$]	58.1 [14a]
[C_3-mim][$F(HF)_{2.3}$]	61 [14a]	[C_8-N_{222}][Tf_2N]	0.33 [14e]	[C_4-mpyr][$F(HF)_{2.3}$]	35.9 [14a]
[C_4-mim][$F(HF)_{2.3}$]	33 [14a]	[C_6-N_{111}][Tf_2N]	0.43 [14e]	[C_6-mpyr][$F(HF)_{2.3}$]	23.7 [14a]
[C_5-mim][$F(HF)_{2.3}$]	27 [14a]	[C_7-N_{111}][Tf_2N]	0.40 [14e]	[C_2-mpip][$F(HF)_{2.3}$]	37.2 [14a]
[C_6-mim][$F(HF)_{2.3}$]	16 [14a]	[C_8-N_{111}][Tf_2N]	0.35 [14e]	[C_3-mpip][$F(HF)_{2.3}$]	23.9 [14a]
[C_1-mim][CF_3BF_3]	15.5 [9c]	[C_1-N_{HHH}][formate]	4.38 [14h]	[C_4-mpip][$F(HF)_{2.3}$]	12.3 [14a]
[C_2-mim][CF_3BF_3]	14.8 [9c]	[C_2-N_{HHH}][formate]	1.216 [14h]	[C_1-mim][$C_2H_5BF_3$]	11.7 [9c]
[C_3-mim][CF_3BF_3]	8.5 [9c]	[C_4-N_{HHH}][formate]	0.31 [14h]	[C_2-mim][$C_2H_5BF_3$]	12.2 [9c]
[C_4-mim][CF_3BF_3]	5.9 [9c]	[C_5-N_{HHH}][formate]	0.153 [14h]	[C_3-mim][$C_2H_5BF_3$]	7.5 [9c]
[C_2-mim][BF_4]	13.6 [9c]	[C_2-S_{11}][Tf_2N]	3.35 [14f]	[C_4-mim][$C_2H_5BF_3$]	5.5 [9c]
[C_3-mim][BF_4]	5.9 [9c]	[C_3-S_{11}][Tf_2N]	3.55 [14f]	[C_1-mim][Tf_2N]	11[b] [17a]
[C_4-mim][BF_4]	3.43 [9c]	[C_4-S_{11}][Tf_2N]	2.25 [14f]	[C_2-mim][Tf_2N]	11[b] [17a]
[C_6-mim][BF_4]	1.04 [9c]	[C_5-S_{11}][Tf_2N	1.78 [14f]	[C_4-mim][Tf_2N]	4.6[b] [17a]
[C_8-mim][BF_4]	0.58 [9c]	[C_3-S_{12}][Tf_2N]	4.47 [14f]	[C_6-mim][Tf_2N]	2.7[b] [17a]
[C_2-mim][$(C_2H_5)_3PF_3$]	4.4 [14b]	[C_4-S_{12}][Tf_2N]	3.35 [14f]	[C_8-mim][Tf_2N]	1.6[b] [17a]
[C_5-mim][$(C_2H_5)_3PF_3$]	1.66 [14b]	[C_5-S_{12}][Tf_2N]	2.5 [14f]	[C_1-vinyl-im][I]	0.215 [14d]
[C_6-mim][$(C_2H_5)_3PF_3$]	1.32 [14b]	[C_1-S_{22}][Tf_2N]	5.8 [14f]	[C_2-vinyl-im][I]	0.197 [14d]
[C_1-allyl-im][Br]	1.55 [14c]	[C_2-S_{22}][Tf_2N]	7.1 [14f]	[C_3-vinyl-im][I]	0.186 [14d]
[C_2-allyl-im][Br]	1.05 [14c]	[C_3-S_{22}][Tf_2N]	5.03 [14f]	[C_4-vinyl-im][I]	0.170 [14d]
[C_3-allyl-im][Br]	0.48 [14c]	[C_4-S_{22}][Tf_2N]	3.7 [14f]	[C_5-vinyl-im][I]	0.158 [14d]
[C_5-allyl-im][Br]	0.17 [14c]	[C_5-S_{22}][Tf_2N]	2.86 [14f]	[C_5-P_{222}][Tf_2N]	1.73 [14g]
[C_8-allyl-im][Br]	0.06 [14c]			[C_8-P_{222}][Tf_2N]	0.98 [14g]
				[C_{12}-P_{222}][Tf_2N]	0.47 [14g]

[a] N_{111} = NMe_3; N_{222} = NEt_3; S_{11} = SMe_2; S_{12} = SMeEt; S_{22} = SEt_2; P_{222} = PEt_3; mim = methylimidazolium; im = imidazolium; mpyr = 1-methylpyridinium; mpip = 1-methylpiperidinium; [b] data taken at 30 °C.

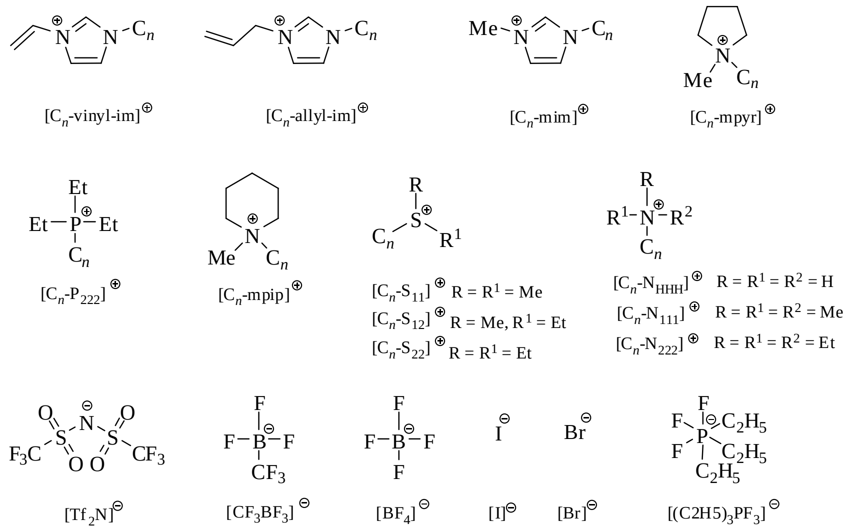


Fig. 5. Structures of cations and anions examined in this study.

tion the symmetry is related to the more ordered state of the system, and thus the C_2 symmetry will affect the IL properties because of the higher degree of ordering, which means that entropy should decrease with the symmetry number. It should be noted that unsymmetrical vinyl- and allyl-sybstituted methylimidazolium ILs (Fig. 3, compds. **7**, **8**) did not show such a behavior, but follow reasonably well the corresponding RVA correlation.

It seems that C_2 symmetry significantly affects the macroscopic properties of ILs. The symmetry influence on the melting points of ILs has already been discussed [19]: in general, the higher the symmetry, the higher the melting points. Based on the above reasoning, it could be assumed that C_2 symmetry will influence the other macroscopic IL properties as well. Let us consider the viscosity and correlate the experimental values for [C_n-mim][Tf_2N] and [C_n-S_{11}][Tf_2N] series using RVA. The correlations are presented in Fig. 4. As can be seen, the rigid compounds with C_2 symmetry deviate from the straight line derived for the remaining members of the series. It is obvious that the C_2 symmetry in these cases plays a key role, and the deviation can be attributed to the higher ordering of these melts. Considering Eq. 6, or in particular the viscosity dependence from the ionic conductivity, it is clear that the observed deviations for the viscosity will have the opposite sign for the IC.

Conclusion

The RVA correlations proposed here show the opportunity for IC prediction of a given homologous series of ILs (Fig. 5) from the experimentally measured data for three members of the group only. Moreover, we believe that if sophisticated computational methods are used to provide data for at least three compounds of one series, it could be combined with the RVA to predict the properties of the remaining members of the series. This approach will reduce considerably expensive computer time and will facilitate the experimental synthetic work in the targeted synthesis of ILs with desired properties. On the other hand, RVA allows the rapid estimation of the maximum ionic conductivity which is achievable for a given cation-anion combination and describe qualitatively the effect of the substituents on the property changes.

The relation found in the case of C_2-symmetrical ILs suggests that the role of the ion symmetry should be further considered in the development of more complicated property-predictive methods. Therefore, targeted syntheses of homologous series of ILs containing rigid C_2-symmetrical members, further combined with quantum chemical simulations, are necessary for a detailed explanation of the C_2 symmetry effect on their physical properties.

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