# Simple Prediction of Some Physical Properties of Ionic Liquids: The Residual Volume Approach

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*Z. Naturforsch.* **2009**, *64b,* 215 – 222; received July 8, 2008

*Dedicated to Professor Mariana Palamareva on the occasion of her retirement from the University of Sofia*

A new method for prediction of fundamental physical properties of ionic liquids (ILs) is proposed. The Residual Volume Approach (RVA) allows the estimation of density and viscosity of unknown ILs, using a simple linear correlation between a given property and a newly defined substituent parameter $\beta^X$. The proposed method has been developed for the density estimation of 50 *n*-alkyl-substituted imidazolium and tetraalkylammonium salts in a homologous series of ILs and has been extended for the estimation of viscosity, which also correlates linearly with the corresponding $\beta^X$. In addition, the parameters $\beta^X$ are temperature and pressure independent, which allows the prediction of these values at any temperature and pressure.

*Key words:* Ionic Liquids, Predictive Methods, Physical Properties, Structure-Property Relationships, Residual Volume Approach

## Introduction

Ionic liquids (ILs) are organic salts with melting points near r. t. (or by agreement below 100 °C). Recently, the unique material and solvent properties of such salts have led to an extraordinary increase of interest in them [1f]. Their fascinating properties favor application in diverse fields, such as synthesis [1d], catalysis [1a], electrochemistry [1b], separation technology, analytical chemistry, and nanotechnology [1e]. Nowadays, an immense number of possible ILs ($> 10^{14}$) [1c] can be easily obtained, but since the experimental study of such a huge number of potential cation-anion combinations together with their many substitution patterns is impossible, the fine-tuning of a certain property to fit a specific task is rather difficult. Therefore, understanding the behavior of ILs at molecular level and further implementing this knowledge in different property-predicting models is a great challenge for the research community, and any success in this field would facilitate their rational design. In this direction, several attempts at quantitative prediction of density [2a – h], viscosity [3a – f], surface tension [4a, b], conductivity [3b, 5] and melting points [2a, 6a – d] have been reported. The significance of these efforts is clear: on the one hand, to diminish the time- and money-consuming experimental work and, on the other, to promote the synthesis of the targeted IL.

Inspired by this work, we report here a facile and rapid method for the estimation of fundamental physical properties of room-temperature ionic liquids (RTILs) using a simple linear correlation between the given IL property and the residual volume of the *n*-alkyl substituents. Thus, we will show that the prediction of density and viscosity is an “easy game”, and that this procedure can be carried out even by a non-specialist. Moreover, the application of this approach to a selected anion-cation combination allows both fine-tuning the desired property by a slight variation of *n*-alkyl substituents and predictions for different temperatures and pressures. This is of great importance from a practical point of view.

## Results and Discussion

### *Residual volume approach*

The proposed Residual Volume Approach (RVA) is a linear correlation between the volume-dependent physical properties of *n*-alkyl-substituted ILs and the newly defined substituent parameters ($\beta^{X}$). The basic idea is that, for any series of ILs differing only by the substituents at a definite position in the cation structure, the change of a given physical property is proportional to the change in the molecular volume of the substituents.

We found the plot of experimental densities ($\rho$) of a series of *n*-alkyl-substituted imidazolium salts [C$_n$mim][Tf$_2$N] at 25 °C against the corresponding molecular volumes $V_\mathrm{m}$ to lie reasonably well on a straight line (correlation coefficient: $R^2$ = 0.98) with a smooth, monotonic decrease in density with increase of the molecular volume. This correlation follows Eq. 1:

$$\rho^{X} = aV^{X} + C \tag{1}$$

where $\rho^{X}$ and $V^{X}$ are the density and the molecular volume of the X-substituted member, respectively, *a* is the slope of the line, and *C* is the intercept. This equation is applicable for any member of the series, and if the density and the molecular volume of the methyl substituted compound are denoted by $\rho^0$ and $V^0$, then:

$$\rho^{0} = aV^{0} + C \tag{2}$$

Eq. 2 may be substracted from Eq. 1 for the same series to give Eq. 3:

$$\rho^{X} - \rho^{0} = a(V^{X} - V^{0}) \tag{3}$$

From this equation it can be seen that the differences in the densities of X- and methyl-substituted compounds are proportional to the differences in their molecular volumes. Since for any series of ILs ($V^{X} - V^{0}$) is constant, a new constant $\beta^{X}$ can be defined, characteristic of a given substituent X. This definition reduces Eq. 3 to Eq. 4:

$$\rho^{X} = a\beta^{X} + \rho^{0} \tag{4}$$

where $\beta^{X}$ (the substituents constant as stated) may be interpreted as being the residual volume of the substituent X, and the slope *a* is a measure of the sensitivity to the substituent molecular volume changes of the cation-anion combination in question. It is worth noting that the slope (parameter *a*) and the intercept ($\rho^0$) are empirical constants which depend on the cation-anion combination only, but are independent of the substituent X. The opposite is valid for the substituent parameters $\beta^{X}$, which depend only on the specific substituent X. The values of $\beta^{X}$ can be calculated from their definition by using of Glasser's empirical equation $V_\mathrm{m}$ (nm$^3$) = $1.66 \times 10^{-3}$ ($M_\mathrm{w}\rho^{-1}$) [7] for the molecular volume calculations ($M_\mathrm{w}$ is the molecular weight), or by using the group additivity approach [2b]. Since it has been shown [2b] that the molecular volume for a given IL in liquid state increases by 0.028 nm$^3$ per methylene group (-CH$_2$-), the calculated substituent parameters $\beta'^{X}$ are as follows: $\beta'^{Me} = 0$ ($\rho^{Me} = \rho^{0}$); $\beta'^{Et} = 0.028$ ($\beta'^{Et} = \beta'^{Me} + 0.028$); $\beta'^{Pr} = 0.056$ ($\beta'^{Pr} = \beta'^{Et} + 0.028$), *etc.* The $\beta'^{X}$ values for methyl to dodecyl, calculated in this way, are listed in Table 1. Table 1 also displays the refined values for $\beta^{X}$ (corrected empirically for a better fit). This shows that the molecular volume is not affected by exactly 0.028 nm$^3$ per methylene group. A possible reason for this is that each new -CH$_2$- group leads to an increase of the degrees of freedom due to conformational flexibility [8], and thus it may be assumed that every additional group's contribution is smaller than that of the previous one, related to the cation-anion combination under study. This assumption has been proved by a parallel correlation of experimental densities of [C$_n$mim][Tf$_2$N] at 25 °C [9] with both $\beta^{X}$ and $\beta'^{X}$ parameters. The analysis shows a better correlation coefficient $R^2$ = 0.997 for $\beta^{X}$ compared to $R^2$ = 0.983 for $\beta'^{X}$. Consequently, the values for the refined $\beta^{X}$ constants should be used.

Table 1. Preliminary calculated ($\beta'$) and refined ($\beta$) constants.

| Substituent | $\beta'^{X}$ (nm$^3$) | $\Delta\beta'^{X\,a}$ | $\beta^{X}$ (nm$^3$) | $\Delta\beta^{X\,a}$ |
|---|---|---|---|---|
| Methyl, (-CH$_3$) | 0 | – | 0 | – |
| Ethyl, (-C$_2$H$_5$) | 0.028 | 0.028 | 0.029 | 0.029 |
| Propyl, (-C$_3$H$_7$) | 0.056 | 0.028 | 0.056 | 0.027 |
| Butyl, (-C$_4$H$_9$) | 0.084 | 0.028 | 0.081 | 0.025 |
| Pentyl, (-C$_5$H$_{11}$) | 0.112 | 0.028 | 0.105 | 0.024 |
| Hexyl, (-C$_6$H$_{13}$) | 0.140 | 0.028 | 0.127 | 0.022 |
| Heptyl, (-C$_7$H$_{15}$) | 0.168 | 0.028 | 0.149 | 0.022 |
| Octyl, (-C$_8$H$_{17}$) | 0.196 | 0.028 | 0.169 | 0.020 |
| Nonyl, (-C$_9$H$_{19}$) | 0.224 | 0.028 | 0.189 | 0.020 |
| Decyl, (-C$_{10}$H$_{21}$) | 0.252 | 0.028 | 0.208 | 0.019 |
| Undecyl, (-C$_{11}$H$_{23}$) | 0.280 | 0.028 | 0.223 | 0.015 |
| Dodecyl, (-C$_{12}$H$_{25}$) | 0.308 | 0.028 | 0.235 | 0.012 |

[a] Difference between two neighbors.

However, the hypothesis may be set up from the above reasoning that in the case of any ILs series

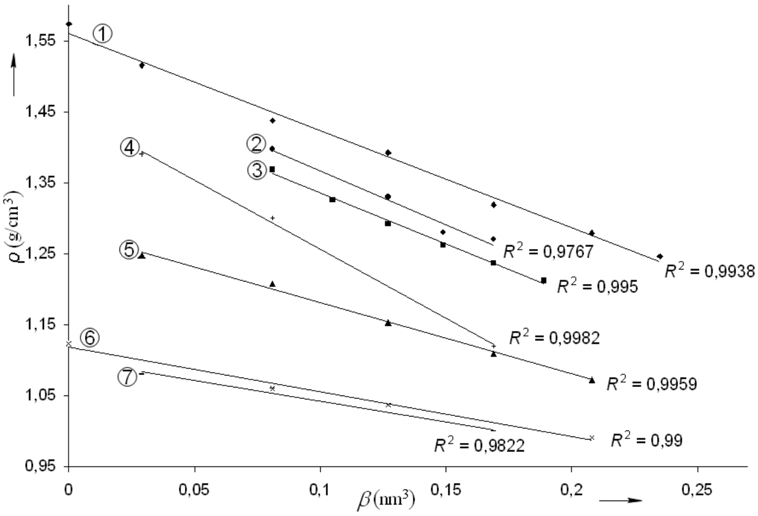

Fig. 1. Correlation between $\beta$ constants and experimental densities for [$C_n$-mim]- and tetraalkylammonium-based ILs at different temperatures: (**1**) [$C_n$-mim][$Tf_2N$] at 20 °C, $n$ = 1, 2, 4, 6, 8, 10, 12 [7]; (**2**) [$C_n$-$N_{111}$][$Tf_2N$] at 20 °C, $n$ = 4 [3e], 6, 7, 8 [10]; (**3**) [$C_n$-mim][$PF_6$] at 25 °C, $n$ = 4, 5, 6, 7, 8, 9 [9]; (**4**) [$C_n$-mim][OTf] at 22 °C, $n$ = 2, 4, 8 [24]; (**5**) [$C_n$-mim][$BF_4$] at 20 °C, $n$ = 2, 4, 6, 8, 10 [7]; (**6**) [$C_n$-Him][lactate] at 80 °C, $n$ = 1, 4, 6, 10 [13]; (**7**) [$C_n$-mim][$N(CN)_2$] at 25 °C, $n$ = 2 [23a], 4, 8 [23b].

for which data on a reasonable number of $n$-alkyl-substituted compounds are available, a plot of $\rho^X$ against $\beta^X$ will give a straight line with a slope of the best fit $a$ and an intercept – the density of the first member of the series (the methyl-substituted compound). Thus, the proposed equation quantifies the effect of substituents on property changes by defining characteristic substituent parameters ($\beta^X$). It can be assumed that Eq. 4 is applicable for any series of ILs differing both in cation and anion, but possessing common substituents. Subsequently, if data for at least three members of a given group are available, it will be possible to predict the values of $\rho^X$ using the corresponding $\beta^X$ constants and the empirically obtained parameters $a$ and $\rho^0$. Based on the above assumption, the application of the current approach has been generalized by correlating the volumetric and transport properties of a vast number of representative ILs and the newly defined substituent constants $\beta^X$.

### *Density correlations*

A data base of available experimental densities (see Table 2 below) was collected from the literature (mentioned in the captions of Figs. 1 – 4). The imidazolium-based ILs are the most frequently investigated molten salts which allowed the applicability of the RVA correlations to be tested on them. A series of ILs based on the quaternary ammonium cations was also taken into account. Unfortunately, there are no data available for suitably substituted cations such as pyrrolidinium and piperidinium, and thus a total number of 50 suitably substituted methylimidazolium (7 series), H-imidazolium (1 series) and tetraalkylammonium (5 series) based ILs containing $[PF_6]^-$, $[BF_4]^-$, $[Tf_2N]^-$, $[OTf]^-$, $[N(CN)_2]^-$ and $[lactate]^-$ as anions were used in this study.

Plots of $\rho = f(\beta)$ for 32 RTILs are shown in Fig. 1. As can be seen, the density decreases with $\beta^X$ for all the ILs examined here, and each series follows a very good linear relationship (correlation coefficient: $R^2$ = 0.977 – 0.998). [$C_n$-$N_{222}$][$Tf_2N$] ($n$ = 6, 7, 8) [10a], [$C_n$-$N_{444}$][$Tf_2N$] ($n$ = 6, 7, 8) [10a], [$C_n$-$N_{111}$][$Tf_2N$] ($n$ = 4, 6, 10, at 25 °C) [10b] and [$C_n$-$N_{113}$][$Tf_2N$] ($n$ = 4, 6, 10) [10b] series have not been included in Fig. 1 because of overlapping, but the plots $\rho = f(\beta)$ in these cases give straight lines with $R^2$ = 0.999, 0.954, 0.994, and 0.994, respectively. Fig. 1 is direct evidence for the hypothesis defined above that the difference in the densities of X- and methyl-substituted compounds ($\rho^X - \rho^0$) are proportional to the difference in their molecular volumes ($V^X - V^0$), and that the residual volume substituent constants $\beta^X$ may be correlated with the experimentally measured densities, giving a linear relationship.

Let us demonstrate how the proposed approach works by implementing it on the [$C_n$-mim][$Tf_2N$] series ($n$ = 1 – 10) at 25 °C. It is worth noting that for better prediction it is necessary for the reference members under study not to be immediate neighbors. Thus, the plot of densities of ethyl-, butyl- and octyl-substituted members [9] against the corresponding $\beta^X$ gives a straight line (correlation coefficient: $R^2$ = 0.997) with slope $a = -1.4105$ and intercept $\rho^0$ = 1.556. The lat-

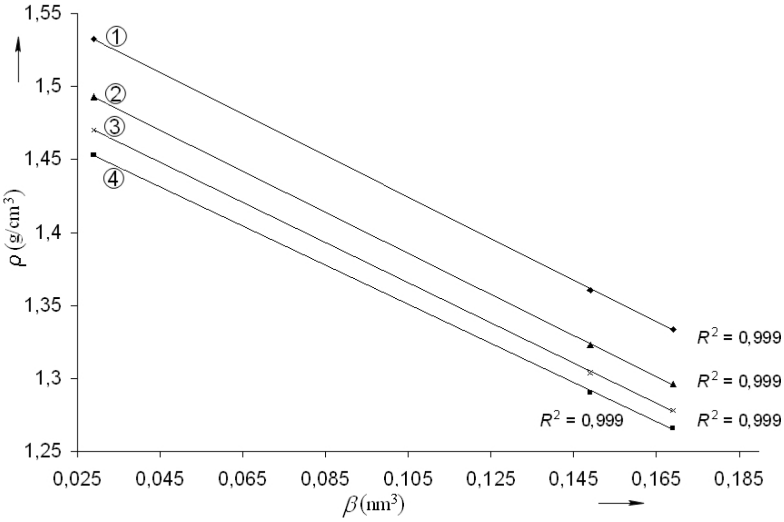

Fig. 2. Correlation between $\beta$ constants and experimental densities for [C$_n$-mim][Tf$_2$N], $n$ = 2, 7, 8, at different pressures and temperatures [2e]: (**1**) 25 MPa and 303.15 K; (**2**) 0.1 MPa and 323.15 K; (**3**) 10 MPa and 353.15 K; (**4**) 30 MPa and 393.15 K.

ter is, in fact, the predicted value of $\rho^{\text{Me}}$ at 25 °C (exp. $\rho^{\text{Me}}$ = 1.554 [11a], 1.570 [11b]). Having the empirical equation $\rho^{\text{X}} = -1.4105\beta^{\text{X}} + 1.556$ and the corresponding $\beta^{\text{X}}$ constants, the density of the remaining members of the group can be easily calculated. The predicted and experimental values (in parentheses [9]), expressed in g cm$^{-3}$, are as follows: $\rho^{\text{Pr}}$ = 1.477 (1.475); $\rho^{\text{Pen}}$ = 1.408 (1.403); $\rho^{\text{Hex}}$ = 1.377 (1.372, 1.371 [12a], 1.3722 [12b]); $\rho^{\text{Hept}}$ = 1.346 (1.344); $\rho^{\text{Non}}$ = 1.290 (1.299); $\rho^{\text{Dec}}$ = 1.263 (1.271). The experimental densities ($Y$) in this case demonstrate a very good agreement with the corresponding predicted densities ($X$): $Y = 0.9988\ X$ (correlation coefficient: $R^2$ = 0.995). The observed relative deviation of 1.22 % shows the good predictive ability of RVA in this case. However, as can be seen from Fig. 1, the [C$_n$-Him][lactate] series also holds a linear correlation even though the experimental data have been taken at 80 °C [13]. This fact suggests that the substituent parameters $\beta^{\text{X}}$ seem to be temperature- and pressure-independent. The latter is easily rationalized since density changes linearly with temperature or pressure [2d, 2e, 14]. This allows us to apply RVA for a prediction of density at different conditions. Fig. 2 presents the plots of $\rho = f\ (\beta)$ for [C$_n$-mim][Tf$_2$N] ($n$ = 2, 7, 8) ILs [2e]. It is clear that the selected representative temperature-pressure combinations hold a linear relationship (correlation coefficient: $R^2$ = 0.999 in all the cases), even for wide ranges of temperature ($303.15 < T < 393.15$ K) and pressure ($0.10 < p < 30.00$ MPa). The equation of the series at 0.1 MPa and 323.15 K is $\rho^{\text{X}} = -1.1857\ \beta^{\text{X}} + 1.5256$ (correlation coefficient: $R^2$ = 0.999). Thus, we are able to predict, for example, the density of butyl- and hexyl-substituted members at these conditions. Then, $\rho^{\text{Bu}}$ = 1.426 g cm$^{-3}$ (lit. $\rho^{\text{Bu}}$ (0.10 MPa / 323.14 K) = 1.414 g cm$^{-3}$ [15a]) and $\rho^{\text{Hex}}$ = 1.359 g cm$^{-3}$ (lit. $\rho^{\text{Hex}}$ (0.10 MPa / 323.14 K) = 1.348 g cm$^{-3}$ [15a, b]). The equation of the series at pressure 25 MPa and temperature 303.15 K is $\rho^{\text{X}} = -1.201\ \beta^{\text{X}} + 1.5659$ (correlation coefficient: $R^2$ = 0.999). Then $\rho^{\text{Bu}}$ = 1.465 g mol$^{-3}$ (lit. $\rho^{\text{Bu}}$ (24.670 MPa / 303.14 K) = 1.450 g cm$^{-3}$ [15a]) and $\rho^{\text{Hex}}$ = 1.398 g mol$^{-3}$ (lit. $\rho^{\text{Hex}}$ (25.860 MPa / 303.14 K) = 1.385 g cm$^{-3}$ [15a]).

Furthermore, our attempt to implement RVA for the methylimidazolium series of ILs containing terminal functional groups in the longer alkyl chain proved successful. The plots $\rho = f\ (\beta)$ of [(NC)-C$_n$-mim][BF$_4$] at 20 °C ($n$ = 2, 3, 4 [16]) and [Ph-C$_n$-mim][Tf$_2$N] at 25 °C ($n$ = 1, 2, 3 [9]) were also linear (correlation coefficient: $R^2$ = 0.982 and 0.994, respectively). In these cases, salts [R-CH$_2$-mim][A] were selected as first members and thus the intercepts in both correlations give the densities for cyanomethyl- and benzyl-substituted methylimidazolium ILs. This shows that RVA can be used not only in the case of $n$-alkyl substituents but also for a subsituent series which differs only by the count of methylene groups.

### *Viscosity correlations*

The viscosity, $\eta$, of an IL is one of its most important material properties because high viscosities form barriers to many applications. For example, many

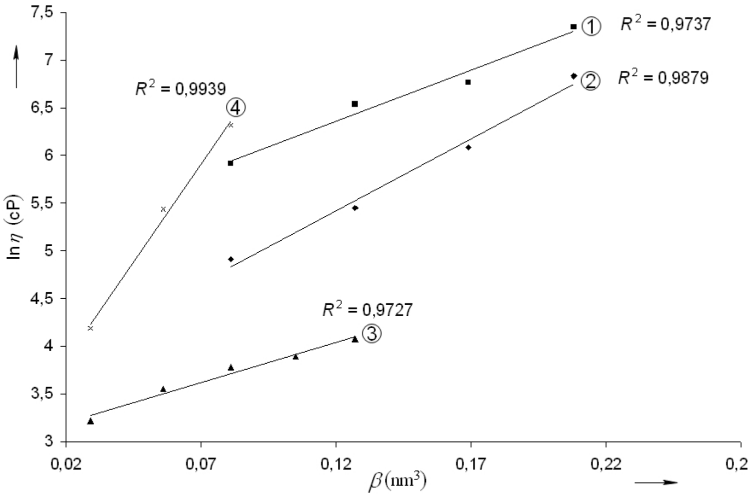

Fig. 3. Correlation between $\beta$ constants and viscosity for [C$_n$-mim][A] at different temperatures: (**1**) [C$_n$-mim][PF$_6$] at 20 °C, $n$ = 4, 6, 8, 10 [25a]; (**2**) [C$_n$-mim][BF$_4$] at 20 °C, $n$ = 4, 6 [20b], 8, 10 [25a]; (**3**) [C$_n$-mim][Tf$_2$N] at 20 °C, $n$ = 2, 3, 4, 5, 6 [25b]; (**4**) [(NC)-C$_n$-mim][BF$_4$] at 25 °C, $n$ = 2, 3, 4 [16].

chemical reactions are slower in ILs than in molecular solvents such as water, alcohols, or acetonitrile [1f]. The lowest viscosity observed to date at 298 K ($\eta$ = 21 cP for [C$_2$mim][(CN)$_2$N] [17]) is still more than twenty times that of water. Since most of the ILs are highly viscous oils an essential aspect of the synthesis of novel systems is the search for a suitably substituted cation-anion combination with low viscosity. In contrast, ILs with high viscosity are applicable as stationary phases in gas-liquid chromatography [18]. However, the simulation of this fundamental physical property is difficult and is just beginning to be explored. Therefore, the development of simple models for data prediction is of great importance. Recently, Slattery *et al.* [3e] showed that the molecular volumes of a series of ILs hold a strong exponential correlation with their viscosities, following an equation of the type:

$$\ln\eta = aV_{\mathrm{m}} + C \tag{5}$$

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 with density above, that the differences in the viscosities should be proportional to the differences in the molecular volumes for a given series. The latter may be expressed by Eq. 6:

$$\ln\eta^{\mathrm{X}} = a\beta^{\mathrm{X}} + \ln\eta^{0} \tag{6}$$

where $\eta^{\mathrm{X}}$ is the viscosity of the X-substituted member, $a$ is the slope of the line, the intercept $\ln\eta^0$ is the viscosity of the methyl-substituted member, and $\beta^{\mathrm{X}}$ is again the correspondinig substituent constant (see Table 1). 16 suitably substituted imidazolium-based ILs (4 series, including [(NC)-C$_n$-mim]) containing [PF$_6$]$^-$, [BF$_4$]$^-$ and [Tf$_2$N]$^-$ as anions were used for proving the validity of Eq. 6. Plots of $\ln\eta = f\ (\beta)$ are shown in Fig. 3. Each series follows a very good linear relationship (correlation coefficient: $R^2$ = 0.973 – 0.994), which is evidence for the proportionality between ($\ln\eta^{\mathrm{X}} - \ln\eta^0$) and $\beta^{\mathrm{X}}$. The viscosity increase with $\beta$ for all the ILs examined here is in agreement with the trend for viscosity to increase with the increase of the number $n$ of carbon atoms in the alkyl group.

The plot of viscosity against the corresponding $\beta^{\mathrm{X}}$ for the [C$_n$-mim][BF$_4$] series ($n$ = 4, 6, 8, 10) at 20 °C (Fig. 3) gives a straight line (correlation coefficient: $R^2$ = 0.988) with slope $a$ = −15.056 and intercept $\ln\eta^0$ = 3.6184. The latter is, in fact, the predicted value of $\ln\eta^0$ for the methyl-substituted compound at 20 °C. Having the empirical coefficients $a$ and $\ln\eta^0$, it is easy to calculate the viscosity of any member of the series by using the equation $\ln\eta^{\mathrm{X}} = -15.056\ \beta^{\mathrm{X}} + 3.6184$. Then, the predicted viscosity for [C$_2$-mim][BF$_4$] at 20 °C is $\eta^{\mathrm{Et}}$ = 58 cP, which is in good agreement with the experimetal value 66.5 cP [19]. It should be mentioned here that the vast number of different viscosity values reported in the literature are confusing. For example, reported data (in cP) for [Bu-mim][BF$_4$] at 25 °C are as follows: 104 [20a], 104 [20b], 120 [20c], 136 [12a], 154 [20d], 180 [20e], 219 [20f]. On the one hand, this discrepancy is due to impurities, since it is well known that a small amount of residual halide or water dramatically affects viscosity [19,21]. On the

Table 2. Abbreviations, full names and experimental data used in this study.

| Abbreviation | Full name | $\rho$ (g cm$^{-3}$), T in °C in parentheses | $\eta$(cP), T in °C in parentheses |
|---|---|---|---|
| [C$_1$-mim][Tf$_2$N] | 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.574 (20) | – |
| [C$_2$-mim][Tf$_2$N] | 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.5154 (20) | 25 (25) |
| [C$_3$-mim][Tf$_2$N] | 1-propyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | – | 35 (25) |
| [C$_4$-mim][Tf$_2$N] | 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.4378 (20) | 44 (25) |
| [C$_5$-mim][Tf$_2$N] | 1-pentyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.3926 (20) | 49 (25) |
| [C$_6$-mim][Tf$_2$N] | 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.3926 (20) | 59 (25) |
| [C$_8$-mim][Tf$_2$N] | 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.3189 (20) | – |
| [C$_{10}$-mim][Tf$_2$N] | 1-decyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.2792 (20) | – |
| [C$_{12}$-mim][Tf$_2$N] | 1-dodecyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.246 (20) | – |
| [C$_4$-mim][PF$_6$] | 1-butyl-3-methylimidazolium hexafluorophosphate | 1.368 (25) | 371 (20) |
| [C$_5$-mim][PF$_6$] | 1-pentyl-3-methylimidazolium hexafluorophosphate | 1.326 (25) | – |
| [C$_6$-mim][PF$_6$] | 1-hexyl-3-methylimidazolium hexafluorophosphate | 1.292 (25) | 690 (20) |
| [C$_7$-mim][PF$_6$] | 1-heptyl-3-methylimidazolium hexafluorophosphate | 1.262 (25) | – |
| [C$_8$-mim][PF$_6$] | 1-octyl-3-methylimidazolium hexafluorophosphate | 1.273 (25) | 866 (20) |
| [C$_9$-mim][PF$_6$] | 1-nonyl-3-methylimidazolium hexafluorophosphate | 1.212 (25) | – |
| [C$_{10}$-mim][PF$_6$] | 1-decyl-3-methylimidazolium hexafluorophosphate | – | 1550 (20) |
| [C$_2$-mim][OTf] | 1-ethyl-3-methylimidazolium trifluoromethanesulfonate | 1.39 (22) | – |
| [C$_4$-mim][OTf] | 1-butyl-3-methylimidazolium trifluoromethanesulfonate | 1.3 (22) | – |
| [C$_8$-mim][OTf] | 1-octyl-3-methylimidazolium trifluoromethanesulfonate | 1.12 (22) | – |
| [C$_2$-mim][BF$_4$] | 1-ethyl-3-methylimidazolium tetrafluoroborate | 1.248 (20) | 66.5 (20) |
| [C$_4$-mim][BF$_4$] | 1-butyl-3-methylimidazolium tetrafluoroborate | 1.208 (20) | 136 (20) |
| [C$_6$-mim][BF$_4$] | 1-hexyl-3-methylimidazolium tetrafluoroborate | 1.153 (20) | 233 (20) |
| [C$_8$-mim][BF$_4$] | 1-octyl-3-methylimidazolium tetrafluoroborate | 1.110 (20) | 439 (20) |
| [C$_{10}$-mim][BF$_4$] | 1-decyl-3-methylimidazolium tetrafluoroborate | 1.072 (20) | 928 (20) |
| [C$_1$-Him][lactate] | 1-methylimidazolium lactate | 1.123 (80) | – |
| [C$_4$-Him][lactate] | 1-butylimidazolium lactate | 1.060 (80) | – |
| [C$_6$-Him][lactate] | 1-hexylimidazolium lactate | 1.037 (80) | – |
| [C$_{10}$-Him][lactate] | 1-decylimidazolium lactate | 0.991 (80) | – |
| [C$_2$-mim][N(CN)$_2$] | 1-ethyl-3-methylimidazolium dicyanamide | 1.08 (25) | – |
| [C$_4$-mim][N(CN)$_2$] | 1-butyl-3-methylimidazolium dicyanamide | 1.06 (25) | – |
| [C$_8$-mim][N(CN)$_2$] | 1-octyl-3-methylimidazolium dicyanamide | 1.00 (25) | – |
| [C$_4$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-butanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.397 (20) | – |
| [C$_6$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-hexanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.33 (20) | – |
| [C$_7$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-heptanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.28 (20) | – |
| [C$_8$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-octanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.27 (20) | – |
| [C$_4$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-butanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.3747 (25) | – |
| [C$_6$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-hexanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.3106 (25) | – |
| [C$_{10}$-N$_{111}$][Tf$_2$N] | *N*,*N*,*N*-trimethyl-1-decanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.2263 (25) | – |
| [C$_6$-N$_{222}$][Tf$_2$N] | *N*,*N*,*N*-triethyl-1-hexanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.27 (20) | – |
| [C$_7$-N$_{222}$][Tf$_2$N] | *N*,*N*,*N*-triethyl-1-heptanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.26 (20) | – |
| [C$_8$-N$_{222}$][Tf$_2$N] | *N*,*N*,*N*-triethyl-1-octanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.25 (20) | – |
| [C$_6$-N$_{444}$][Tf$_2$N] | *N*,*N*,*N*-tributyl-1-hexanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.15 (20) | – |
| [C$_7$-N$_{444}$][Tf$_2$N] | *N*,*N*,*N*-tributyl-1-heptanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.14 (20) | – |
| [C$_8$-N$_{444}$][Tf$_2$N] | *N*,*N*,*N*-tributyl-1-octanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.12 (20) | – |
| [C$_4$-N$_{113}$][Tf$_2$N] | *N*-butyl-*N*,*N*-dimethyl-1-propanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.3483 (25) | – |
| [C$_6$-N$_{113}$][Tf$_2$N] | *N*-hexyl-*N*,*N*-dimethyl-1-propanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.2846 (25) | – |
| [C$_{10}$-N$_{113}$][Tf$_2$N] | *N*-decyl-*N*,*N*-dimethyl-1-propanaminium bis[(trifluoromethyl)sulfonyl]imide | 1.2007 (25) | – |
| [NC-C$_2$-mim][BF$_4$] | 1-cyanoethyl-3-methylimidazolium tetrafluoroborate | 2.15 (22) | 66 (22) |
| [NC-C$_3$-mim][BF$_4$] | 1-cyanpropyl-3-methylimidazolium tetrafluoroborate | 1.87 (22) | 230 (22) |
| [NC-C$_4$-mim][BF$_4$] | 1-cyanbutyl-3-methylimidazolium tetrafluoroborate | 1.71 (22) | 553 (22) |
| [Ph-C$_1$-mim][Tf$_2$N] | 1-benzyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.491 (25) | – |
| [Ph-C$_2$-mim][Tf$_2$N] | 1-phenethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.47 (25) | – |
| [Ph-C$_3$-mim][Tf$_2$N] | 1-phenylpropyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | 1.455 (25) | – |

other hand, attention should be paid to the viscosity measurements of ILs containing long-chain alkyl substituents. In some cases they may show non-Newtonian flow behavior [22] caused by network formation due

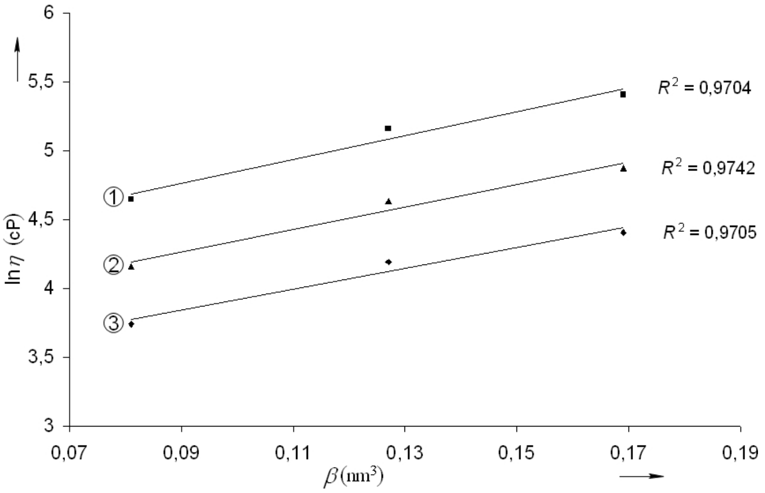

Fig. 4. Correlation between $\beta$ constants and experimental viscosities for [C$_n$-mim][BF$_4$], $n$ = 4, 6, 8, at different temperatures [20b]: (**1**) 298.15 K; (**2**) 308.15 K; (**3**) 318.15 K.

to associative interactions and thus may lead to wrong data. Therefore, a sufficiently large data base on the fundamental physical properties of standardized ILs has to be established not only for process and product design but also for the development of adequate correlations and of predictive methods for the estimation of these properites of unknown ILs.

Having in mind that $\beta^{\mathrm{X}}$ values are temperature- and pressure-independent we went further and implemented RVA for the viscosity of [C$_n$-mim][BF$_4$] at different temperatures. Indeed, good correlations were also observed in this case (Fig. 4), which allows the estimation of this property at different conditions. However, it should be mentioned that the above correlations will only be correct if the RVA is applied on ILs with proven high purity. Moreover, in some cases $\rho^0$ and $\ln\eta^0$ make sense as empirical constants only, since the first members, as well as some other members of the series, may be solids. However, we believe that the range between two liquid members in a homologous series should also hold only liquids, except if some specific, unpredictable interactions lead to a solid product.

## Conclusion

A new method for the prediction of volumetric and transport properties of ILs has been developed. The method is based on simple linear correlations between newly defined substituent parameters $\beta^{\mathrm{X}}$ and fundamental macroscopic physical properties of ILs – density and viscosity. In addition, it has been shown that the method can be applied successfully for property estimation at different temparatures and pressures. A correlation of this type is clearly meaningful and suggests that same changes in the structure of different ILs produce proportional changes on given structure-dependent properties. The reported results demonstrate the influence of $n$-alkyl substituents on the property changes and also show the possibility for fine-tuning density and viscosity by slight variations in the structure of a given anion-cation combination. The residual volume approach proposed by us is empirical in nature, and thus it is of great importance that it is further developed and validated.

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