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Temperature-dependent structure-property modeling of viscosity for ionic liquids

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Abstract

In this paper we present the methodology for assessing the ionic liquids' viscosity at six temperature points (25, 35, 45, 50, 60 and 70 [^{0}C]), which utilizes only the *in silico* approach. The main idea of such assessment is based on the "correction equation" describing the correlation between experimentally measured viscosity and theoretically derived density (calculated with use of molecular mechanics), given at 6 different temperature points. The equation allows for recalculating the viscosity of ILs at 25^{0}C to determine the viscosity of ILs at other, higher temperature. Since the equation needs the basic viscosity value (at 25^{0}C) we additionally developed QSPR model that allows predicting it. According to our model, the viscosity of ILs is dependent to the size and branching of the cation and size, shape, symmetry and the vertical electron binding energy of IL's anion. With those novel tools, it is possible to predict the viscosity of new ionic liquids at different temperatures without the need of experimental measurements.

Keywords: ionic liquid, viscosity, temperature, QSPR, experimental

1. Introduction

Chemistry of Ionic Liquids (ILs) is nowadays a very important field of research and its impact on today's science and technology is becoming more significant. Many technologies and processes are improved to use ionic liquids as an alternative to the previously employed materials and solvents. This owes to the fact, that ILs are considered to be "greener" chemicals, with less negative impact on the environment than the classical solvents.[1,2] They are also "adjustable", which means that their properties can be tuned to the desired purpose.[3,4] Since the popularity of IL is rising, there is an increasing need for new information concerning their properties and behavior. In our work, we combined the experimental and computational approach, in order to deliver new methodology of acquiring data concerning IL's viscosity (as a property of high importance – especially in the field of electrochemistry [5]) and its change under the varying temperature. Moreover, considering that the enormous amount of possibilities in the field of ionic liquids synthesis makes the experimental approach an insufficient source of information, we designed our methodology to be completely computational. This way every (even just theoretically designed) ionic liquid can be a subject of viscosity analysis.

We attempted to develop a mathematical formula, which we called a "correction equation". The purpose of this equation was to calculate the viscosity of ILs in the selected temperature, based on the value of viscosity at initial temperature point – in our case: 25^0C. Quite similar approach was already successfully applied in the previous contributions.[6–12] However, the equations used to predict the viscosity in altering temperature were previously developed to describe other kinds of fluids, glasses, polymers, etc., rather than ionic liquids. Among the equations used in the other works

we can find for example: Ahrrenius,[6,7,11,12] Vogel-Fulcher-Tammann,[6,8,10–12] Litovitz[8,12] or Orric Erbar equation.[9] Those equations are describing viscosity in dependency of the temperature with a good accuracy, confirming their applicability in the field of ILs. However, all of the known equations work on the basis of experimentally determined coefficients, which are only dedicated to one specific ionic liquid. Therefore, predicting the viscosity of IL in the varying temperature has to be preceded by the experiment, which was on the contrary to our intention.

Since the above-mentioned correction equation operates on the known value of viscosity, a second computational tool was needed, in order to derive it. We decided to use modeling based on quantitative structure-properties relationship (QSPR).[12,13] The QSPR paradigm is based on defining the relationship that tries to numerically explain the observed values of a given physicochemical property (so-called the endpoint) in terms of several independent variables encoded by so-called molecular descriptors. In the other words, QSPR model interpolates the lacking data from the calculated molecular parameters and a suitable mathematical model established for a group of similar chemicals.[14,15] We developed QSPR model on the basis of data delivered in our experiment. However, the correction equation can be used with any other source of information concerning the value of viscosity at 25^0C, including other QSPR models.

With the proper experimental measurements, molecular dynamics and chemometric analysis, we attempted to develop a complex theoretical methodology of determining the ILs' viscosity in various temperature points. With this combined approach, we made such predictions possible for new ionic liquids with known structure, for which the experimental measurements are not needed. Thus, our work was aimed at: (i) developing a universal algorithm for transferring the viscosity of ILs at

25^0C for another temperature value as well as (ii) creating a mathematical model (based on the experimental data) that allows predicting the initial viscosity value.

2. Methodology

2.1 Experimental measurements

2.1.1. Viscosity measurement

Ionic liquids with a total concentration of impurities of less than 2% were purchased from IoLiTec (Ionic Liquids Technologies, Germany) and used as obtained.

Measurement of the viscosity has been performed on a BROOKFIELD LVDV-III ULTRA programmable Viscometer/Rheometer (Brookfield Engineering Laboratories Inc., Middleboro, Massachusetts,USA). The liquid (volume 6.7ml) has been placed in a stainless steel cylinder (SC4-13-RPY) in which the measurement spindle (SC4-18) has been immersed. The cylinder has been heated by a BROOKFIELD TC-series Circulating Baths (temperature accuracy +/- 1°C). The B.E.V.I.S (Brookfield Engineering Viscometers Instruction Set) programing method, included in the Rheocalc® software, has been used to automatically carry out the sequence of measurements. Each liquid has been tested at different temperatures (27 to 70°C, step 9°C) and different spindle rotation speeds (1 to 200rpm, step 10rpm). After that, the measurement was repeated a second time with the decreasing speed from 200rpm to 1rpm. At each set point a dwell time of 10sec was hold before taking the measurement value.

To determine the viscosity, the simple graphical method based on the analysis of the non-newtonian flow was used. For each ionic liquid at each concentration and temperature, the plot of viscosity versus spindle speed was analyzed (Figure 1).

The viscosity's variation lower than 1% means that viscosity is stabilized regardless of the spindle speed. These stabilized values were chosen as final values of viscosity.

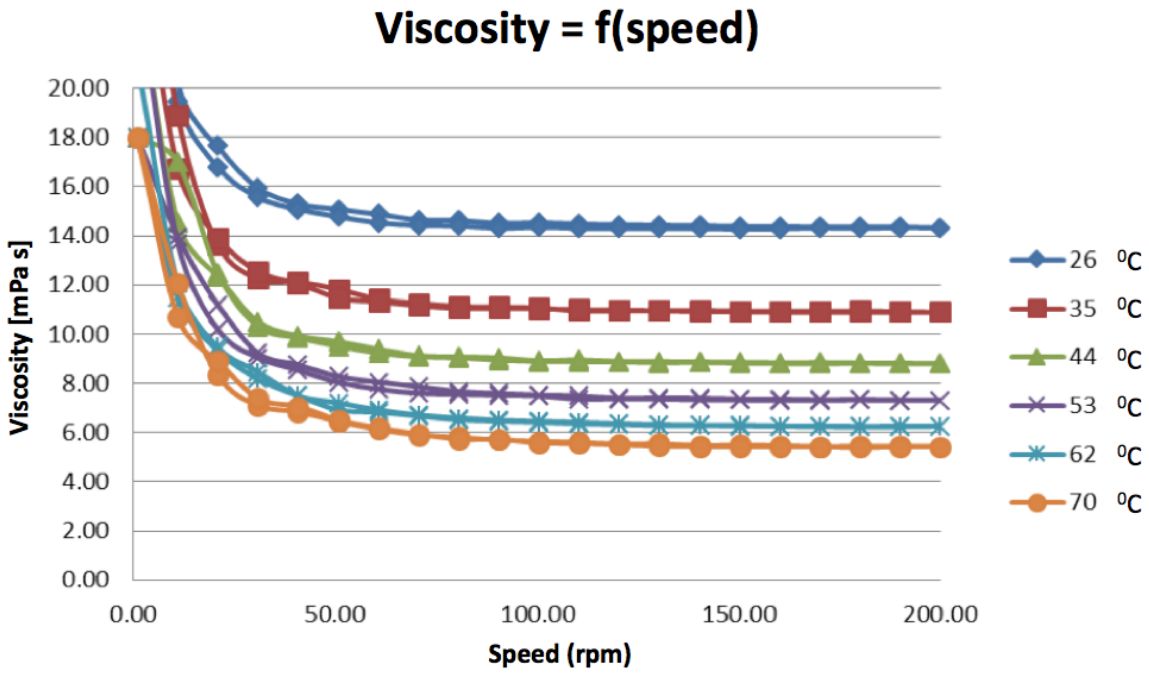


Figure 1. An example of viscosity measurement based on non-newtonian flow analysis graphical method for IL0003 (1-Ethyl-3-methylimidazolinium dicyanamide).

2.1.2. QSPR modeling

In order to obtain a set of molecular descriptors reflecting the structural variability in the studied compounds we applied a two-step protocol that included: (i) optimization of the molecular geometry of the studied compounds with quantum-mechanical cacluations and (ii) calculation of the descriptors based on the optimized molecular structures.

The optimized structures (of the cations and anions together) were obtained by performing calculations at the level of the Density Functional Theory (DFT) and *ab initio*

perturbational methods that include electron correlation. For DFT, the Becke's Three Parameter Hybrid Method with the LYP (Lee-Yang-Parr) correlation functional (B3LYP)[16,17] was employed. *Ab initio* calculations were performed using the second-order Møller-Plesset (MP2) perturbational method. In both types of calculations we applied the 6-311++G(d,p)[18,19] Pople's style, one-electron basis set, whose usefulness has been proven in the previous studies of structurally similar ionic liquids.[20] All calculations were performed with the *Gaussian09 (Rev.A.02)* software package.[21] In order to avoid erroneous results from the default direct SCF calculations, the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u (the keyword SCF=NoVarAcc). The geometry optimizations were performed using tight convergence thresholds (i.e., 10^{-5} hartree/bohr for the root mean square first derivative).

The optimized structures were used for calculation of the molecular descriptors for QSPR modeling. A matrix of 2920 descriptors was calculated using DRAGON software.[22] The matrix included 1460 and 1460 descriptors corresponding to cations and anions, respectively.

The compounds, for which the viscosity data have been measured, were splitted into two sets: training set (used for developing the QSPR model) and validation set (employed to examine the model's ability to predict the viscosity based on compounds not previously involved in training). By using 'three-to-one' method of splitting[23] every third compound, sorted along with the increasing value of viscosity, has been included in the validation set, whereas the remaining compounds formed the training set. In effect, we obtained training set containing 17 ILs (74% of all compounds) and validation set containing 6 ILs (26% of all compounds). For more details please refer to Table S1 in Supporting Information.

Finally, QSPR model for disclosing relationship between the viscosity originating from experiments and structural descriptors was developed. Molecular descriptors to be utilized in QSPR model were selected by applying Holland's genetic algorithm (GA)[24] implemented in the QSARINS software. [25,26] The model was developed following the recommendations of the Organization for Economic Cooperation and Development (OECD).[27,28] We have applied the multiple linear regression technique (MLR) in which the response **y** (viscosity) is expressed as a linear combination of independent variables $\mathbf{x_i}$ (molecular features) (eq. 1):

$$\mathbf{y} = b_0 + b_1\mathbf{x}_1 + b_2\mathbf{x}_2 + \ldots + b_n\mathbf{x}_n \quad (1)$$

The coefficients vector b was calculated, assuming minimization of the squared residuals, according to the formula (eq. 2):

$$\mathbf{b}=(\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{y} \quad (2)$$

where: **X** is the descriptor matrix containing an additional (first) column with ones, which is necessary to calculate the intercept (b_0).

The model's goodness-of-fit, robustness and predictive power were finally verified by calculating the commonly used parameters listed in Table 1.[27–31] Additionally, model's predictive ability was also tested with the use of literature data for ten ionic liquids with similar parameters calculated. The additional validation set can be found in Table S2 in Supporting Information.

Table 1. Measures of goodness-of-fit, robustness and predictive ability of a QSPR model according to OECD recommendations[27,28]

Paramether	Coefficient

Measure of goodness-of-fit	$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i^{obs} - y_i^{pred})^2}{\sum_{i=1}^{n}(y_i^{obs} - \tilde{y}^{obs})^2}$	$RMSEC = \sqrt{\frac{\sum_{i=1}^{n}(y_i^{obs} - y_i^{pred})^2}{n}}$
Measure of stability of the model	$Q^2_{CV} = 1 - \frac{\sum_{i=1}^{n}(y_i^{obs} - y_i^{predcv})^2}{\sum_{j=1}^{n}(y_j^{obs} - \tilde{y}^{obs})^2}$	$RMSECV = \sqrt{\frac{\sum_{i=1}^{n}(y_i^{obs} - y_i^{predcv})^2}{n}}$
Measure of external predictivity	$Q^2_{EXT} = 1 - \frac{\sum_{j=1}^{k}(y_j^{obs} - y_j^{pred})^2}{\sum_{j=1}^{k}(y_j^{obs} - \hat{y}^{pred})^2}$	$RMSEP = \sqrt{\frac{\sum_{i=1}^{k}(y_j^{obs} - y_j^{pred})^2}{k}}$
	$CCC = \frac{2\sum_{j=1}^{k}(y_j^{obs} - \hat{y}^{obs})(y_j^{pred} - \hat{y}^{pred})}{\sum_{j=1}^{k}(y_j^{obs} - \hat{y}^{obs})^2 + \sum_{j=1}^{k}(y_j^{pred} - \hat{y}^{pred})^2 + k\,(\hat{y}^{obs} - \hat{y}^{pred})^2}$	
	$r_m^2 = r^2\left(1 - \sqrt{r^2 - r_0^2}\right)$ $\quad \overline{r_m^2} = \frac{r_m^2 + r'^2_m}{2}$ $\quad \Delta r_m^2 = \lvert r_m^2 - r'^2_m \rvert$	

where: y_j^{obs} – experimental (observed) value of the property for the i^{th} compound from the training set; y_i^{pred} – predicted value for i^{th} compound from the training set; $\tilde{y}^{obs}$ – the mean experimental value of the property in the training set; n – the number of compounds in the training set; y_i^{predcv} – cross-validated predicted value or i^{th} compound; y_j^{obs} – experimental (observed) value of the property for the j^{th} compound from the validation set; y_j^{pred} – predicted value or j^{th} compound from the validation set; $\hat{y}^{obs}$ – the mean experimental value of the property in the validation set; k – the number of compounds in the validation set; r^2 – determination coefficient of the regression function calculated using the experimental and the predicted data of the prediction set; r_0^2 – determination coefficient of the regression function calculated using the experimental and the predicted data of the prediction set forcing the origin of the axis; r_m^2/r'^2_m – coefficient calculated using the experimental data on the ordinate/abscissa axis; $\check{r}_m^2$ – mean value of r_m^2; Δr_m^2 – difference between r_m^2 and r'^2_m;

The applicability domain (AD) of the QSPR model is a theoretical space defining the chemicals for which can the model be reliably applied. It was reviewed by determination of the interpolation region described by the training data set and further verified graphically by Williams plot. [32]

All steps of model development and validation were performed in QSARINS software.[25,26]

2.1.3. Density calculation – molecular mechanics

Molecular dynamics simulations have been applied to obtain theoretical density for all 23 ionic liquid studied at seven different temperatures: 20, 25, 35, 45, 50, 60 and 70 [^{0}C]. The general AMBER force field (GAFF) with AM1-BCC charges scaled by 0.8 was chosen for parameterization of all ions except BF_4^- (AM1 parameters are not available for boron atoms). Wu et al.[33] parameterization with charges scaled by 0.8 was used for of BF_4^-. The use of scaled charges models charge transfer observed for *ab initio* calculations of ionic pairs was used as a less computationally expensive alternative to polarizable force fields.[34] Density is less sensitive to the parameterization than dynamic properties of ionic liquids[35]. GAFF can reproduce a variety of thermodynamic and transport properties with similar accuracy to that of ionic liquid specific force fields.[36] Cubic boxes of 64 nm^3 in size (or larger boxes of 216 nm^3 for two ionic liquids with cations with long alkyl chains, methyltrioctylammonium bis(trifluoromethylsulfonyl)imid and trihexyltetradecylphosphonium chlorid) and containing 100 ion pairs were generated using Packmol.[37] Ionic liquid boxes were simulated with periodic boundary conditions by using LAMMPS package.[38] To reduce the number of the non-bonding interactions, 10 Å cut-off of was used The electrostatic interactions were carried out with the particle-particle particle-mesh method. A Nosé-Hoover thermostat and barostat were used to control temperature and pressure, with time constant of 0.1 and 1.0 ps, respectively. Time step of 1 fs was used for all production simulations except simulations of 1-ethyl-3-methylimidazolium diethylphosphat and trihexyltetradecylphosphonium chlorid which employed 0.5 fs time step. At each temperature, the system was simulated for 1 ns, and trajectories of last 0.2 ns were used to calculate average density.

3. Results and discussion

3.1 Correction equation for viscosity in different temperatures

Accordingly to the first objective highlighted in the Introduction section, we attempted to develop a universal algorithm for transferring the viscosity of ILs at 25^0C for another temperature value. There are many contributions, where the temperature-dependence is described quantitatively.[6–11] However, all the equations used for such description are based on the coefficients that has to be determined empirically from experimental data and are different for each ionic liquid. The accuracy of such description is very high. Nevertheless, our intention was to omit the experiment in the process of ILs' viscosity determination entirely. Therefore, we chose a different path of investigation and tried to develop an algorithm, useful for the same purpose but based only on the information that can be delivered by the means of computational chemistry.

There is a direct relationship between viscosity and density. We used this fact, because the density of ionic liquids in different temperatures can be precisely determined with use of the molecular mechanics approach. In the further stage of our work, the viscosity would be simply calculated from the density.

Therefore, we calculated densities of the entire set of investigated ILs (Table S3 in the electronic Supporting Information) with the molecular mechanics method. The detailed description of density calculations is presented in the Methodology Section.

In the next step, for 23 ILs we correlated the density calculated in six temperatures with the viscosity measured at the same temperatures (Table S3 and Table S4 in the electronic Supporting Information). The values of the r-Pearson's correlation coefficient for most of them were higher than 0.96 (Table S3 in the electronic Supporting Information). Based on that we proposed a universal equation to calculate the viscosity of ILs at different temperatures (eq. 4).

$$\eta_{T_X} = 10^{[log10(\eta_{T_{25}}) - A*(T_X - 25)*d_{T_X}]} \quad (4)$$

where:

η_{TX} – viscosity at temperature X^{0}C, η_{T25} – viscosity at 25^{0}C, d_{TX} – density calculated for temperature X^{0}C, A – coefficient characteristic for each IL, T_X – temperature X^{0}C

However, the coefficient A in eq. 4 has to be still determined empirically for each IL. Although the experimental determination of ILs' characteristic coefficients has been reduced to just one parameter (in contrast to many experimental parameters required in case of commonly used equations for temperature-dependent viscosity calculations), it did not solve the problem of omitting the experimental work yet.

Our further analysis showed, that there is a strong correlation between vector of experimentally determined A coefficients and the vector expressed as a ratio of logarithm of viscosity (at 25^{0}C) and density (at 25^{0}C) for each IL. A simple data transformation of the ratio vector (division by 110) allowed us to reproduce the experimentally determined A vector very well (Figure 2). We modified the equation 4 accordingly to this fact.

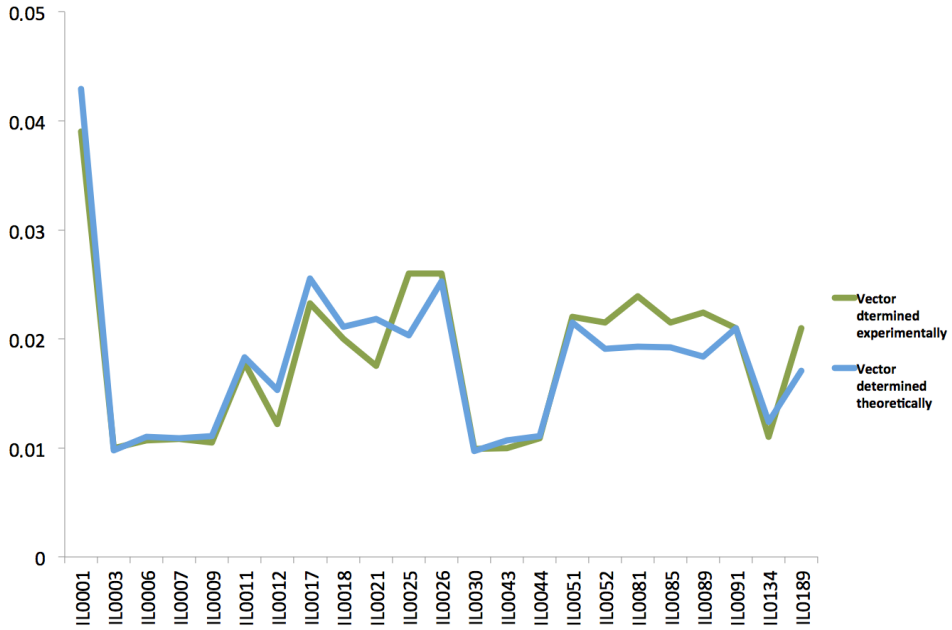


Figure 2. Plot representing the similarities between two vectors used as substituents for the correction equation.

The finally derived correction equation is as follows (eq. 5):

$$\eta_{T_X} = 10^{\left[log10\left(\eta_{T_{25}}\right) - \frac{log10\left(\eta_{T_{25}}\right)}{d_{T_{25}} * 110} * (T_X - 25) * d_{T_X}\right]} \quad (5)$$

where:

η_{TX} – viscosity at temperature X^{0}C, η_{T25} – viscosity at 25^{0}C, d_{TX} – density calculated for temperature X^{0}C, d_{T25} – density calculated for 25^{0}C, T_X – temperature X^{0}C

In order to validate the equation (eq. 5), we performed a comparison between the viscosities calculated at all six temperatures, with the viscosities obtained experimentally. The average correlation coefficient (r^2) between the experimental and calculated viscosity performed for 23 ILs (Figure 3) was 0.9678, which confirms accuracy of the predictions. Moreover, the average value of the Root Mean Square Error

of prediction (RMSE) expressed as the percent of value of viscosity at 25^0C was at 4.6% (Table 2).

Table 2. Parameters describing accuracy of viscosity predictions for particular ILs

IL name	IL symbol	r^2	RMSE $[\%\eta_{T25}]$
trihexyltetradecylphosphonium chlorid	IL0001	0.916	8%
1-Ethyl-3-methylimidazolinium dicyanamide	IL0003	0.988	2%
1-Ethyl-3-methylimidazolium tetrafluoroborat	IL0006	0.985	3%
1-Ethyl-3-methylimidazolium thiocyanamide	IL0007	0.993	2%
1-Ethyl-3-methylimidazolium triflat	IL0009	0.985	3%
1-Butyl-3-methylimidazolium hexafluorophosphat	IL0011	0.997	2%
1-Butyl-3-methylimidazolium tetrafluoroborate	IL0012	0.915	8%
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imid	IL0017	0.985	4%
1-Hexyl-3-methylimidazolium hexafluorophosphat	IL0018	0.995	2%
1-Methyl-3-octylimidazolium tetrafluoroborat	IL0021	0.822	16%
1-Methyl-3-propylimidazolium iodid	IL0025	0.962	6%
1-Hexyl-3-methylimidazolium iodid	IL0026	0.997	2%
Triethylsulfonium bis(trifluoromethylsulfonyl)imid	IL0030	0.987	3%
Ethylammonium nitrat	IL0043	0.980	3%
1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imid	IL0044	0.990	3%
1-Butyl-3-methylimidazolium iodid	IL0051	0.994	2%
1-Ethyl-3-methylimidazolium diethylphosphat	IL0052	0.982	4%
1-Butyl-3-methylpyridinium tetrafluoroborat	IL0081	0.940	7%
1-Butyl-4-methylpyridinium tetrafluoroborat	IL0085	0.983	4%
1-Butylpyridinium tetrafluoroborat	IL0089	0.941	7%
1-Ethyl-3-methylimidazolium hydrogensulfat	IL0091	0.990	3%
1.2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imid	IL0134	0.976	4%
1-Ethyl-3-methylimidazolium acetat	IL0189	0.956	6%
mean		**0.968**	**4.6%**

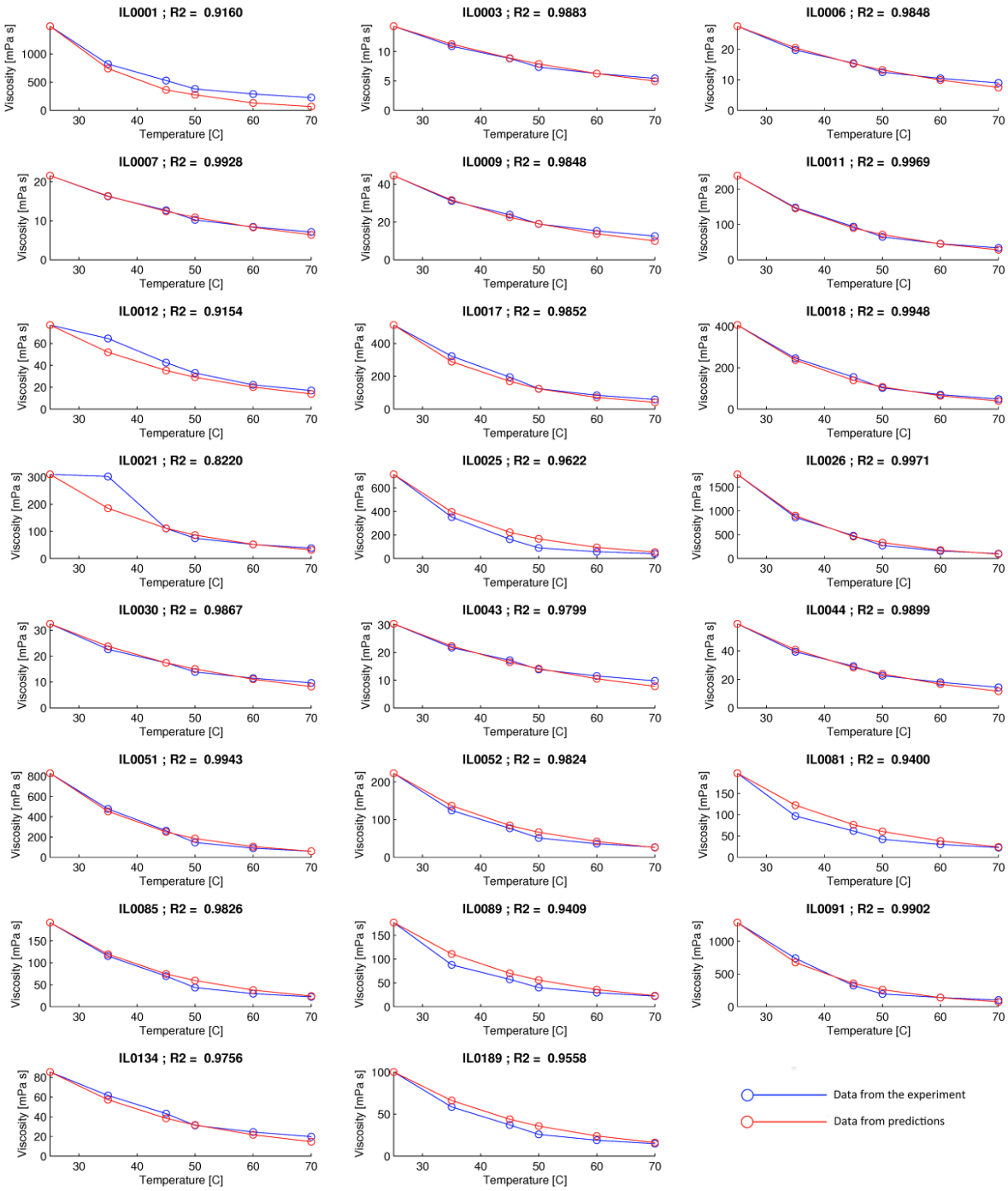


Figure 3. Plots of experimentally measured and predicted viscosity at six different temperature points for 23 ILs.

Although the predictive ability of our equation was generally satisfying, we have also identified one outlying case: 1-Methyl-3-octylimidazolium tetrafluoroborate (marked as IL0021 on Figure 3). Data for IL0021 did not follow the overall trend,

indicating significantly lower value of r^2 = 0.8220 and higher RMSE = 16%. We may suspect, that it was caused by experimental inaccuracy. While analyzing the plot of viscosity against the temperature for 1-Methyl-3-octylimidazolium tetrafluoroborate, one can see that for the first and second measuring points (25^0C and 35^0C), the viscosity was nearly constant. On the contrary, all other tested ILs indicated the decrease of viscosity between those two temperatures, and for most of them, that was the largest change of the viscosity reported. It is also worth to note, that all the further predictions for viscosity values at higher temperatures for 1-Methyl-3-octylimidazolium tetrafluoroborate have maintained the decreasing trend, determining the viscosity accurately. Another argument supporting this conclusion is that the previous reports concerning very detailed viscosity measurements for this IL,[39] suggested that the trend of its change should be similar to the trend occurring in other ILs. This is the case, where computational methods might be used for identifying uncertain experimental results and making suggestion to repeat the experiments.

Finally, we compared our method with other methods of temperature-dependent viscosity predictions. As we mentioned before, numerous equations can be fitted to the experimental data (by calculation of IL specific coefficients) and therefore, can be used as a model to predict the viscosity in other temperature. The example of such approach can be found in the Seoane et al[11] work. They demonstrated the performance of Ahrrenius, Vogel-Fulcher-Tammann, modified Vogel-Fulcher-Tammann, fluidity and Litovitz equations for estimating the viscosity in different temperatures. Presented approach allows for comparison of the fitness (expressed as R^2) and accuracy (expressed as Standard Relative Deviation) of applied calculation methods since they were all fitted to the same viscosity dataset. In general, the fitting and accuracy of our approach is slightly lower than those obtained by Seoane et al. for other methods. The

lowest R^2 in Seoane's work is 0.9987 and the highest SRD is 4.2758. This fact may be a consequence of employing theoretical data in our model, which are usually less accurate than the experimental ones. Nonetheless, the fitting and predictive parameters of our method are still high and comparable with methods presented by Seoane et al.

There are also some contributions based on a slightly different approach called Rough Hard Spheres (RHS). The method first proposed by Chandler can also be a useful way to predict IL's viscosity in varying temperature. Recent findings proved method's high accuracy in such predictions. In works of Gaciño et al.[40] and Hossain et al.[41], the errors of the method, expressed as Average Absolute Deviations (AAD), are on the level of 2.31% (Gaciño et al.) and 1.15% (Hossain et al.), when based on the set of 19 and 48 ILs respectively. Errors of our approach are expressed as RMSE values and therefore the direct comparison between those two methods is impossible.

Nevertheless, our goal was to develop the mathematical approach to predict the viscosity of IL's on the basis of their molecular structures only. In fact, no further experimental parameterization of the equation is required for our approach. Therefore, the utility of the viscosity prediction method presented in this work is very high, even if the fitness and accuracy of the predictions are not as high as in previously presented methods.

3.2. QSPR model for viscosity at 25^0C

In order to perform calculation with use of the developed correction equation, the initial value of viscosity of ionic liquid at 25^0C is necessary. It is possible to obtain such vale basing only on the structure of the ionic liquid with the use of proper QSPR model. Since we derived all the data needed for QSPR modeling during the experimental

work, we decided to develop such model, fulfilling the second objective pointed out in the Introduction section. We performed a series of calculations using genetic algorithm in order to select appropriate molecular descriptors. In each iteration of its performance, GA is creating a set of QSPR models and performs a proper validation of the used descriptors, in order to type the most suitable descriptors to be employed in the final model. After several attempts with various GA presets, we noticed that Weighted Holistic Invariant Molecular (WHIM) descriptors were the most frequently appearing in the selected set. Therefore we narrowed our further attempts to WHIM descriptors only. This allowed determining the group of three descriptors, which finally we included in the model.

In the next step we used MLR technique, in order to create QSPR model for viscosity prediction (eq. 3):

$$\eta_{T25} = 2.175(\pm 0.071) + 0.335(\pm 0.078)\mathbf{Dm^C} - 0.358(\pm 0.079)\mathbf{E1m^A} - 0.259(\pm 0.074)\mathbf{G3i^A} \qquad (3)$$

N=23, t=17, v=6, F=20.40, R^2=0.826, $RMSE_C$=0.254, Q^2_{CV}=0.650, $RMSE_{CV}$=0.361, Q^2_{Ext}=0.830, CCC=0.903, $\check{r}_m^2$=0.648, Δr^2_m=0.160, $RMSE_{Ext}$=0.244, *p*=1.54e-13, $p\mathrm{Dm^C}$=8.79e-4, $p\mathrm{E1m^A}$=5.29e-4, $p\mathrm{G3i^A}$=4.10e-3,

where:

η_{T25} – viscosity at 25^{0}C, $\mathrm{Dm^C}$ – total accessibility index weighted by mass calculated for cation, $\mathrm{E1m^A}$ – 1st component accessibility directional WHIM index / weighted by mass calculated for anion, $\mathrm{G3i^A}$ – 3rd component symmetry directional WHIM index / weighted by ionization potential calculated for anion, N – number of compounds, t – number of compounds in the training set, v – number of compounds in the validation set, F – distribution parameter, *p* – statistical significance of the intercept, $p\mathrm{Dm^C}$ – statistical significance of $\mathrm{Dm^C}$ descriptor, $p\mathrm{E1m^A}$ – statistical significance of $\mathrm{E1m^A}$ descriptor, $p\mathrm{G3i^A}$ – statistical significance of $\mathrm{G3i^A}$ descriptor,

High value of F parameter (F=20.40) as well as the satisfactory results of the Y-scrambling procedure (Figure 4C) proves the model's statistical significance. The model was characterized by high goodness-of-fit. Model's robustness was satisfactory. Lower value of Q^2_{CV} was a result of strong diversification of ionic liquids in the training set. We also proved model's good predictive capabilities by performing the external validation. Both, fitting quality and predictive abilities were additionally confirmed by analyzing the plot of ILs' experimental vs. predicted viscosity values (Figure 4A).

Since the validation set used for the verification of model's predictive abilities was relatively small, we decided to perform an additional, external validation using the literature data. We collected the values of viscosity for the set of ten ionic liquids that were structurally similar to the compounds tested experimentally in this work. The second validation also proved model's good predictive abilities ($2^{nd}Q^2_{Ext}$=0.795, 2^{nd}CCC=0.898, $2^{nd}\check{r}_m^2$=0.742, $2^{nd}\Delta r^2_m$=0.037, $2^{nd}RMSE_{Ext}$=0.232).

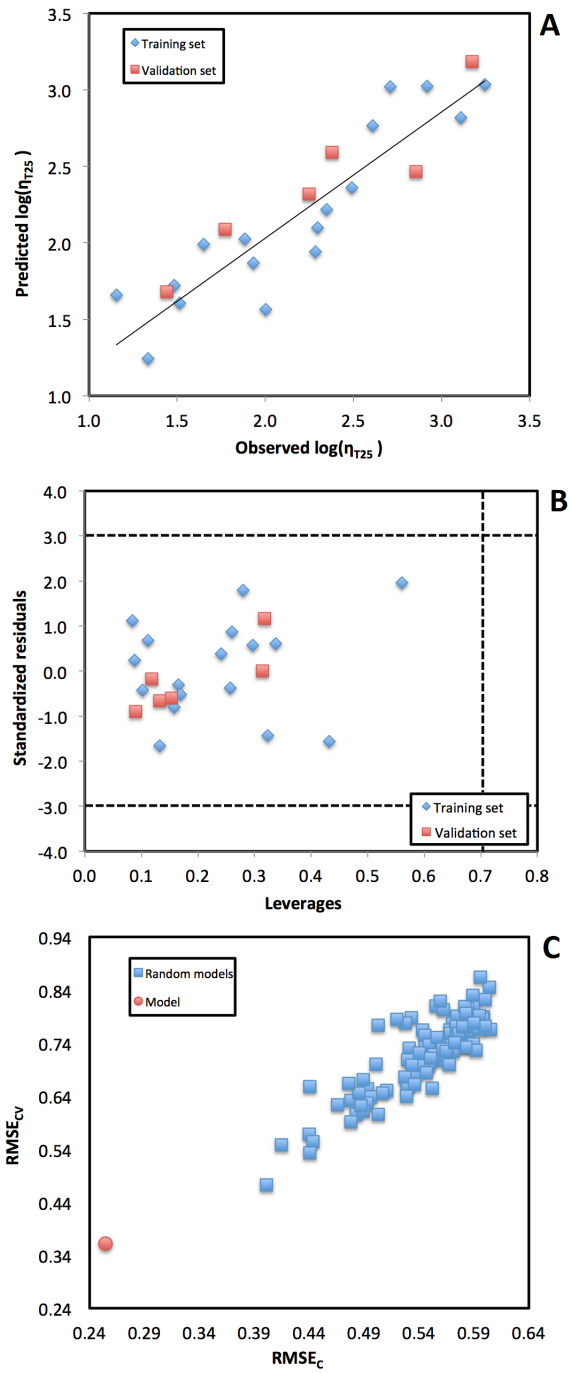


Figure 4. A) Plot representing ILs' predicted vs. experimentally measured viscosity values, B) Williams plot, C) Y-scrumbling plot.

Model's applicability domain was veryfied by analysis of Williams plot (Figure 4B). All tested ILs were located within the area delimited by +/- three standard deviations of normalized residual values, and restricted by critical leverage value

(h*=0.706). It proved that no predictions were obtained as a result of model extrapolation and that the set of ILs chosen for modeling can be considered as structurally similar.

The developed QSPR model is a linear combination of three WHIM descriptors. The WHIM molecular descriptors are calculated by using the matrix of score values (projection of atoms along the principal axes) determined by Principal Component Analysis (PCA) on cartesian coordinates of atoms in the compound's molecular model.[42] WHIM descriptors deliver information about the molecule's 3D structure, regarding molecular size, shape, symmetry and atom distribution. WHIM descriptors could be weighted according to the six different weighting schemes (by molecular mass, van der Waals volume, Mulliken electronegativity, polarizability, elecrotopological indices by Kier and Hall, and unweight values). WHIM descriptors can also be divided into two groups: (1) directional indices (calculated on the projections of the individual atom along each individual principal axis) and (2) non-directional (global) indices (related only to the global view of the molecule).[42]

Mechanistic interpretation of the obtained model using only three WHIM descriptors is intuitive. The first descriptor is Dm^C – total accessibility index weighted by mass, calculated for the cation. It is a non-directional WHIM index that describes the total distribution of density of atoms in a molecule. Density of atoms correlates with accessibility, symmetry and branching of the particular IL's cation. In the case of a small and symmetric cation like triethylsulfonium the value of Dm^C is 0.138. Dm^C value increases with an increasing size and branching of the cation and with simultaneously decreasing symmetry. For example (Figure 5), the value of Dm^C changes from 0.146 for 1-ethyl-3-methylimidazolium, though 0.215 for 1-hexyl-3-methylimidazolium, up to 0.230 for trihexyltetradecylphosphonium. The values of Dm^C are positively correlated

with the viscosity values (i.e., smaller cations that exhibit lower values of Dm^C are characterized by lower viscosity as well). Our finding stays with good accordance to the previous studies, [43–46] proving that long alkyl side chains, resulting in high steric hindrance, make ILs more viscous. Additionally, there is a report[47] suggesting that viscosity strongly correlates with the number of hydrogen bonds. Cations with long side chains have larger accessibility space; therefore hydrogen bonds determining higher viscosity of ILs may occur more often.

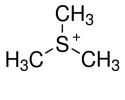
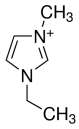
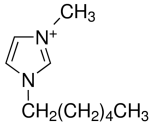
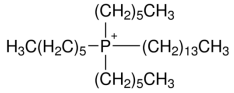
Structure of the IL's cation				
Dm^C	0.138	0.146	0.215	0.230

Figure 5. Values of Dm^C for different structure of the ILs' cations

The last two descriptors employed in the QSPR model are directional WHIM descriptors calculated for anion. $E1m^A$ is the first component accessibility directional WHIM index weighted by mass and $G3i^A$ is the third component symmetry directional WHIM index weighted by ionization potential. $E1m^A$ is related to the size, shape and symmetry of the anion and it is negatively correlated with the viscosity. Size, shape and symmetry are closely related to the accessibility space available for intermolecular interactions. Indeed, more spherical anions (e.g. $PF6^-$, $BF4^-$ or halides) have low values of $E1m^A$ descriptor, which results in the high values of viscosity (Figure 6). This conclusion is supported by the earlier contributions demonstrating that anionic size and shape have considerable impact on the viscosity.[48,49] Generally, the viscosity increases with

increasing molecular weight of the anion. However, spherical anions (like BF_4^-) make IL more viscose than such anions as $N(CN)_2^-$ or SCN^- where intermolecular frictions are generated by the rod-shape of those anions.[49]

According to our findings the vertical electron binding energy of the anion (represented here by $G3i^A$ descriptor) has a significant influence on the viscosity. When the charge is located symmetrically in the molecule (e.g for I^- and PF_4^-), the values of $G3i^A$ descriptor are maximal (Figure 6). Interestingly, we found that the structure of the cation is also indirectly affecting the value of $G3i^A$ descriptor. Overall distribution of the ionization charge can be different for the same anion, as it depends on its symmetry. In our work, chemical structures (molecular models) of the ions constituting the studied ILs were optimized together (each optimization was performed on the system of cation-anion pair), therefore the final symmetry of the anion might be affected by the presence of different cations. For example (Table 3), there are two values of $G3i^A$ for the same anion bis(trifluoromethylsulfonyl)imid, dependently on the cation present in the liquid.

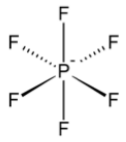
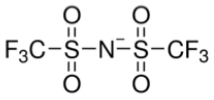
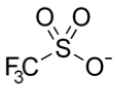
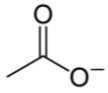
Structure of the IL's anion	I^-				
$E1m^A$	0.000	0.240	0.611	0.913	1.114
$G3i^A$	1.000	1.000	0.427/1.000	0.364	0.574

Figure 6. Values of Dm^C for different structure of the ILs' anions

Table 3. Experimental values of viscosity and calculated descriptors for particular ILs, used in the QSPR model

IL's symbol	IUPAC name	$\log\eta_{T25}$	Dm[C]	E1m[A]	G3i[A]
IL0030	Triethylsulfonium bis(trifluoromethylsulfonyl)imid	1,513	0,138	0,611	1,000
IL0009	1-Ethyl-3-methylimidazolium triflat	1,650	0,146	0,913	0,364
IL0189	1-Ethyl-3-methylimidazolium acetat	2,001	0,146	1,114	0,574
IL0018	1-Hexyl-3-methylimidazolium hexafluorophosphat	2,609	0,214	0,240	1,000
IL0017	Methyltrioctylammonium bis(trifluoromethylsulfonyl)imid	2,710	0,223	0,611	0,427
IL0091	1-Ethyl-3-methylimidazolium hydrogensulfat	3,109	0,146	0,220	0,279
IL0026	1-Hexyl-3-methylimidazolium iodid	3,247	0,215	0,000	1,000

Our model was properly developed and validated and it offers a detailed mechanistic interpretation. It is a good tool to be used as an initial source of information to the correction equation. However, some of the already published models also have good predictive abilities and are developed by the use of even larger and more diversified set of ionic liquids that ours.[13,50–53] Since this is not obligatory to use our model's predictions in correction equation, we recommend use of the other QSPR models as well, considering the IL's fitness to models applicability domain as a decisive factor.

4. Conclusions

We developed a correction equation, allowing recalculating viscosity of ILs at 25^0C to determine the viscosity of ILs' at other, higher temperature points. The range of temperatures covered by this equation is 45^0C (from 25^0C to 70^0C). The correction equation's performance was proven accurate by both R^2 and RMSE coefficients as well as observed vs. predicted viscosity values plot analyzes.

In addition, we developed a QSPR model, describing quantitatively the relationship between ILs' structure and viscosity in 25^0C. The model acquired satisfactory parameters and therefore can be used for predicting ILs' viscosity. We also

pointed out that size and branching of the cation and size, shape, symmetry and the vertical electron binding energy of IL's anion are the features responsible for the viscosity of ILs. Model's predictions can be used as a source of information to the correction equation.

To our knowledge, this complex approach using QSPR and correction equation algorithm is the first one, allowing predicting the viscosity of ILs in various temperatures, based only on ILs' molecular structures. No additional experiments are needed to parameterize any of those tools. The additional advantage of our tools is that they can be used separately, as two different and independent measures.

Additional analyzes, that could improve both QSPR model and correction equation performance, as well as extend the range of their applicability, are planned in future work.

List of symbols

x	vector of variables
X	matrix of variables
X^T	transposed matrix of variables
η_{TX}	viscosity at temperature X^0C
η_{T25}	viscosity measured at 25^0C
d_{TX}	density calculated for temperature X^0C
d_{T25}	density calculated for 25^0C
T_X	temperature X^0C
Dm^C	total accessibility index weighted by mass calculated for cation
$E1m^A$	1st component accessibility directional WHIM index / weighted by mass calculated for anion
$G3i^A$	3rd component symmetry directional WHIM index / weighted by ionization potential calculated for anion
N	number of compounds used to develop a QSPR model
t	number of compounds in the training set
v	number of compounds in the validation set
F	distribution parameter
p	statistical significance of the intercept
pDm^C	statistical significance of Dm^C descriptor
$pE1m^A$	statistical significance of $E1m^A$ descriptor
$pG3i^A$	statistical significance of $G3i^A$ descriptor

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