



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 [°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 °C to determine the viscosity of ILs at other, higher temperature. Since the equation needs the basic viscosity value (at 25 °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.

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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 °C. 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: Arrhenius [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

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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 °C, 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 °C 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 6.7 ml) 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 (27–70 °C, step 9 °C) and different spindle rotation speeds (1–200 rpm, step 10 rpm). After that, the measurement was repeated a second time with the decreasing speed from 200 rpm to 1 rpm. 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 (Fig. 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.

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

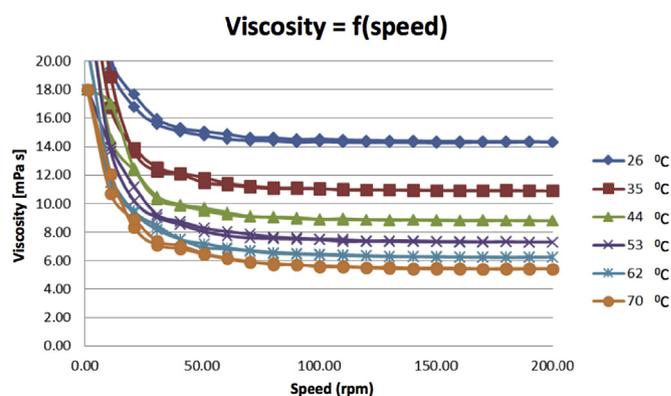


Fig. 1. An example of viscosity measurement based on non-newtonian flow analysis graphical method for IL0003 (1-Ethyl-3-methylimidazolium dicyanamide).

geometry of the studied compounds with quantum-mechanical calculations 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

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