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Regular Article

Which structural features stand behind micelization of ionic liquids? Quantitative Structure-Property Relationship studies

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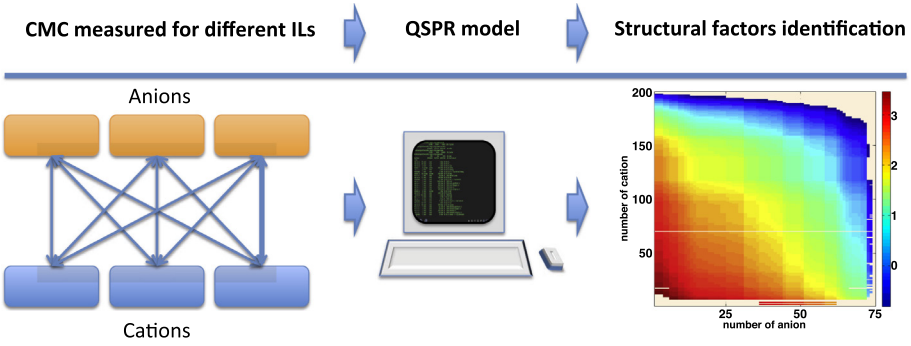
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Different ions constituting ionic liquids (ILs) change their properties, including the Critical Micelization Concentration (CMC). It is possible to identify and quantitatively describe specific structural ions' features having influence on the micelization of ILs. Moreover, it should be possible to verify, whether the phenomenon of micelization is governed by the influence of the single ion only, rather than being a sum of both ions' mutual influence.

Experimental: The qualitative and quantitative description of the structural properties responsible for micelles formation was performed with the use of the Quantitative Structure-Property Relationship (QSPR) approach. Structural features were expressed with help of the molecular GEometry, Topology, and Atom-Weights AssemblY (GETAWAY) descriptors system. The QSPR model was properly validated and its quality and usability was additionally proven by applying it to predict the CMC for 15,000 computationally designed ILs. It was the first model to the CMC assessment for ILs.

Findings: The analysis showed that longer (containing big hydrophobic domain), less spherical and not "folded" cations as well as bigger anions are the main factors causing the decrease of CMC. According to the presented model, the influence of cations and anions is independent.

Abbreviations: QSPR, Quantitative Structure-Property Relationship; IL, ionic liquid; CMC, critical micelization concentration; GETAWAY, GEometry, Topology, and Atom-Weights AssemblY descriptors; IFT, interferential tension measurement; ST, surface tension measurement; EC, electric conductivity measurement; GA, Genetic Algorithm; MLR, Multiple Linear Regression; R^2/Q^2, determination coefficient; CCC, Concordance Correlation Coefficient; RMSE, Root Mean Square Error; MAE, Mean Average Error; AD, applicability domain; OECD, Organization for Economic Co-operation and Development; H8e, H autocorrelation of lag 8 weighted by Sanderson electronegativity; R7p+, R maximal autocorrelation of lag 7 weighted by polarizability; HTi, H total index weighted by ionization potential.

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1. Introduction

Ionic Liquids (ILs) are the subject of intensive studies in recent years, mainly because of their untypical properties. Among these most interesting ones, there are: high thermal and chemical stability [1–3], low vapor pressure [4], high electric conductivity [5] and ability to dissolve both polar and nonpolar chemicals. Because of those features, the spectrum of ILs' applications is growing fast and the use of ILs offers a promising alternative to the classical solvents [6].

Nowadays, attention of many researchers is focused on investigating, which structural features are responsible for ILs' particular properties (physicochemical or toxicological) or ILs' specific behavior. Since every IL is in fact a combination of cation and anion, altering one of ions will likely succeed with modifying IL's properties. The biggest concern is to answer which properties would be affected by such modification and to what extent such alteration would occur. Knowledge on that matter could make it possible to design ionic liquids with predefined, wished properties. In the light of those facts, we decided to investigate IL's micelization ability, and try to describe its relation with IL's structure qualitatively and quantitatively.

The choice of this particular property was not unintentional. Many ionic liquids indicate structural similarities to surfactants [7]. Therefore the micelization can easily occur for them. This process is important from both technological and environmental point of view. Ionic liquids are already employed in many technological procedures (like for example extraction), in which their amphiphilic character plays an important role [8–11]. There are also some reports, proving their applicability as co-surfactants in various technological processes [12–14]. Moreover micelization can affect ionic liquid's synthesis, purification and regeneration routes [15]. Therefore ability to predict the Critical Micelization Concentration (CMC) value quantitatively can be helpful from the very practical point of view. There are also important environmental aspects connected to the micelization process. Micelization can be directly related with the risk and the exposure assessment for ILs. Since amphiphilic compounds are capable of interacting with cell membranes and other nonpolar surfaces, both toxicity and biodegradation of those compounds can be directly related to their physicochemical properties responsible for ILs self-assembling. Consequently, the CMC might be an important indicator, delivering information about toxicity and biodegradability of ILs [16]. Also, the antibacterial and anti-fungal potential is directly related to CMC [17]. Ability of creating micelles is also proven to have a direct impact on the environmental transport of ionic liquids [15,18]. Therefore, a more thorough insight into the potential for micelization of each ionic liquid can help to understand and assess their environmental fate, as well as to deliver some new, useful information about possible threats connected with the use of ILs.

The aim of this study was to provide a new insight into the knowledge about the ionic liquids' micelization process. Basing on the information delivered throughout the process of Quantitative Structure-Property Relationship (QSPR) modeling, we expected to identify and quantitatively describe specific structural features having influence on micelization of ILs. So far, such approach was not applied for ionic liquids. Moreover, we attempted to verify, whether the phenomenon of micelization is governed by the influence of the single ion only, rather than being a sum of both ions' mutual influence. We also presented a practical use of the developed QSPR model, which could be employed for computational CMC assessment for existing and theoretically designed ILs.

2. Methodology

2.1. Data collection

The QSPR method utilizes experimental data for the model development. Data concerning the critical micelization concentration for ionic liquids was collected from the available scientific literature (Table 1). All CMC values listed in the Table 1 were measured experimentally in the temperature ranging between 295 and 297 [K], with one of three different methods. Because no single publication provided dataset sufficient for QSPR modeling, therefore, we intentionally used CMC data obtained with slightly different experimental approaches (Interferential tension measurement (IFT), Surface tension measurement (ST), Electric conductivity measurement (EC)). This allowed us to create dataset of 59 structurally diversified IL's with the CMC ranging between the 0.098 and 902 [mM]. CMC values were logarithmically transformed in purpose of data linearization. The normality of CMC values distribution was tested and proven by Shapiro-Wilk test (p-value = 0.28). The distribution plot is presented in the Electronic Supplementary Information 1 (Fig. S1).

2.2. Structure optimization protocol and molecular descriptors calculation

In the QSPR approach, information concerning structural features of chemical compounds is encoded as numerical values of molecular descriptors. Each of them brings a separate (however, not always unique) piece of information about the chemical's structure.

Certain groups of molecular descriptors have to be calculated on the basis of 3D coordinates, describing the localization of each particular atom in the compound's molecular 3D model. Therefore, in order to guarantee the accuracy and the repeatability of calculations, they have to be performed on the optimized molecular models – models representing the chemical compound in its most suitable spatial conformation (characterized by the lowest potential energy).

Molecular models of all 59 ionic liquids were created in the ChemSketch [32] software. Structures (of each anion and each cation separately) were thereafter optimized with semi-empirical PM7 method implemented in MOPAC [33] software. This method is recommended for the geometry optimization of ionic liquids [34]. After the optimization the molecular descriptors were calculated with the use of the DRAGON [35] software. We obtained 1328 descriptors for each ion (cation and anion separately), therefore the total number of 2656 descriptors for each IL.

2.3. QSPR model's development

The Quantitative Structure-Property Relationship method was used in order to develop the model determining the influence of certain structural features of ILs on the value of their CMC.

At the initial stage (model's calibration), set of n = 59 compounds listed in the Table 1 was divided into the training set (counting t = 42 compounds) and the validation set (counting v = 17 compounds) with the use of Kennard-Stone [36] algorithm. Until the validation step, all the following procedures were performed with use of the training set only. The proper descriptors selection was performed in the QSARINS software with the use of the Genetic Algorithm (GA) implemented therein [37]. The purpose of the GA application was to reduce the descriptors-compounds ratio, to avoid model's overfitting. The GA was applied to each subgroup of descriptors system separately (see Table S1 in ESI1 for full