

Daniel Rauber

Optimizing Ionic Liquids for Broad Applications

Ionic liquids are organic salts with extraordinarily low melting points. Most representatives of this modern class of materials are liquid under ambient conditions. Low temperature molten salts combine the characteristics of conventional molecular liquids with those of classical high temperature molten salts, resulting in a unique combination of properties. The features of ionic liquids include intrinsic conductivity, good dissolution capacities, negligible vapor pressure and often high chemical, thermal and electrochemical stability. Thanks to this range of properties, ionic liquids have transformed from an academic curiosity to being implemented in or considered for a broad range of applications. These implementations also include many sustainable technologies, for instance electrochemical devices, the exploitation of renewable resources, or processes that save chemicals and energy.

Each potential application has specific requirements for the combination of properties the ionic liquid must have to improve the results. The chemical space available for modifications of ionic liquids is extremely large. Hence, the investigation of structure-property relationships is indispensable to facilitate the design process. As part of this optimization, two inherent limitations of ionic liquids compared to their molecular counterparts must be considered. The first limitation are their melting points, as many representatives are solid at room temperature, akin to classical molten salts. This of course limits their usage where the liquid state is a prerequisite. The second disadvantage is the comparatively high viscosity that is generally at least one order of magnitude higher than those of molecular solvents. Viscosity is reciprocally connected to other dynamic properties, hence a decrease in the viscosity of ionic liquids also increases their conductivity and mass transport, which is generally desired, especially if ionic liquids are used for instance as electrolytes or as medium for substance transport or reactions.

Our research mainly focuses on the structure-property relations of ionic liquids by combination of chemical synthesis, various characterization techniques, spectroscopic measurements and computational methods (Fig. 1a)). Functional groups are commonly incorporated into the organic cation of ionic liquids as a chemical tool for modifying the substance behavior via

the molecular structure [1]. In contrast, tuning the ionic liquid properties via the anion constitution demands quite different strategies [2]. Unfortunately, a very general trend is that the melting points of ionic liquids increase upon cation functionalization, while their dynamics slow down. These findings mainly result from unfavorable electronic and steric effects resulting in higher interionic interactions induced by the functionalization. However, there is one functional group where the contrary is observed – the ether group. The incorporation of ether groups in the side chains of ionic liquids significantly accelerates dynamics (exemplarily shown in Fig. 1b)) and lowers liquefaction temperatures. Even more, crystallization is not observed for many samples, but rather only glass formation at low temperatures, thus expanding the temperature range of these ionic liquids. We could show in various works, that these beneficial properties are systematically observed for different types of cations and anions as well as different positions of the ether oxygen in the side group. Furthermore, the effect is enhanced by increasing the number of ether side groups [3].

By combining experimental and computational methods we were able to rationalize the findings as the result of an altered cation conformation. While the alkyl groups attached to the positive charged cation center (ammonium or phosphonium) preferred a linear conformation, the ether group adopted a minimum of the N-C-C-O dihedral angle of approximately 60° leading to a curled cationic structure (Fig. 1c)). This curled structure reduces the size of the cation and gives a more spherical geometry, which is favorable to increase dynamics. Furthermore, the conformation of the ether side chains also shields the charged cation center. This leads to decreased and less specific interionic interactions (Fig. 1d) + e)) accompanied with increased configurational entropy, destabilizing the crystal lattice and increasing molecular motion. In addition, we were able to identify that the formation of intramolecular hydrogen bonds and non-specific long-range interactions contributed approximately equally in the formation of the curled cation structures.

In summary, structure-property relations are necessary to obtain insights into the vast and highly diverse class of ionic liquids, where an intricate interplay between molecular composition and macroscopic properties is common. The shared goal within the community is to find highly fluid ionic liquids with wide temperature windows, as such ionic liquids are required for a broad range of applications. We found that the functionalization of ionic liquid cations with ether groups, especially using multiple ether side chains, fulfills these requirements and identified the altering of the cation conformation as the underlying reason for the property boost. Tuning properties by ion

Dr. Daniel Rauber
Physikalische Chemie und Didaktik der Chemie
Universität des Saarlandes
Campus B 2-2, D-66123 Saarbrücken
daniel.rauber@uni-saarland.de
<https://www.uni-saarland.de/en/chair/kay/ionische-fluessigkeiten.html>

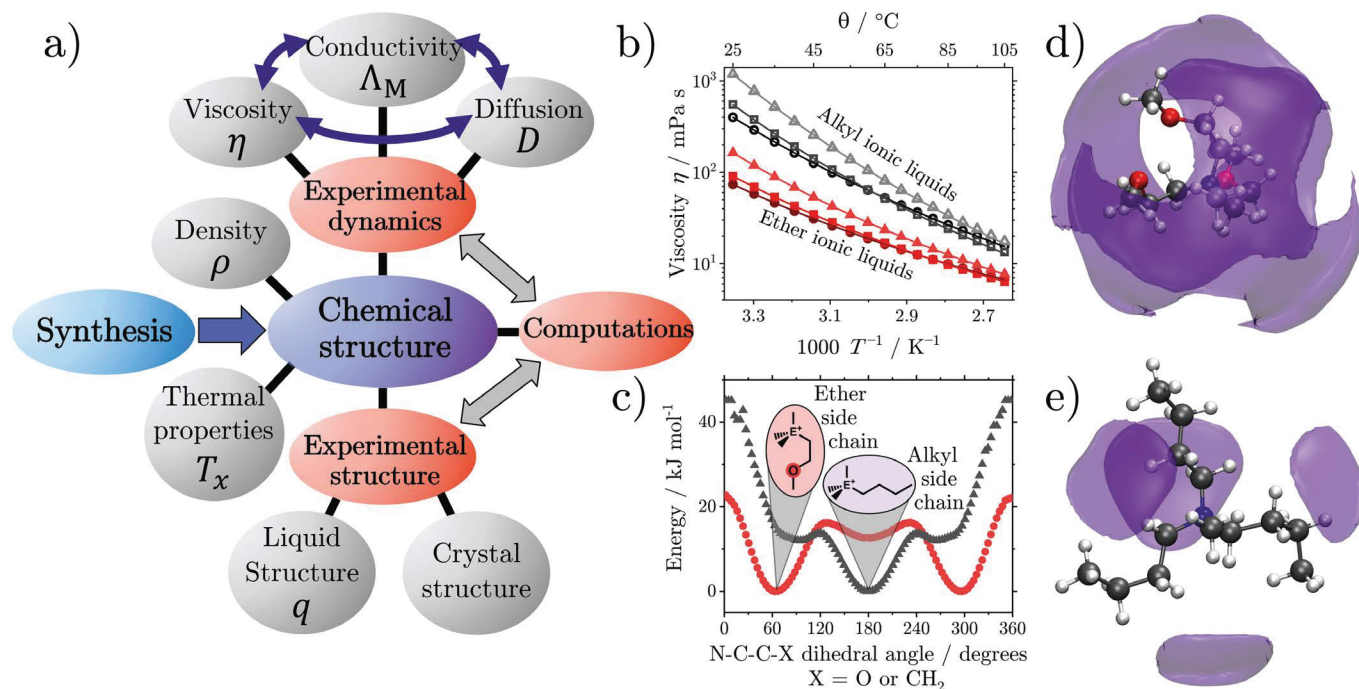


Fig. 1: a) Combination of methods to investigate the structure-property relations of ionic liquids. b) Markedly lowered viscosity of the ether ionic liquid compared to the alkylated counterparts (various anions shown with the same symbols). c) Altered minima of the N-C-C-X dihedral angle leading to a change in the conformation of the cation. The ether side chain (X = O) adopts a curled geometry, while the energetic minimum for the alkylated group (X = CH₂) is the linear conformation. Spatial distribution functions of the anions (bis(trifluoromethanesulfonyl)imide) obtained from molecular dynamics simulations for d) the cation with three ether side groups (tris(2-methoxyethyl)methylammonium) and e) with alkyl side chains (tributylmethyl ammonium cation).

conformation therefore adds a novel and powerful strategy to the molecular design of ionic liquids towards specific technical implementations.

References

- [1] Daniel Rauber, Frederik Philippi, Björn Kuttich, Julian Becker, Tobias Kraus, Patricia Hunt, Tom Welton, Rolf Hempelmann, Christopher W.M. Kay : *PCCP* 2021 **23**, 21042 – 21064.
- [2] Frederik Philippi, Daniel Rauber, Oriele Palumbo, Kateryna Goloviznina, Jesse McDaniel, David Pugh, Sophia Suarez, Carla C. Fraenza, Agilio Padua, Christopher W. M. Kay, Tom Welton, *Chem. Sci.* 2022 **13**, 9176 – 9190.
- [3] Frederik Philippi, Daniel Rauber, Björn Kuttich, Tobias Kraus, Christopher W.M. Kay, Rolf Hempelmann, Patricia Hunt, Tom Welton, *PCCP* 2020 **22**, 23038 – 23056.

Dr. Daniel Rauber

Studied chemistry at Karlsruhe Institute of Technology and Johannes Gutenberg University Mainz. He then joined the group of Prof. Dr. Rolf Hempelmann at Saarland University to obtain his PhD. He is currently PostDoc in the Group of Prof. Dr. Christopher Kay dealing with magnetic resonance spectroscopy. His research covers fundamental physico-chemical investigation on ionic liquids and the transfer of these findings into applications, such as tribology, the exploitation of sustainable resources and electrochemical devices. As a result, he has national and international cooperations with scientists from many adjacent disciplines, such as physics, material science, biotechnology and pharmacy. In 2022 he received the Ewald Wicke prize of the German Bunsen Society for Physical Chemistry. He likes being in nature, is a do-it-yourself enthusiast, and fan of cats.

