

Vilniaus universitetas  
Fizinių ir technologijos mokslų centras  
Kauno technologijos universitetas  
Vilniaus Gedimino technikos universitetas (VILNIUS TECH)  
Lietuvos fizikų draugija

# 45-oji LIETUVOS NACIONALINĖ FIZIKOS KONFERENCIJA

*2023 m. spalio 25-27 d., Vilnius*

## **PROGRAMA IR PRANEŠIMŲ TEZĖS**



VILNIAUS  
UNIVERSITETO  
LEIDYKLA

2023

Bibliografinė informacija pateikiama

Lietuvos integralios bibliotekų informacinės sistemos (LIBIS) portale [ibiblioteka.lt](http://ibiblioteka.lt).

**ISBN 978-609-07-0981-8** (skaitmeninis PDF)

**DOI:** <https://doi.org/10.15388/LNPC.2023>

Leidinį rengė

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Knygos internete [knygynas.vu.lt](http://knygynas.vu.lt)

Mokslo periodikos žurnalai [zurnalai.vu.lt](http://zurnalai.vu.lt)

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## Joninių skysčių struktūros ir BMR spektrinių savybių modeliavimas MD simuliacijomis bei jungtiniais QM/MM metodais

### Structural and NMR properties of ionic liquid systems modelled by an integrated MD-QM/MM approach

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Molecular dynamics (MD) simulations combined with the quantum mechanics/molecular mechanics (QM/MM) models have proven to be a powerful computational technique for accurate predictions of electronic properties of extensive molecular systems. MD simulations are employed to sample the phase space of molecular system of interest under specific thermodynamic conditions, and then QM/MM calculations of electronic properties are performed where the central part of the molecular system is described by an electronic structure method and the rest of the system is modelled by a classical force field. Polarizable force fields can also be used for the classical subsystem to allow for mutual polarization interactions between quantum and classical regions.

In this presentation we will discuss our recent attempts to describe the structural and nuclear magnetic resonance (NMR) properties of ionic liquid (IL) systems using this integrated MD-QM/MM scheme based on classical MD simulations and density functional theory. ILs and their mixtures with traditional molecular solvents have already found numerous applications in both industry and laboratory. However, it is of importance to disclose the molecular mechanisms behind the physicochemical properties of IL systems in order to facilitate their practical applications.

To gain insight into ion pairing phenomenon, we have conducted classical MD simulations of the 1-decyl-3-methyl-imidazolium chloride contact ion pair as well as of free ions in water, acetonitrile, and dichloromethane [1]. The QM/MM model was used to predict NMR chemical shift for the so-called H2 proton in the imidazolium ring of the cation, which has displayed high sensitivity to the nature of the solvent. The chemical shift of the H2 proton was found to be primarily modulated by hydrogen bonding with the chloride anion, while the influence of the solvents though differing in polarity and capabilities for hydrogen bonding is less important. By comparing experimental and computational results, we were able to get quantitative information concerning chemical equilibrium between contact ion pairs and free ions established in each solvent.

We have also scrutinized the molecular mechanism behind the observed non-monotonic dependence of the <sup>1</sup>H NMR chemical shift of water on the composition of the aqueous mixtures of the 1-butyl-3-methyl-

imidazolium chloride IL [2]. We have found that complex chemical equilibrium between various water-ionic aggregates is established in these mixtures. This equilibrium is changing with the varying composition of the mixture, leading to this peculiar evolution of the chemical shift of water. Extensive classical MD simulations of these mixtures were carried out, and QM/MM approaches were applied to predict the NMR chemical shifts. The proliferation of strongly hydrogen-bonded complexes between chloride anions and water molecules is found to be the reason behind the increasing chemical shift of water when its molar fraction in the mixture is low and decreasing. The model shows that the chemical shift of water molecules that are trapped in the IL matrix without direct hydrogen bonding to the anions is considerably smaller than the chemical shift predicted for the neat water. The <sup>1</sup>H NMR spectrum of neat [C4mim][Cl] was predicted and found to be in very reasonable agreement with the experimental data. The experimentally observed strong dependence of the chemical shift of the H2 proton on the composition of the mixture was rationalized as well.

We will also briefly discuss our very recent extensive computational NMR studies of the molecular mechanism behind the increased solubility of drug molecules in aqueous solution of choline based ILs and of structural properties of the aqueous mixtures of 1-butyl-3-methylimidazolium nitrate.

Support from the Research Council of Lithuania (grant no. S-MIP-22-74) is acknowledged. Computational resources were provided by the Swedish National Infrastructure for Computing (SNIC) at HPC2N and at PDC, Sweden, and by the High Performance Computing Center “HPC Saulėtekis” at Vilnius University, Lithuania.

*Keywords: ionic liquids, molecular dynamics simulations, quantum mechanics, nuclear magnetic resonance.*

#### Literature

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