

KARL KARU

Computer modeling
of ionic liquid properties and behavior
at the molecular and interfacial levels



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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications.

The publications are sequenced to follow the structure of the thesis.

- I. Karu, K.;** Ruzanov, A.; Ers, H.; Ivaništšev, V.; Lage-Estebanez, I.; Garcia de la Vega, J. M. (2016). Predictions of Physicochemical Properties of Ionic Liquids with DFT. *Computation*, 4(3), 25.
- II. Karu, K.;** Misin, M.; Ers, H.; Sun, J.; Ivaništšev, V. (2018). Performance of SCAN density functional for a set of ionic liquid ion pairs. *International Journal of Quantum Chemistry*, 118(3), e25582.
- III. Karu, K.;** Elhi, F.; Põhako-Esko, K.; Ivaništšev, V. (2019). Predicting Melting Points of Biofriendly Choline-Based Ionic Liquids with Molecular Dynamics. *Applied Sciences*, 9(24), 5367.

Author's contribution:

- Publication I:** The author developed the computational workflow, ran all calculations, performed the data analysis, participated in writing the manuscript.
- Publication II:** The author performed most of the DFT computations, conducted the analysis of the results, and participated in writing the manuscript.
- Publication III:** The author performed the MD simulations and DFT computations, conducted the analysis of the results, and participated in writing the manuscript.

LIST OF RELATED PUBLICATIONS

The author contributed to the following publications:

- IV.** Elhi, F.;* **Karu, K.**;* Rinne, P.; Nadel, K.-A.; Järvekülg, M.; Aabloo, A.; Tamm, T.; Ivaništšev, V.; Põhako-Esko, K. (2020). Understanding the behavior of fully non-toxic polypyrrole-gelatin and polypyrrole-PVdF soft actuators with choline ionic liquids. *Actuators*, 9(2), 40.
- V.** **Karu, K.**;* Roos Nerut, E.;* Tao, X.; Kislenko, S. A.; Põhako-Esko, K.; Voroshylova, I. V.; Ivaništšev, V. (2024). Ionic liquid–electrode interface: Classification of ions, saturation of layers, and structure-determined potentials. *Electrochimica Acta*, 503, 144829.

* Contributed equally to this work

Author's contribution:

- Publication IV:** The author performed the DFT and MD simulations, developed the workflows for predicting ionic conductivity and actuator strain, and participated in writing the manuscript.
- Publication V:** The author performed the DFT calculations of the electrochemical windows, contributed to making the MD simulation and analysis workflows, and participated in writing the manuscript.

LIST OF ACRONYMS AND NOTATIONS

Chemical nomenclature

Anions shown in Figures 2–4

$[\text{BF}_4]^-$	– Tetrafluoroborate
$[\text{B}(\text{CN})_4]^-$	– Tetracyanoborate
$[\text{C}(\text{CN})_3]^-$	– Tricyanomethanide
$[\text{FEP}]^-$	– Tris(pentafluoroethyl)trifluorophosphate
$[\text{FSI}]^-$	– Bis(fluorosulfonyl)imide
$[\text{N}(\text{CN})_2]^-$	– Dicyanamide
$[\text{OTF}]^-$	– Trifluoromethanesulfonate
$[\text{PF}_6]^-$	– Hexafluorophosphate
$[\text{S}_4]^-$	– Sulfonyl-based anion
$[\text{SCN}]^-$	– Thiocyanate
$[\text{TFSI}]^-$	– Bis(trifluoromethanesulfonyl)azanide

Cations shown in Figures 2–4

$[\text{Am}_4]^+$, $[\text{N}_{2214}]^+$, $[\text{TEPA}]^+$	– Ammonium
$[\text{BMIm}]^+$ and $[\text{Im}_4]^+$	– 1-Butyl-3-methylimidazolium
$[\text{BMPyr}]^+$ and $[\text{Pyr}_4]^+$	– 1-Butyl-1-methylpyrrolidinium
$[\text{BPy}]^+$ and $[\text{Py}]^+$	– Butylpyridinium
$[\text{Ch}]^+$	– Choline

Computational methodology

B2PLYP	– B3LYP functional including MP2 correlation energy
B3LYP	– Becke’s three-parameter exchange functional with Lee-Yang-Parr correlation
BLYP	– Becke’s 88 exchange functional with Lee-Yang-Parr correlation
CCSD(T)	– Coupled cluster single double (triple) method
CHELPG	– Charges from Electrostatic Potentials using a Grid-based method
CP	– Boys–Bernardi counterpoise correction
D3 / D4	– Grimme’s dispersion correction (versions 3 and 4)
DFT	– Density Functional Theory
DFTB	– Density Functional Tight-Binding
DLPNO	– Domain-based local pair natural orbital (approximation)
gCP	– Geometrical counterpoise correction
GFN2-xTB	– Geometry, Frequency, Noncovalent, and eXtended Tight-Binding (method)
M06-L	– Minnesota 06 local functional
MD	– Molecular Dynamics
ML	– Machine Learning
MP2	– Second-order Møller–Plesset perturbation theory

<i>NPT</i>	– Simulation ensemble with constant Number of particles, Pressure, and Temperature
<i>NVT</i>	– Simulation ensemble with constant Number of particles, Volume, and Temperature
OPLS-AA	– Optimized Potential for Liquid Simulations All-Atom force field
PBE	– Perdew–Burke–Ernzerhof functional
R^2	– Coefficient of determination in curve fitting
r ² SCAN-3c	– Composite method based on r2SCAN with dispersion and counterpoise corrections
SCAN	– Strongly Constrained and Appropriately Normed functional
SCAN0	– SCAN functional with 25% Hartree–Fock exchange
SCS-MP2	– Spin-component scaled MP2
SMILES	– Simplified Molecular Input Line Entry System
Δ SCF	– Delta self-consistent field method

Quantities and descriptors

D	– Diffusion coefficient
EA	– Electron Affinity
ECW	– Electrochemical Window
E_a	– Activation energy
$E_{\text{disp}}, E_{\text{int}}$	– Dispersion and Interaction energies
HOMO–LUMO gap	– an energy gap between the Highest Occupied and Lowest Unoccupied Molecular Orbitals
IE	– Ionization Energy
r and R	– Contact and lateral radii of ions
T_m	– Melting temperature
η	– Viscosity
θ_M	– Maximum packing density
σ	– Surface charge density
φ_M and φ_S	– Potentials of Monolayer charge and Saturation

1. INTRODUCTION

Ionic liquids are recognized for their unique properties, including negligible vapor pressure, high thermal and chemical stability, and a wide electrochemical window. Unlike traditional solvents, ionic liquids consist entirely of ions, allowing fine-tuning of their physicochemical properties by selecting specific cation–anion combinations. Such adaptability makes ionic liquids relevant to electrochemical and other technological applications. Specific combinations of these properties enable their use in domains such as green chemistry, energy storage, and electrochemical devices.

Advances in computational methods have significantly enhanced the study of ionic liquids. Density functional theory and molecular dynamics simulations enable the prediction of their properties, design of novel ionic liquids, and understanding of interfacial behaviors at the molecular level. These approaches complement experimental techniques by providing cost-effective tools for high-throughput screening and optimization of ionic liquids for targeted applications.

This thesis examines ionic liquids computationally, with three primary objectives: (1) to establish workflows for ionic liquids property prediction, (2) to elucidate ionic liquids’ molecular structure, and (3) to investigate interfacial behaviors of ionic liquids at charged surfaces. The articles compiled in this work highlight advancements in high-throughput computations, the influence of ion geometries on interfacial properties, and the customization of ionic liquids for environmentally friendly applications.

By integrating theoretical and computational frameworks, this research relates calculated molecular properties to bulk and interfacial properties. The findings contribute to the enhancement of ionic liquid-based electrochemical systems, such as actuators and supercapacitors, thus, addressing energy storage and sustainability challenges.

1.1. Literature overview

Computational techniques

Density functional theory (DFT) is widely used for predicting IL properties, providing detailed insights into electronic structures and enabling accurate predictions of various properties. DFT approaches are frequently employed to calculate energies, optimize geometries, predict properties such as ionization energies and electron affinities, and evaluate various parameters that correlate electronic and geometric structures with macroscopic properties.

Advanced DFT approaches, including hybrid functionals and many-body interaction corrections, have improved the accuracy of energetic and structural predictions. These methods are used to predict transport properties and reactivity parameters, enabling their integration with experimental results to validate theoretical findings.

Density Functional Tight Binding (DFTB) differs from DFT in its computational efficiency and approximation approach. While DFT explicitly calculates electronic densities and solves the Kohn–Sham equations, DFTB simplifies this by expanding the energy as a series around a reference density, often reducing computational demands by orders of magnitude, while preserving essential quantum mechanical details.

The GFN-xTB, a family of DFTB-based methods, enhances these principles with features like anisotropic multipole electrostatics and density-dependent dispersion corrections. This family of methods is particularly well-suited for large-scale systems and for conformational analysis, non-covalent interaction studies, and property predictions, balancing accuracy with efficiency [1].

DFTB, particularly GFN2-xTB, has been instrumental in predicting the properties of ILs. ILs were explicitly included in the training set for GFN2-xTB, enabling reliable predictions of their structural and energetic properties. The method was used to develop parameters for force fields in Publications III and IV [2,3]. These papers focused on capturing the complex behavior of ILs in bulk and interfacial configurations, highlighting the motivation to create computationally efficient yet accurate methods for describing IL systems.

Molecular dynamics (MD) simulations often integrate DFT-based force fields, providing insights into IL structure and dynamics at interfaces and under external fields [4]. Machine learning (ML) and quantitative structure-activity relationship (QSAR) models are increasingly used for predicting IL properties. ML algorithms trained on extensive datasets can rapidly identify patterns and predict properties, offering scalability and adaptability for high-throughput screening. However, their reliability depends heavily on the quality and diversity of the training data, and they often struggle to generalize beyond the initial dataset [5]. QSAR models, by contrast, rely on established chemical descriptors and statistical correlations, making them interpretable but prone to errors when extrapolating beyond well-characterized systems [6].

This thesis emphasized the need for methods that could bridge the gap between molecular-level precision and macroscopic observables. For example, in Publications III and IV the use of GFN2-xTB to parameterize interactions addressed challenges in modeling IL systems with dominant Coulomb interactions. These efforts underscored the importance of combining computational methods with experimental validations to enhance predictive accuracy for IL properties and behaviors at molecular and interfacial levels.

Electrochemical window prediction

The electrochemical window (ECW) of ILs, determined by their anodic and cathodic limits, is critical for electrochemical applications. Several methods estimate ECW, each with specific requirements, benefits, and limitations.

An early approach used the HOMO–LUMO gap, which provided a basic estimate of ECW by considering the frontier orbital energies of ions. While computationally efficient, this method often overestimated ECW due to systematic

errors in estimating the LUMO energy. Later advancements employed adiabatic and vertical ionization energies and electron affinities, enabling more reliable predictions of ECW. This approach recognized that each ion could have multiple configurations in isolation, within ion pairs, and when solvated in the IL bulk. Accounting for these configurations and their solvation effects represented a significant methodological improvement.

Solvation effects can be evaluated using implicit models or explicitly, for example, using the DFT-MD techniques. These methods enable detailed consideration of reorganization energies and local versus global minima configurations, often weighted appropriately. While they offer enhanced accuracy and allow the application of Marcus' theory, they are computationally demanding and resource-intensive.

By addressing solvation and structural variability, these approaches provide more reliable predictions of ECW but at the cost of computational efficiency.

Thermodynamic cycle-based methods extend beyond the electron transfer approach by also considering bond breakage. These methods require detailed quantum chemical data and often molecular dynamics simulations to parameterize the solvation environment as well as to account for reaction paths with breakage and formation of chemical bonds. This approach provides superior accuracy at a moderately increased computational cost [7].

Thermodynamic cycle-based frameworks have been expanded to include comprehensive databases of electrochemical windows, as demonstrated by Wang et al., who applied a systematic cycle-based analysis to over 300 electrolytes, highlighting patterns and guiding the design of new ILs [8].

Marcus' theory offers another layer of refinement by simulating reorganization energies associated with electron transfer processes. This approach provides valuable insights into redox behavior but requires both quantum chemical and kinetic data for accurate predictions.

Finally, molecular dynamics (MD) integrated frameworks directly evaluate ion pairing and solvation dynamics. By simulating realistic environments, these models deliver comprehensive predictions of ECW but demand significant computational resources [9,10].

Viscosity modeling

The study of viscosity in ILs has long been interesting due to its direct correlation with conductivity and diffusion coefficients. These properties are essential for the application of ILs in energy storage and electrochemical systems. Historically, viscosity has been studied more extensively than other transport properties due to the abundance of experimental data, making it a preferred focus for theoretical modeling [10].

The foundational work by Eyring et al. in 1941 described viscosity as: $\eta = (N_A h / V_m) \cdot \exp(\Delta G / (RT))$, where N_A is Avogadro's number, h is Planck's constant, V_m is molar volume, ΔG is the energy of activation for the jump, R is

the gas constant, and T is temperature. This approach laid the groundwork for future theoretical developments.

In 2010, Han et al. expanded this model by incorporating probabilities for creating and occupying holes in a pseudolattice model. Their equation added corrections for degrees of freedom and Lennard-Jones potential effects, further refining predictions. However, Lennard-Jones potentials were deemed inadequate for ionic liquids, necessitating more sophisticated models for their complex interactions.

In 2019, Karu combined DFT with pseudolattice formalism to address the shortcomings of traditional Lennard-Jones models [2,3,11]. They developed a semi-empirical approach correlating experimental activation energies with calculated interaction energies. The activation energy of viscosity was expressed as a linear function of the interaction energy scaled by Madelung-type constants.

Their method used DFT to calculate interaction energies (E_{int}) and dispersion energies (E_{disp}) and correlated them with experimental viscosities. The derived semi-empirical equation was: $\ln(\eta) = \ln(A) + E_a / (RT)$, where E_a is the activation energy, and A is a pre-exponential factor influenced by the molar volume (V_m).

Dispersion forces, which were previously underrepresented, were integrated into the model using correction factors derived from dispersion energies. Bernard et al. found a similar correlation, underscoring the critical role of dispersion forces in viscosity modeling of ILs [12].

Machine Learning Approaches for Predicting Viscosity and Conductivity

Machine learning (ML) has recently emerged as a transformative tool for predicting ILs' properties, especially viscosity and conductivity. ML approaches have demonstrated the ability to handle large datasets and uncover complex non-linear relationships, significantly advancing predictive accuracy.

For viscosity prediction, models such as Gradient Boosting Machines, e.g., CatBoost, and deep neural networks have achieved strong performance metrics, with R^2 values exceeding 0.99 in some cases. These models integrate features derived from molecular structures, such as SMILES notations, to enhance the granularity of predictions. CatBoost, for instance, effectively combines chemical descriptors with domain-specific physics insights, providing robust predictions across diverse IL systems [13].

In conductivity prediction, neural architectures like Transformers and graph-based networks, e.g., Message Passing Neural Networks, have leveraged large datasets to model ion-pair interactions. These approaches consistently outperform traditional regression models, reducing errors by up to 20% compared to earlier techniques [14].

Moreover, advances in interpretable ML methods have enhanced the trustworthiness of these predictions. Techniques like SHapley Additive exPlanations (SHAP) and Partial Dependence Plots (PDP) clarify the influence of molecular descriptors and environmental factors on predictions, ensuring models align with known chemical principles [13].

While traditional empirical methods, like Quantum Structure Property Relationships (QSPR), provide quick approximations, ML-driven methodologies now set the standard for precision and scalability in IL property modeling. This evolution underscores the role of ML in pushing the boundaries of IL research, providing unparalleled predictive accuracy and insights for practical applications, each with unique advantages and challenges. QSPR method uses empirical correlations between molecular structures and transport properties. These models are extensively parameterized, requiring careful calibration against experimental data for specific IL families. Despite their accuracy, QSPR models lack generalizability beyond their training datasets.

The Conductor-like Screening Model for Realistic Solvation (COSMO-RS) is another approach widely used for viscosity predictions. COSMO-RS calculates thermodynamic properties based on continuum solvation models, integrating molecular surface charge densities. This method is effective but computationally demanding and highly dependent on accurate solvation parameters [15].

Volume-based thermodynamics links viscosity to the molecular volume and free energy of activation for molecular movement. This method often provides quick estimates but requires extensive parameterization for specific IL classes, limiting their versatility for novel systems [16].

More recently, ML approaches have been applied to viscosity modeling. ML models, trained on large experimental datasets, offer high-speed predictions for diverse IL systems. However, their predictive power depends heavily on the quality and diversity of the training data, and they struggle with extrapolating beyond the range of their dataset [12].

Each of these approaches complements DFT-based methods by offering tailored solutions for specific applications, emphasizing the diverse toolkit available for modeling IL viscosities.

Melting point prediction

Predicting the melting points of ILs remains a challenging task due to the complex interplay of molecular interactions governing phase transitions. Various computational approaches have been developed, each with unique advantages and limitations.

QSPR method utilizes molecular descriptors to establish correlations between structural features and melting points. Early works focused on simple linear models for specific IL families, such as imidazolium and benzimidazolium salts, using descriptors such as HOMO–LUMO gaps, orbital populations, and partial charges. Despite their simplicity and interpretability, QSPR models are heavily reliant on the quality and diversity of training datasets, often failing to generalize beyond closely related chemical structures [17].

MD-based methods provide a direct route for estimating melting points by analyzing diffusion coefficients during annealing. Techniques such as the pseudo-supercritical path (PSCP) and voids method have demonstrated high accuracy but require prior knowledge of the IL crystal structure. This prerequisite

limits their application in high-throughput screening, as synthesizing and characterizing the crystal structure negates the computational advantage. Recent advancements circumvent this limitation by using Coulombic potential wells to generate initial solid-phase structures, improving robustness and reducing dependence on experimental crystal data [2].

Thermodynamic cycles calculate the Gibbs free energy of fusion as a function of temperature and extrapolate to determine the melting point. This approach provides detailed thermodynamic insights but is computationally intensive and sensitive to the accuracy of lattice and solvation energies [18].

Semi-empirical quantum methods, such as GFN-xTB with Hirshfeld partitioning, refine force fields for MD simulations. These models improve melting point predictions by incorporating cluster-derived charges, which better reflect condensed phase environments compared to isolated ion charges [2].

Challenges and limitations

Predicting the properties of ILs involves accounting for intermolecular interactions and the surrounding environment. Current computational approaches often struggle to balance accuracy and scalability, particularly for complex systems like ILs [11].

Melting point prediction

For melting point predictions, methods like QSPR and MD-based simulations face challenges in generalizing across diverse IL families. QSPR models depend heavily on the quality and diversity of training datasets, often failing to extrapolate accurately for novel structures [17]. MD simulations, while accurate for known crystal structures, require detailed prior knowledge, limiting their applicability in high-throughput workflows. Semi-empirical quantum methods, such as GFN-xTB, have made strides in improving predictions but remain sensitive to parameterization and computational costs [2].

Viscosity prediction

Viscosity prediction methods must account for the nonlinear effects of temperature, pressure, and molecular structure on transport properties. Empirical approaches like QSPR and COSMO-RS require extensive parameterization and fail to capture generalizable trends for novel ILs. ML-based models, though promising, often depend on large datasets and are limited by their black-box nature, necessitating advanced interpretability tools to validate predictions [13]. Current methods also inadequately account for the role of long-range electrostatic and dispersion forces, which are critical for understanding ionic interactions [12].

Electrochemical window prediction

ECW predictions remain particularly challenging due to the absence of methods that incorporate interfacial effects. Simulating charge transfer at interfaces is computationally intensive and requires specialized techniques. Publication V on

IL–electrode interfaces represents a step toward integrating interfacial effects into predictions of electrochemical stability. The development of computational methods for such calculations is essential for capturing the unique properties of ILs at interfaces, which are critical for applications in energy storage and catalysis [19].

Bridging the gap

The current thesis emphasized bridging the gap between molecular-level precision and macroscopic observables. Presented studies, including the development of force fields using GFN2-xTB, have focused on addressing challenges in modeling IL interactions, particularly in systems with strong non-covalent forces. Combining semi-empirical techniques with experimental validations is significant for enhancing predictive accuracy across properties, ensuring that computational methods are robust, scalable, and aligned with experimental realities.

1.2. Research aims

This research aimed to bridge the gap between molecular-level precision and macroscopic observables in ILs by developing reproducible workflows, benchmarking novel computational methods, and ensuring open-source accessibility for broader applicability. The first aim was to create computational workflows to screen IL candidates for various applications, focusing on their electrochemical, thermal, and transport properties. High-throughput computational techniques were leveraged to evaluate IL performance systematically. Another goal was to validate the SCAN functional for accurately predicting interaction energies, dipole moments, and thermodynamic properties. Benchmarking against reference methods and optimizing parameters for IL-specific applications ensures reliability.

Designing workflows for stability and viscosity prediction involved integrating DFT-based calculations and ML models to correlate molecular descriptors with experimental data. That ensured model reliability and scalability. A comprehensive methodology was developed for melting point prediction using MD simulations and thermodynamic cycles. Incorporating pseudolattice models and solid-liquid diffusion analysis improved prediction accuracy. For interfacial properties such as electro-mechanical stability (θ_M), innovative approaches were introduced by integrating semi-empirical models with MD and DFT calculations, simplifying and scaling interfacial simulations for practical applications.

All computational workflows were developed to be reproducible. Namely, open-source tools and open data were provided to ensure workflows were accessible and standardized. Frameworks like NaRIBaS were used to automate workflows [20], standardize input parameters, and improve data handling [21,22].

2. METHODS

2.1. Density Functional Theory calculations

DFT calculations were used throughout the PhD studies to predict various properties and/or provide input for other methods. Details are summarized in Table 1, including specifics on the used software. DFT-based methods were applied to single ions and ion pairs. More efficient DFTB and MD methods were used on larger clusters and bulk liquids. Different methods were chosen based on the needs of the specific study.

DFT functionals used in Publications I–V are:

- BLYP – Becke’s 88 exchange functional and Lee, Yang, and Parr’s correlation functional [23,24]
- B3LYP – BLYP with Becke’s exchange functional augmented by Hartree–Fock exchange energy [25]
- B2PLYP – B3LYP, which includes the correlation energy from the second-order Møller–Plesset (MP2) perturbation theory [26]
- SCAN – strongly constrained and appropriately normed functional [27]
- SCAN0 – SCAN with 25% Hartree–Fock exchange energy
- r²SCAN-3c – composite method based on SCAN with a custom triple-zeta Gaussian basis set, D4 dispersion correction, and a geometrical counterpoise correction (gCP) [28]
- M06-L – Minnesota 06 local functional [29]
- PBE – Perdew–Burke–Ernzerhof functional [30]

Reference data were obtained using two *ab initio* methods:

- DLPNO-CCSD(T) – domain-based local pair natural orbital coupled cluster method with singles, doubles, and perturbative triplets excitations [31,32]
- SCS-MP2 – spin-component scaled MP2 [33]

The calculations employed the following basis sets:

- Def2-SVP, Def2-TZVP, Def2-TZVPP, Def2-QZVPP – Ahlrichs’ type basis sets with double- ζ split valence (-SV-), triple- ζ split valence (-TZ-), quadruple- ζ split valence (-QZ-), polarization functions (-P), extra polarization functions (-PP) [34,35]
- 6-311++G(3df,3pd) – Gaussian type basis set with 6-311G for first-row atoms and the McLean-Chandler basis sets for second-row atoms, with diffuse functions on heavy atoms and hydrogen, 3 sets of d functions and 1 set of f functions on heavy atoms and 3 sets of p functions and 1 set of d functions on hydrogen [36,37]

The following empirical corrections were applied as required:

- D3, D4 – Grimme’s dispersion correction, vers. 3 and 4 [38–40]
- gCP – geometrical counterpoise correction [41]
- CP – Boys–Bernardi counterpoise correction [42]

The calculated properties and descriptors included:

- Geometry/energy – where geometry denotes the relative spatial coordinates of atoms, and energy denotes the final single point energy of the subject compound
- Dipole moment – the spatial integral of the total charge density, comprising both the positive nuclear charges and the negative electron density, multiplied by the position vector
- Partial charge – unless otherwise noted, charges from electrostatic potentials using a grid-based method (CHELPG) to accurately reproduce the electrostatic potential [17,43]
- Molar volume – volume of the ions estimated from the single point calculation as the volume, where the electron density surpasses 0.001 electrons/Bohr³

Table 1 summarizes how the different methods, basis sets, and corrections, and software were combined to generate the results.

Table 1: DFT methods, basis sets, empirical corrections, software packages, and calculated properties used in Publications I–V.

Publication	Method	Basis set	Corrections	Software	Properties
I	BLYP	Def2-TZVP	D3, gCP	Orca 3.0.3	Geometry
I	B3LYP	Def2-TZVP	D3, gCP	Orca 3.0.3	Energy, Partial charges, Dipole moment
II	B2PLYP	Def2-TZVPP	D3, CP	Orca 3.0.3	Geometry, Energy, Dipole moment
II	DLPNO-CCSD(T) ^a	Def2-TZVPP ^b	-	Orca 3.0.3	Energy, Dipole moment
II	SCS-MP2 ^a	Def2-TZVPP; Def2-QZVPP ^c	-	Orca 3.0.3	Energy
II	SCAN	6-311++G (3df,3pd)	D3 ^d , CP	Gaussian 03 ^e	Energy, Dipole moment
II	SCAN0	6-311++G (3df,3pd)	D3 ^d , CP	Gaussian 03 ^e	Energy, Dipole moment
II	M06-L	Def2-TZVPP	D3, CP	Orca 3.0.3	Energy, Dipole moment
II	PBE	Def2-TZVPP	D3, CP	Orca 3.0.3	Energy, Dipole moment
III	PBE	Def2-SVP	-	Orca 4.0.2	Geometry, Partial charges
IV ^f	PBE	Def2-SVP	-	Orca 4.0.2	Geometry, Partial charges
IV ^f	B3LYP	Def2-TZVP	-	Gaussian 09	Energy, Molar volume
V ^f	r ² SCAN-3c	See footnote ^g	D4, gCP ^g	Orca 5.0.2	Energy

a – *ab initio* wave function method

b – extrapolated to complete basis set using SCS-MP2 energies

c – effective core potentials were used for iodine [44]

d – rescaled dispersion correction, because it was not yet sufficiently parametrized

e – developer’s version of Gaussian 03, because SCAN was not publicly available at the time

f – related publications

g – corrections and a custom basis set are already included in the method

2.1.1. Electrochemical window

Electrochemical window (ECW) – a measure of electrochemical stability – can be predicted from calculated single-point energies using the delta self-consistent field (Δ SCF) method [45,46]. According to the Δ SCF method, the ionization energy (IE) of a cation is defined as the difference between the electronic energies of the cation and its reduced form. Similarly, electron affinity (EA) for an anion is defined as the difference between the electronic energies of the anion and the oxidized anion:

$$IE_{\text{ion}} = E(\text{Cation}^+) - E(\text{Cation}^*), EA_{\text{ion}} = E(\text{Anion}^-) - E(\text{Anion}^*)$$

For a more accurate analysis, solvation has to be accounted for – either by a continuum model or, more expensive, by a specific MD simulation. However, in this work, the aim was to reproduce experimental properties with scalable DFT calculations. For this reason, a modified Δ SCF method was used. At the first approximation, taking into account the inter-ionic interactions and neglecting the interfacial interactions, the Δ SCF procedure was carried out with the ion pairs, therefore, accounting for the solvation of an ion with its counter-ion:

$$IE_{\text{pair}} = E(\text{Pair}) - E(\text{Pair}^-), EA_{\text{pair}} = E(\text{Pair}) - E(\text{Pair}^+)$$

By combining the $1/4IE_{\text{pair}}$ with $3/4IE_{\text{ion}}$ and $1/4EA_{\text{pair}}$ with $3/4EA_{\text{ion}}$, the EA and IE values for the ILs were calculated, respectively. It was found that scaling factors of $1/4$ and $3/4$ align the $IE + EA$ sum to the ECW values in Table 6 of Reference [47]. The physical meaning of this scaling factor is closely related to the Madelung constant difference [48]. Effectively, such an approach can be extended to account for the solvation energy of the species involved in redox reactions at the interface. Thus, the EA and IE values of the ion pairs can be and were used to estimate the relative electrochemical stabilities of the ILs, as ECW:

$$ECW = - (EA + IE) / e,$$

where e is the elementary charge.

Note that, as in Publication IV, the ECW was not of primary interest; the EA and IE values were calculated only for individual ions, and the ECW formula was then applied to those values. It should also be stressed that when estimating ECW based on $EA_{\text{ion/pair}}$ and $IE_{\text{ion/pair}}$ values, one has to take into account that a cation may oxidize and an anion may reduce, or both could participate in chemical reactions.

2.1.2. Interaction energy of an associate

The interaction energies (E_{int}) of ion pairs, consisting of a single anion and a single cation, were calculated as the difference between the energy of the ion pair and its components:

$$E_{\text{int}} = E_{\text{pair}} - E_{\text{anion}} - E_{\text{cation}}$$

In the current thesis, each geometry in the formula above was optimized separately. Sometimes in the literature, a similar quantity is calculated as a binding energy, where the individual ions are fixed in their geometries within the pair.

2.1.3. Activation energy of viscosity

The calculated E_{int} values were used to predict the activation energy of viscosity. First, experimental viscosity–temperature dependence data were used to calculate the experimental activation energy based on the Arrhenius equation:

$$\ln \eta = \ln A - E_{\text{a}}^{\text{exp}} / (RT),$$

where $E_{\text{a}}^{\text{exp}}$ is the activation energy evaluated from viscosity–temperature dependence, A is a constant, R is the universal gas constant, and T is temperature. This was performed using simple linear regression, with $E_{\text{a}}^{\text{exp}}/R$ as the fitted slope. The experimental viscosity data were obtained from the literature (see Table 1 in Publication I).

Activation energy of viscosity ($E_{\text{a}}^{\text{calc}}$) was estimated using E_{int} and its dispersion energy E_{disp} component using the following formula:

$$E_{\text{a}}^{\text{calc}} = a_i E_{\text{int}} - b E_{\text{disp}}$$

The normalization factors a_i and b were defined as:

$$a_i = 0.165 \times q_i^2, \quad b = 0.5 \times 0.165$$

In the formulae above, 0.165 was a Madelung-type constant accounting for the fact that viscosity naturally happens in a larger phase (see Appendix A in Publication I). The E_{int} part was scaled with a charge component (q_i^2) which was taken to be 0.85 e or 0.74 e for ion pairs with smaller or larger partial charge transfer, respectively – the distinction was made based on CHELPG charge analysis, see Publication I.

In further unpublished work, an attempt was made to fit the pre-exponential factor $\ln A$ to enable a full computational workflow for estimating viscosity. It was hypothesized that $\ln A$, which can be seen as the activation energy for viscosity, was proportional to the conformational properties of the ions or ion pairs. Therefore, conformer searches were conducted and fit $\ln A$ to be inversely proportional to the number of possible conformers and their energies relative to the global minimum. I.e., if an ion has numerous conformations close to its minimum energy level, then its activation energy for lateral movement throughout the condensed phase is also low. However, the combined $E_{\text{a}}^{\text{calc}}$ and $\ln A$ results were, at best, moderate.

2.2. Density Functional Tight-Binding calculations

DFTB was employed via the Geometry, Frequency, Noncovalent, and eXtended Tight-Binding method (GFN2-xTB) as implemented in the xTB software [49], to estimate partial charges of atoms in ionic associates larger than ion pairs. DFTB was chosen because such associates are resource-intensive in DFT.

In practice, trajectories for bulk liquids were obtained via MD simulations, and selected “snapshots” were then recalculated using DFTB. Hirshfeld partial charges were extracted from single-point GFN2-xTB calculations. New atomic partial charges were calculated by averaging the charges of the corresponding atoms within all “snapshots”. Ions more than 15 Å from the geometric center of the box were excluded because the GFN2-xTB calculations were run without periodic boundary conditions, and such ions might have been affected by boundary effects. Finally, the obtained averaged charges were used in subsequent MD simulations.

GFN2-xTB was also used for conformer search of IL pairs and associates. First, the output from a conformer search served as a starting point for adding new IL pairs in the existing DFT workflows, e.g., for estimating ECW, because optimizing new ion pairs or larger associates is very time-consuming, especially if one needs to ensure they reach a global minimum on the energy surface.

Second, conformer search was used to analyze the abundance of different conformers and their relative energies for various IL pairs. This exploratory analysis was run to establish a correlation between E_{int} and $\ln A$ of viscosity, as mentioned in the previous section.

2.3. Molecular Dynamics simulations

Classical MD was run using OPLS-AA-type force fields [50]. The force field parameters for choline and TFSI ions were obtained from References [51,52]. All other force fields were developed using the generic OPLS-AA atom types [21,22]. The Ligandbook repository was used as the starting point for most anions in Publications III and IV [53].

Initial partial charges were calculated using DFT, see Sec. 2.1. Subsequently, MD workflows were run as per the following sections to obtain condensed phases. After that, final partial charges were found using DFTB, as described in Sec. 2.3, and replaced in the force fields per atom type in each ion. The corresponding workflows were restarted with the updated charges. Naturally, this process was repeated for each IL system to provide more realistic partial charges.

In Publications III and IV, Gromacs 5.1.4 was used, while in Publication V, Gromacs 2020 was used [54]. Initial geometries for all simulations were generated using Packmol [55] from individual ion geometries. MDanalysis [56] and VMD [57] software were used to analyze trajectories.

2.3.1. Workflow for melting point prediction

The MD workflow for predicting melting points is summarized in Figure 1 and was structured as follows:

- An initial ionic cluster was packed with Packmol, and a short MD run was performed with a steep integrator
- Solid phases were obtained in a 200 ps *NVT* simulation, where T lowered from 1000 K to 1 K in 100 ps and kept at 1 K for 100 ps
- Coulombic potential wells [58,59] were introduced, and the system was re-organized in six consecutive 500 ps *NVT* simulations
- After the removal of potential wells, the system was equilibrated at 175 K for 2.5 ns with an *NPT* ensemble; then the temperature was increased to 475 K over 30 ns
- The diffusion coefficient (D) dependence on T was fitted during annealing between two distinct phases and reported the temperature of the phase transition
- The above steps were repeated for each IL with two initial packing densities and eight different potential well configurations.

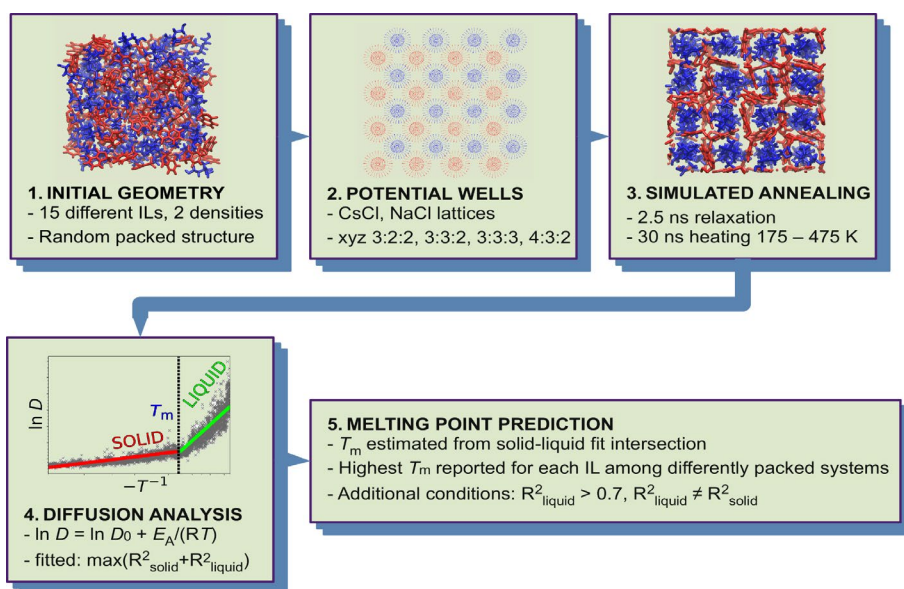


Figure 1. MD workflow for predicting the melting temperature (T_m) of an IL without a known crystal structure. An initially random-packed system was reorganized using Coulombic potential wells arranged in CsCl- or NaCl-type lattices, relaxed after removal of the wells, and annealed from 175 to 475 K. The solid- and liquid-phase regions were identified by linear fits to $\ln D$ as a function of negative inverse temperature, $-T^{-1}$, and T_m was obtained from the intersection of the fits. For each IL, two initial densities and eight potential-well configurations were tested. The highest estimate with R^2 for the solid fit of at least 0.7 and R^2 for the liquid fit of at least 0.9 was reported.

The sizes of the initial systems were chosen so that the orthorhombic simulation unit cell would extend by more than 2.8 nm in all dimensions (yielding 128–350 ion pairs, depending on ion size). Two different packing densities were chosen based on the anion: sulfonimides were packed at 1.4 kg/dm³ and 1.6 kg/dm³; carboxylic and benzoic acids were packed at 1.0 kg/dm³, 1.2 kg/dm³, or 1.4 kg/dm³. In the annealing step, volume (and thus density) was not constrained. For each system, eight configurations of potential wells were obtained by combining CsCl and NaCl ionic lattices with lattice-vector ratios of 3:2:2, 3:3:2, 3:3:3, and 4:3:2 for *x:y:z* coordinates, respectively. The potential wells interact with ions purely electrostatically, scaling linearly with distance, thereby attenuating attraction very close to the center of the well, since the wells lack Lennard-Jones repulsion.

With each system, six consecutive runs were made, each a 500 ps *NVT* simulation. The interaction strength of the potential wells is toned down with each subsequent run. In runs one, three, and five only the anions were allowed to move while the positions of the cations were restrained. In simulations two, four, and six the cations moved while the anions were restrained. The temperature was decreased from 1000 K to 1 K within 400 ps and held at 1 K for the final 100 ps of each simulation run. For the simulated annealing step, the potential wells were removed, and the system was equilibrated at 175 K for 2.5 ns with an *NPT* ensemble. After this, the temperature was increased to 475 K over 30 ns at 10 K/ns. A pressure of 1 bar and a compressibility of $4.5 \cdot 10^{-5}$ bar⁻¹ were imposed using the isotropic Berendsen pressure coupling algorithm and velocity-rescaling temperature coupling. A cut-off of 1.3 nm was defined for van der Waals and electrostatic interactions. The particle-mesh Ewald model was used with 0.1 nm Fourier spacing for long-range electrostatics.

Diffusion coefficient *D* was calculated during annealing from the mean square displacement during annealing. *D* follows the Arrhenius equation:

$$\ln D = \ln D_0 - E_a / (RT),$$

where *E_a* is the activation energy, *R* is the universal gas constant, and *T* is the temperature. Thus, the logarithmic *D*–*T* dependence of a phase with a single mechanism of diffusion is linear.

Finally, the obtained *D*–*T* dependence was distributed into two regions, solid and liquid, by maximizing the correlation coefficients of the linear fits of both phases. While doing that, there is a significant change required in slope between the two phases; the fits for the solid phase are $R^2 \geq 0.7$, and for the liquid phase $R^2 \geq 0.9$. These requirements were added to ensure that two distinct phases are detected. Melting temperature is the *T* value at the boundary between the two-phase fits.

For each IL, the maximum eligible melting temperature is reported across the different systems, as it corresponds to the most stable (and thus probably the most realistic) solid phase.

2.3.2. Workflow for maximal surface charge density

To determine the maximum surface charge density, a one-electrode model with counterions was used. The electrode was a graphene-like slab with a size $4.26\text{ nm} \times 3.94\text{ nm}$ (640 carbon atoms). Five replicas with the same type of counter-ion and a variable number of such ions were created. The electrode in each system was charged so the overall charge of the system would be zero, assuming ionic charge is $\pm 1e$.

A steep energy minimization run was conducted for 10 ps with 1 fs timestep, followed by a 20 ps equilibration step with 0.5 fs timestep, generating velocities for $T = 100\text{ K}$. Next, a 1 ns *NVT* run was performed with a 1 fs timestep and velocities corresponding to 353 K. The Verlet cut-off scheme was employed, and *xy*-periodic boundary conditions (i.e., parallel to the electrode surface) were applied with the particle-mesh Ewald and 3dc Ewald correction. For details see Ref. [19] and references there.

The trajectories of the 1 ns *NVT* simulation runs were analyzed, excluding the first 10 ps of each trajectory. The density profile of a central atom type for each counter-ion was extracted with the VMD software (e.g., the phosphorus for PF_6^-). On one side, the contact layer is bordered by the electrode. On the other side, the contact layer was terminated at a distance where the cross-sectional density of the central atom type dropped below a given threshold. The density was then integrated over all slices in this region to evaluate the packing density of the contact layer.

This approach was implemented in custom Python code and visually validated in VMD. This ensured that rotational conformations of counter-ions were not accidentally assigned as the formation of a second layer, and that the formation of adlayers in the hollow spaces of the contact layer would correctly be assigned as the formation of a second layer.

2.4. Machine Learning modeling

The limited precision of the MD-based melting point predictions motivated the development of an alternative ML-based approach. This workflow integrated experimental IL properties and computational descriptors to predict melting points. Experimental properties (density, melting point, refractive index, molecular weight, and ionic conductivity) were accessed from the NIST IL Database [60]. To maximize data quality and consistency, the dataset excluded metal-containing compounds and mixtures (ILs containing more than one cation or anion). This selection resulted in a dataset of approximately 418 ion pairs.

For each ion pair, the molecular geometry was generated from the SMILES code and optimized in a vacuum as single pairs and isolated ions. Two categories of descriptors served as model inputs. First, topological descriptors included the number of hydrogen-bond donor groups (H–Cl, H–Br, H–O, and H–N bonds), the number of hydrogen-bond acceptor groups (Cl, Br, O, and N atoms lacking a formal positive charge), and the number of C–H bonds. Second, chemical

descriptors – from DFT (PBE+D4+gCP/DEF2-SVP) and DFTB (GFN2-xTB) calculations – included interaction energy, dipole moment, partial charge, dispersion energy, HOMO–LUMO gap, and conformation energy (defined as the energy difference between ions in the pair geometry and in the relaxed geometry).

The XGBoost algorithm was used to fit a model for predicting melting points [61]. The dataset was split into a training set (80%) and a test set (20%) using random sampling. The model training utilized 1000 estimators with a learning rate of 0.1, as defined in the XGBoost Python package. Precision metrics (root mean square error and mean absolute error) were calculated using the test set. The Scikit-Learn package was employed to evaluate property–melting point relationships [62].

3. RESULTS

Chemically diverse ILs were studied to examine how ion composition, electronic structure, and molecular shape affect the properties discussed in this section. In Publication I, as illustrated in Figure 2, the conventional IL set combined cations containing aromatic nitrogen centers, such as pyridinium and imidazolium, with cations containing saturated quaternary nitrogen centers, such as ammonium and pyrrolidinium. The anions represented halides, borates, phosphates, sulfonates, sulfonimides, and cyanide-containing species. This set included fluoride-containing anions, e.g., $[\text{TFSI}]^-$ – bis(trifluoromethanesulfonyl)azanide, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, and $[\text{FEP}]^-$ – tris(pentafluoroethyl)trifluorophosphate; and cyanide-containing anions, such as $[\text{B}(\text{CN})_4]^-$, $[\text{C}(\text{CN})_3]^-$, $[\text{N}(\text{CN})_2]^-$, and $[\text{SCN}]^-$. The chemical variation focused on separating the effects of cation and anion properties on interaction energies, charge distribution, electrochemical stability, and the activation energy of viscosity [9,11].

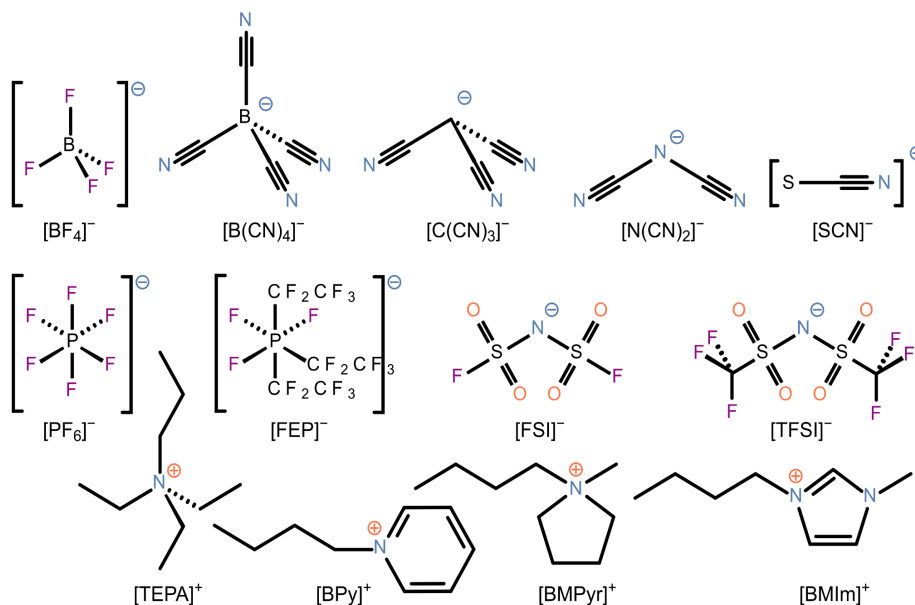


Figure 2. Two-dimensional chemical structures of the anions and cations combined to form the set of 48 conventional IL ion pairs used to evaluate interaction energies, charge transfer, electrochemical stability, and the activation energy of viscosity. Anions are shown in the upper rows and cations in the lower row. Cl^- , Br^- , and I^- were also included in the calculations but are not shown. Ion abbreviations and chemical names are given in the List of acronyms and notations.

In Publications III and IV, as illustrated in Figure 3, the set of ions represented biofriendly choline-based ILs. Choline cation $[\text{Ch}]^+$ was combined with anions derived from carboxylic acids, including acetate, isobutanoate, lactate, isovalerate, 2-methylbutanoate, malonate, glutarate, and citrate. The benzoic acid derivatives comprised benzoate, salicylate, acetylsalicylate, and ibuprofenate, while acesulfamate and saccharinate represented sulfonimide-derived anions. $[\text{Ch}][\text{TFSI}]$ was included as a reference to a commonly studied fluorinated IL. This set focused on examining melting points and actuator behavior in ILs selected primarily for low toxicity and biodegradability [2,3].

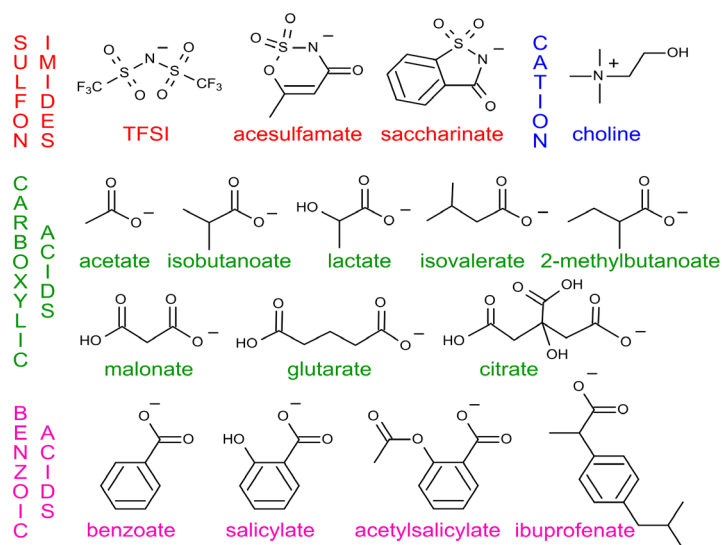


Figure 3. Two-dimensional chemical structures of $[\text{Ch}]^+$ and the anions used to construct the 15 choline-based ILs studied by MD. The anions are grouped as sulfonimide-derived, carboxylate, and benzoate species. $[\text{Ch}][\text{TFSI}]$ was included as a fluorinated reference IL. This set was used for melting point prediction and for comparison of biofriendly IL electrolytes. Ion abbreviations and chemical names are given in the List of acronyms and notations.

For the interfacial study in Publication V, as illustrated in Figure 4, ions were classified according to their packing at a charged surface. Ball-like spherical ions retained a similar orientation as the surface charge increased, forming compact contact layers. Head-tail ions contained a charged head connected to an alkyl tail and changed their packing through head and tail reorientation. Roly-poly ions changed between parallel and perpendicular orientations as the contact layer became denser. Teeter-totter ions contained two similar groups connected through a central atom and largely retained their interfacial orientation as the surface charge increased.

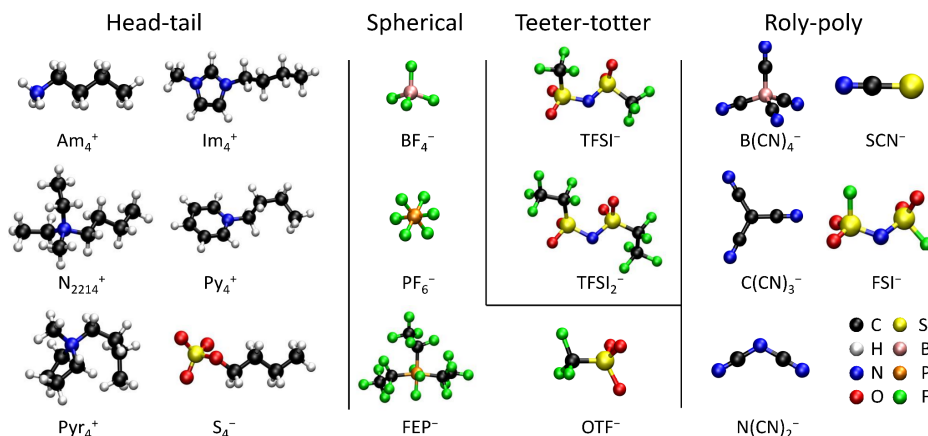


Figure 4. Ball-and-stick models of representative ions assigned to four structural classes according to their packing at a charged surface: head-tail, spherical or ball, teeter-totter, and roly-poly. Head-tail and roly-poly ions can reorient as the contact layer becomes denser, whereas spherical and teeter-totter ions largely retain their orientation. The atom colors are identified in the figure. Ion abbreviations and chemical names are given in the List of acronyms and notations.

Together, the sets in Figures 2–4 cover conventional, biofriendly, fluorine and cyanide-containing, aromatic, aliphatic, rigid, and flexible ions. The chemical and structural classifications provided a common basis for testing computational methods and, as discussed below, predicting interaction energies, transport-related quantities, strain, melting points, electrochemical stability as ECW, maximum packing densities, and structure-determined interfacial potentials.

3.1. Calculation of interaction energy

Ion-pair interaction energy was used to compare performance of density functionals. This quantity characterizes cohesion in ILs and correlates with viscosity, diffusion coefficients, and surface tension. The reference interaction energies were calculated using DLPNO-CCSD(T)/CBS. The reference interaction energies span from -410 to -290 kJ mol $^{-1}$, covering both strongly and weakly associated ion pairs. The DFT calculated E_{int} values were compared directly with the reference energies [9].

Figure 5 shows that SCAN+CP+D3* functional is close to this line across most of the energy range. The deviations increase for several strongly interacting ion pairs. In particular, [BPy][Cl], [BPy][Br], and [BPy][I] lie below the diagonal, indicating that SCAN+CP+D3* predicts interaction energies that are too negative, arising from the self-interaction error, as shown in previous work [63].

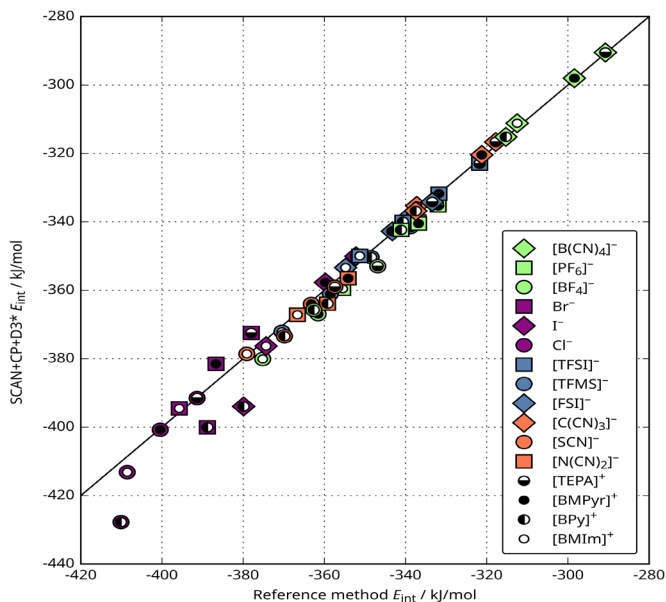


Figure 5. Interaction energies E_{int} calculated with SCAN, CP, and refitted D3 compared with the DLPNO-CCSD(T)/CBS reference values for the individual ion pairs. See Sec. 2.1 for details on notation. Points below the diagonal line correspond to interaction energies that are too negative, most notably for $[\text{BPy}]^+$ -halide anion ion pairs. The surrounding marker identifies the anion and the inner symbol identifies the cation. Ion abbreviations are given in the List of acronyms and notations.

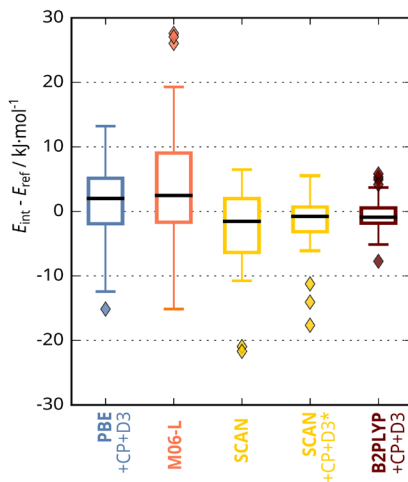


Figure 6. Box-and-whisker distributions of the interaction-energy error, $E_{\text{int}} - E_{\text{ref}}$, relative to DLPNO-CCSD(T)/CBS. Boxes summarize the central distribution and diamonds denote outlying ion pairs. SCAN with CP and refitted D3 gives a narrow distribution centered close to zero, comparable to the more expensive B2PLYP method with CP and D3.

Figure 6 compares the distributions of interaction-energy errors for the best-performing variant of each tested functional: SCAN, SCAN(+CP+D3), PBE+CP+D3, M06-L, and B2PLYP+CP+D3. All methods reproduce the general energy range, but their error distributions differ. SCAN+CP+D3* gives a narrow distribution centered close to zero, whereas PBE+CP+D3 and M06-L show broader variation. Here * implies that the D3 was refitted to minimize the standard deviation to 2.9 kJ mol⁻¹. B2PLYP+CP+D3 yields a comparable standard deviation of 2.7 kJ mol⁻¹, although its computational cost is much higher due to the inclusion of MP2 [9]. Note that in the case of SCAN+CP+D3* refitting the D3 parameters corrected the bias rather than narrowing the remaining spread. This result suggests that further refinement of the dispersion contribution may improve the accuracy of interaction energy predictions where the dispersion is an essential component [9].

The interaction energy results indicate that SCAN is an efficient method for IL associates. Its accuracy and nonhybrid form make it suitable for computational screening and DFT-based molecular dynamics simulations, where repeated electronic-structure calculations limit the use of more expensive methods. At the time of Publication II, calculations with the SCAN calculations required a developer version of Gaussian 03. Later studies showed computational instability of SCAN, which motivated the development of a regularized r²SCAN functional and a composite r²SCAN-3c functional with included dispersion and counterpoise corrections [28,64]. In 2026, the Materials Project incorporated r²SCAN calculations into its core database. Yet, despite much success, self-interaction error remains the most relevant issue for SCAN [65].

The dipole moment analysis provides the most straightforward way to test the impact of the self-interaction error on the electronic density. Across the full dataset, SCAN yielded a mean absolute deviation of 0.131 D, compared with 0.216 D for PBE, 0.110 D for M06-L, and 0.043 D for B2PLYP relative to the reference DLPNO-CCSD(T). SCAN therefore described dipole moments more accurately than PBE but less accurately than M06-L, which is known to resile the SIE [63]. This comparison is useful because both dipole moments and interaction energies depend strongly on charge separation within the ion pair. Although atomic partial charges were not compared directly, the combined energy and dipole results provide indirect evidence for the quality of the charge distribution predicted by SCAN.

The main limitation appears for ion pairs containing chloride, bromide, and iodide. For these systems, SCAN gave the largest standard deviation of the dipole moment error among the tested nonhybrid functionals. These deviations were attributed to the self-interaction error, which increases partial charge transfer in ion pairs with closely spaced frontier orbitals. Introducing exact exchange through SCAN0 reduced the mean absolute dipole-moment deviation to 0.056 D, comparable to B2PLYP, while remaining at a much lower computational cost. These results show that SCAN performs well for most IL ion pairs, but systems with pronounced charge transfer require a hybrid functional or a direct SIE correction [9].

3.2. Prediction of viscosity

Next, it was examined whether the E_{int} of an ion pair could describe a dynamic property of the corresponding IL. Viscosity arises from collective molecular motion, whereas the calculations considered isolated ion pairs. The question was therefore whether the energetic cost of local ionic rearrangement retains a systematic relation to the experimentally derived activation energy of viscosity [11].

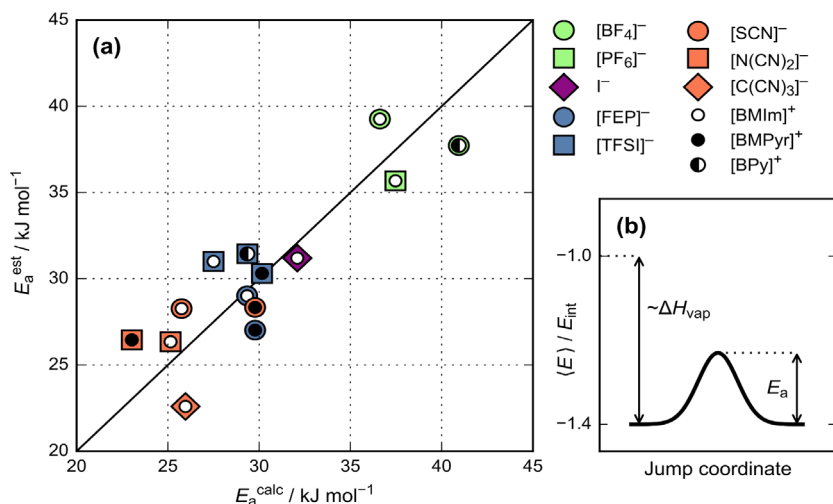


Figure 7. (a) Activation energy of viscosity estimated from the ion pair interaction and dispersion energies (on the y-axis, in the text denoted as E_a^{calc}) compared with the value obtained from the experimental viscosity–temperature dependence (on the x-axis, in the text denoted as E_a^{exp}). The surrounding marker identifies the anion and the inner symbol identifies the cation. Ion abbreviations are given in the List of acronyms and notations. (b) Schematic potential energy profile for a diffusional jump. E_a is the barrier between neighboring local environments, whereas approximately ΔH_{vap} is required to remove the ion pair completely from the liquid.

Figure 7a shows that the computational and experimental activation energies follow the diagonal across the studied ILs. The calculated values (using Eqs. in Sec. 2.1.3) span approximately 25–40 kJ mol^{-1} and reproduce the main differences between the anion families. ILs containing $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ have high activation energies, consistent with strong cation–anion association. The cyanide-based anions $[\text{N}(\text{CN})_2]^-$ and $[\text{C}(\text{CN})_3]^-$ generally give lower values, while $[\text{TFSI}]^-$ and $[\text{FEP}]^-$ occupy an intermediate region. The remaining scatter indicates that E_{int} is a useful descriptor, but it does not capture all structural contributions to ionic motion [11].

The physical interpretation of the established correlation is illustrated in Figure 7b. An ion moves through the liquid by leaving one local ionic environment and entering another. This diffusional jump requires a partial disruption of the surrounding interactions, thereby creating the activation barrier E_a . Complete removal of an ion pair from the liquid requires a much larger amount of energy, approximately equal to the enthalpy of vaporization. The activation energy is therefore related to only a fraction of the total cohesive energy. Within the pseudolattice description, this fraction corresponds to the difference between the interaction energies of the stable and transition configurations. Stronger cation–anion interactions deepen the local energy minimum and generally increase the barrier to translational motion [11].

The agreement in Figure 7a supports the use of E_{int} values for rapid estimates of E_a . This interpretation assumes that the dominant mass-transport mechanism remains similar across the studied ILs. Differences in ion packing, accessible conformations, entropy, and diffusion pathways can alter the established relationship and explain the observed scatter. The approach therefore, predicts a transport-related energy descriptor rather than true viscosity [11].

3.3. Prediction of strain

The interaction energy model described above provides an estimate of the activation energy, which represents the temperature-dependent contribution to viscosity. Calculation of absolute viscosity also requires the pre-exponential factor A in the equations presented in Section 2.1.3. Conductivity can likewise be related to viscosity through transport equations. A reliable description of collective ionic motion requires structural information in addition to interaction energies and ion volumes. It was therefore tested whether a simulation-derived structural descriptor could predict a more complex macroscopic response: the strain difference of an electromechanical actuator, whose response relies on ion movement in an IL electrolyte [11].

The strain was compared with ion size and ionic conductivity. A volume-based interpretation suggests that larger migrating ions produce greater electrode expansion, while high conductivity supports rapid ion redistribution. These descriptors captured part of the actuator response. The high strain produced by [Ch][Ib] relative to [Ch][Mal] and the other studied choline ILs indicated that the mechanically active species were ionic clusters rather than individual ions [3].

The MD simulations revealed cation–cation correlations associated with interactions between the ammonium and hydroxyl groups of choline. Short-range packing reflects a combination of steric, Coulombic, and hydrogen-bonding interactions. The second maximum of the cation–cation radial distribution function provided a clearer distinction between the studied ILs because the oscillatory shell structure was more regular in this region. Therefore, the natural logarithm of this peak height was converted into a descriptor of the interaction associated with the second cation–cation shell [3].

Figure 8 compares the measured strain differences for PPy-PVdF actuators with those predicted using the cation–cation correlation descriptor. The data follow the diagonal across the six choline ILs studied. The linear relation has $R^2 = 0.92$ and an intercept close to zero [3]. This agreement supports the interpretation that strain depends on the structure of the migrating ionic clusters. Wider or more strongly correlated cationic shells interact more strongly with neighboring polymer chains and produce a larger mechanical response. The anion modifies the cation–cation correlation, so each choline IL forms clusters with distinct mechanical effects. Therefore, positive ionic clusters were identified as the mobile species responsible for the observed trend in the PPy-PVdF actuators [3].

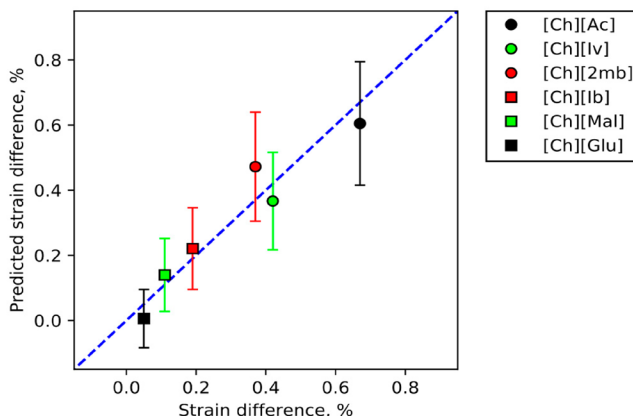


Figure 8. Measured and predicted strain differences for PPy-PVdF actuators containing six choline-based ILs. The dashed diagonal denotes equality between prediction and experiment, and the error bars correspond to plus or minus one standard error. Ac, Iv, 2mb, Ib, Mal, and Glu denote acetate, isovalerate, 2-methylbutanoate, isobutanoate, malonate, and glutarate, respectively, and are illustrated in Figure 3.

3.4. Predicting melting points

3.4.1. Prediction of pure IL melting points

15 choline-based ILs were examined using an MD workflow for melting-point prediction (Sec. 2.2). Fourteen systems combined choline with biofriendly carboxylate, benzoate, or sulfonimide-derived anions, while [Ch][TFSI] served as a reference. The aim was to test whether melting points could be estimated before synthesis when the crystal structures were unknown [2].

Melting-point prediction requires a representative solid phase. Crystallization of ILs is too slow to be simulated directly by atomistic MD, and crystal structures were known for only four of the studied compounds. Therefore, ordered solids were generated using Coulombic potential wells arranged in several NaCl- and CsCl-type lattices. Gradual weakening and removal of the wells allowed the ions

to relax from these initial arrangements. Then each solid was heated and identified melting from the change in the temperature dependence of ionic self-diffusion [2].

Figure 9 shows the melting point analysis for choline ibuprofenate. The initial solid structure was generated at 1.2 kg dm^{-3} using potential wells arranged in a CsCl lattice with a 4:3:2 vector ratio. The temperature dependence of the diffusion coefficient revealed two distinct regimes: a low-temperature solid phase with limited diffusion (red fit, $R^2 = 0.87$) and a steeper high-temperature liquid phase (green fit, $R^2 = 0.91$). The intersection of these fits yielded a predicted melting point of 330 K, whereas the experimental value was 342 K [2,3].

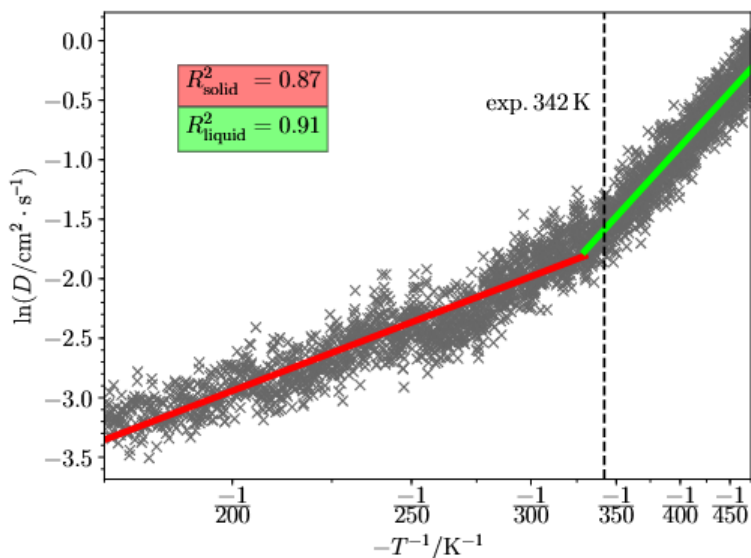


Figure 9. Dependence of the diffusion coefficient (D) on temperature (T) during simulated annealing of choline ibuprofenate, shown as $\ln D$ versus negative inverse temperature, $-T^{-1}$. Red and green lines fit the solid and liquid regimes, with $R^2 = 0.87$ and $R^2 = 0.91$, respectively. Their intersection gives $T_m = 330 \text{ K}$. The vertical dashed line marks the experimental value of 342 K.

The simulated phase transition was gradual rather than abrupt. During this interval, the structure still resembled the initial solid, although ionic mobility had already increased. Different diffusion mechanisms may have different activation energies and pre-exponential factors, which may explain the curvature of the diffusion–temperature dependence. The melting point was therefore defined from the intersection of the solid and liquid fits, and correlation criteria were applied to exclude trajectories without sufficiently distinct regimes [2].

Across the entire dataset, the predicted melting points yielded a root-mean-square error of 18–24 K, depending on the selected experimental reference. The workflow gave this error without using experimental crystal structures or a training set of related compounds. The method can thus be used to screen ILs before synthesis and crystallization.

Still, several experimental factors affect the accuracy of the method. Reported melting point values can vary for the same ILs due to differences in water content, residual conjugate acids, other impurities, and experimental heating rates. Some choline salts formed glassy or poorly crystalline phases, which complicates comparison with a simulated ordered solid. From the computational point of view, multiple diffusion mechanisms broaden the simulated transition region, while force field parametrization affects the balance between Coulombic and non-Coulombic interactions.

The influence of heating rate was tested because direct heating simulations can shift the observed phase transition. The predicted melting points depended on the applied rate and tended to converge for most ILs. Faster heating usually produced lower melting-point estimates, opposite to the increase expected from superheating. This trend was tentatively attributed to local overheating or to the response of the velocity-rescaling temperature-coupling algorithm to rapid heating. Ultimately, the rate of 10 K ns^{-1} reproduced the experimental ordering across most of the systems studied [2].

As shown in Figure 10, simulations at several heating rates also enabled extrapolation to 0 K ns^{-1} , representing infinitely slow heating. The extrapolated values approached the experimental results for most ILs. Across the full dataset, the resulting root-mean-square error was 19–23 K, similar to the 18–24 K obtained at 10 K ns^{-1} . Exclusion of choline 2-methylbutanoate, which behaved as an outlier, reduced the extrapolated error to 12–18 K. Heating-rate extrapolation therefore provides a direct measure of rate sensitivity and can improve individual predictions [2].

The partial charge model had a stronger effect than the heating rate. Charges derived from isolated ions constrained the total ionic charges to $\pm 1\text{ e}$ and produced strongly overestimated melting points. Uniform scaling to $\pm 0.8\text{ e}$ weakened the Coulombic interactions and improved several predictions, although this empirical correction did not represent the charge distribution within the condensed phase. Therefore, Hirshfeld charges were calculated from GFN2-xTB calculations of ionic clusters extracted from MD trajectories. Incorporation of these condensed-phase charges markedly improved the melting-point predictions for most tested systems. This result shows that both effective ionic charge and intramolecular charge distribution control the simulated stability of the solid phase [2].

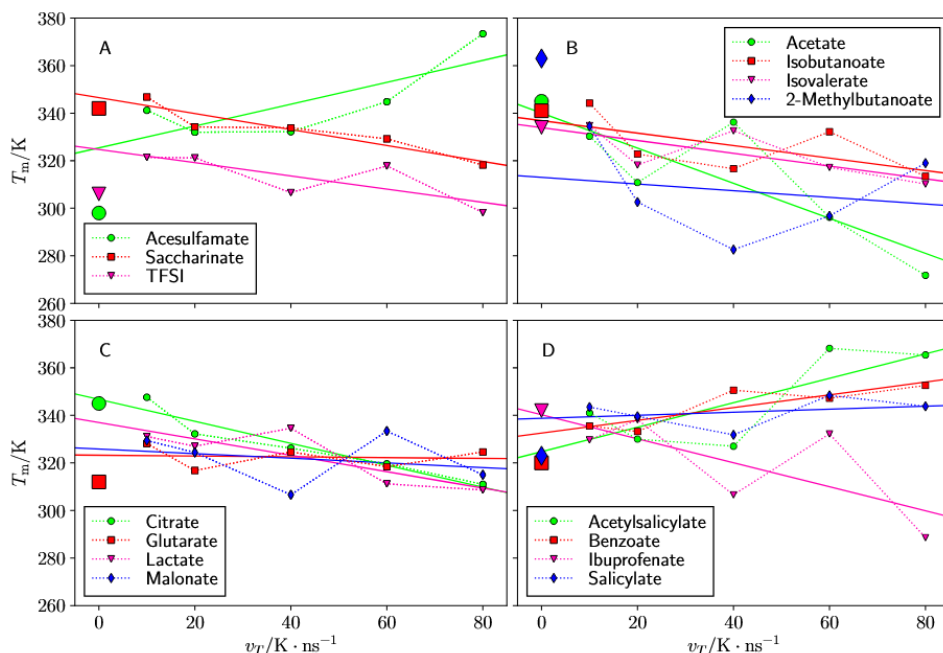


Figure 10. Dependence of the predicted melting temperature T_m on the heating rate v_T for (A) choline sulfonimides, (B) choline carboxylates containing one carboxyl group, (C) choline carboxylates containing two carboxyl groups, and (D) choline benzoates. Small markers show the MD estimates at the simulated heating rates. Large markers at $v_T = 0 \text{ K ns}^{-1}$ show the experimental T_m values, and the solid regression lines extrapolate the simulated results to the limit of infinitely slow heating.

3.4.2. Prediction of IL mixtures' melting point

In subsequent unpublished work, the same MD workflow was applied to choline-based IL mixtures. Each simulation contained 210 ion pairs, regardless of the resulting simulation box dimensions. Exploratory simulations with water present were also performed to examine how residual water could shift the phase transition. These calculations remained preliminary because the effect depended strongly on composition and water content. The solid-generation and annealing procedure followed the method developed for pure ILs [2].

For the mixtures, the melting point analysis was revised. The pure liquid workflow assigned a single melting temperature from the intersection of the fitted solid and liquid diffusion regimes. The diffusion–temperature curves of the mixtures often showed broader transitions. Therefore, a temperature interval was defined for the phase change rather than one discrete value. The lower and upper limits represented the region in which the diffusion behavior changed from the solid-like to the liquid-like regime, as illustrated in Figure 11.

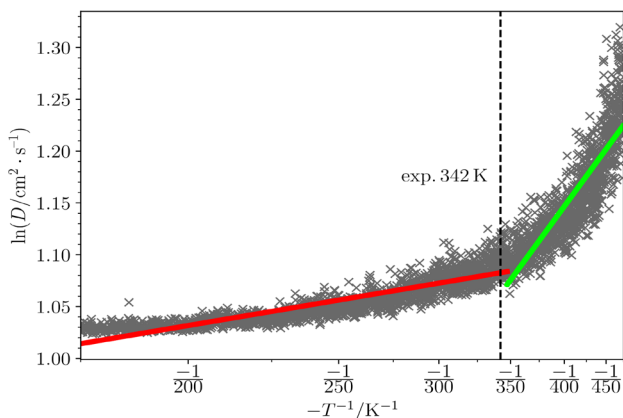


Figure 11. Representative dependence of $\ln D$ on $-T^{-1}$ during simulated annealing of a choline-based IL system in the mixture study. The red and green lines fit the solid-like and liquid-like regimes, respectively, and the vertical dashed line marks the experimental reference temperature of 342 K. In the mixture analysis, the data between the two fitted regimes were treated as a phase-transition interval rather than assigning a single T_m .

For most systems, the available experimental melting temperatures fell within the predicted phase-transition ranges. Choline 2-methylbutanoate was the main exception. This compound was also the largest outlier in the pure IL study, indicating that its behavior is difficult to represent with the present force field and transition-detection procedure [2].

Composition-dependent melting ranges were also constructed for IL mixtures. These calculations reproduced the expected decrease in melting temperature for several compositions. The uncertainty of the predicted transition range was of the same order as the melting-point depression caused by mixing. The resulting phase diagrams, therefore, did not distinguish the composition trend with sufficient precision for publication.

Experimental reference values introduced significant uncertainty. Melting temperatures of choline-based ILs are sensitive to water content, residual conjugate acids, and other impurities. Such factors shift both pure-component melting points and mixture phase boundaries. The experimental values used to develop and assess the model therefore contained uncertainty comparable in magnitude to the simulated melting-point shifts. Consequently, distinguishing errors in force field parametrization and phase-transition analysis from variation in reference measurements proved difficult.

3.4.3. Prediction of melting point with machine learning

The limitations of the MD-based workflow motivated the development of an alternative ML-based approach. The ML models took into account experimental and computational data, as described in Sec. 2.4. Herewith the precision of the

tested ML models was relatively unaffected by the choice between DFT and DFTB methods: the PBE/DEF2-SVP approach yielded a mean average error of 25 K and a root mean square error of 43 K, while the faster GFN2-xTB calculations gave a mean average error of 29 K and a root mean square error of 42 K.

Despite similar precision, the DFT-based calculations struggled with convergence; only 240 of 418 ion pair calculations terminated successfully with PBE/DEF2-SVP, compared to 348 successes with GFN2-xTB. However, the GFN2-xTB method has managed to optimize ill-defined geometries that the more rigorous DFT calculations failed to converge. Manual handling of problematic geometries, which were automatically generated from SMILES using OpenBabel, would likely improve the precision for both DFT and DFTB within the presented workflow.

The choice of descriptors affected the prediction errors more than the choice of computational method. For the PBE/DEF2-SVP method, an ML model that included all descriptors produced a mean average error of 25 K and a root mean square error of 43 K. Models excluding either computational or experimental descriptors yielded mean average errors exceeding 30 K and root mean square errors of 50 K.

Table 2 summarizes the permutation importance of descriptors for the PBE/DEF2-SVP method, where a value closer to “1” indicates that the descriptor completely and uniquely determines the estimate, and “0” indicates complete independence. Partial charge and the number of hydrogen bond donors were identified as the most important descriptors for the ML modeling. Hence, the partial dependence for partial charge in Figure 12 indicates that charges closer to unity decrease the predicted melting point.

Table 2: Permutation importance of descriptors in the ML model based on PBE/DEF2-SVP calculations.

Weight	Descriptor
0.1701 $\pm$ 0.3990	Partial charge
0.1050 $\pm$ 0.0804	Number of hydrogen bond donors
0.0811 $\pm$ 0.1043	Dipole moment
0.0584 $\pm$ 0.0379	Density
0.0472 $\pm$ 0.1951	Ionic conductivity
0.0198 $\pm$ 0.0308	Dispersion energy
0.0144 $\pm$ 0.0278	Number of C–H bonds
–0.0186 $\pm$ 0.0277	Interaction energy
–0.0197 $\pm$ 0.0397	Molecular weight
–0.0231 $\pm$ 0.0182	Refractive index
–0.0531 $\pm$ 0.0806	Conformation energy
–0.0580 $\pm$ 0.2022	Number of hydrogen bond acceptors
–0.0590 $\pm$ 0.0667	HOMO–LUMO gap

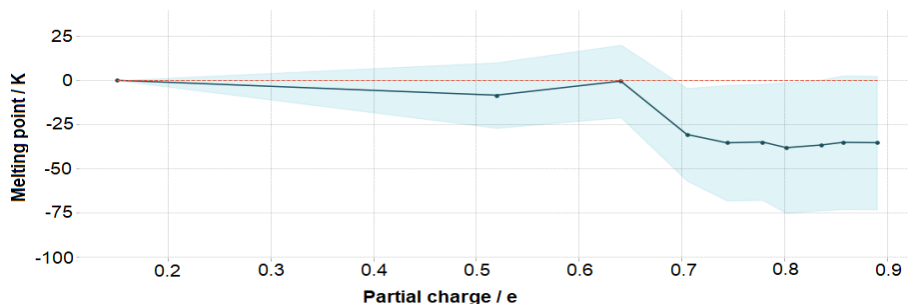


Figure 12. Partial dependence of the ML-predicted melting temperature T_m on the partial ionic charge, expressed in units of the elementary charge e , for the model based on PBE/DEF2-SVP descriptors. The curve shows the average change in predicted T_m relative to the model baseline. The shaded region shows the variation of the estimate, and the dashed red line marks zero change. Partial charges closer to unity lower the predicted T_m . This data is unpublished.

The ML-based melting point prediction workflow took an order of magnitude less time to develop and two orders of magnitude less time/cost to execute than the MD-based workflow in Publication III. While its prediction errors remained higher than those of Publication III, it included hundreds of ILs compared to 15 ILs in Publication III and is easily extendable with new ILs, thereby improving the predictive power of the model.

Overall, considering performance, speed, and robustness, it is hard to see any upside to the MD-based melting point prediction in this thesis, i.e., when the crystal structure is unknown and a potentially large number of ILs are of interest. However, adapting such an ML workflow to study mixtures and find eutectic compositions would be yet another challenge.

3.5. Prediction of the potential of decomposition

The resistance of ILs toward oxidation and reduction was estimated from calculated EA and IE values, as described in Sec. 2.1. These quantities describe the energetic cost of adding or removing an electron and therefore provide direct descriptors of cathodic and anodic decomposition, in the case of a reaction limited by an electron transfer step. The modified Δ SCF approach used in this study included the stabilizing effect of the counter-ion, which provided a first approximation to the ionic environment while retaining computational efficiency [11].

Figure 13 presents the EA and IE values for 48 ion pairs. Ion pairs in the lower-left region have the highest predicted resistance toward both reduction and oxidation. Movement to the right indicates lower resistance to reduction, while movement upward indicates lower resistance to oxidation. Separating the points into groups shows that electrochemical stability depends on the electronic properties of both ions rather than on either component alone [11].

The variation in Figure 13 is closely connected to the charge distribution within the ion pairs. Electron transfer becomes more favorable when the electronic structures of the cation and anion permit greater charge redistribution. Charge transfer from the anion to the cation was therefore examined using CHELPG charge analysis. Figure 14 shows that the calculated charge transfer ranges from approximately $0.05e$ to $0.45e$ across the studied ion pairs. The systematic variation across both cation and anion families confirms that charge transfer is a property of the complete ion pair [11].

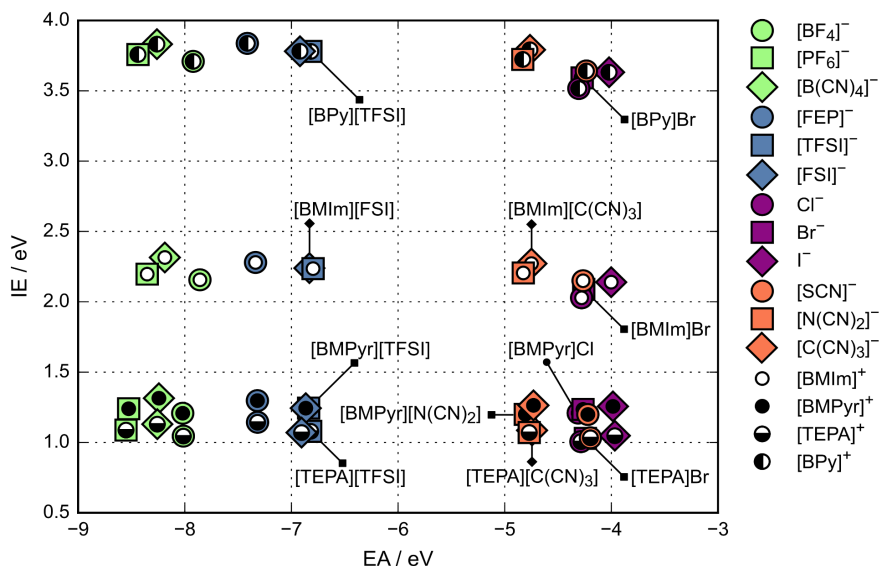


Figure 13. Electron affinity (EA) and ionization energy (IE) of the 48 ion pairs, calculated using the modified Δ SCF method with the counter-ion included as a first approximation to the ionic environment. In the sign convention used here, ion pairs in the lower-left region have the greatest predicted resistance to both reduction and oxidation. Movement to the right or upward indicates decreasing resistance to reduction or oxidation, respectively. The surrounding marker identifies the anion and the inner symbol identifies the cation. Ion abbreviations are given in the List of acronyms and notations.

Larger charge transfer indicates that the ions redistribute electron density more readily. This behavior is consistent with a lower resistance of the anion toward oxidation and of the cation toward reduction. Charge distribution, therefore, provides a natural link between the electronic structure of an ion pair and its predicted decomposition limits. Figure 14 also explains part of the grouping observed in Figure 13: ion combinations with stronger charge transfer tend to occupy regions associated with lower relative electrochemical stability [11].

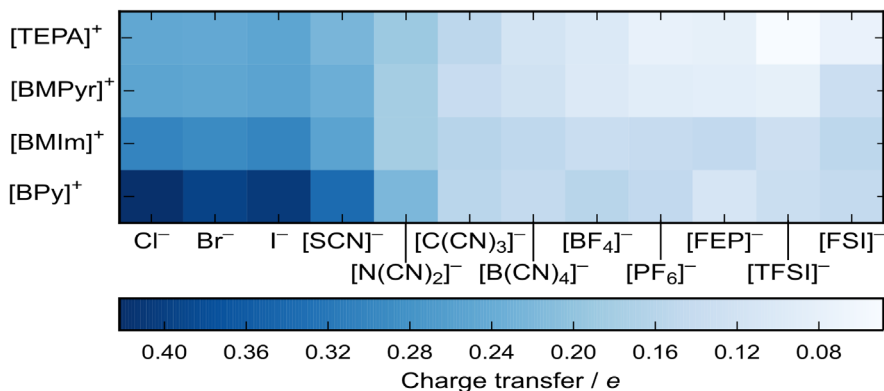


Figure 14. CHELPG charge transfer from anion to cation for the set of conventional ion pairs. Rows identify the cation and columns identify the anion. Darker cells correspond to greater anion-to-cation electron density redistribution. Ion abbreviations are given in the List of acronyms and notations.

This interpretation requires care because charge transfer, electron affinity, and ionization energy are sensitive to the SIE of density functional approximations. The error can produce excessive delocalization of electron density between ions and therefore distort both the calculated charges and the predicted decomposition energies. This effect was reduced by using a hybrid functional for the single-point calculations, while recognizing that the remaining charge-related values are best used for relative comparison rather than as exact decomposition potentials [11]. In the later study, single-ion EA and IE values were used to estimate ECW values for a larger set of ILs. Both conventional and alternative redox assignments were considered by allowing the cation or anion to define either decomposition limit. These calculations provided upper estimates because they excluded solvation, electrode interactions, specific reaction pathways, and the electrical double-layer structure. The values were therefore used to compare ILs and to define approximate limits for interfacial processes [19].

3.6. Prediction of the potential of monolayer charge

The potential of monolayer charge (φ_M) is the electrode potential at which a monolayer of counter-ions exactly screens the surface charge density (σ). In the phenomenological model, this condition corresponds to $\sigma = -\theta_M$, where θ_M is the maximum packing density of ions in the contact layer. At this point, the contact layer compensates the electrode charge without requiring charge compensation by the following ionic layers. φ_M was therefore used as a structure determined reference point for distinguishing true monolayer formation from saturated over-screening [19].

This distinction is needed because ordered interfacial layers are often interpreted as evidence of crowding, even when the experiment does not directly identify both counter-ions and co-ions in the interfacial layers [66]. Earlier theories and simulations introduced the competition between overscreening and crowding as a central feature of IL electrical double layers [67,68]. Later simulations connected the overscreening-to-crowding transition to the maximum density of counter-ions in the contact layer [69,70]. θ_M and φ_M were therefore treated as practical reference quantities for judging whether a proposed crowded state is physically reachable within the ECW [19]. This approach, developed in Publication V, was further improved to show that φ_M is well-defined in simulations and can serve as the criterion for the overscreening-to-crowding transition [66,71].

In Publication V, φ_M was estimated from θ_M and the geometry of the ions. After shifting the surface charge plane to the idealized metal position [72], the estimate becomes $\varphi_M = \theta_M r / (\epsilon_r \epsilon_0)$, where r is the contact radius of the ion, ϵ_r is the relative permittivity, and ϵ_0 is the vacuum permittivity [72].

Figure 15 illustrates how the one- and two-electrode MD simulations can be used to estimate θ_M and φ_M . Curves show $|\theta|$ as a function $|\sigma|$; Circles and diamonds show simulations with one and two electrodes, respectively. The dashed diagonal marks $|\theta| = |\sigma|$, corresponding to exact screening of the electrode charge. Therefore, the plateau defines the maximum packing density θ_M . Note that the one- and two-electrode simulations give the same limiting θ_M , even though the two-electrode model reaches this limit at smaller $|\sigma|$. This difference is a consequence of overscreening. In the two-electrode model, co-ions remain beyond the counter-ion contact layer and contribute to charge compensation. The inflection point before the plateau corresponds to the saturation of the contact layer and the potential φ_S . After that point, further surface charging proceeds mainly through co-ion desorption from the second layer, rather than simple counter-ion adsorption. The plateau then marks the stricter condition $\sigma = -\theta_M$, where exact screening by the counter-ion monolayer is achieved [19].

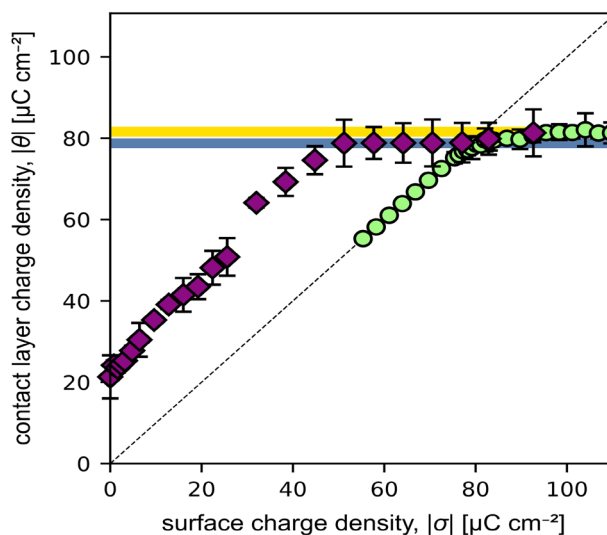


Figure 15. Absolute contact layer charge density ($|\theta|$) as a function of the absolute electrode surface charge density ($|\sigma|$) for $[\text{PF}_6]^-$. Circles and diamonds show simulations with one and two electrodes, respectively. Error bars show the variation in the calculated contact layer density. The dashed diagonal marks $|\theta| = |\sigma|$, corresponding to exact screening of the electrode charge. The plateau and horizontal bands define the maximum packing density (θ_M).

3.7. Prediction of the potential of saturation

Figure 16 compares the simulated θ_M with the calculated potential of monolayer charge (φ_M) for the IL ions shown in Figure 4. The vertical dashed lines at -2 and 2 V indicate the practical potential range relative to the potential of zero charge – a widest ECW. The calculated φ_M values lie outside this range for the common IL ions studied, indicating that exact monolayer screening is generally inaccessible under practical electrochemical conditions. However, for many IL ions, the estimated values of φ_S , given in the supporting information of Publication V, fit into the potential range of ± 2 V relative to the potential of zero charge. φ_S marks the point at which the counter-ion contact layer becomes saturated [70]. Beyond φ_S , further electrode charging occurs mainly through co-ion desorption from the second layer rather than continued counter-ion accumulation. Thus, φ_S precedes the monolayer condition φ_M and remains within the overscreening regime [70,19,66].

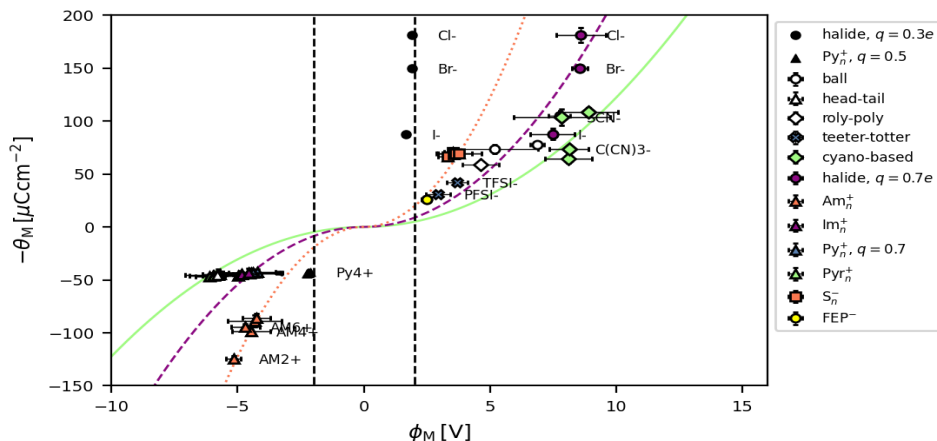


Figure 16. Simulated maximum packing density (θ_M), and calculated potential of monolayer charge (ϕ_M) for the set of ILs described in Figure 4. Marker shapes distinguish ion classes and charge scaling cases, as indicated in the legend. Ion abbreviations and quantities are defined in the List of acronyms and notations. Vertical dashed lines at -2 and 2 V indicate the practical potential range relative to the potential of zero charge and show that exact monolayer screening is generally inaccessible for common IL ions.

Publication V estimated ϕ_S for the studied ions using the ionic bilayer model and the structure-dependent parameters obtained from MD simulations [73]. In contrast to ϕ_M , which remained outside the typical ECW of the common ions studied, the estimated ϕ_S values were generally within or close to ± 2 V relative to the potential of zero charge [19]. This result indicated that saturation of the contact layer is experimentally more accessible than exact screening by a counter-ion monolayer.

The distinction between ϕ_S and ϕ_M changes the interpretation of experimentally observed ordered adlayers as discussed in Ref. [66] along with comparison of experimental and computational studies. For common ILs, such structures are more consistent with a saturated contact layer in the overscreening regime than with true crowding. Therefore, ϕ_S provides a practical structure-based reference for interpreting potential-dependent ordering and changes in interfacial properties at IL–electrode interface.

3.8. Drawing the map for IL electrochemistry

Among all calculated properties, two descriptors were identified as primarily relevant to electrochemical applications: the ECW and the activation energy of viscosity. Electrochemical stability refers to an IL’s resistance to oxidation and reduction, while activation energy describes the temperature dependence of ion transport. Their combination, therefore, reflects the balance between electrochemical stability and ionic mobility [11].

The calculated descriptors do not equal experimental redox potentials or ionic conductivity. Moreover, the estimated ECW omits electrode effects, interfacial structure, solvation, and decomposition pathways. The calculated E_a describes only the temperature-dependent contribution to viscosity and excludes the pre-exponential factor required for absolute viscosity. Yet, both quantities are obtainable from compact ion pair calculations and provide consistent data across large chemical sets, thus, enable high-throughput screening of ILs [11].

Figure 17 presents the estimated activation energy of viscosity as a function of the calculated ECW value. A suitable electrolyte should occupy the lower-right region of the plot, where a wide electrochemical window is combined with a low activation energy. The distribution of the points shows a general trade-off. Several ILs with wide predicted electrochemical windows also have high activation energies, while systems with low activation energies often have narrower windows [11].

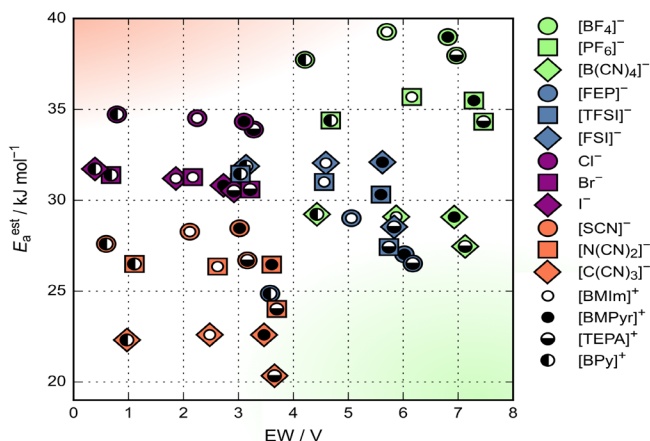


Figure 17. Calculated activation energy of viscosity (E_a^{calc}) as a function of the calculated electrochemical window (ECW) for the set of ILs described in Figure 2. The surrounding marker identifies the anion and the inner symbol identifies the cation. Ion abbreviations are given in the List of acronyms and notations. The green lower right region combines a wide ECW with a low E_a^{calc} and is, therefore, preferred for electrolyte screening.

Several families approach the desired region. These include ILs containing cyanide-based or fluorinated anions combined with quaternary ammonium or pyrrolidinium cations. In particular, $[\text{B}(\text{CN})_4]^-$, $[\text{C}(\text{CN})_3]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{TFSI}]^-$, and $[\text{FEP}]^-$ provide combinations of moderate activation energies and relatively wide predicted electrochemical windows. The map, therefore, allows to identify ion combinations that balance transport and electrochemical stability before applying more detailed calculations or experimental testing [11].

4. CONCLUSIONS

This thesis developed computational workflows connecting molecular and interfacial descriptors to measurable ionic liquid properties. The research combined density functional theory, density functional tight-binding, molecular dynamics, machine learning, and automated analysis to identify systems for experimental study. Among electronic structure methods, the corrected Strongly Constrained and Appropriately Normed functional provided an effective balance between accuracy and computational cost for ion pairs. Dispersion and counterpoise corrections reduced systematic errors, aligning interaction energies with expensive benchmark methods, though charge-related quantities remained sensitive to self-interaction error in strongly charge-transferring pairs.

Density functional tight-binding calculations improved the force field partial charges, while molecular dynamics enabled direct analysis of collective structure. Preliminary machine learning models proved suitable for broad screening, though mixture optimization remains limited by descriptor and reference-data quality. The workflows successfully estimated interaction energies, viscosity activation energies, actuator strain, melting points, decomposition limits, and interfacial potentials. Interaction energies captured variations in viscosity activation, while cation-cation correlations described strain differences in actuators. Notably, the melting-point workflow predicted choline-based ionic liquid properties with root-mean-square errors of 18–24 Kelvin, requiring no known crystal structures.

For electrochemical applications, the electrochemical window and activation energy of viscosity formed a practical screening map. These results establish a clear hierarchy for ionic liquid research: corrected density functional theory supports molecular screening, density functional tight-binding enhances condensed-phase parametrization, molecular dynamics resolves collective structure, and machine learning extends screening to larger chemical sets. Future work must validate whether capacitance estimates from the saturation model agree quantitatively with explicit electrode simulations and experimental measurements.

5. SUMMARY IN ESTONIAN

ioonsete vedelike omaduste ja käitumise arvutuslik modelleerimine molekulaarsel tasandil ja piirpindadel

Antud doktoritöö eesmärgiks oli välja töötada arvutuslikud töövood lihtsustamiseks eksperimentaalseks uurimiseks sobivate süsteemide identifitseerimist. Arendati töövooge, mis seovad molekulaarsed ja interfaasi kirjeldajad ionsete vedelike (IL) eksperimentaalselt mõõdetavate ja rakendustes olulise ionsete IL-de füüsiko-keemiliste omadustega nagu näiteks elektrokeemilised või termililise omadused. Selleks kombineeriti tihedusfunktsionaalteooria (DFT), tihedusfunktsionaali tiheda sideme meetod (DFTB), molekulaardünaamika (MD), masinõpe ja automatiseeritud analüüs.

Elektroonse struktuuri meetoditest pakkus korrigeeritud Strongly Constrained and Appropriately Normed funktsionaal optimaalseima tasakaalu tulemuse täpsuse ja ühe ionpaari arvutusliku maksumuse vahel. Süstemaatilisi vigu õnnestus vähendada dispersiooni ja vastandpunkti korrigeerimisega, mis viisid interaktsiooni energia kooskõlla arvutuslikult kallimate võrdlusmeetoditega. Tugeva laenguülekandega ionpaarides jäid laenguga seotus suurused siiski tundlikuks iseendaga interakteerumisest tekkiva vea suhtes.

DFT, MD ja masinõppe mudelite kombinatsioon osutus sobivaks mitmesuguste omaduste ulatuslikuks sõelumiseks. Väljatöötatud töövood võimaldasid edukalt hinnata IL-de omadusi nagu interaktsioonienergiad, viskoossuse aktivatsioonienergiad, elektroaktiivsete polümeersete täiturite deformatsiooni, sulamispunkte, lagunemiskiire ja faasidevahelisi potentsiaale. Interaktsioonienergiad kirjeldasid viskoossuse aktivatsioonienergia varieeruvust, samas kui katioonidevahelised korrelatsioonid selgitasid täiturite deformatsiooni erinevusi. DFTB sideme meetodil tehtud arvutused parandasid jõuväljade osalaenguid, samal ajal kui MD võimaldas otseselt analüüsida kollektiivset struktuuri. Siiski selgus, et IL-de segude optimeerimist piiravad endiselt kirjeldajate ja võrdlusandmete kvaliteet.

Erinevate omaduste uurimisest järeldus, et elektrokeemiliste rakenduste jaoks praktilise sõelumiskaardi moodustasid elektrokeemilise aken ja viskoossuse aktivatsioonienergia. Töö tulemused löid selge hierarhia IL-de uurimiseks: korrigeeritud DFT toetab molekulaarset sõelumist, DFTB meetod parandab kondenseerunud faasi parameetrite määramist, MD võimaldab lahendada kollektiivse struktuuri ning masinõpe laiendab sõelumist suuremate keemiliste süsteemide kogumitele. Edasises töös tuleb valideerida, kas küllastusmudeli abil saadud mahtuvuse hinnangud langevad kvantitatiivselt kokku nii elektroodide simulatsioonide kui ka eksperimentaalsete mõõtmistega.

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8. PUBLICATIONS

CURRICULUM VITAE

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List of publications:

- Karu, K.;** Ruzanov, A.; Ers, H.; Ivaništšev, V.; Lage-Estebanez, I.; Garcia de la Vega, J. M. (2016). Predictions of Physicochemical Properties of Ionic Liquids with DFT. *Computation* 4(3), 25.
- Karu, K.;** Misin, M.; Ers, H.; Sun, J.; Ivaništšev, V. (2018). Performance of SCAN density functional for a set of ionic liquid ion pairs. *International Journal of Quantum Chemistry*, 118(3), e25582.
- Karu, K.;** Elhi, F.; Põhako-Esko, K.; Ivaništšev, V. (2019). Predicting Melting Points of Biofriendly Choline-Based Ionic Liquids with Molecular Dynamics. *Applied Sciences*, 9(24), 5367.
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- Elhi, F.;;* **Karu, K.;*** Rinne, P.; Nadel, K.-A.; Järvekülg, M.; Aabloo, A.; Tamm, T.; Ivaništšev, V.; Põhako-Esko, K. (2020). Understanding the behavior of fully non-toxic polypyrrole-gelatin and polypyrrole-PVdF soft actuators with choline ionic liquids. *Actuators*, 9(2), 40.
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- Kislenko, S. A.; Moroz, Y. O.; **Karu, K.**; Ivaništšev, V. B.; Fedorov, M. V. (2018). Calculating the Maximum Density of the Surface Packing of Ions in Ionic Liquids. *Russ. J. Phys. Chem.*, 92, 999–1005.
- Ruzanov, A.; **Karu, K.**; Ivaništšev, V. B.; Nazmutdinov, R. R.; Lust, E. (2016). Interplay between the hydrophilicity of metal electrodes and their interfacial capacitance, *Electrochimica Acta*, 210, 615–621.

Participation in international conferences:

- Karu, K.**; Põhako-Esko, K.; Ivaništšev, V.; Determining the melting points of biocompatible ionic liquids and their mixtures with molecular dynamics. Poster presentation, 2018 *Baltic Electrochemistry Conference*.
- Karu, K.**; Tasouli, F.; Skaltsa, K.; Time to deterioration in function/symptoms endpoints under the estimand framework: considerations on plausible strategies and associated estimators. Oral presentation, 2023 *PSI Annual Conference*.
- Karu, K.**; Tasouli, F.; Skaltsa, K.; Common challenges in the analysis of patient-reported outcome (PRO) data. Oral presentation, 2023 *PSI Annual Conference*.
- Tasouli, F.; Daskalopoulou, C.; **Karu, K.**; Kral, P.; Simulation-based performance evaluation of time-varying effect models for intensive longitudinal data. Poster presentation, 2023 *PSI Annual Conference*.
- Karu, K.**; Kral, P.; Ho, C. N.; Keith, M.; Griffiths, P.; Brooks, L.; A simulation study to assess the missing diary data rule for bi-weekly Dysphagia Symptom Questionnaire (DSQ) scores. 2022 *ISOQOL Annual Conference*.
- Karu, K.**; Griffiths, P.; Visualizing equivalence in simulated data. Poster presentation, 2022 *PSI Annual Conference*.
- Skaltsa, K.; Kral, P.; **Karu, K.**; Sensitivity analysis for time to health-related quality of life (HRQoL) deterioration endpoints under not at random assumptions. Poster presentation, 2022 *PSI Annual Conference*.

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Karu, K.; Ruzanov, A.; Ers, H.; Ivaništšev, V.; Lage-Estebanez, I.; Garcia de la Vega, J. M. (2016). Predictions of Physicochemical Properties of Ionic Liquids with DFT. *Computation* 4(3), 25.
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Cella, D.; Choueiri, T. K.; Hamilton, M.; Blum, I. S.; Ivanescu, C.; **Karu, K.;** Ejzykiewicz, F.; Motzer, R. J. (2024). The Relationship Between Health-Related Quality of Life and Overall Survival in Patients With Advanced Renal Cell Carcinoma in CheckMate 214. *The Oncologist*, 29(6), 511–518.

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Rahvusvahelistel konverentsidel osalemine:

- Karu, K.**; Põhako-Esko, K.; Ivaništšev, V.; Determining the Melting points of biocompatible ionic liquids and their mixtures with molecular dynamics. Poster presentation, 2018 *Baltic Electrochemistry Conference*.
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- Skaltsa, K.; Kral, P.; **Karu, K.**; Sensitivity analysis for time to health-related quality of life (HRQoL) deterioration endpoints under not at random assumptions. Poster presentation, 2022 *PSI Annual Conference*.

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