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Theoretical Investigation of the Molecular Structure and Physicochemical Properties of Imidazolium Ionic Liquids Based on DFT Calculations

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Abstract. Imidazolium ionic liquids are tunable salts whose properties arise from electrostatic attraction, hydrogen bonding, dispersion, charge transfer, conformational freedom, and solvation. This paper presents a literature-grounded theoretical investigation of their molecular structure and physicochemical behavior using density functional theory (DFT). Representative EMIM and BMIM salts are compared using conformer searches, dispersion-aware optimization, solvation, orbital, and QTAIM/NCI analyses. Recent work confirms that anions dominate local coordination and redox response, while side chains control packing and viscosity. Isolated ion-pair DFT explains local interactions but cannot alone predict bulk transport or phase behavior; multiscale validation is therefore essential.
Keywords: *imidazolium; ionic liquids; DFT; hydrogen bonding; electronic structure; physicochemical properties.*

1. Introduction

Ionic liquids (ILs) are salts that melt below 100 degrees C. Imidazolium ILs are especially important because their aromatic cation is stable and readily modified, while exchange of the counterion provides a broad range of polarity, miscibility, conductivity, viscosity, and thermal behavior. These properties are not simple sums of cation and anion contributions. They emerge from a dense network of Coulomb attraction, C-H...anion contacts, dispersion, conformational disorder, and local charge transfer. Recent calculations further show that one ion pair may possess several low-energy arrangements; a global conformational search is therefore necessary before structure-property conclusions are made [1].

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DFT offers an efficient quantum-mechanical description of optimized geometry, vibrational frequencies, charge distribution, frontier orbitals, and noncovalent interactions. During 2025-2026 it was used to analyze CO2 binding in fluorinated imidazolium systems [1], proton transfer in 1-methylimidazolium carboxylates [2], anion-dependent hydration [3], condensed-phase charges for conductivity models [4], selective anion exchange [5], and electrochemical stability in ether-functionalized salts [6]. The aim here is to integrate these findings into a concise and reproducible theoretical framework without presenting unverified numerical calculations.

2. Theoretical Methodology

Representative EMIM and BMIM ion pairs should be constructed with Cl-, OAc-, BF4-, PF6-, DCA-, OTf-, and NTf2-. For each system, the anion must be placed near C2-H, C4/5-H, the alkyl region, and any ether or hydroxyl group; flexible anions and side chains require several rotamers. Low-cost prescreening can be followed by optimization with a dispersion-corrected hybrid functional and a polarized basis set containing diffuse functions. M06-2X/6-311++G(d,p)-type calculations are common in recent studies [5,7,10], but the functional should be validated for the chosen ion family. Frequency analysis must confirm the absence of imaginary modes and supply zero-point and thermochemical corrections.

The ion-pair interaction energy is defined as follows:

Delta Eint = Eion pair - (Ecation + Eanion)

Negative values indicate stabilization, although gas-phase calculations normally overstate Coulomb binding. Basis-set superposition error should be checked when energy differences are small. Continuum solvation screens long-range electrostatics, whereas explicit water molecules reveal competing contacts; the strongest approach combines an explicit first shell with an outer continuum. Electrostatic-potential maps and method-consistent partial charges identify electron-rich and electron-poor regions. HOMO-LUMO analysis provides qualitative redox information, while QTAIM, NCI, and NBO analyses distinguish directional hydrogen bonding, charge transfer, dispersion, and steric repulsion. The Kohn-Sham gap must not be treated as a direct experimental electrochemical window.

3. Results and Discussion

3.1. Molecular structure and anion effect

The imidazolium positive charge is delocalized over the ring, but C2-H is generally the most acidic and accessible

hydrogen-bond donor. Compact basic anions such as Cl- form short, directional contacts and strongly associated pairs. Acetate can form bifurcated C-H...O interactions and may participate in proton transfer. BF4- and PF6- distribute charge over several fluorine atoms, producing more diffuse coordination. DCA- contains accessible nitrogen acceptors, whereas flexible NTf2- frustrates packing and generates several similar minima. Comparative DFT work on seven BMIM salts showed that water reorganizes around each anion differently and that electrostatics dominates IL-water stabilization [3].

Table 1

Main structural variables and predicted consequences

Variable	DFT interpretation and expected property trend
Cl- or OAc-	Localized, strong coordination; greater association and hydrophilicity, often accompanied by higher viscosity.
BF4- or PF6-	Diffuse C-H...F contacts; weaker local directionality and increased hydrophobic character for PF6-.
DCA- or NTf2-	Delocalized charge and inefficient packing; conditions that can support lower viscosity and higher mobility.
Long/functional side chain	More dispersion and nonpolar segregation; ether or hydroxyl groups introduce competing coordination sites [6].

3.2. Electronic structure and electrochemical behavior

Formal ionic charges are idealized. DFT commonly predicts partial charge transfer whose magnitude changes with local coordination and composition. Verma, Thorat, and Shah derived composition-dependent charges for EMIM mixtures containing BF4-, DCA-, OTf-, and NTf2-. Using these condensed-phase charges improved density and ionic-conductivity predictions over a fixed-charge model [4]. The anion often contributes strongly to the HOMO and therefore to oxidation, while cationic orbitals can control reduction. Ether substitution and chain length shift interaction energies, calculated gaps,

hydrogen-bond distances, viscosity, conductivity, and electrochemical response [6]. Functional chromophores can introduce additional frontier orbitals, as reported for anthracene-linked imidazolium salts [7].

3.3. Physicochemical properties

Strong ion pairing does not guarantee a superior liquid. It can raise viscosity, slow diffusion, and reduce effectively mobile charges. Bulky asymmetric ions may have weaker local coordination but lower melting points because they disrupt crystal packing. Density depends on molecular volume and packing; viscosity also reflects contact lifetime, free volume, and collective rearrangement. Consequently, a single Delta Eint cannot uniquely predict melting point, density, or viscosity. Machine-learning models developed in 2025 combine curated experimental density and viscosity data with atomistic descriptors, illustrating the benefit of data-DFT integration [9].

Water is a major structural variable rather than a passive impurity. It competes for anion sites, weakens some cation-anion contacts, alters spectra, and may increase conductivity while narrowing electrochemical stability. Thermal stability is likewise governed by accessible decomposition pathways and anion nucleophilicity, not merely pair binding. Integrated experiment/DFT studies are therefore preferred. Momeni and Rad-Moghadam linked selective anion exchange and thermal behavior to calculated dication-anion configurations [5], while Vranes and co-workers combined physicochemical measurements, antimicrobial tests, and DFT/ADMET analysis for oxychlorine BMIM salts [8].

4. Application-Oriented Design

Electrolytes require a compromise between weak coordination, high mobility, low viscosity, chemical compatibility, and resistance to oxidation and reduction. CO2 capture favors accessible interaction sites and free volume, but strong absorption must be balanced against regeneration energy; recent multiple-minimum calculations show that several IL-CO2 cluster geometries must be evaluated [1]. Catalytic applications may instead benefit from strong local organization that stabilizes a transition state. Rational screening should therefore rank candidates against application-specific objectives rather than one universal descriptor [11].

5. Limitations

An isolated ion pair describes local electronic structure, whereas a real IL is a dense and dynamically

heterogeneous network. Continuum solvation cannot reproduce coordination-shell fluctuations; small clusters require extensive sampling; periodic DFT is expensive; and molecular dynamics depends on force-field quality. In addition, atomic charges are method-dependent, harmonic spectra omit anharmonic condensed-phase effects, and the HOMO-LUMO gap is not an experimental electrochemical window. Reproducible reports must state conformers, functional, basis set, dispersion correction, solvation model, temperature, standard state, BSSE treatment, and software version.

6. Conclusions

DFT is a powerful molecular tool for imidazolium ILs when used within its proper scale. Anion identity chiefly controls direct coordination, hydration, charge transfer, and redox localization; cation side chains chiefly control accessibility, dispersion, packing, and interfacial organization. Multiple conformers, dispersion-aware optimization, frequency verification, and explicit solvation are essential. For melting behavior and transport properties, DFT descriptors should be linked to molecular dynamics, periodic calculations, experiments, or machine learning. The 2025-2026 literature confirms that this multiscale strategy provides the most defensible route from molecular structure to practical ionic-liquid design.

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