



Review

Magnetic ionic liquids in analytical chemistry: A review



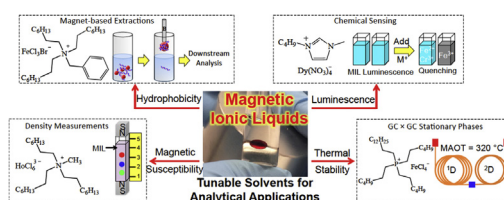
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HIGHLIGHTS

- Review of magnetic ionic liquid applications in analytical chemistry.
- MILs can be designed for extractions, chromatography, and chemical sensing.
- Relationships between MIL structure and physicochemical properties examined.
- Advantages of MILs in magnet-based technologies are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic ionic liquids (MILs) have recently generated a cascade of innovative applications in numerous areas of analytical chemistry. By incorporating a paramagnetic component within the cation or anion, MILs exhibit a strong response toward external magnetic fields. Careful design of the MIL structure has yielded magnetoactive compounds with unique physicochemical properties including high magnetic moments, enhanced hydrophobicity, and the ability to solvate a broad range of molecules. The structural tunability and paramagnetic properties of MILs have enabled magnet-based technologies that can easily be added to the analytical method workflow, complement needed extraction requirements, or target specific analytes. This review highlights the application of MILs in analytical chemistry and examines the important structural features of MILs that largely influence their physicochemical and magnetic properties.

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1. Introduction

Following their discovery over a century ago, ionic liquids (ILs) have contributed to significant advances in the chemical sciences. ILs are a class of molten salts exhibiting melting points at or below 100 °C. Commonly composed of organic cations and organic/inorganic anions, ILs possess a number of advantageous physicochemical properties including negligible vapor pressure at ambient temperatures, high thermal stability, wide electrochemical window, and tunable solvation properties [1]. Owing to readily interchangeable and customizable cations and anions, an estimated 10^{18} possible combinations of ILs can be generated [2]. Although initially applied largely in electrochemistry [3], catalysis [4], and organic synthesis [5], rational design of the chemical structure of ILs has fueled their rapid expansion in the field of analytical chemistry [6,7].

Recently, a new subclass of ILs known as magnetic ionic liquids (MILs) has been the subject of intensified interest in numerous analytical applications. These magnetic solvents are produced by the incorporation of a paramagnetic component in either the cation or anion of the IL structure [8–10]. Often comprised of transition metal or lanthanide metal ions, MILs possess similar physicochemical properties to conventional ILs while also exhibiting a strong response to external magnetic fields. Although the compound had been previously reported [11], the paramagnetic behavior of the 1-butyl-3-methylimidazolium tetrachloroferrate(III) ([BMIM⁺][FeCl₄⁻]) MIL was first demonstrated by Hayashi et al. using superconducting quantum interference device (SQUID) magnetometry [8]. This discovery was significant because it had been previously assumed that metal-based ILs lacked the long-range interactions responsible for paramagnetic phenomena [12]. Subsequently, MILs based on other transition metals including manganese [13] and cobalt [14] were prepared and similarly shown to be paramagnetic liquids. Rare earth metals including neodymium [15], gadolinium [13], and dysprosium [16] were also incorporated into MILs resulting in luminescent materials with considerably higher magnetic moments.

Although early research in MILs was oriented toward synthesis and fundamental studies, the paramagnetic properties and structural tunability of MILs have been an inspiration for new magnet-based technologies. Unlike ferrofluids that require suspended magnetic particles to convey magnetic properties to the bulk material, MILs are transparent and exist as neat magnetic solvents [13], as thoroughly discussed in a recent review of MILs [17]. MILs also exhibit low volatility, circumventing the need for flammable dispersants or stabilizing organic solvents that are often employed in ferrofluids to prevent particle agglomeration [18]. By modifying the chemical structure of the cation or anion, MILs can be designed to possess physicochemical properties that are desirable for specific applications. For example, functionalizing MILs with long aliphatic groups to impart hydrophobic character enables their use in aqueous extraction systems. This Review will focus on the

physicochemical and magnetic properties of MILs that influence their performance in analytical applications, as well as provide an overview of the applications of MILs in analytical chemistry.

2. Magnetic ionic liquid design and structural considerations for analytical applications

2.1. Magnetic susceptibility

The ability to precisely control the motion of MILs by application of a magnetic field represents an important advantage of these materials over conventional ILs. Fig. 1 shows an example of the manipulation of a MIL using a neodymium magnet. By incorporating different paramagnetic metals in either the cation or anion of the IL structure, the magnetic susceptibility of MILs can be tuned for a specific application. Higher magnetic moments may be advantageous for MIL solvents when employed in analytical extractions, manipulation within microfluidic devices, magnet-based sensors, and a host of other applications. The earliest reports of MILs were focused on their preparation [11] and evaluation of the magnetic properties of Fe(III)-containing MILs, including the popular [BMIM⁺][FeCl₄⁻] salt which exhibited an effective magnetic moment (μ_{eff}) of 5.8 Bohr magnetons (μ_B) [8,19]. Upon varying the length of the alkyl group on the imidazolium cation, Yoshida and co-workers observed little difference in the magnetic susceptibility of the resulting MILs paired with [FeCl₄⁻] or [FeBr₄⁻] anions [20]. However, when combining the trihexyl(tetradecyl)phosphonium ([P₆₆₆₁₄⁺]) cation with anions containing different metal components (e.g. Mn(II), Co(II), and Gd(III)), MILs with a wider range of magnetic susceptibilities were generated [13]. MILs based on Fe(III) and Mn(II) possessed similar magnetic susceptibilities, while Co(II)-based MILs exhibited lower susceptibility values. Significantly greater magnetic susceptibilities were observed for the [P₆₆₆₁₄⁺]₃[GdCl₆³⁻] MIL, which is the expected outcome for single-ion lanthanide metals when compared to transition metals. Motivated by the considerably higher μ_{eff} afforded by lanthanide metals, Mallick and co-workers investigated MILs possessing Dy(III) thiocyanate anions [16]. MILs with the chemical formula [C₆MIM]_{5-x}[Dy(SCN)_{8-x}(H₂O)_x] ($x = 0-2$) exhibited μ_{eff} values as high as 10.6 μ_B , owing to the magnetoactive anion with 4f⁹ electron configuration. Bwambok and co-workers also studied MILs containing various transition metal and rare earth metal centers including Fe(III), Mn(II), Gd(III), Ho(III), and Dy(III) [21]. When the same metal-based anion was combined with different cations, namely, [BMIM⁺], 1-butyl-2,3-dimethylimidazolium ([BDMIM⁺]), [Aliquat⁺], and L-alanine methyl ester ([AlaCl⁺]), the authors observed changes in the magnetic susceptibility per unit volume of MIL.

In addition to changing the identity of the paramagnetic metal, the magnetic properties of MILs may also be modulated by utilizing a multi-cationic platform with two or more paramagnetic anions within the chemical structure. Brown and co-workers synthesized

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