

Advances in analytical chemistry using the unique properties of ionic liquids

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Ionic liquids (ILs) are regarded as non-molecular solvents, as they are composed entirely of cations and anions. ILs possess several excellent unique properties (e.g., low volatility, high thermal stability, specific electrochemical characteristics, easy design, tunable viscosity, and miscibility with water or organic solvents). These properties make ILs attractive candidates for various analytical applications, the number of publications on which has increased exponentially in the past decade.

This article presents an overview of representative applications of ILs in advances in analytical chemistry that benefited from the unique properties of ILs, including the development achieved by using ILs as extraction solvents, dissolution solvents and separation media.

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1. Introduction

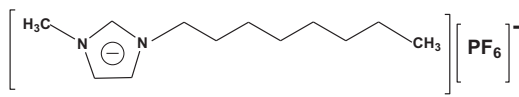
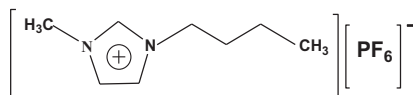
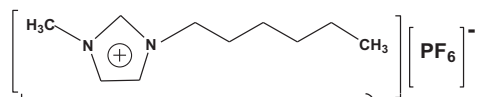
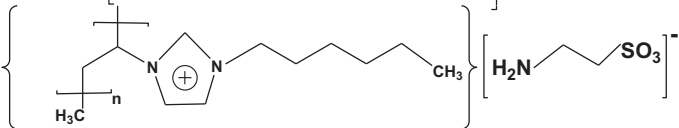
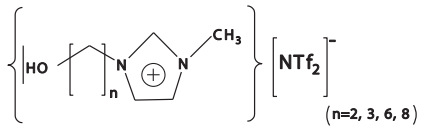
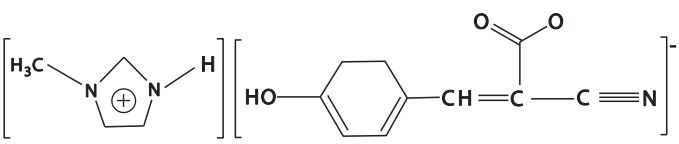
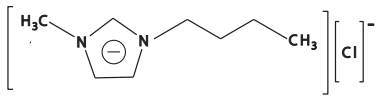
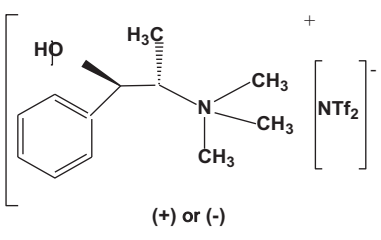
Room-temperature ionic liquids (ILs) are composed only of positively and negatively charged ions, and exist as liquids at relatively low temperatures ($<100^{\circ}\text{C}$) [1]. Almost all of the ILs have been composed of organic cations and various anions. Typical cations are asymmetrically substituted nitrogen-containing compounds (e.g., imidazolium, pyridinium, quaternary ammonium, and the quaternary phosphonium group). Both inorganic anions (e.g., Cl^- , Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$) and organic anions (e.g., trifluoromethylsulfonate $[\text{CF}_3\text{SO}_3]^-$, bis[(trifluoromethyl) sulfonyl]imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, trifluoroethanoate $[\text{CF}_3\text{CO}_2]^-$) are able to serve as the anionic counterparts [2,3]. As reported, theoretically, available combinations of cations and anions can give rise to as many as 10^{18} kinds of IL [4].

In contrast to common organic solvents, ILs have several outstanding properties (e.g., negligible vapor pressure, good thermal stability, wide electrochemical windows, intrinsic conductivity, excellent design, and varying solvation interaction) [5]. Due to these characteristics, ILs are involved in a lot of fields {e.g., synthesis

[6], catalysis [7], chemical industry [8] and analytical chemistry} to compensate for the limitations of classical organic solvents. The unique properties of ILs give rise to a great number of applications in analytical chemistry, and comprehensive review articles on this field have been published [2,3,9–14]. In these reviews, ILs were proposed as promising materials to address the various challenges within the scope of analytical chemistry. Nevertheless, it is of great interest to comment explicitly on the significant advances in analytical chemistry resulting from the application of ILs. Table 1 lists the structures, the properties and the applications of a few representative ILs.

The goal of this review is to highlight the advances using ILs in analytical chemistry benefiting from the unique properties of ILs. We try to overview this progress in the major sub-disciplines of analytical chemistry, including extraction, separation, characterization and detection. Due to the large amounts of publications related to this topic, we do not attempt to refer all the publications, and virtually only the more representative reports are selected for conciseness.

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| Structure | Name | Properties used | Functions | Comments | Ref. |
|---|---|--|--|---|---------|
|  | 1-Octyl-3-methylimidazolium hexafluorophosphate | Negligible volatility and high viscosity | Extraction media in LPME and HFSLM | Large volume drop, long surviving time, high enrichment factor, and high selectivity | [16,21] |
|  | 1-Butyl-3-methylimidazolium hexafluorophosphate | Negligible volatility | Extracting media for the coupling between SDME and GC/MS | Avoiding interference of organic solvent peaks | [18] |
|  | 1-Hexyl-3-methylimidazolium hexafluorophosphate | Temperature dependent aqueous solubility | Extraction solvents in dispersive liquid-phase microextraction | Eliminating the use of dispersing organic solvents | [25] |
|  | Poly(VHIM-aurate) | Long-term stability | Coatings of solid-phase microextraction | High extraction-to-extraction reproducibility | [31] |
|  | (1-hydroxyalkyl-3-methylimidazolium, n = 2,3,6,8) bis(trifluoromethylsulfonyl)imide | Designability | Extraction solvents | Functional groups of ILs influencing protein partitioning | [36] |
|  | Methylimidazolium α -cyano-4-hydroxycinnamate | Low vapor pressure | Matrices for MALDI-MS | Homogeneous solutions, and improved shot-to-shot reproducibility | [50] |
|  | 1-Butyl-3-methylimidazolium chloride | Dual nature in separation | Coatings of GC capillary column | Separating compounds with different polarity | [58] |
|  | <i>N,N</i> -Dimethylphedrinium bis(trifluoromethylsulfonyl)imide | Chirality in separation | Chiral stationary phase of GC capillary column | Excellent separation of various chiral compounds including alcohols, diols, sulfoxides, epoxides, and acetylated amines | [74] |

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