



Ionic liquids for mass spectrometry: Matrices, separation and microextraction

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ABSTRACT

Applications of ionic liquids (ILs) for mass spectrometry (MS) are a burgeoning area and are promising for real applications. However, the research of ILs for MS is in its infancy and there are a large potential for further applications under the ashes. This review article provided an overview of the current state and the research progress of ILs applications for MS. ILs offered several advantages, such as low vapor pressure, soft ionization, high sensitivity, better separation and microextraction, effectively disperse nanoparticles for nanoprobe technologies, and stable under vacuum and for storage in solution form, that led to several applications for MS and assured that ILs carry a brilliant future for analytical purposes. A plethora of ILs with different properties can be designed by various combinations of acid and base moieties and were applied as multifunctional materials. Thus, ILs provided many platforms such as green solvents for microextraction, stationary phases for separation and matrices for laser desorption/ionization mass spectrometry (LDI-MS). Comparison among the organic matrices, ILs and nanoparticles were also highlighted.

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Abbreviations: [C₈MIM][PF₆], 1-octyl-3-methylimidazolium hexafluorophosphate; TCIL-DLLME, Temperature-controlled ionic liquid dispersive liquid-liquid microextraction; US-IL-DLLME, Ultrasound-assisted ionic liquid dispersive liquid-liquid microextraction; LC-QqLIT-MS/MS, High-performance liquid chromatography with a hybrid triple quadrupole-linear ion trap-mass spectrometer; [CMIM][PF₆], 1-Hexyl-3-methylimidazolium hexafluorophosphate; [C₄MIM][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [C₆MIM][N(SO₂CF₃)₂], 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; IL-USA-ME, Ionic-liquid based ultrasound-assisted emulsification microextraction; USA-TC-IL-DLME, ultrasound-assisted temperature-controlled ionic-liquid dispersive liquid-phase microextraction; HPLC, High-performance liquid chromatography; [HMIM][PF₆], 1-hexyl-3-methylimidazolium hexafluorophosphate; FAAS, Flame atomic absorption spectrometry; [C₄MIM][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; APDC, Ammonium pyrrolidine dithiocarbamate; ETAAS, Electrothermal atomic absorption spectrometry; GFAAS, Graphite furnace atomic absorption spectrometry; [BMIM][NTf₂], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; CYPHOS IL101, tetradecyl(trihexyl) phosphonium chloride ionic liquid; BmimBr, 1-butyl-3-methylimidazolium bromide; MAILE, Microwave-assisted ionic liquid extraction; SPME, Solid phase microextraction; GC-MS, Gas chromatography-mass spectrometry; VOCs, Volatile organic compounds; MPIHS, 1-methyl-3-phenethyl-1H-imidazolium hydrogen sulfate ionic liquid; MMHg, Monomethyl mercury; IHg, Inorganic mercury; HF-LPME, Hollow fiber supported liquid phase microextraction; [emin]Br, 1-ethyl-3-methylimidazolium bromide; [hmin]Br, 1-hexyl-3-methylimidazolium bromide; [bmim]SO₄, 1-butyl-3-methylimidazolium methanesulfonate; [bmin]BF₄, 1-butyl-3-methylimidazolium tetrafluoroborate; [Cmim]Cl, 1-dodecyl-3-ethylimidazolium chloride; [C₁₂mim]Br, 1-dodecyl-3-methylimidazolium bromide; [C₁₂mim]CF₃SO₄, 1-dodecyl-3-methylimidazolium trifluoromethanesulfonate; [C₁₂mim]NO₃, 1-dodecyl-3-methylimidazolium nitrate; [C₁₂mim]HSO₄, 1-dodecyl-3-methylimidazolium hydrogen sulfate; RRLC-ESI-MS/MS, Rapid resolution liquid chromatography-electrospray tandem mass spectrometry; [C₄MIM][PF₆], 1-Butyl-3-methylimidazolium hexafluorophosphate; [C₆MIM][PF₆], 1-hexyl-3-methylimidazolium hexafluorophosphate; [C₈MIM][PF₆], 1-octyl-3-methylimidazolium hexafluorophosphate; [C₄MIM][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate; [EMIM][BF₄], 1-ethyl-3-methylimidazole tetrafluoroborate; [C₄MIM]NO₃, 1-butyl-3-methylimidazolium nitrate; ETV-ICP-MS, Electrothermal vaporization inductively coupled plasma mass spectrometry; HS-SDME, Headspace- Single-Drop Microextraction; DUNE, Dynamic ultrasonic nebulisation extraction; PLE, Pressurized liquid extraction; UA-DLLME, Ultrasonic-assisted dispersive liquid-liquid microextraction.

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1. Introduction

Ionic liquids (ILs) are salts in liquid phase at room temperature. ILs have low melting point below 100°C (212°F). The main reason for the low melting point is due to the charge diffuse of ILs ions. ILs consists of ions and can be called as liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. The first prototype represented the ionic liquids was ethyl ammonium nitrate with chemical formula $[C_2H_5NH_3]^+[NO_3]^-$ and melting point 12°C [1]. Ionic liquids offered several features such as low vapor pressure, non-flammable, electrically conducting, offered a wide numbers of

different structures, were stable under vacuum, and have good thermal stability. There are several review articles [2–16], book chapters [17–20] that discussed the properties and applications of ILs as solvent, catalysis or chemical engineering. Because of the unique properties of ILs, they are integrated in many trends such as analytical chemistry [21–29], electrochemistry [30], catalysis [31,32], and others [33]. The wide applications of ILs can be confirmed by the increase of publication when a search was run with “ionic liquids” (Fig. 1A). These interests are varied for many aspects such as analytical chemistry, chromatography/separation/microextraction, material chemistry, environmental, catalysis, electrochemistry, energy

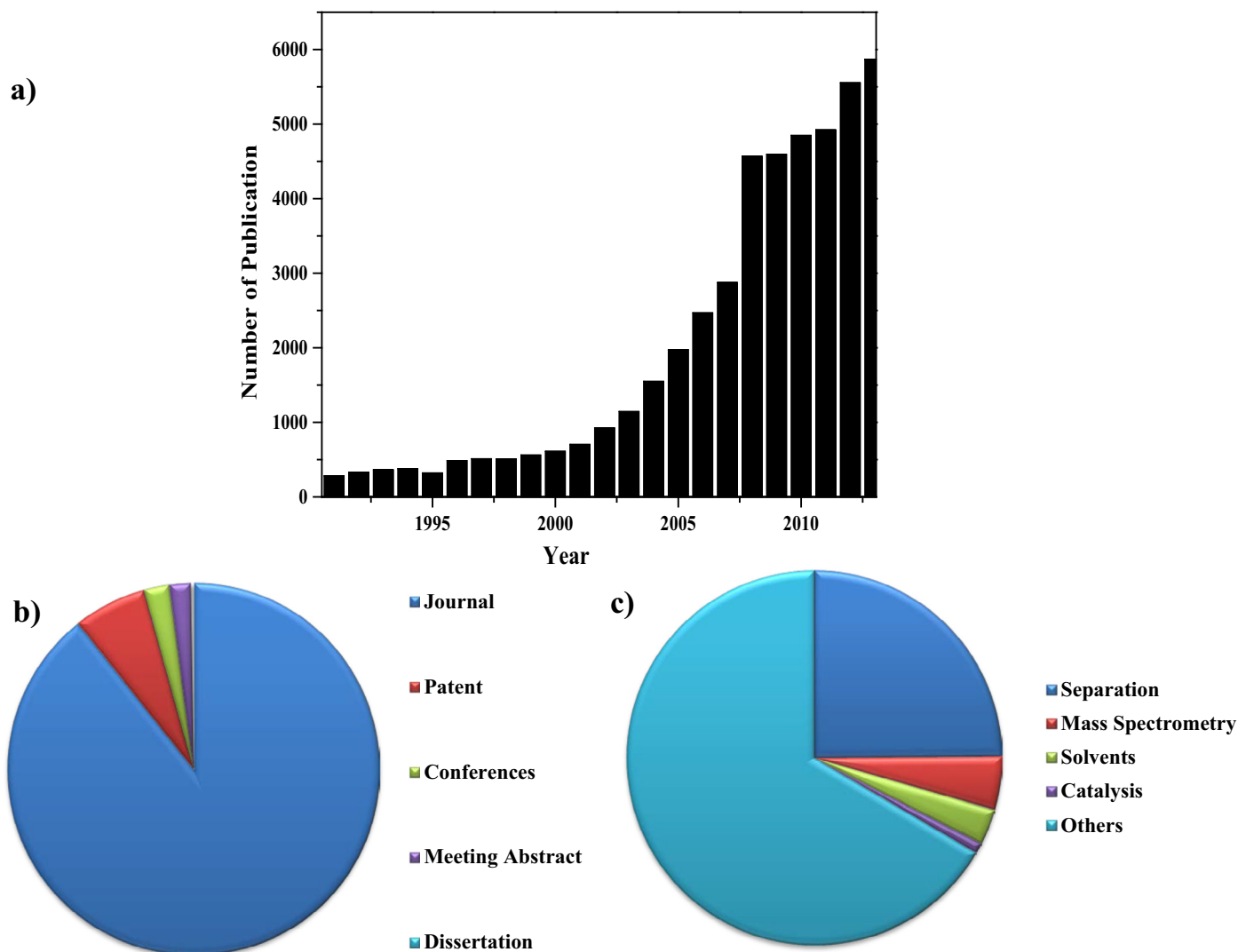


Fig. 1. a) Scientific publication of ionic liquids over the years. Data were collected from Web of Science by using the word 'ionic liquids'; b) types of the scientific publications and c) the applications of ILs.

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