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Opportunities and shortcomings of ionic liquids in single-drop microextraction

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ABSTRACT

The synergistic combination of ionic liquids (ILs) and single-drop microextraction (SDME) involves a powerful coupling toward the development of sustainable analytical methodologies. This overview provides a survey of the literature regarding IL-SDME, including a database on relevant physicochemical properties of ILs for their application in SDME, the strategies implemented to combine IL-based SDME methods efficiently with analytical instrumentation, and a critical evaluation of the analytical applications involving IL-based SDME methodologies. Overall, this work identifies current inefficiencies, challenges and opportunities of this convenient, yet underexploited, analytical approach.

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Contents

Abbreviations: [(NH_2C_6) C_1Pyrr], 1-(6-aminohexyl)-1-methylpyrrolidinium; [BETI], bis(perfluoroethylsulfonyl)imide; [BF_4], Tetrafluoroborate; [Br], Bromide; [C_4C_1Py], 1-butyl-3-methylpyridinium; [C_4C_1Pyrr], 1-butyl-1-methylpyrrolidinium; [CF_3COO], trifluoroacetate; [CF_3SO_3], Trifluoromethanesulfonate; [CH_3COO], Acetate; [Cl], Chloride; [C_nC_1IM], 1-alkyl-3-methylimidazolium; [DC_nIM], 1,3-dialkylimidazolium; [$EtSO_4$], ethanesulfonate; [FAP], Tris(pentafluoroethyl)trifluorophosphate; [$MeDGSO_4$], Diethyleneglycolmonomethylethersulfate; [$MeSO_4$], Methanesulfonate; [$N(CN)_2$], dicyanamide; [$N_{4,1,1,1}$], butyl*trimethylammonium*; [NTf_2], Bis(trifluoromethylsulfonyl)imide; [$P_{14,6,6,6}$], Tetradecyl(trihexyl)phosphonium; [PF_6], Hexafluorophosphate; [SCN], thiocyanate; 2,4,6-TCA, 2,4,6-trichloroanisole; 5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; APDC, Ammonium pyrrolidine dithiocarbamate; BTEX, Benzene, toluene, ethylbenzene and xylene; CE, Capillary electrophoresis; CV-AFS, Cold-vapor atomic fluorescence spectrometry; D-SDME, Direct single-drop microextraction; ECD, Electron-capture detection; EE, Extraction efficiency; EF, Enrichment factor; ETAAS, Electrothermal atomic absorption spectrometry; ETV-ICP-MS, Electrothermal vaporization inductively-coupled plasma mass spectrometry; FID, Flame-ionization detection; FLD, Fluorescence detection; GC, Gas chromatography; GC-MS/MS, Gas chromatography-tandem mass spectrometry; HPLC, High-performance liquid chromatography; HS-SDME, Headspace single-drop microextraction; IL, Ionic liquid; IMS, Ion-mobility spectrometry; LOD, Limit of detection; LOQ, Limit of quantification; LPME, Liquid-phase microxtraction; MALDI-TOF-MS, Matrix-assisted laser-desorption/ionization time-of-flight mass spectrometry; MeIQx, 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline; MMT, Methylcyclopentadienyl-manganese tricarbonyl; MS, Mass spectrometry; PAH, Polycyclic aromatic hydrocarbons; PAN, 1-(2-pyridylazo)-2-naphthol; PDA, Photodiode-array detection; PFA, Perfluoroalkoxy; PTV, Programmed temperature vaporization; QD, Quantum dot; RSD, Relative standard deviation; SDME, Single-drop microextraction; SDS, Sodium dodecyl sulfate; TAN, 1-(2-thiazolylazo)-2-napthol; UV, Ultraviolet.

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1. Introduction

The environmental and human impact of chemical processes has encouraged scientists to the introduction of safer and cleaner alternatives. In this sense, Anastas introduced the concept of Green Chemistry as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous subtances", together with 12 principles that provided a roadmap for development and application of safer, more benign chemical processes [1]. A number of miniaturized strategies have been developed with the aim of greening sample preparation. In this regard, the introduction of single-drop microextraction (SDME) in the mid-1990s represented an important boost toward a dramatic reduction of solvent consumption in analytical methodologies involving conventional liquid-liquid extraction [2–4]. Even though solvent consumption and waste generation could be substantially minimized by replacing conventional solvent extraction with SDME, some toxic organic solvents, such as benzene, were systematically employed in SDME-based methodologies in recent years.

The fifth principle of Green Chemistry states that it is necessary to search for alternatives that could replace harmful organic solvents, thus contributing to reducing the unfavorable environmental impact of chemical processes. Scientific efforts therefore focus on the search for greener substances that could improve selectivity, sensitivity and accuracy of techniques. In this way, ionic liquids (ILs) are commonly considered promising green solvents [5]. ILs are defined as a class of non-molecular ionic solvents with low melting points (by convention, below 100°C) [6]. A typical IL consists of a large nonsymmetrical organic cation (e.g., imidazolium, pyrrolidinium, pyridinium, tetraalkyl ammonium or tetraalkyl phosphonium) and a smaller organic/inorganic anion (e.g., tetrafluoroborate, hexafluorophosphate, bromide).

ILs are characterized by a unique set of physicochemical properties that include: negligibly low vapor pressure, broad temperature range in the liquid state, thermal stability, high viscosity and density, and affinity to organic or inorganic compounds. Additionally, due to the appropriate selection of the anion, the cation, and the length of the substituent alkyl chain, it is possible to control their physicochemical properties, and, thus, to obtain an IL for virtually every specific application. This is why they are called "designer solvents" [7]. Due to their physicochemical properties, ILs have found a broad range of applications in many areas of analytical chemistry, namely sample preparation [8], analytical separation [9,10] and detection systems [11]. Fig. 1 presents the main milestones in the development of ILs.

The implementation of ILs in SDME thus involved a step forward, as the use of volatile organic solvents as extractants can be avoided. Furthermore, the physicochemical properties of ILs provide advantageous conditions for several extraction processes. IL-SDME fulfills several principles of Green Analytical Chemistry (GAC), including the use of miniaturized systems, dramatic reduction of analytical waste, removal of toxic reagents and solvents, and increased operator safety.

2. Fundamental aspects of SDME

SDME is a miniaturized sample-preparation technique based on the partitioning of target analytes between the sample solution and the extractant phase. SDME enables the achievement of high EFs due to the highly reduced extractant phase-to-sample volume ratio. Unlike alternative liquid-phase microxtraction (LPME) [12,13], the extractant phase is exposed to the tip of a capillary or, more commonly, a syringe needle during the extraction process and shows a nearly spherical configuration in SDME.

Drop stability during the microextraction process is an essential condition for the successful application of the technique. The mechanical equilibrium of a microdrop hanging at the end of a capillary or a syringe needle is given by the balance between forces acting over the drop. When the profile of the drop at the boundary with the capillary is nearly vertical, the maximum drop volume that can be formed can be expressed as:

$$V_{d_{\max}} = \frac{2\pi R_m \sigma}{\Delta\rho g} \quad (1)$$

where R_m is the external capillary radius, σ is the interfacial tension, $\Delta\rho$ is the density difference between the interior droplet phase and the exterior matrix phase, and g is the gravitational acceleration [14]. Drop volumes larger than $V_{d_{\max}}$ are not physically stable and, thus, result in droplet detachment. It is worth mentioning that the drop can experience certain perturbations during the microextraction process due to the agitation of the sample, so the droplet can be detached from the needle tip. Therefore, drop volumes below the $V_{d_{\max}}$ value are recommended for higher reliability.

Two SDME modes are commonly used (Fig. 2), namely direct SDME (D-SDME) and headspace SDME (HS-SDME). We describe below basic aspects of both SDME modes.

2.1. D-SDME

In direct-SDME (Fig. 2A), the extractant phase is directly immersed into a continuously stirred liquid-sample solution for extraction of target analytes or analyte derivatives. D-SDME is a versatile SDME mode in terms of analyte type, as both volatile and nonvolatile compounds can be extracted. However, its applicability is reduced in the case of heterogeneous samples, as the presence of suspended materials can affect the mechanical stability of the hanging drop. Furthermore, certain experimental parameters, such as extraction time, temperature and agitation, can also affect the stability of the microdrop and should be therefore carefully selected. The extractant phase must be immiscible with the sample, and show a reduced solubility and a low toxicity.

Under equilibrium conditions, the concentration of analyte in the extractant drop is given by:

$$C_d^{\infty} = K_{dS} C_S^{\infty} = \frac{K_{dS} C_S^0 V_S}{V_S + K_{dS} V_d} \quad (2)$$

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