

Ionic liquids in magnetic-assisted microextraction procedures: A step forward for faster and selective sample preparation

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Abstract

Magnetic separations utilize an extraction material with paramagnetic properties, permitting them to be controlled under a magnetic field and contributing to a simplification of the sample preparation step. Ionic liquids represent an alternative class of solvents to conventional extraction materials, which may be toxic and possess limited selectivity or extraction efficiency. Several studies have proposed the use of ionic liquids in magnetic-assisted microextraction procedures. In some cases, the ionic liquid is combined with other materials such as magnetic nanoparticles, generating a hybrid material able to be used in magnetic-assisted procedures. In other cases, magnetic ionic liquids, which possess inherent magnetism, are directly used as magnetic extraction materials. This review provides an overview of these two possibilities towards magnetic-assisted extraction procedures.

Keywords: ionic liquids, ionic liquid-based surfactants, polymeric ionic liquids, magnetic ionic liquids, magnetic separation, microextraction

Resumo

Separações magnéticas utilizam um material magnético de extração com propriedades paramagnéticas, permitindo seu controle sob um campo magnético e contribuindo para a simplificação da etapa de preparo de amostras. Líquidos iônicos representam uma classe alternativa de solventes aos materiais convencionais de extração, os quais podem ser tóxicos e possuem seletividade limitada ou eficiência limitada de extração. Vários estudos tem proposto o uso de líquidos iônicos em procedimentos de micro extração assistidos por meios magnéticos. Em alguns casos, o líquido iônico é combinado com outros materiais, como nanopartículas magnéticas, gerando materiais híbridos capazes de serem utilizados em procedimentos assistidos por meios magnéticos. Em outros casos, líquidos iônicos magnéticos, os quais possuem magnetismo inerente, são diretamente utilizados como materiais magnéticos para extração. Esta revisão fornece uma visão geral dessas duas possibilidades em direção a procedimentos de extração assistidos por meios magnéticos.

Palavras-chave: líquidos iônicos, surfactantes baseados em líquidos iônicos, líquidos iônicos poliméricos, líquidos iônicos magnéticos, separação magnética, micro extração.

1. Introduction

With the recent advances in instrumentation and automation towards chromatography and related techniques, sample preparation is a bottleneck in any analytical methodology [1]. Thereby, current trends in analytical chemistry are focused on the development of simpler, miniaturized, and faster methods for sample preparation, often following the principles of Green Analytical Chemistry [2] while ensuring proper preconcentration of the target analytes. In this sense, microextraction procedures represent a valid alternative to conventional extraction techniques.

Two main microextraction modes can be distinguished from one another based on whether the extraction material is a solid or a liquid: solid phase-based microextraction (SPME) [3] and liquid-phase based microextraction (LPME) [4], respectively. The use of all these microextraction techniques under their different modes generates a wide range of possibilities for carrying out an analysis. Furthermore, a simplification of both types of microextraction procedures has been possible due to the introduction of magnetic separations. Magnetic separations utilize an extraction material with paramagnetic properties, permitting them to be controlled under a magnetic field [5]. Analytes are enriched in the extraction material and can be subsequently separated from the remaining components of the sample with the aid of a strong Fe-Nd-B magnet [6]. Thus, the method avoids common centrifugation and filtration steps.

Ionic liquids (ILs) are non-molecular solvents with melting points below 100 °C. They possess a wide variety of physicochemical properties, including low to negligible vapor pressure at room temperature, and high chemical and electrochemical stability [7]. ILs are composed completely of ions. In general, they possess organic cations containing nitrogen or phosphorous atoms such as imidazolium, ammonium or phosphonium, and inorganic or organic anions [8]. There are two important aspects that makes ILs interesting

materials. First, small modifications to the IL structure are accompanied by a dramatic change in a number of IL properties, including water solubility and viscosity. Furthermore, the incorporation of different moieties within the IL structure can promote different interactions with analytes, resulting in impressive solvation capabilities for different compounds.

ILs represent an alternative to conventional extraction materials that often may be toxic and have limited selectivity or extraction efficiency. Thus, a large number of applications have reported the use of ILs in microextraction studies [9,10]. Furthermore, an increasing number of studies employ magnetic assisted-procedures together with ILs [11,12]. There are two possibilities for incorporating ILs in magnetic assisted-microextraction procedures: (i) the combination of the IL with other materials such as magnetic nanoparticles (MNPs) or microspheres (MMPs), generating a hybrid material with paramagnetic properties, and (ii) the use of magnetic ionic liquids (MILs) which are a subclass of ILs possessing inherit magnetism.

Within this review, we provide an overview in the use of ILs and their derivatives towards magnetic-assisted microextraction procedures. The review is focused on applications that combine the use of microextraction procedures with chromatography and related techniques.

2. Microextraction procedures based on hybrid materials containing an ionic liquid component

This section describes magnetic-assisted microextraction procedures using extraction materials possessing a magnetic core (in general, MNPs) coated/decorated with an IL (MNP@IL). The extraction performance of the material is related to the nature of the IL [13]. These MNP@IL hybrid materials can be prepared by the following two routes: the first route implies the *in situ* formation of the hybrid material (the combination of the MNPs and the IL) during the microextraction

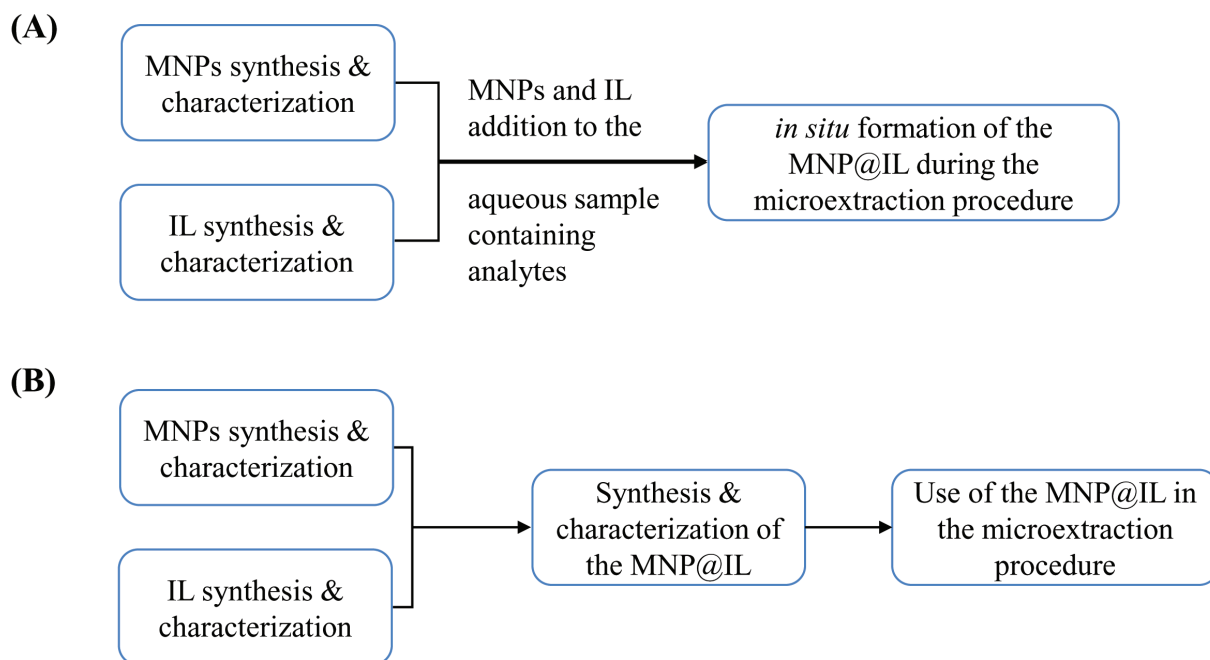


Fig. 1. Scheme of the preparation of hybrid materials based on MNP@IL: (A) *in situ* formation of the hybrid material during the microextraction step, and (B) synthesis and characterization of the material prior its use in the microextraction procedure.

step [11,14] (route (A) of Figure 1). The second route involves the synthesis and characterization of the MNP@IL material prior its use in the microextraction procedure (route (B) of Figure 1).

Regarding the magnetic core, a larger number of magnetic-based extraction procedures use MNPs composed of magnetite ($\alpha\text{-Fe}_3\text{O}_4$) [11,14]. However, bare Fe_3O_4 MNPs tend to aggregate, and they can also experience oxidation in air or biodegradation. For that reason, they are protected with layers of other materials such as silica, generating core-shell structures ($\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs) [15], as shown in Figure 2. Furthermore, there are different strategies of functionalization of the surface of the MNPs to create specific moieties able to interact with the corresponding IL (or IL derivative). These strategies include the use of 3-chloropropyltriethoxysilane [15] or 1,6-diisocyanatohexane [16] as coupling agents, among others. In addition, other studies have described the combination of Fe_3O_4 MNPs with carbon-based

materials, including graphene oxide ($\text{Fe}_3\text{O}_4@\text{GO}$ MNPs [17] or $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}$ MNPs [18]), or multi-walled carbon nanotubes ($\text{Fe}_3\text{O}_4@\text{MWCNTs}$ MNPs [19]). Other magnetic-assisted procedures use $\text{Fe}_3\text{O}_4@ \beta\text{-cyclodextrin/attapulgit}$ [20], barium ferrite nanoparticles [13] or $\text{Fe}_3\text{O}_4@\text{diatomaceous earth}$ [21] as a magnetic core.

Regarding the IL component of these magnetic materials, they will be discussed in the following sections related to the type of microextraction method employed: dispersive liquid-liquid microextraction with magnetic retrieval (m-DLLME) or magnetic-assisted micro-solid phase extraction (m- μ -SPE).

2.1 Dispersive liquid-liquid microextraction with magnetic retrieval

Dispersive liquid-liquid microextraction (DLLME) is a type of LPME procedure based on the use of two types of solvents: a water immiscible solvent acting as an extraction solvent, and a dispersive solvent that is miscible with both the sample and the extraction solvent

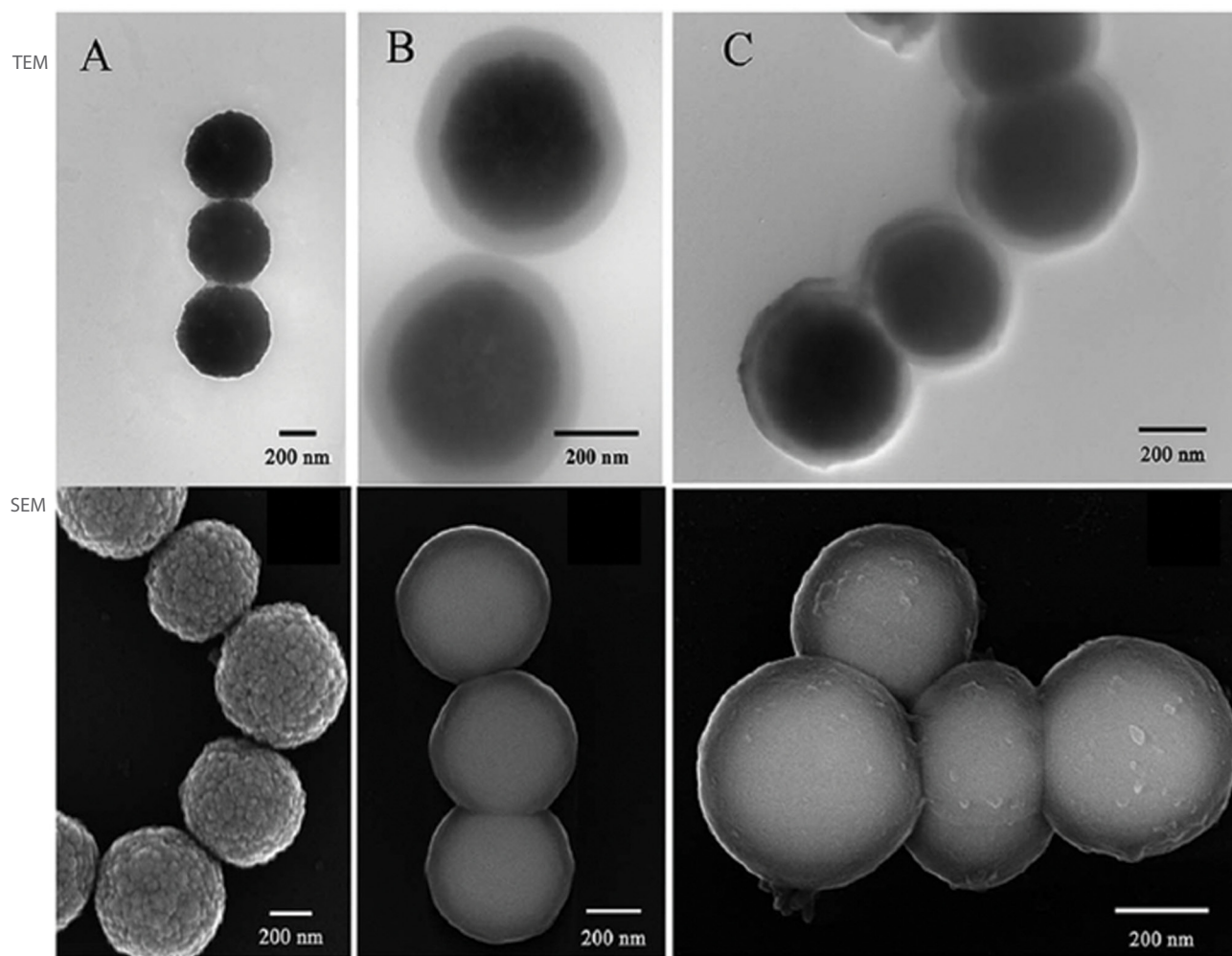


Fig. 2. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of (A) Fe_3O_4 MNPs, (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs, and (C) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PIL}$ MNPs. Reproduced with permission from reference [15].

[22]. The addition of these two components to the aqueous sample forms a cloudy solution that promotes a rapid partitioning of the analytes into the extraction solvent. In some cases, the application of high temperatures, or the use of microwaves, ultrasound, vortex or any other stirring method has also been reported [10]. The classical DLLME method then requires centrifugation and filtration steps for the separation and isolation of the extraction phase from the sample matrix.

IL-DLLME processes with magnetic retrieval (m-IL-DLLME) avoid the centrifugation and filtration steps of classical DLLME, simplifying the procedure and reducing the extraction time. In these approaches,

the IL acts as the extraction solvent. After the formation of the cloudy solution, MNPs are added to the extraction vial. Weak interactions between the MNPs and the IL containing the extracted analytes are established, and the hybrid material can be isolated using a strong magnet. Analytes are then subsequently eluted from the material. Thus, the hybrid material is prepared using the first route of Figure 1(A).

It is important to mention that some authors have used the DLLME with magnetic retrieval term [23] whereas others use the terminology of dual magnetic microextraction (DMME), describing the methodology

as a combination of DLLME with a subsequent step of μ -SPE [13].

Hydrophobic ILs containing imidazolium cations and the bis[(trifluoromethyl)sulfonyl]imide ($[\text{NTf}_2^-]$) [13,20] or hexafluorophosphate ($[\text{PF}_6^-]$) [23] anions are used as extraction solvents in m-IL-DLLME procedures. In addition, hydrophilic ILs have been employed for *in situ* DLLME procedures with magnetic retrieval [14,24]. In these approaches, the hydrophilic IL is mixed with an anion exchange reagent such as lithium $[\text{NTf}_2^-]$ ($\text{Li}[\text{NTf}_2^-]$) [24], sodium dicyanamide ($\text{Na}[\text{N}(\text{CN})_2^-]$) [14] or sodium diethyldithiocarbamate ($\text{Na}[\text{DDTC}^-]$) [14]. The mixture of both reagents in a 1:1 ratio promotes a metathesis reaction, generating a hydrophobic IL in which analytes are extracted. After that, a magnet is held in the extraction vial for the magnetic separation followed by elution of the analytes.

Yang *et al.* proposed an effervescence-assisted m-IL-DLLME procedure for the determination of four fungicides in water, followed by high performance liquid chromatography with ultraviolet detection (HPLC-UV) [25]. A magnetic effervescent tablet composed of Fe_3O_4 MNPs, sodium carbonate, sodium dihydrogen phosphate and 1-hexyl-3-methylimidazolium $[\text{NTf}_2^-]$ ($[\text{C}_6\text{MIM}^+][\text{NTf}_2^-]$) was added to the aqueous sample as the extraction material [25]. Sodium carbonate and sodium dihydrogen phosphate act as effervescence precursors, generating CO_2 bubbles that assisted the dispersion of the $\text{Fe}_3\text{O}_4@$ IL MNPs, as shown in Figure 3. After that, a magnet is placed at the bottom of the extraction tube to promote magnetic separation. After separation of the sample matrix, analytes are eluted with ethanol [25].

Table 1 [11,15,18-20,24-29] shows representative examples of m-IL-DLLME applications. It is important to highlight that the majority of the procedures have utilized HPLC as a subsequent analytical technique with a wide variety of detection systems, including UV [20] or mass spectrometry [24].

2.2. Magnetic-assisted micro-solid phase extraction

Micro-solid phase extraction (μ -SPE) is the miniaturized version of solid phase extraction (SPE) [30]. Analytes are extracted in a small amount of sorbent material, which is placed in a cartridge (static μ -SPE) [31] or is dispersed on the matrix sample (dispersive μ -SPE, or μ -dSPE) [3]. Analytes are then eluted from the sorbent material using a low volume of a solvent, followed by analytical determination. The classical μ -dSPE requires centrifugation and/or filtration steps to separate the matrix sample and the extraction material prior to the elution. Thus, magnetic-assisted μ -dSPE (m- μ -dSPE) represents an interesting alternative in sample preparation as these steps can be avoided, contributing to the simplification of the procedure.

Hybrid materials containing an IL component have been used in m- μ -dSPE procedures to improve the extraction performance of the methodology. Table 1 also summarizes some of these m- μ -dSPE approaches. The majority of these applications use MNP@IL materials

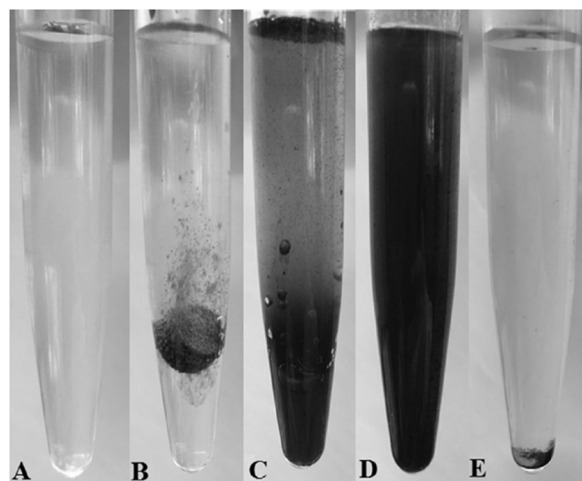


Fig. 3. Steps used during the effervescence-assisted m-IL-DLLME procedure reported in [25]: (A) aqueous sample, (B) addition of the magnetic effervescent tablet, (C) dispersion of the MNP@IL by CO_2 bubbles, (D) extraction vial after dispersion (the disintegrated tablet was homogeneously distributed into the aqueous sample), and (E) MNP@IL MNPs sedimented at the bottom of the extraction vial after magnetic separation. Reprinted with permission from reference [25].

Table 1. Representative magnetic assisted-microextraction procedures based on hybrid materials containing an ionic liquid component

Analites	Sample	Extraction procedure ^a	Extraction material ^b	Analytical technique ^c	LOD ^d (µg·L ⁻¹)	RSD ^e (%)	RR ^f (%)	Ref.
fungicides	water	m-DLLME assisted by vortex	Fe ₃ O ₄ @βCD/AP @ [C ₆ MIM ⁺][NTf ₂ ⁻] MNPs	HPLC-UV	0.02–0.04	2.9–4.2	97–115	[20]
acaricides	tea infusion	m-DLLME assisted by vortex	ZnO@ Fe ₃ O ₄ @ [C ₈ MMIM ⁺][NTf ₂ ⁻] MNPs	HPLC-DAD	0.44–1.0	4.4–7.4	83.0–104	[26]
endocrine disrupting phenols	water	in situ m-DLLME using [C ₄ MIM ⁺][Cl] ^h and Li[NTf ₂ ⁻]	Fe ₃ O ₄ @ [C ₄ MIM ⁺][NTf ₂ ⁻] MNPs	HPLC-MS	0.004–0.62	0.5–9.3	78.8–103	[24]
fungicides	water	effervescence-assisted m-DLLME	magnetic effervescent tablet with Fe ₃ O ₄ @ [C ₆ MIM ⁺][NTf ₂ ⁻] MNPs	HPLC-UV	0.02–0.10	2.4–4.9	84.6–113	[25]
bisphenol A	plastic tableware	LLE followed by m-µ-dSPE assisted by stirring and temperature	Fe ₃ O ₄ @ SiO ₂ @ [C ₈ MIM ⁺][PF ₆ ⁻] MNPs	HPLC-UV	0.09	1.2	99.4–101	[27]
triazole herbicides	water	m-µ-dSPE assisted by ultrasound	Fe ₃ O ₄ @ MWCNT@ [AC ₄ C ₄ IM ⁺][Cl] ⁻ MNPs	GC-MS	0.05–0.22	6.9–11	84.7–111	[19]
preservatives	vegetables	modified QuEChERS (LLE followed by m-µ-dSPE)	Fe ₃ O ₄ @ SiO ₂ -NH ₂ @ GO @poly ^g [VC ₈ IM ⁺][Br ⁻] MNPs	GC-MS	0.82–6.6 µg·kg ⁻¹	1.8–12	83.3–118	[18]
sulfonylurea herbicides	soil	m-µ-dSPE assisted by vortex	Fe ₃ O ₄ @ SiO ₂ -PEG @poly ^g [VMIM ⁺][Cl] ⁻ MNPs	HPLC	1.6–2.9	3.2–4.5	77.4–97.6	[15]
endocrine disrupting phenols	water and tea infusion	m-µ-dSPE assisted by ultrasound	mixed hemimicelles of Fe ₃ O ₄ @ [C ₁₂ C ₁₂ IM ⁺][Br ⁻] & [C ₁₆ MIM ⁺][Br ⁻] (1:1 ratio) MNPs	HPLC-DAD	0.1–0.6	1.6–13	89.2–112	[11]
cephalosporins	urine	m-µ-dSPE assisted by ultrasound	Mixed hemimicelles of Fe ₃ O ₄ @GO @ [C ₁₆ MIM ⁺][Br ⁻]	HPLC-UV	0.6–1.9	< 6.3	82.1–96.8	[28]
non-steroidal anti-inflammatory drugs	human blood	SFE, followed by m-µ-dSPE assisted by vortex	Fe ₃ O ₄ @ SiO ₂ @ [N _{1,1,18, TMSP} ⁺][Cl] ⁻ MNPs	HPLC-UV	0.2–0.5	8.0–10	92.0–97.1	[29]

^a Abbreviations: LLE for liquid-liquid extraction, m-DLLME for dispersive liquid-liquid microextraction with magnetic retrieval, m-µ-dSPE for magnetic-assisted dispersive micro-solid phase extraction, and SFE for supercritical fluid extraction.

^b **IL abbreviations:** **Cations:** [AC₄C₄IM⁺] for 1-(3-aminopropyl)-3-propylimidazolium, [C₄MIM⁺] for 1-butyl-3-methyl imidazolium, [C₆MIM⁺] for 1-hexyl-3-methylimidazolium, [C₈MIM⁺] for 1-octyl-3-methylimidazolium, [C₁₀MMIM⁺] for 1-octyl-2,3-dimethylimidazolium, [C₁₂C₁₂IM⁺] for 1,3-didodecylimidazolium, [C₁₆MIM⁺] for 1-hexadecyl-3-methylimidazolium, [N_{1,1,18, TMSP}⁺] for dimethyloctadecyl[3-(trimethoxysilylpropyl)] ammonium, [VC₈IM⁺] for 1-vinyl-3-octylimidazolium, and [VMIM⁺] for 1-vinyl-3-methylimidazolium.

Anions: [Br⁻] for bromide, [Cl⁻] for chloride, [NTf₂⁻] for bis[(trifluoromethyl)sulfonyl]imide, and [PF₆⁻] for hexafluorophosphate.

Others: βCD/AP for β- cyclodextrin/attapulgit, GO for graphene oxide, MNPs for magnetic nanoparticles, and MWCNTs for multi-walled carbon nanotubes.

^c Abbreviations: DAD for diode array detection, GC for gas chromatography, HPLC for high-performance liquid chromatography, MS for mass spectrometry, and UV for ultraviolet detection.

^d Limit of detection.

^e Relative standard deviation.

^f Relative recovery.

^g "Poly" denotes a polymeric ionic liquid.

generated using route (B) of Figure 1. Regarding the nature of the IL, both hydrophobic and hydrophilic ILs can be attached to the magnetic core of the hybrid material (Table 1). Amino functionalized dicationic ILs were coated on the surface of Fe@GO composite and used as magnetic adsorbent for the extraction of bovine hemoglobin [17]. Furthermore, Fe₃O₄@MWCNT@[AC₄C₄IM⁺][Cl⁻] (being [AC₄C₄IM⁺][Cl⁻] the 1-(3-aminopropyl)-3-propylimidazolium chloride IL) was prepared for the determination of triazole fungicides in water [19]. The IL was synthesized on the surface of MWCNTs and chemically attached via CONH- groups.

Polymeric ionic liquids (PILs) have also been used to generate hybrid materials for m-μ-dSPE. PILs are polymers generated by the polymerization of an IL monomer [32]. The majority of PILs employed for sample preparation are of the polycationic type where the backbone of the polymer is in the cationic component and the anionic component is responsible for the ionic conductivity of the material. Zhang *et al.* synthesized an epitope molecularly imprinted polymer using a cyclodextrin-based IL as functional monomer for the specific recognition of cytochrome in aqueous solutions [33]. The epitope polymer shell was coated on Fe₃O₄@SiO₂ MNPs functionalized with [3-(methacryloyloxy)propyl]trimethoxysilane, and characterized by transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS), and thermogravimetric analysis (TGA) [33]. The authors demonstrated a superior adsorption capacity and recognition ability when both β-cyclodextrins and ILs were used together with the Fe₃O₄@SiO₂ MNPs [33]. Another interesting hybrid material was based on Fe₃O₄@SiO₂@GO@PIL MNPs, synthesized using 1-vinyl-3-octylimidazolium bromide ([VC₈IM⁺][Br⁻]) as IL monomer [18]. The hybrid material was used as an adsorbent in a modified QuEChERS method for the determination of 20 preservatives in vegetables, followed by gas chromatography-mass spectrometry (GC-MS) [18]. With this method, good clean-up performance and

limits of detection down to 6.6 μg·kg⁻¹ were achieved (Table 1).

Hydrophilic ILs with long alkyl chains, able to act as IL-based surfactants, have also been employed in m-μ-dSPE. When these ionic surfactants are in solution at a concentration near or slightly below their critical micelle concentration (CMC), they can form monolayers or bilayers on the surface of a solid with opposite charge (the MNPs in this particular case). These layers of surfactants are termed hemimicelles and admicelles, respectively [34]. Mixed hemimicelles occur when both aggregation types are present together [11,35]. In hemimicelles, the hydrophobic chain of the surfactant is exposed to the sample while in admicelles, the ionic headgroup of the surfactant is exposed to the sample. Thus, both non-polar and polar analytes can be extracted using mixed hemimicelles. It is important to point out that mixed hemimicelles of IL-based surfactants on the surface of MNPs are generated using route (A) of Figure 1. Several methods describe the use of mixed hemimicelles based on ILs [35]. Furthermore, a successful method for phenol determination was developed using mixed hemimicelles of double salts of IL-based surfactants supported on Fe₃O₄ (Fe₃O₄@DSIL MNPs) [11]. Under optimum conditions, two different IL-based surfactants were mixed to generate a DSIL, namely 1,3-didodecylimidazolium bromide ([C₁₂C₁₂IM⁺][Br⁻]) and 1-hexadecyl-3-methylimidazolium bromide ([C₁₆MIM⁺][Br⁻]) (1:1 ratio) [11].

In another interesting study, non-steroidal anti-inflammatory drugs were determined in biological fluids by subsequently employing two extraction techniques: supercritical fluid extraction (SFE) and m-μ-dSPE using [29] (Table 1). A small matrix effect was observed when the developed technique was applied for the analysis of blood samples [29].

3. Microextraction procedures based on magnetic ionic liquids

Magnetic ionic liquids (MILs) are a subclass of ILs designed to contain a paramagnetic component in the cation or anion of the IL structure, exhibiting a strong response to external magnetic fields [36]. MILs can be clearly differentiated from MNP@IL and MMP@IL hybrid materials, previously discussed in Section 2, that are magnetic suspensions of nanometer to micrometer size. In comparison, MILs are transparent and exist as neat magnetic solvents [37]. Thus, MILs are considered a second generation of paramagnetic fluids, as their magnetism is on the atomic scale [38]. Furthermore, MILs

possess some of the unique physicochemical properties of ILs, including low vapor pressure at room temperature and impressive solvation capabilities for both polar and non-polar compounds, and they can be easily tuned for specific applications. The majority of MILs contain transition metal (Fe(III), Co(II), Mn(II), Ni(II)...) or lanthanide metal (Gd(III), Nd(III), Dy(III)...) complexes as anions [36]. Figure 4 shows representative examples of MILs used for analytical applications. The type of paramagnetic anion, and also the cationic platform, can assist in modulating the magnetic properties of the MIL.

The inherit magnetism of MILs makes them interesting extraction materials in magnetic separations. Up to date, they have been employed in different modes

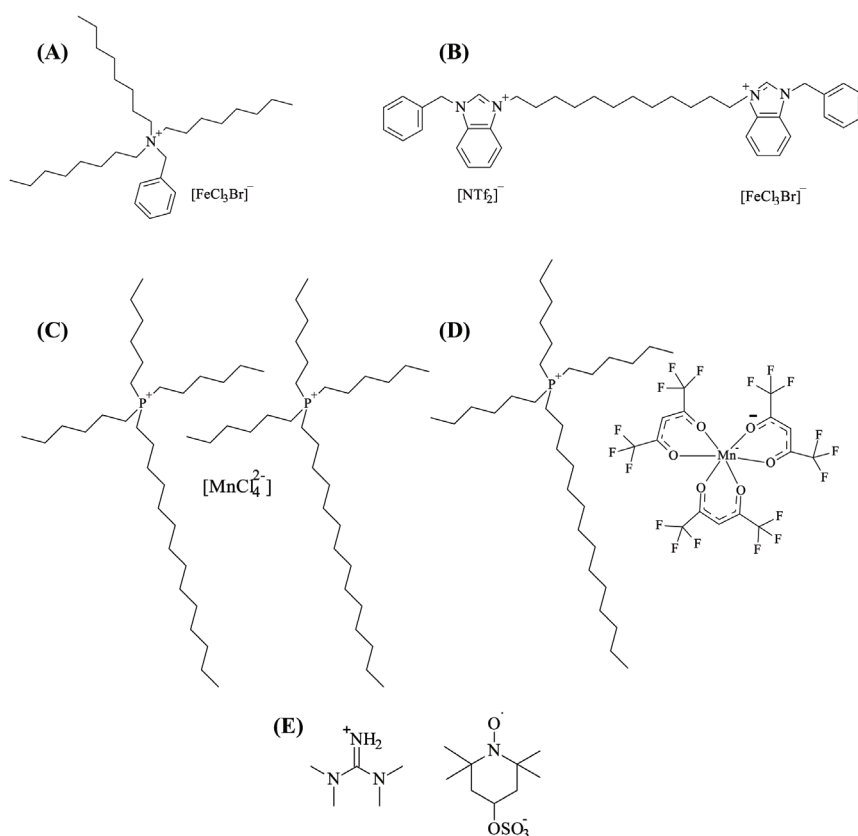


Fig.4 Representative examples of the MILs used in magnetic-assisted microextraction procedures, with (A) bencyltriocetylammmonium bromotrichloroferrate(III) ($[\text{N}_{8,8,8\text{Bn}}^+][\text{FeCl}_3\text{Br}]^-$), (B) 1,12-di(3-benzylbenzimidazolium)dodecane bis([trifluoromethyl)sulfonyl]imide bromotrichloroferrate (III) ($[(\text{BBnIM})_2\text{C}_{12}^{2+}][\text{NTf}_2][\text{FeCl}_3\text{Br}]^-$), (C) trihexyltetradecylphosphonium tetrachloromanganate(II) ($[\text{P}_{6,6,6,14}^+][\text{MnCl}_4]^{2-}$), (D) trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)manganate(II) ($[\text{P}_{6,6,6,14}^+][\text{Mn}(\text{hfacac})_3]^-$), and (E) 1,1,3,3-tetramethylguanidine 4-sulfonate 2,2,6,6-tetramethylpiperidine 1-oxyl ($[\text{TMG}^+][\text{TEMPO-OSO}_3]^-$).

Table 2. Representative magnetic assisted-microextraction procedures based on the use of magnetic ionic liquids (MILs).

Analites	Sample	Extraction procedure ^a	Extraction material ^b	Analytical technique ^c	LOD ^d ($\mu\text{g}\cdot\text{L}^{-1}$)	RSD ^e (%)	RR ^f (%)	Ref.
phenols	water	m-DLLME	$[\text{N}_{1,8,8}^+][\text{FeCl}_4^-]$	HPLC-DAD (direct injection of the MIL)	1.05–33.0	3.6–7.2	89–94	[42]
polycyclic aromatic hydrocarbons	water and tea infusion	m-DLLME, followed by back-extraction	$[\text{N}_{8,8,8}^+][\text{FeBrCl}_3^-]^9$, $[\text{N}_{8,8,8,\text{MOB}}^+][\text{FeBrCl}_3^-]$, or $[(\text{BBnIM})_2\text{C}_{12}^{2+}][\text{NTf}_2^-, \text{FeCl}_3\text{Br}^-]$	HPLC-FD	0.005–0.02	1.0–13	91.5–119	[6]
triazine herbicides	vegetable oils	m-DLLME, followed by back-extraction	$[\text{C}_6\text{MIM}^+][\text{FeCl}_4^-]$ & carbonyl iron powder to enable magnetic separation	HPLC-UV	1.31–1.49	1.9–7.5	93.7–107	[43]
organic pollutants	water	m-DLLME	$[\text{P}_{6,6,6,14}^+][\text{MnCl}_4^{2-}]^9$, or $[\text{Aliquat}^+][\text{MnCl}_4^{2-}]$	HPLC-UV	0.05–1.0	0.3–17	71.5–108	[40]
organic pollutants	water	m-HS-SDME	$[\text{P}_{6,6,6,14}^+][\text{MnCl}_4^{2-}]^9$, or $[\text{Aliquat}^+][\text{MnCl}_4^{2-}]$	HPLC-UV	0.04–1.0	2.3–15	69.2–110	[40]
free fatty acids	milk	vacuum HS-SDME	$[\text{P}_{6,6,6,14}^+][\text{MnCl}_4^{2-}]$, $[\text{Aliquat}^+][\text{MnCl}_4^{2-}]$, $[\text{P}_{6,6,6,14}^+][\text{Mn}(\text{hfacac})_3^-]^9$, or $[\text{P}_{6,6,6,14}^+][\text{Dy}(\text{hfacac})_4^-]$	HSD-GC-MS	14.5–216	2.5–13	79.5–94.4	[44]
chloramphenicol	water	magnetic-assisted ABS	$[\text{TMG}^+][\text{TEMPO-OSO}_3^-]$ & potassium phosphate	HPLC-UV	0.14	4.45	90–110	[41]
UV filters	water	SBDLME	$[\text{P}_{6,6,6,14}^+][\text{Dy}(\text{hfacac})_4^-]$, $[\text{P}_{6,6,6,14}^+][\text{Co}(\text{hfacac})_3^-]$, $[\text{P}_{6,6,6,14}^+][\text{Ni}(\text{hfacac})_3^-]^9$	or HSD-GC-MS	0.01–0.03	1.4–15	89–115	[45]
phenolic acids	apple	LLE & m- μ -dSPE	molecularly imprinted polymer using $[\text{AlC}_8\text{IM}^+][\text{FeCl}_4^-]$	HPLC-UV	0.31–1.72	1.1–6.3	81–100	[46]

^a Abbreviations: ABS for aqueous biphasic system, LLE for liquid-liquid extraction, m-DLLME for dispersive liquid-liquid microextraction with magnetic retrieval, m- μ -dSPE for magnetic-assisted dispersive micro-solid phase extraction, m-HS-SDME for magnetic-assisted headspace single-drop microextraction, vacuum HS-SDME for headspace single-drop microextraction under reduced pressure conditions, and SBDLME for stir-bar dispersive liquid microextraction.

^b **IL abbreviations: Cations:** $[\text{Aliquat}^+]$ for trioctylmethylammonium, $[(\text{BBnIM})_2\text{C}_{12}^{2+}]$ for 1,12-di(3-benzylbenzimidazolium)dodecane, $[\text{C}_6\text{MIM}^+]$ for 1-hexyl-3-methylimidazolium, $[\text{N}_{1,8,8}^+]$ for trioctylmethylammonium, $[\text{N}_{8,8,8}^+]$ for benzyloctylammonium, $[\text{N}_{8,8,8,\text{MOB}}^+]$ for methoxybenzyloctylammonium, $[\text{P}_{6,6,6,14}^+]$ for trihexyltetradecylphosphonium, and $[\text{TMG}^+]$ for 1,1,3,3-tetramethylguanidine

Anions: $[\text{Co}(\text{hfacac})_3^-]$ for tris(hexafluoroacetylaceto)cobaltate(III), $[\text{Dy}(\text{hfacac})_4^-]$ for tetra(hexafluoroacetylaceto)dysprosate(III), $[\text{FeBrCl}_3^-]$ for bromotrichloroferrate(III), $[\text{FeCl}_4^-]$ for tetrachloroferrate(III), $[\text{MnCl}_4^{2-}]$ for tetrachloromanganate(II), $[\text{Mn}(\text{hfacac})_3^-]$ for tris(hexafluoroacetylaceto)manganate(II), $[\text{Ni}(\text{hfacac})_3^-]$ for tris(hexafluoroacetylaceto)nickelate(II), $[\text{NTf}_2^-]$ for bis[(trifluoromethyl)sulfonyl]imide, and $[\text{TEMPO-OSO}_3^-]$ for 2,2,6,6-tetramethylpiperidine 1-oxyl.

^c Abbreviations: FD for fluorescence detection, HPLC for high-performance liquid chromatography, HSD for headspace desorption, GC for gas chromatography, MS for mass spectrometry, PCR for polymerase chain reaction, and UV for ultraviolet detection.

^d Limit of detection.

^e Relative standard deviation.

^f Relative recovery.

^g Selected as optimum MIL.

^h Molecularly imprinted polymer based on a MIL monomer.

of LPME and SPME, as will be discussed in the following sections.

3.1. Magnetic-assisted liquid phase microextraction

MILs have been employed in two different modes of LPME, including m-DLLME [39] and magnetic-assisted single-drop microextraction (m-SDME) [40]. Furthermore, they have been used as a component of aqueous biphasic systems (ABSs) [41]. Representative examples of these types of applications using MILs are listed in Table 2 [6,40-46].

Regarding m-DLLME, the majority of works use MILs containing Fe(III) anions such as tetrachloroferrate(III) ($[\text{FeCl}_4^-]$) [43] or bromotrichloroferrate(III) ($[\text{FeBrCl}_3^-]$) [47,48], in combination with imidazolium [43], phosphonium [47] or ammonium [47] cations, as in Figure 4(A). Dicationic-based MILs have also been used as extraction solvents in m-DLLME, specifically 1,12-di(3-hexadecylbenzimidazolium) dodecane bis[(trifluoromethyl)sulfonyl]imide bromotrichloroferrate(III) ($[(\text{C}_{16}\text{BnIM})_2\text{C}_{12}^{2+}][\text{NTf}_2^-, \text{FeBrCl}_3^-]$) for the determination of DNA in albumin [47] and 1,12-di(3-benzylbenzimidazolium) dodecane bis[(trifluoromethyl)sulfonyl]imide bromotrichloroferrate (III) ($[(\text{BBnIM})_2\text{C}_{12}^{2+}][\text{NTf}_2^-, \text{FeBrCl}_3^-]$) for polycyclic aromatic hydrocarbons (PAHs) in water [6] (Figure 4(B)). In these cases, the hydrophobicity of the MIL was increased through the use of the dicationic structures while the combination of the two anions serves to control their water solubility without losing the magnetic susceptibility of the material. Other m-DLLME procedures with $[\text{FeCl}_4^-]$ -based MILs required the addition of extra materials such as carbonyl iron powder [49] or Fe_3O_4 MNPs [50] to enable the magnetic separation. The magnetic susceptibility of the tested MILs (1-butyl-3-methylimidazolium tetrachloroferrate(III), $[\text{C}_4\text{MIM}^+][\text{FeCl}_4^-]$ [49] and 1-hexyl-3-methylimidazolium tetrachloroferrate(III), $[\text{C}_6\text{MIM}^+][\text{FeCl}_4^-]$ [50]) was not

sufficient for being collected using an external magnetic field. In other cases, the high viscosity of the MIL did not allow direct injection of the MIL microdroplet after m-DLLME and a further step of back-extraction is required [6,43].

Fe(III) anions undergo hydrolysis in water at room temperature and have a strong absorbance at wavelengths in the UV-Visible region, which represents drawbacks for some analytical applications [39]. As an alternative, MILs containing the tetrachloromanganate(II) ($[\text{MnCl}_4^{2-}]$) anion have been developed and used in m-DLLME [39,40] (Table 2). Particularly, trioctylmethylammonium tetrachloromanganate(II) ($[\text{Aliquat}^+]_2[\text{MnCl}_4^{2-}]$) and trihexyltetradecylphosphonium tetrachloromanganate(II) ($[\text{P}_{6,6,6,14}^{+}]_2[\text{MnCl}_4^{2-}]$) were applied for the determination of different groups of pollutants in water [39,40]. The structure of $[\text{P}_{6,6,6,14}^{+}]_2[\text{MnCl}_4^{2-}]$ is represented in Figure 4(C).

Concerning SDME, it is a powerful microextraction technique based on the use of a small droplet of extraction solvent that is directly exposed to the sample (direct immersion SDME, DI-SDME) or using the headspace as intermediate phase (headspace SDME, HS-SDME) [51]. In general, the extraction solvent droplet is suspended with the aid of a microsyringe. However, in m-SDME procedures using MILs as extraction solvent, the common microsyringe is substituted by a rod magnet. With this configuration, a higher microdroplet volume can be hung on the rod magnet for prolonged sampling time, even under strong stirring [40]. Despite this advantage, only a few studies have reported the use of MILs as extraction solvents in m-SDME [40,44,48]. Two of these applications have compared the analytical performance of the m-SDME method with m-DLLME [40,48]. In the first application, three different Fe(III)-based MILs were used in m-DI-SDME and m-DLLME for the determination of DNA [48]. In the second approach, a comparison between m-HS-SDME and m-DLLME was established using $[\text{MnCl}_4^{2-}]$ -based MILs for the determination of organic pollutants [40]. In general, comparable results were

obtained using both types of methodologies. More recently, two MILs containing the $[\text{MnCl}_4]^{2-}$ anion and other novel MILs, namely trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)manganate(II) ($[\text{P}_{6,6,6,14}^+][\text{Mn}(\text{hfacac})_3^-]$) and trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)dysprosate(III) ($[\text{P}_{6,6,6,14}^+][\text{Dy}(\text{hfacac})_4^-]$), were employed in m-SDME [44] (Figure 4(D), Table 2). In this particular application, a m-HS-SDME method under low pressure conditions (termed as vacuum HS-SDME) was developed for the first time for the determination of free fatty acids in milk [44]. The procedure was combined with headspace desorption (HSD)-GC-MS. This new generation of MILs containing transition or rare earth metals coordinated with bidentate organic ligands are extremely hydrophobic and possess low viscosity and high magnetic susceptibility [52].

A new type of guanidinium-based MIL that does not contain any metal center has been applied in ABS for the determination of chloroamphenicol in water [41] (Table 2). ABS are two immiscible aqueous-rich phase systems based on the combination of two types of components, in general salt-salt, polymer-polymer or salt-polymer combinations [53]. Both types of components are water soluble, but above a certain concentration, they separate into two phases to generate the ABS. When ABS are used with extraction purposes, one of the aqueous phase will be enriched in the analytes. In the developed MIL-ABS approach, the ABS was generated using aqueous solutions of 1,1,3,3-tetramethylguanidine 4-sulfonate 2,2,6,6-tetramethylpiperidine 1-oxy ($[\text{TMG}^+][\text{TEMPO-OSO}_3^-]$) [41] (Figure 4(E)). Potassium phosphate was used as a salt to promote the phase separation followed by collection of the MIL phase containing chloroamphenicol using an external magnet, and directly injected in HPLC-UV for further determination [41].

3.2. Magnetic-assisted solid-phase microextraction

MILs have also served as platforms for performing SPME extractions. Thus, they have been

used as extraction materials in two SPME modes: stir bar dispersive liquid-liquid microextraction (SBDLME) [45] and m- μ -dSPE [46]. Table 2 summarizes some of the analytical figures of merit of these developed procedures.

SBDLME is a novel technique that combines the principles and advantages of stir bar sorptive extraction (SBSE) and DLLME. The procedure is based on the use of a Nd-core magnetic stir bar as in SBSE, a paramagnetic extraction material (a MIL in this particular case) and high stirring rates during extraction [45]. The MIL is initially retained in the stir bar due to its magnetism but, after increasing stirring rate, the rotational forces of the stir bar surpass the magnetic field and the MIL disperses into the sample solution as fine microdroplets similar to DLLME. Figure 5 shows the dispersion of a MIL during SBDLME. When the stirring is stopped, the MIL containing extracted analytes returns to the stir bar. This new approach has been successfully applied for the determination of UV filters [45] and PAHs [54] in water, both in combination with HSD-GC-MS. Different MILs were tested as possible extraction solvents, including $[\text{P}_{6,6,6,14}^+][\text{Dy}(\text{hfacac})_4^-]$ [54], trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)cobaltate(II) ($[\text{P}_{6,6,6,14}^+][\text{Co}(\text{hfacac})_3^-]$) [45] and trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)nickelate(II) ($[\text{P}_{6,6,6,14}^+][\text{Ni}(\text{hfacac})_3^-]$) [45,54].

A molecularly imprinted polymer generated using a MIL as monomer has been prepared and used in m- μ -dSPE for the determination of phenolic acids in aqueous extracts of apple samples [46]. The molecularly imprinted polymer was prepared by suspension polymerization using 1-allyl-3-octylimidazolium tetrachloroferrate(III) ($[\text{AIC}_8\text{IM}^+][\text{FeCl}_4^-]$) as MIL monomer, ethylene glycol dimethyl acrylate as crosslinker and chlorogenic acid as template molecule. Furthermore, Fe_3O_4 MNPs were combined with the final polymer to ensure an adequate magnetic susceptibility and to enable magnetic separation during the m- μ -dSPE procedure [46].

4. Conclusions

ILs and derivatives have been successfully used as extraction materials in magnetic-assisted procedures. Two different types of paramagnetic fluids have been generated using ILs: (i) hybrid materials based on MNP@ILs, MNP@PILs or MNP@IL-based surfactants, and (ii) MILs, that are species with inherent magnetism. A simplification of the microextraction procedure is achieved using magnetic materials, as common filtration and centrifugation steps are avoided with these methodologies. The IL-character of the material contributes to highly sensitive and/or selective procedures for the monitoring of a wide variety of analytes and towards environmental, biological and food analysis. Furthermore, MILs have appeared as a new generation of

paramagnetic fluids. Compared to hybrid materials, they are easily synthesized and characterized, and they have served as a tool for developing and exploiting the use of new microextraction procedures, including vacuum HS-SDME and SBDLME. Thus, it can be expected that an increasing number of studies will be published regarding this field in the following years.

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Fig. 5. Images of a stir-bar coated with the trihexyltetradecylphosphonium tetrachloronickelate(II) ($[P_{6,6,6,14}^+][Ni(hfacac)_3^-]$) MIL (A), and the dispersion of the MIL during a SBDLME procedure (B). Reprinted with permission from reference [45].

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