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In situ formation of hydrophobic magnetic ionic liquids for dispersive liquid-liquid microextraction☆

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ABSTRACT

A new class of magnetic ionic liquid (MIL) containing paramagnetic cations has been applied for *in situ* dispersive liquid-liquid microextraction in the determination of both polar and non-polar pollutants, including ultraviolet filters, polycyclic aromatic hydrocarbons, alkylphenols, a plasticizer and a preservative in aqueous samples. The MILs were based on cations containing Ni(II) metal centers coordinated with four N-alkylimidazole ligands and chloride anions. The MILs were capable of undergoing *in situ* metathesis reaction with the bis[(trifluoromethyl)sulfonyl]imide ($[NTf_2^-]$) anion during the microextraction procedure, generating a water-immiscible extraction solvent containing the preconcentrated analytes. The MIL was then isolated by magnetic separation, followed by direct analysis using reversed-phase high performance liquid chromatography with diode array detection. Among all of the studied MILs, those containing the N-butylimidazole and N-benzylimidazole ligands ($[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$, respectively) exhibited the best extraction performance. The method under optimum conditions required 5 mL of sample at pH 3, 20 mg of $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ or 30 mg of $[Ni(BeIM)_4^{2+}]2[Cl^-]$, 300 μL of acetone or acetonitrile as dispersive solvent (depending on the MIL), a 1:2 M ratio of MIL to $[NTf_2^-]$, and 3 min of vortex. The developed method achieved higher extraction efficiency compared to the conventional MIL-dispersive liquid-liquid microextraction mode, with extraction efficiencies of 46.8–88.6% and 65.4–97.0% for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs (at a spiked level of 81 $\mu g\,L^{-1}$), respectively, limits of detection down to 5.2 $\mu g\,L^{-1}$, and inter-day relative standard deviation lower than 16%.

1. Introduction

Magnetic ionic liquids (MILs) are a subclass of ionic liquids (ILs) designed to contain a paramagnetic component in the cation or anion, allowing for a strong response to external magnetic fields [1–3]. These solvents possess many of the unique properties of ILs, including low to negligible vapor pressure at room temperature, variable viscosity, and impressive solvation capabilities for both polar and non-polar compounds. MILs are clearly differentiated from other magnetic materials such as magnetic nanoparticles, as they are transparent and exist as neat magnetic solvents, and are often considered a second generation of paramagnetic fluids [4].

Dispersive liquid-liquid microextraction (DLLME) is a powerful extraction and preconcentration technique that provides high enrichment factors while being simpler and faster than other liquid-phase microextraction procedures [5]. The technique is based on the rapid addition of an extraction and dispersive solvent mixture to an aqueous solution containing analytes. A cloudy solution of microdroplets is formed, maximizing the interface between phases and promoting the rapid partitioning of the analytes into the extraction solvent. The analyte-rich extraction phase can then be isolated by centrifugation and/or filtration. The *in situ* DLLME mode is an adaptation of the classical DLLME method that uses ILs as extraction solvents [6,7]. In this particular approach, a water soluble IL is mixed with an anion-exchange reagent, which undergoes an *in situ* metathesis reaction to form a water immiscible IL that acts as extraction solvent [6,7]. As a consequence, higher enrichment factors can generally be achieved in comparison to conventional DLLME [8–10].

MILs have been applied as extraction solvents in DLLME [1,2,6,7,11–18]. In these applications, the inherit magnetism of MILs makes it possible to replace the common centrifugation and filtration steps performed for isolating the extraction solvent by the magnetic separation of the MIL with

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a strong magnet. However, the majority of MILs designed with analytical purposes contain paramagnetic anions such as tetrachloroferrate(III) ($[FeCl_4^-]$) [11,12], bromotrichloroferrate(III) ($[FeBrCl_3^-]$) [13,14], tetrachloromanganate(II) ($[MnCl_4^{2-}]$) [15,16], tris(hexafluoroacetylaceto)nickelate(II) ($[Ni(hfacac)_3^-]$) [17] or tris(hexafluoroacetylaceto)dysprosate(III) ($[Dy(hfacac)_4^-]$) [18]. These types of MILs possess some limitations for their use in DLLME. For example, Fe(III)-based MILs can undergo hydrolysis in water at room temperature and have a strong absorbance in the UV–vis region, and Mn(II)-based MILs possess relatively high viscosity. Acetylacetonate-based MILs are generally not compatible with common reversed-phase (RP) phases used in high performance liquid chromatography (HPLC). In addition, the use of any of these types of MILs in the *in situ* DLLME mode is limited as the paramagnetic component will be exchanged during the metathesis reaction, impeding the subsequent magnetic separation step.

In this study, we report a new generation of MILs containing paramagnetic cations that are suitable for *in situ* DLLME with magnetic separation. The MILs are composed of cations containing Ni(II) centers coordinated with four ligands of N-alkylimidazole and chloride anions. These MILs are able to undergo metathesis reaction with the bis[(trifluoromethyl)sulfonyl]imide ($[NTf_2^-]$) anion [19]. The MILs are used for *in situ* DLLME in combination with HPLC for the determination of a group of both polar and non-polar pollutants, including UV filters, polycyclic aromatic hydrocarbons (PAHs), alkylphenols, a plasticizer and a preservative. This study reports the first application of MILs for *in situ* DLLME.

2. Experimental

2.1. Chemicals, reagents, materials and samples

Ten organic pollutants were determined including UV filters, PAHs, alkylphenols, a plasticizer and a preservative. Benzophenone-3 (BP3, 98.0%), octocrylene (OCR, ≥98.0%), homosalate (HS, pharmaceutical secondary standard) and 2-ethylhexyl salicylate (ES, ≥99.0%), 4-nonylphenol (NP, analytical standard), 1-chloro-4-nitrobenzene (CNB, 99%) and biphenyl (Bip, 99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Fluorene (Fl, analytical standard) and anthracene (Ant, analytical standard) were obtained from Supelco (Bellefonte, PA), and 4-octylphenol (OP, 99%) was acquired in Alfa Aesar (Heysham, England).

Individual stock solutions of each analyte were prepared in acetonitrile with concentrations of 1300 mg L^{-1} for Ant, 2100 mg L^{-1} for NP, and 5000 mg L^{-1} for the remaining analytes. An intermediate stock solution containing all analytes was prepared in acetonitrile by dilution of the stock solutions to a concentration of 150 mg L^{-1}. Standard working solutions were prepared by dilution of the intermediate solution in ultrapure water with concentrations between 0.015–1.5 mg L^{-1}. Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Up to five different MILs were developed and tested as extraction solvents in *in situ* MIL-DLLME. All MILs possessed the same type of chemical structure based on tetraalkylimidazolenickelate(II) chloride ($[Ni(RIM)_4^{2+}][Cl^-]$) with different alkyl substituents (R) in the ligands of the cation, with methyl- (M), vinyl- (V), butyl- (C_4), benzyl- (Be), and -methoxybenzyl (MOBe). Stock solutions of the MILs at 50 mg L^{-1} were prepared in ultrapure water in all cases, with the following exceptions: a concentration of 20 mg mL^{-1} for the $[Ni(BeIM)_4^{2+}][Cl^-]$ MIL, and the use of acetonitrile instead of ultrapure water as solvent for the $[Ni(MOBeIM)_4^{2+}][Cl^-]$ MIL. For the synthesis of the MILs, 1-vinylimidazole (99%), 1-butylimidazole (98%), 1-benzylimidazole (99%), 1-methoxybenzylimidazole (99%) and $NiCl_2$ (98%) were purchased from Sigma-Aldrich. The reagent 1-methylimidazole (99%) was obtained in Acros Organic (New Jersey, USA).

Sodium chloride, sodium hydroxide, hydrochloric acid and tetrahydrofuran (certified ACS reagents) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Formic acid (≥95%), acetonitrile, methanol and acetone (HPLC grade) were obtained from Sigma-Aldrich. Lithium bis[(trifluoromethyl)sulfonyl]imide ($[Li^+][NTf_2^-]$) was purchased from SynQuest Laboratories (Alachua, FL, USA). An aqueous solution of $[Li^+][NTf_2^-]$ (400 mg L^{-1}) was used for *in situ* DLLME extractions.

2.2. Instrumentation

An Agilent Technologies 1260 Infinity II HPLC equipped with quad pumps, vial sampler and diode array detector (DAD) was employed for the separation and detection of analytes. The separation was carried out using a RP-Ultra C_8 analytical column (250 mm L × 4.6 mm ID × 5 μm particle size, with carbon loading of 12%) obtained from Restek (Bellefonte, PA, USA) and equipped with an Ultra C_8 guard column (10 mm L × 4.0 mm ID). The analytical column was maintained at 40 °C and the vial sampler injected 10 μL in all cases. The separation of analytes was achieved using a binary mobile phase composed of a 0.02% (v/v) aqueous formic acid solution (pH 3.0) and acetonitrile at a constant flow rate of 1 mL·min^{-1}. Linear gradient elution was performed according to the following program: from 60% of acetonitrile to 90% in 16.5 min, then up to 100% of acetonitrile in 3.5 min, and finally maintaining 100% for 5 min. The DAD was operated at 260 nm for the detection of CNB and BP3, 254 nm for Bip, Fl and Ant, and 220 nm for the remaining analytes.

2.3. Procedures

2.3.1. Synthesis of magnetic ionic liquids

Synthesis of the MILs was carried out according to a recently reported method [19], with some modifications. For the $[Ni(C_4IM)_4^{2+}][Cl^-]$ MIL, 4.0 mmol of $NiCl_2$ was reacted with 16 mmol of N-butylimidazole overnight at room temperature using water as solvent. The solvent was then removed under reduced pressure and the solid product was dried in a vacuum oven at 60 °C. The composition of the product was found to be consistent with the formula $[Ni(C_4IM)_4^{2+}][Cl^-]$ based on elemental analysis [19]. The $[Ni(MIM)_4^{2+}][Cl^-]$ and $[Ni(VIM)_4^{2+}][Cl^-]$ MILs were prepared using the same procedure, except for substituting N-butylimidazole with N-methylimidazole or 1-vinylimidazole, respectively. The $[Ni(BeIM)_4^{2+}][Cl^-]$ and $[Ni(MOBeIM)_4^{2+}][Cl^-]$ MILs were prepared using either N-benzylimidazole or N-methoxybenzylimidazole and performing the reaction at 80 °C to increase the solubility of the N-alkylimidazole in water.

2.3.2. In situ *dispersive liquid-liquid microextraction*

An aqueous solution containing all analytes was placed in a 7 mL glass vial (Supelco). The pH was adjusted to 3.0–10 by adding 0.5 M HCl or 0.5 M NaOH and the NaCl content was adjusted to 0–10% (w/v), depending on the experiment. An aqueous solution containing 10–40 mg of the MIL in the $[Cl^-]$-form and 100–500 μL of dispersive solvent (acetone, acetonitrile, methanol or tetrahydrofuran) was then added to the extraction vial. A volume between 21.4–85.8 μL of the ion-exchange reagent ($[Li^+][NTf_2^-]$, 400 mg L^{-1}) was subsequently added to achieve a MIL:$[Li^+][NTf_2^-]$ molar ratio of 1:1, 1:2 or 1:3. The total volume was 2–5 mL, depending on the experiment. The vial was closed using a screw hole cap with a polytetrafluoroethylene (PTFE)/silicone septa, and the ternary mixture was vortexed for 1–5 min at 2000 rpm to facilitate the metathesis reaction. The water immiscible MIL containing the preconcentrated analytes was then isolated by magnetic separation. A NdFeB rod

magnet (0.5 cm D × 5 cm thick, B = 0.66 T) from K&J Magnetics, Inc. (Pipersville, PA, USA) was directly introduced into the extraction vial, and the MIL was transferred to a 2 mL glass vial (Agilent Technologies) and diluted to 100 μL with acetonitrile to reduce the viscosity. Finally, 10 μL was subjected to HPLC-DAD. Figure S1 of the Supplementary Material (SM) shows a scheme of the procedure, including images highlighting the magnetic separation of the MIL using a rod magnet.

The optimum conditions involving the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL included no salt, a total volume of 5 mL, pH 3, 20 mg of MIL (0.4 mL of 50 mg L^{-1} aqueous solution), 300 μL of acetone and 42.8 μL of 400 mg L^{-1} $[Li^+][NTf_2^-]$ (1:2 M ratio), and 3 min of vortex.

The optimum conditions using the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL required the addition of 30 mg of MIL (1.5 mL of 20 mg L^{-1} aqueous solution), 300 μL of acetonitrile and 53.5 μL of 400 mg L^{-1} $[Li^+][NTf_2^-]$ (1:2 M ratio). The remaining conditions were similar to those used for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL.

2.3.3. Quality assurance and quality control procedures

During method development, the extraction efficiency of the procedure was evaluated by determining the corresponding enrichment factors (EF) and/or the extraction efficiency (ER) of the experiments performed during the optimization. The EF values were determined as the ratio between the predicted concentration obtained using the HPLC-DAD curves (without performing any microextraction procedure, according to Table S1 of the SM) and the spiked concentration of each analyte. The ER values, expressed as a percentage, were calculated by the ratio between the EF and the maximum enrichment factor ($E_{F,max}$). The $E_{F,max}$ is the maximum preconcentration that can be achieved with the method, and was calculated by the ratio of the initial volume and the final volume after extraction.

For validation of the methodology, calibration curves of each analyte using the entire *in situ* MIL-DLLME-HPLC-DAD methodology were obtained by using external calibration. The limits of detection (LODs) and limits of quantification (LOQs) were determined as the concentration corresponding to three and ten times the signal-to-noise ratio, respectively. The reproducibility was estimated as the relative standard deviation (RSD) obtained after performing both intra- and inter-day experiments at two spiked levels. The relative recovery (RR), expressed as a percentage, was calculated as the ratio of the predicted concentration obtained using the calibration curves of the entire method and the spiked concentration of each analyte.

3. Results and discussion

3.1. Ensuring compatibility of hydrophobic MILs in RP-HPLC

In this study, the hydrophobic MILs obtained after *in situ* DLLME ($[Ni(RIM)_4^{2+}]2[NTf_2^-]$) were diluted with acetonitrile and directly injected to HPLC. In order to ensure HPLC compatibility, two aspects related to the nature of both the cation and anion of the MIL were considered.

Firstly, it is important to consider that silica bonded phases used in RP-HPLC contain a considerable fraction of free silanol groups that can be detrimental to the separation, especially in the separation of organic bases at common pH values of the mobile phases (between 3 and 8) [20,21]. Several strategies have been used to avoid the adverse effects from silanol groups, including the use of certain additives that act as silanol suppressors, such as tertiary amines [22], ILs [20], and divalent metals [23]. At low concentrations levels, these species preferentially interact with the free silanol groups *via* ion-exchange [20]. Furthermore, in the case of ILs, a second interaction between the alkyl groups of the cation and the hydrophobic groups of the functionalized silica is possible, especially at high IL concentrations [20]. With this background, it is possible to expect both ion-exchange and hydrophobic interactions between the cations of the MIL and the stationary phase. In this particular study, these interactions were not desired as they resulted in increased pressure in the HPLC system due to the high volume of the MIL. To avoid this effect, an endcapped C_8 stationary phase was selected for the separation of the analytes to reduce the percentage of exposed free silanol groups. Finally, a binary mobile phase composed of acetonitrile and aqueous formic acid solution at pH 3 was employed to reduce the amount of deprotonated free silanol groups. Using these conditions, pressure issues were eliminated after successive injections of the MIL. In any case, injection of the MIL was also possible using other endcapped reversed phase HPLC stationary phases, such as C_{18}.

Attention was also paid to the anion (*i.e.*, $[NTf_2^-]$) of the MIL injected in the HPLC. It was observed that a minimum acetonitrile mobile phase composition of 55% was required to ensure the solubility of all MILs. Finally, 60% of acetonitrile was selected as the initial condition of the linear gradient elution program to ensure the adequate separation of the analytes.

With all of the aforementioned considerations and the conditions detailed in Section 2.2, a broad peak corresponding to the elution of MIL was observed in the 1–5 min elution period of the chromatogram using 220 nm as the detection wavelength, as shown in Figure S2 of the SM. Relatively low absorption of the MIL was observed at 254 nm and 280 nm. In any case, the MIL did not co-elute with any of the studied analytes. The retention times of the analytes are shown in Table S1 of the SM shows the analytical performance of the HPLC-DAD method, obtained by injection of the standard analyte solutions (without performing a preconcentration step).

3.2. Screening of MILs using in situ dispersive liquid-liquid microextraction

In this study, all MILs examined were based on the coordination of Ni(II) ion centers with N-alkylimidazole ligands to form the paramagnetic compound. The influence of substituent groups appended to the imidazole ligands was studied by performing experiments using 4 mL of sample containing the analytes at 500 μg L^{-1}, 30 mg of MIL, 300 μL of acetonitrile as dispersive solvent, 1:2 MIL:$[Li^+][NTf_2^-]$ molar ratio, and 3 min of vortex. The results are shown in Fig. 1. It was noted that no hydrophobic MIL was obtained after the *in situ* DLLME procedure when the $[Ni(VIM)_4^{2+}]2[Cl^-]$ and the $[Ni(MIM)_4^{2+}]2[Cl^-]$ MILs were used under the aforementioned experimental conditions. In these cases, instead of the formation of a liquid microdroplet, a white precipitate was observed likely due to a change in the coordination of Ni(II) or the complete destruction of the MIL and the formation of hydroxylated complexes with the Ni(II) anions. This behavior could be attributed to the poor stability of Ni(II) complexes when they are coordinated with N-alkylimidazole ligands containing short alkyl groups, such as -vinyl or -methyl [24]. For example, the reported stability constant (log β_1) of the $[Ni(MIM)_4^{2+}]$ cation in aqueous solution at 25 °C is 3.05, while for the $[Ni(C_4IM)_4^{2+}]$ cation the reported value is 3.30 (values determined by potentiometry using the Rydberg equation [24]). Among the remaining MILs, the highest extraction efficiencies were achieved when the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs were employed. In comparison, lower extraction efficiency was achieved for all analytes when the $[Ni(MOBeIM)_4^{2+}]2[Cl^-]$ MIL was studied, likely due to the higher viscosity of the $[Ni(MOBeIM)_4^{2+}]2[NTf_2^-]$ MIL compared to $[Ni(BeIM)_4^{2+}]2[NTf_2^-]$, which limited its dispersion in the aqueous sample.

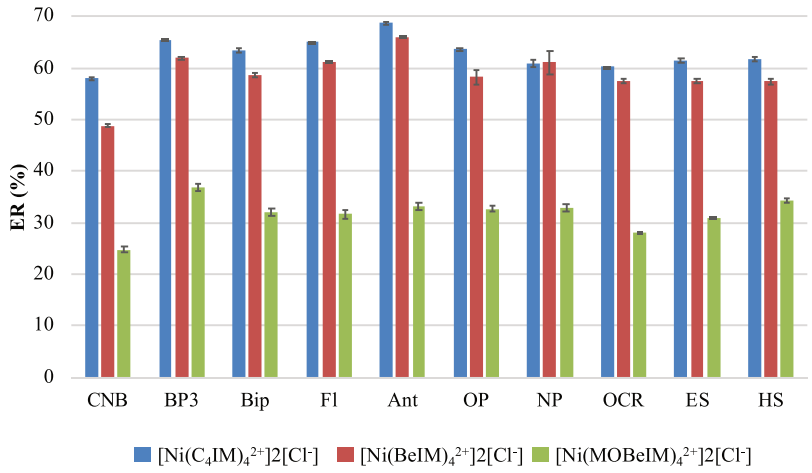

Fig. 1. Influence of the MIL type in the *in situ* DLLME-HPLC-DAD method. Experimental conditions (n = 3): 500 μg L^{-1} spiked level, 4 mL total sample volume, 30 mg of MIL, 300 μL of acetonitrile, 1:2 MIL:[Li^+][NTf_2^-] molar ratio, vortex (2000 rpm, 1 min), magnetic separation, dilution to 100 μL with acetonitrile, and HPLC-DAD injection (10 μL).

3.3. Optimization of the microextraction procedures

The entire methodology was optimized using the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] and [$Ni(BeIM)_4^{2+}$]2[Cl^-] MILs. Among all of the parameters that influenced the extraction, the vortex speed was fixed to 2000 rpm to achieve adequate dispersion of the MIL and rapid formation of the hydrophobic microdroplet. The final acetonitrile dilution step to 100 μL was also kept constant to decrease the viscosity of the final microdroplet and to achieve adequate analyte preconcentration. The remaining parameters were optimized using a one-factor-at-a-time optimization approach. The studied parameters for the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL included the sample volume, type of metathesis reagent, MIL:[Li^+][NTf_2^-] molar ratio, amount of MIL, type and volume of dispersive solvent, pH, NaCl content and vortex time. For the [$Ni(BeIM)_4^{2+}$]2[Cl^-] MIL, the behavior of the two MILs was similar for some parameters, and the optimum conditions obtained for the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL were also used for the $Ni(BeIM)_4^{2+}$]2[Cl^-] MIL.

3.3.1. Effect of sample volume

The sample volume has a direct influence on the preconcentration of analytes. In general, larger samples volumes are beneficial in LPME as the enrichment factor of the method increases. For that reason, the influence of the sample volume was studied in the range between 2–5 mL for the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL. Figure S3 of the SM shows the obtained results. As expected, an increase in the EF values was observed when the sample volume increased. For that reason, 5 mL was selected for subsequent experiments.

3.3.2. Effect of type and amount of metathesis reagent

Different salts such as [Li^+][NTf_2^-], [K^+][PF_6^-], [NH_4^+][PF_6^-], or [Na^+][PF_6^-] have been used in *in situ* DLLME to promote the metathesis reaction [7,25]. Among all of these salts, the influence of [Li^+][NTf_2^-] and [K^+][PF_6^-] in the *in situ* DLLME method was studied using the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL. The experiments were carried out using 5 mL of sample volume, 30 mg of MIL, 300 μL of acetonitrile, a 1:2 MIL: anion-exchange molar ratio, and 1 min of vortex. When the [K^+][PF_6^-] salt was used to promote the metathesis reaction, no hydrophobic microdroplet was obtained. However, a white precipitate was observed as described in Section 3.2. Therefore, [Li^+][NTf_2^-] was selected as the optimum anion-exchange reagent.

The influence of the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL:[Li^+][NTf_2^-] molar ratio was studied in the range between 1:1 and 1:3. When experiments using a 1:1 M ratio were performed, the aqueous solution after extraction became turbid and no hydrophobic microdroplet was observed, likely because the generated [$Ni(C_4IM)_4^{2+}$]2[NTf_2^-] MIL was soluble in water at the studied concentration. The results obtained using 1:2 and 1:3 are presented in Figure S4 of the SM. The highest ER values were achieved using the 1:2 M ratio, whereas a significant decrease in the ER was observed when the 1:3 M ratio was employed. In this case, an excess of the [Li^+][NTf_2^-] salt can saturate the MIL, resulting in less preconcentration of the analytes. This phenomenon was previously observed in other reported *in situ* IL-DLLME procedures [26]. A 1:2 MIL:[Li^+][NTf_2^-] molar ratio was selected as optimum for the remaining experiments.

3.3.3. Effect of MIL amount

The amount of MIL generally has a significant effect in the extraction performance of the method. For that reason, this parameter was studied in the range between 10 and 40 mg for the two studied MILs. As shown in Fig. 2, the observed behavior for all analytes was similar using both MILs as the lowest ER values were obtained using 10 mg of MIL, likely due to the MIL being completely saturated. When the amount of MIL was increased, the ER values also increased until a maximum was reached. For the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL, the maximum ER values were achieved using 20 or 30 mg, whereas 30 mg were required for the [$Ni(BeIM)_4^{2+}$]2[Cl^-] MIL. Larger amounts of MILs caused a significant decrease in the ER. In these cases, it was observed that larger microdroplet volumes were generated during the *in situ* DLLME procedure, which decreased the maximum preconcentration factor. In view of these results, 20 mg and 30 mg were selected as optimum values for the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] and [$Ni(BeIM)_4^{2+}$]2[Cl^-] MILs, respectively.

3.3.4. Effect of type and volume of dispersive solvent

In the most conventional DLLME mode, dispersion of the extraction solvent is achieved by the use of a dispersive solvent, a suitable solvent that must be miscible in both the aqueous sample and the extraction solvent. In the *in situ* IL-DLLME mode, the use of dispersive solvent is not always mandatory as the metathesis reaction promotes the formation of the cloudy solution. However, some authors have reported the addition of dispersive solvent in *in situ* IL-DLLME to further increase the extraction efficiency [10,27]. For this reason, different conditions including the use of various dispersive solvents (acetonitrile, methanol, acetone or tetrahydrofuran) as well as no-dispersive solvent were evaluated for both MILs. The results are presented in Fig. 3(A). In the case of the [$Ni(C_4IM)_4^{2+}$]2[Cl^-] MIL, the highest ER values were achieved using 20 mg of MIL and dispersive solvent, indicating that the presence

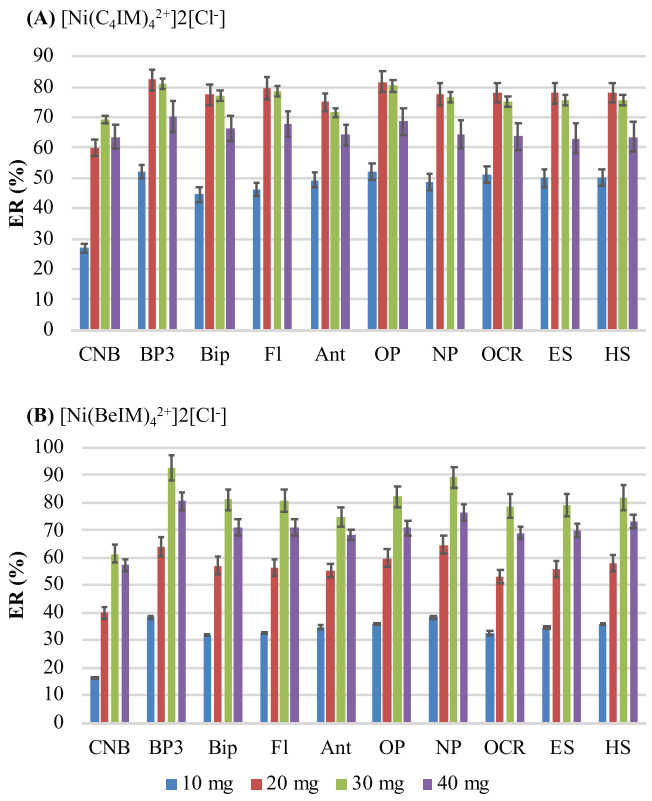

Fig. 2. Influence of the amount of MIL in the *in situ* DLLME-HPLC-DAD method using **(A)** $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and **(B)** $[Ni(BeIM)_4^{2+}]2[Cl^-]$. Experimental conditions (n = 3): 500 μg L^{-1} spiked level, 5 mL total sample volume, 10–40 mg of MIL, 300 μL of acetonitrile, 1:2 MIL:$[Li^+][NTf_2^-]$ molar ratio, vortex (2000 rpm, 3 min), magnetic separation, dilution to 100 μL with acetonitrile, and HPLC-DAD injection (10 μL).

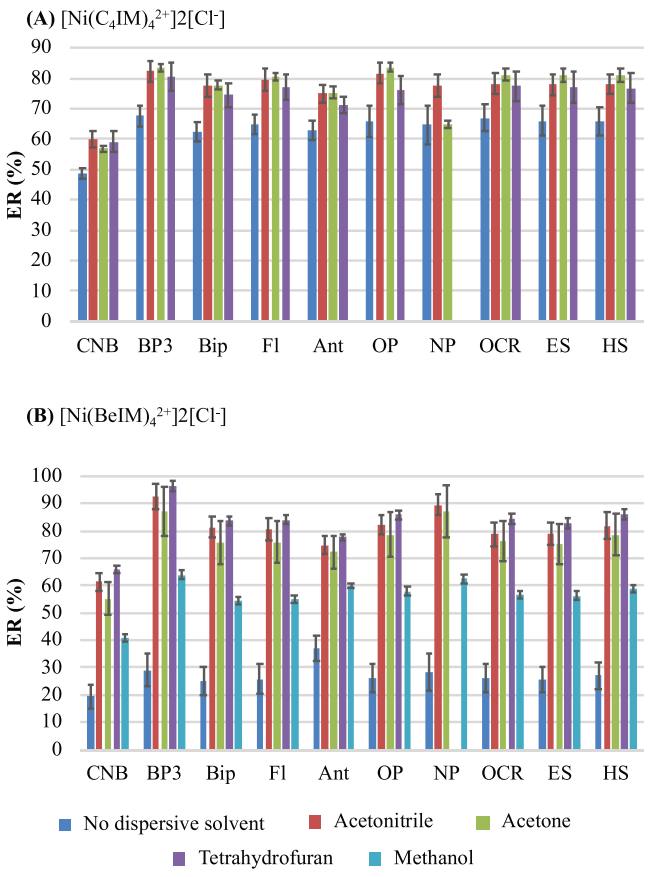

Fig. 3. Influence of the dispersive solvent type in the *in situ* DLLME-HPLC-DAD method using **(A)** $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and **(B)** $[Ni(BeIM)_4^{2+}]2[Cl^-]$. Experimental conditions (n = 3): 500 μg L^{-1} spiked level, 5 mL total sample volume, 20 mg of $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ or 30 mg of $[Ni(C_4IM)_4^{2+}]2[Cl^-]$, 300 μL of acetonitrile, acetone, tetrahydrofuran or methanol, or no dispersive solvent, 1:2 MIL:$[Li^+][NTf_2^-]$ molar ratio, vortex (2000 rpm, 3 min), magnetic separation, dilution to 100 μL with acetonitrile, and HPLC-DAD injection (10 μL). Note: experiments with no dispersive solvent were performed using 40 mg of MIL instead of 20 mg in the case of $[Ni(C_4IM)_4^{2+}]2[Cl^-]$.

of the dispersive solvent significantly aids in dispersion of the MIL. If different dispersive solvents are compared, methanol was discarded because it prompted the formation of a white precipitate after extraction. Tetrahydrofuran provided slightly lower ER for the majority of analytes, with the exception of NP for which quantification was not possible for the appearance of an interfering peak at the same retention time as the analyte. Among the remaining solvents, acetone provided slightly higher ER and was selected as the optimum extraction solvent when the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL was employed.

The behavior of the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL was slightly different (Fig. 3(B)). Reproducible results were achieved with this MIL when extractions were performed using the selected optimum amount of MIL (30 mg) and no dispersive solvent or 300 μL of methanol. These better results can be related to the higher stability and hydrophobicity of the $[Ni(BeIM)_4^{2+}]2[NTf_2^-]$ MIL. The highest ER values were achieved when tetrahydrofuran was used as dispersive solvent (with the exception of NP, for the same aforementioned reasons), followed by acetonitrile. At the end, acetonitrile was selected as the optimum extraction solvent for the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL.

The effect of dispersive solvent volume was studied in the range between 100–500 μL for both MILs. The results are shown in Figure S5 of the SM. Both MILs exhibited similar behavior regarding this parameter. The ER increased for all analytes when the volume of dispersive solvent increased from 100 to 300 μL, indicating that 100 μL was not sufficient for adequate dispersion of the MIL. Finally, a decrease in the ER was observed using dispersive volumes larger than 300 μL, likely due to partial solubilization of the MIL. Finally, an optimal dispersive solvent volume of 300 μL was selected for both MILs.

3.3.5. *Effect of pH and ionic strength of the aqueous sample*

The pH has two different effects in the *in situ* DLLME procedure using MILs. Firstly, basic pH values can ionize BP3, OP, NP, ES, and HS, causing a diminution of the ER for these analytes. In addition, the pH can also affect the stability of the metal complex of the MIL cation. Previous studies with similar metal complexes have examined their stabilities in the pH range between 3 and 8 [24]. For all of these reasons, the influence of pH on the extraction efficiency of the method was evaluated for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL by evaluating the pH in the range between 3 and 10. The pH was controlled by adding a proper volume of 0.5 mol·L^{-1} of HCl or NaCl, and the results are presented in Figure S6 of the SM. The results indicated a decrease in the ER values for all analytes when the pH was increased, indicating a direct relation of pH and stability of the MIL. These results are in accordance with the microdroplet volume; that is, when the pH increased, lower microdroplet volumes were obtained resulting in destabilization of the metal complex. In addition, it is important to mention that a hydrophobic microdroplet was not observed after performing experiments at pH 10, likely for the same reasons. In view of these results, an optimal pH value of 3 was selected.

The influence of ionic strength on the extraction efficiency was evaluated for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL by comparing experiments performed in ultrapure water with those in which the NaCl content was adjusted to 5% and 10% (w/v), as shown in Figure S7

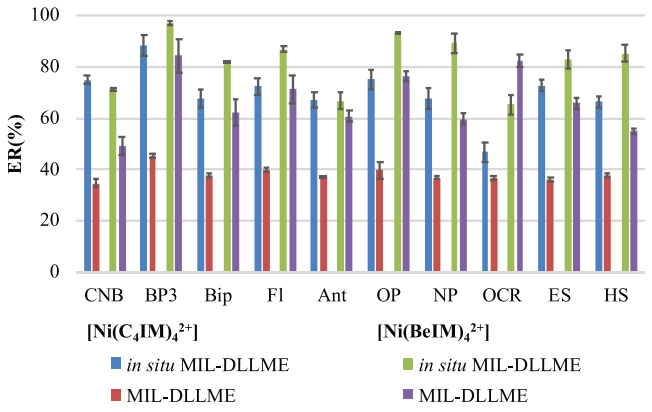

Fig. 4. Comparison of *in situ* MIL-DLLME- and MIL-DLLME. Experimental conditions (n = 3): a spiked level of 81 μg L^{-1} was used in all cases. For the *in situ* MIL-DLLME method, optimum conditions were used for both the [Ni(C$_4$IM)$_4^{2+}$]2[Cl$^-$] and [Ni(BeIM)$_4^{2+}$]2[Cl$^-$] MILs. For MIL-DLLME, the following conditions were employed: 40 mg of [Ni(C$_4$IM)$_4^{2+}$]2[NTf$_2^-$] dissolved in 300 μL of acetone (or 45 mg of [Ni(BeIM)$_4^{2+}$]2[NTf$_2^-$] dissolved in 300 μL of acetonitrile), vortex (2000 rpm, 3 min), magnetic separation, dilution to 100 μL with acetonitrile, and HPLC-DAD injection (10 μL).

of the SM. For all analytes, except CNB, no significant change in the ER was observed when NaCl was increased from 0 to 5% (w/v). However, a decrease in the ER was observed using 10% (w/v). In this case, a larger microdroplet volume was obtained, which can limit the dispersion of the generated solvent and possibly impede analyte mass transfer. For CNB, an increase in the ER was observed when the NaCl content was increased, likely due to the salting out effect. In the optimum procedure, no NaCl was used.

3.3.6. *Effect of vortex time*

Vortex was applied during the microextraction procedure to accelerate the metathesis reaction and, at the same time, provide better dispersion of the MIL in the aqueous sample. The effect of vortex time was studied for both MILs in the range between 1 and 5 min. The obtained results are presented in Figure S8 of the SM. Identical behavior of two MILs was observed as maximum ER values were achieved using 3 min of vortex. Shorter vortex times provided lower ER, likely because the metathesis reaction was not complete. Vortex times longer than 5 min also provided lower ER, possibly due to stability limitations of the MIL cation. A vortex time of 3 min was selected as optimum for both MILs.

3.4. *Comparison of* in situ *MIL-DLLME and MIL-DLLME*

To prove the beneficial effect of the *in situ* metathesis reaction in DLLME, both *in situ* MIL-DLLME and MIL-DLLME were compared. For the *in situ* MIL-DLLME approach, experiments were performed at the optimum conditions described in Section 3.3. For the MIL-DLLME method, the MIL in the [NTf$_2^-$]-form was directly employed as extraction solvent. The MIL was dissolved in the dispersive solvent and the mixture was directly added to the aqueous sample. In particular, 40 mg of [Ni(C$_4$IM)$_4^{2+}$]2[NTf$_2^-$] MIL was dissolved in 300 μL of acetone to recover ~18 mg of MIL. Similarly, 45 mg of [Ni(BeIM)$_4^{2+}$]2[NTf$_2^-$] MIL was dissolved in 300 μL of acetonitrile to recover ~35 mg of MIL. The MIL-DLLME experiments were designed to mimic the same extraction conditions used in the *in situ* DLLME mode, and to recover the same volume with both methods during the magnetic separation. As shown in Fig. 4, the MIL-DLLME approach provided lower ER values than the *in situ* MIL-DLLME method for both MILs, with the exception of OCR using the [Ni(BeIM)$_4^{2+}$]2[NTf$_2^-$] MIL. In this case, higher ER values were achieved using MIL-DLLME. If both MILs are compared, a more pronounced decrease in ER was observed for the [Ni(C$_4$IM)$_4^{2+}$]-based MIL, with an average 44% diminution *versus* a 22% diminution on average for the [Ni(BeIM)$_4^{2+}$]-based MIL. These results demonstrate that the proposed *in situ* MIL-DLLME is more advantageous for the extraction and preconcentration of the selected group of pollutants.

3.5. *Analytical performance*

The *in situ* DLLME methods using both selected MILs were validated by constructing the corresponding calibration curves. Table 1 shows the analytical performance of both methods, including calibration slopes, correlation coefficient (R), LODs and LOQs.

Wide linear ranges were achieved, ranging between 15–1500 μg·L^{-1} for the [Ni(C$_4$IM)$_4^{2+}$]2[Cl-] MIL, and between 15–1200 μg·L^{-1} (with 15–800 μg·L^{-1} for Ant) for the [Ni(BeIM)$_4^{2+}$]2[Cl-] MIL. The R values were higher than 0.9959 and 0.9968 for [Ni(C$_4$IM)$_4^{2+}$]2[Cl-] and [Ni(BeIM)$_4^{2+}$]2[Cl-], respectively.

The sensitivity of the method was evaluated using the calibration slopes, with slopes ranging between $(3.3 \pm 0.1)\cdot 10^2$ and $(63 \pm 2)\cdot 10^2$ for the [Ni(C$_4$IM)$_4^{2+}$]2[Cl$^-$] MIL, and from $(3.3 \pm 0.1)\cdot 10^2$ to $(83 \pm 2)\cdot 10^2$ for the [Ni(BeIM)$_4^{2+}$]2[Cl$^-$] MIL. The sensitivity was the lowest for NP and maximum for Ant using both

Table 1
Analytical performance of the developed *in situ* MIL-DLLME methods.

Analyte	[Ni(C$_4$IM)$_4^{2+}$]2[Cl$^-$][a]					[Ni(BeIM)$_4^{2+}$]2[Cl$^-$][b]				
	(Slope ± SD[c])·10^{-2}	R[d]	S$_{y/x}$[e]	LOD[f] (μg·L^{-1})	LOQ[g] (μg·L^{-1})	(Slope ± SD[c])·10^{-2}	R[d]	S$_{y/x}$[e]	LOD[f] (μg·L^{-1})	LOQ[g] (μg·L^{-1})
CNB	13.7 ± 0.4	0.9968	63	4.2	14	15.7 ± 0.2	0.9993	26	0.46	1.5
BP3	8.7 ± 0.2	0.9980	31	5.2	15	9.0 ± 0.2	0.9991	17	0.64	2.1
Bip	25.5 ± 0.6	0.9986	62	0.87	2.9	27.5 ± 0.4	0.9994	43	0.35	1.2
Fl	23.7 ± 0.5	0.9984	76	0.93	3.1	24.8 ± 0.5	0.9990	50	0.23	0.77
Ant	63 ± 2	0.9959	351	0.13	0.43	83 ± 2	0.9983	160	0.012	0.041
OP	8.7 ± 0.2	0.9986	26	1.4	4.6	9.1 ± 0.2	0.9983	24	1.6	5.2
NP	3.3 ± 0.1	0.9982	11	2.7	8.8	3.3 ± 0.1	0.9971	12	1.4	4.8
OCR	6.2 ± 0.2	0.9975	25	1.1	3.7	6.3 ± 0.2	0.9968	23	0.52	1.7
ES	3.7 ± 0.1	0.9976	15	1.8	6.1	3.8 ± 0.1	0.9976	12	0.86	2.9
HS	3.9 ± 0.1	0.9978	15	4.7	15	4.0 ± 0.1	0.9975	13	0.87	2.9

[a] Calibrations in the range of 15–1500 μg·L^{-1}, and for 8 calibration levels.
[b] Calibrations in the range of 15–1200 μg·L^{-1} (15–800 μg·L^{-1} for Ant), and for 7–8 calibration levels.
[c] Standard deviation of the slope.
[d] Correlation coefficient.
[e] Standard deviation of the residuals (or error of the estimate).
[f] Limit of detection, calculated as 3 times the signal-to-noise ratio.
[g] Limit of quantification, calculated as 10 times the signal-to-noise ratio.

Table 2
Reproducibility, extraction efficiency, and relative recovery obtained in the *in situ* DLLME method using the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL.

Analytes	Spiked level: 81 μg·L^{-1}					Spiked level: 300 μg·L^{-1}			
	RSD (%)[a]		E_F[b]	E_R (%)[c]	RR (%)[d]	RSD intraday (%)[e]	E_F[b]	E_R (%)[c]	RR (%)[d]
	Intraday[e]	Interday[f]							
CNB	1.6	6.0	35.7	71.4	98.2	3.7	31.9	63.7	102
BP3	1.5	6.3	55.1	97.0	95.6	3.7	48.1	96.2	101
Bip	4.5	6.7	41.0	82.0	93.5	3.6	39.1	78.1	96.6
Fl	2.4	5.8	43.4	86.8	91.8	4.1	39.6	79.2	98.5
Ant	8.5	9.3	33.4	66.8	96.6	6.9	34.1	68.3	97.7
OP	5.4	5.9	46.6	93.2	94.8	1.7	41.1	82.2	100
NP	7.6	13	44.6	89.3	83.0	6.2	39.3	78.6	89.8
OCR	11	16	32.7	65.4	101	6.5	29.5	58.9	85.7
HS	8.9	9.1	41.5	82.9	90.6	5.0	33.2	66.5	86.9
ES	8.1	11	42.6	85.2	92.3	5.4	33.5	66.9	87.5

[a] Relative standard deviation.
[b] Enrichment factor (with $E_{F,max} = 50$).
[c] Real extraction efficiency.
[d] Relative recovery.
[e] Extractions performed during the same day (n = 3).
[f] Extraction performed in 3 non-consecutive days (n = 9).

Table 3
Reproducibility, extraction efficiency, and relative recovery obtained in the *in situ* DLLME method using the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL.

Analytes	Spiked level: 81 μg·L^{-1}					Spiked level: 300 μg·L^{-1}			
	RSD (%)[a]		E_F[b]	E_R (%)[c]	RR (%)[d]	RSD intraday (%)[e]	E_F[b]	E_R (%)[c]	RR (%)[d]
	Intraday[e]	Interday[f]							
CNB	4.5	5.0	37.5	75.0	114	3.9	27.0	53.9	96.4
BP3	8.1	6.1	44.3	88.6	108	5.5	39.2	78.4	92.7
Bip	9.4	8.0	33.8	67.6	96.5	4.7	32.6	65.1	90.2
Fl	7.9	6.5	36.3	72.5	105	3.3	33.2	66.3	92.5
Ant	8.8	13	33.6	67.2	102	2.3	28.7	57.3	101
OP	8.4	8.6	37.6	75.1	104	1.4	34.0	67.9	92.6
NP	13	14	33.9	67.9	108	4.1	32.7	65.3	88.2
OCR	13	14	23.4	46.8	94.4	6.0	26.7	53.4	83.4
HS	5.6	6.7	36.4	72.7	104	4.1	29.2	58.4	83.6
ES	6.6	5.9	33.2	66.4	103	4.3	28.4	56.8	83.8

[a] Relative standard deviation.
[b] Enrichment factor (with $E_{F,max} = 50$).
[c] Real extraction efficiency.
[d] Relative recovery.
[e] Extractions performed during the same day (n = 3).
[f] Extraction performed in 3 non-consecutive days (n = 9).

MILs. However, if both MILs are compared, a 1.2–24% higher calibration slope was achieved using the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL.

LODs in the microgram per liter level were achieved, ranging between 0.13–5.2 μg L^{-1} for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL, and between 0.012–1.6 μg L^{-1} for the $[Ni(BeM)_4^{2+}]2[Cl^-]$ MIL.

Results regarding the reproducibility, extraction efficiency (EF, ER) and accuracy are presented in Tables 2 and 3. The reproducibility, expressed as RSD, was obtained by performing experiments at two spiked levels (81 and 300 μg L^{-1}). For the lower spiked level, both intra-day (n = 3) and inter-day (n = 9, 3 non-consecutive days) experiments were performed. The inter-day RSD ranged between 5.0–14%, and from 5.8 to 16% for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs, respectively. The ER for the lower spiked level ranged between 46.8–88.6% for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL and between 65.4–97.0% for the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL. This ER values are especially higher for this microextraction procedure. The lowest and highest ER values were achieved for OCR and BP3, respectively, using both MILs. These results indicated that the behavior of both MILs in the extraction of the selected group of pollutants was similar, but the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL provided slightly higher extraction efficiency and sensitivity. Satisfactory RR values were also obtained in ultrapure water, with values ranging between 94.4–114% and 83.0–101% for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs, respectively.

The developed methods were compared with other IL-DLLME methods reported in the literature for the determination of similar analytes (Table S3 of the SM [8,12,13,26]). It is important to highlight that the majority of these methods reported similar LODs to the proposed method, despite some of them utilizing mass spectrometry [26] or fluorescence detection [13]. In comparison to classical *in situ* DLLME methods [8,26], the proposed methods are faster and did not require centrifugation, which can be beneficial for performing *in field* analysis. In comparison to MIL-DLLME [12,13], the proposed methods are also faster and allowed for the direct injection of the MIL in the HPLC system.

3.6. Analysis of real samples

After optimization of the method, it was applied for the analysis of water samples, including tap, lake and pool water. No analytes were detected in any of the analyzed samples. A study of reproducibility and RR was carried out by spiking the samples with analytes at 81 μg L^{-1}. Fig. 5 shows representative chromatograms obtained after the analysis of spiked tap water. The obtained results regarding this type of sample are shown in Table S4 of the SM. The RSD was lower than 19% and 15% for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs, respectively, and acceptable RR values were achieved, from 67.7 to 120% and

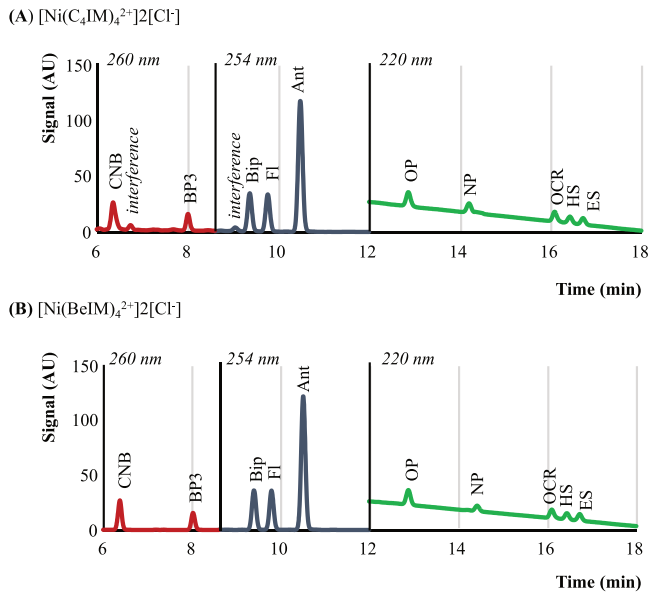

Fig. 5. Representative chromatograms obtained in the analysis of spiked tap water (spiked level of 81 μg L^{-1}) using the *in situ* DLLME method with the **(A)** $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and **(B)** $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs.

86.5–96.6% for $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs, respectively. These results also indicated that there was no significant matrix effect in this type of sample.

Reproducibility and RR studies performed in both spiked lake and pool water revealed the presence of matrix effects. In these cases, we hypothesized that the presence of interfering ions in the sample can cause the partial destruction of the MIL if some of the N-alkylimidazole ligands coordinated with the Ni(II) are substituted by ions within the samples. Furthermore, these ions may also interfere in the metathesis reaction with the $[NTf_2^-]$ ion, leading to lower RRs. Two series of experiments were performed to address this question and avoid the use of matrix matched calibrations: (1) experiments varying the MIL:$[Li^+][NTf_2^-]$ molar ratio in lake and pool water, and (2) studies in which an excess amount of N-butylimidazole or N-benzylimidazole, depending on the MIL, was added during the extraction with these real samples. Regarding the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL (Figure S9 of the SM), the external calibration method can be used if 1:1.5 MIL:$[Li^+][NTf_2^-]$ molar ratio is employed for the analysis of lake water, whereas 1:1.5 MIL:$[Li^+][NTf_2^-]$ molar ratio provided satisfactory results for CNB, Bip, Fl, and OCR in the case of pool water. For the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ MIL (Figure S10 of the SM), the use of 1:1.5 MIL:$[Li^+][NTf_2^-]$ molar ratio also provided satisfactory results for the determination of CNB, Bip, Fl, and OCR in the case of pool water. In the remaining cases, the matrix effect was still significant, indicating that matrix matched calibrations and/or standard addition calibrations are required.

4. Conclusions

For the first time, hydrophobic MILs have been successfully generated *in situ* for DLLME in the determination of a group of organic pollutants, including UV filters, PAHs, alkylphenols, a plasticizer, and a preservative. The MILs were specifically designed to contain a paramagnetic component in the cation. Thus, the paramagnetic component was not lost during the *in situ* metathesis reaction with the $[NTf_2^-]$ anion, and magnetic separation was easily applied after the microextraction procedure for the isolation of the extraction solvent, thereby avoiding the use of centrifugation.

Among all of the studied MILs, the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs provided the highest extraction efficiency for the determination of the selected group of compounds. The beneficial effect of the *in situ* metathesis reaction during the DLLME procedure was demonstrated for these two MILs by comparing the proposed method with an analogous DLLME method using MILs in the $[NTf_2$-]-form.

The *in situ* DLLME method, under optimum conditions, provided up to 88.6% and 97.0% real extraction efficiency for the $[Ni(C_4IM)_4^{2+}]2[Cl^-]$ and $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MILs, respectively. Both MILs exhibited similar behavior, but the $[Ni(BeIM)_4^{2+}]2[Cl^-]$ MIL provided slightly higher extraction efficiency and sensitivity, possibly due to the presence of the benzyl group in the cation of the MIL, which can promote π–π interactions with the analytes. As an additional advantage, the method was fast (~4 min per extraction), and the paramagnetic features of the extraction solvent have great potential for automation [28].

The method was successfully applied for the analysis of tap water, with acceptable reproducibility and recovery. The analysis of pool and lake water revealed the presence of matrix effects. This effect could be partially suppressed by controlling the extraction conditions by either decreasing the initial amount of $[NTf_2^-]$ anion or adding extra N-alkylimidazole ligand to the extraction vial.

Ongoing work is focused on performing additional studies to address matrix effects, avoiding the use of matrix matched calibrations and/or standard addition to the sample. One alternative is to tailor the MIL structure in order to increase the stability of the MIL in the analyzed aqueous samples. In general, two alternatives can be employed to increase the stability of the MIL: (1) use of longer alkyl chains substituents appended to the N-alkylimidazole ligands (*e.g.* octyl or decyl-alkyl chains), or (2) employ different metal centers than Ni(II), including Co(II), Mn (II), or Dy(III).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2018.12.032.

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