Supramolecular solvents based on quaternary ammonium salts and perfluorinated compounds for dispersive liquid-liquid microextraction of phthalates

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In this study, eight hydrophobic supramolecular (SUPRA) solvents composed of tetrabutylammonium chloride and tetradecyltrimethylammonium bromide as amphiphiles and four perfluorinated compounds (hexafluoroisopropanol, trifluoroacetic acid, pentafluoropropionic acid and heptfluorobutyric acid) as coacervation-inducing agents were developed. The SUPRA phase volumes were determined as a function of individual concentrations of the system components. The extraction properties of the SUPRA solvents for the extraction of phthalates from the model aqueous solutions were investigated and their applicability as sample diluents for the reversed-phase HPLC separations of phthalates was tested. Finally, the solvent consisting of tetradecyltrimethylammonium bromide and hexafluoroisopropanol was applied for dispersive liquid-liquid microextraction of phthalates from wastewater samples prior to HPLC analysis. Under optimised extraction conditions, the enrichment factors were around 75. The calibration curves were linear ($R^2 \geq 0.9965$) for the concentration level between 1.00 and 50.0 μg/L and the detection limits were in the range 0.3–0.6 μg/L. The recoveries of the phthalates of the developed method for the spiked wastewater samples were 93.1–104.4%, with the relative standard deviation values less than 7.4%.

Keywords: supramolecular solvents, perfluorinated constituents, dispersive liquid-liquid microextraction, phthalates

INTRODUCTION

In the past two decades, there has been an increasing and fully justified emphasis on the miniaturisation of traditional sample preparation techniques. The main advantages of the miniaturised extraction methods are the high sample throughput, the ease of operation, low costs, small sample amounts required and an extremely low solvent consumption.

Dispersive liquid-liquid microextraction (DLLME), introduced by Rezaee et al. in 2006, is, perhaps, the most popular microextraction technique used in the last decade. In the typical DLLME procedure, a hydrophobic and high-density extraction solvent is quickly dispersed into a conical tube containing the aqueous sample by means of the so-called dispersant solvent, which is miscible in both the extraction solvent and sample. The microemulsion formed by hundreds of microdroplets allows a large surface area to exist between the different phases, favouring the instant transfer of the analytes from the donor phase to the extraction solvent. After extraction, phase separation is achieved by centrifugation, where the settled phase is easily collected with
a microsyringe for later measurement in the analytical instrument. However, one of the weakest aspects of DLLME techniques is the limited number of the effective extractants. Heavier than water hydrophobic solvents are preferred because such solvents sediment at the bottom of the centrifuge tube and can be simply collected by using a microsyringe.

For that reason, during the last years, several types of alternative solvents such as ionic liquids, deep eutectic solvents and supramolecular solvents were proposed for DLLME. Because most of these solvents consist of two components, some of their properties (e.g. viscosity, density and hydrophobicity) can be tuned by combining properly the different constituents.

Supramolecular (SUPRA) solvents are defined as water-immiscible nano/microstructured liquids formed from a sequential self-assembly of different amphiphilic molecules, such as surfactants and long-chain carboxylic acids. The production of SUPRA solvents occurs through two steps including (i) aggregation of an amphiphile, providing supramolecular assemblies, micelles, or vesicles in a homogeneous solution and (ii) coacervation, producing water-immiscible liquids (SUPRA phase) that separate from the bulk solution. The coacervation step requires the action of external factors such as electrolyte, pH, temperature and organic solvent. In SUPRA self-assembly, various non-covalent interactions (hydrophobic, electrostatic, hydrogen bond, etc.) cooperatively control the assembly process and the final structure of the solvent. These SUPRA solvents possess exceptional extraction capabilities due to their great surface and their different polarity environments. Moreover, they can be synthesised in situ during the analysis, making them really attractive for microextraction approaches.

The first time that SUPRA solvents were employed for DLLME was in 2009. In this application, Ballesteros-Gómez et al. used a SUPRA phase formed by decanoic acid and tetrahydrofuran (THF) as coacervation agent for the determination of benzo[a]pyrene, bisphenol A, and ochratoxin from beverages. Since then, a lot of works have been published on the use of SUPRA solvents in DLLME. However, most of the works published employed similar approaches, using alkanoic acids (i.e. decanoic acid and octanoic acid) as amphiphilic substances and THF as coacervation agent.

The fluoroalcohol-induced coacervation of amphiphiles in aqueous media was originally discovered and characterised by Khaledi and co-workers. In recent years, several types of hexafluorosopropanol-induced SUPRA solvents have been proposed and applied for conventional liquid-liquid extraction and DLLME of organic pollutants from aqueous samples. These studies demonstrate that due to their strong hydrogen bond donor ability and high density perfluorinated compounds should be very promising alternative coacervation-inducing agents.

In the present work, eight hydrophobic SUPRA solvents composed of tetrabutylammonium chloride and tetradecyltrimethylammonium bromide as amphiphiles and four perfluorinated compounds (hexafluorosopropanol, trifluoroacetic acid, pentafluoropropionic acid and heptafluorobutyric acid) as coacervation-inducing agents were investigated and applied for DLLME of phthalates from wastewaters.

EXPERIMENTAL

Reagents and solutions
Tetrabutylammonium chloride (TBAC, purity ≥99%), tetradecyltrimethylammonium bromide (TDTMAB, purity ≥98%), hexafluorosopropanol (HFIP, purity ≥99%), trifluoroacetic acid (TFA, for HPLC, purity ≥99%), pentafluoropropionic acid (PFPA, purity ≥97%), heptafluorobutyric acid (HFBA, purity ≥98%), naphthalene (NAPH, purity ≥99%), acetonitrile (for HPLC, gradient grade, purity ≥99.9%) and methanol (ACN, for HPLC, gradient grade, purity ≥99.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dimethyl-(DMP), diethyl-(DEP), dibutyl-(DBP) and bis(2-ethylhexyl)-(DEHP) phthalates were used as model analytes. All of them were obtained from Sigma-Aldrich, and their purity was higher than 99%. Stock solutions (100 mg/L) of all the phthalates and the internal standard (naphthalene) were prepared in methanol. Stock solutions of TBAC and TDTMAB (200 mmol/L) were prepared in water. All solutions were stored in a refrigerator at 4°C.
**Instrumentation**

Chromatographic separations were performed on an Agilent 1290 Infinity II LC system (Agilent, Waldbronn, Germany) equipped with a ternary pump, thermostatted column compartment, photodiode array detector and an autosampler. InfinityLab Poroshell 120 EC-C18 (3.0 × 150 mm, 2.7 μm, Agilent) column, maintained at 25°C, was used in the experiments. Separations were performed with ACN/water mobile phases at a flow rate of 0.5 mL/min under linear gradient elution conditions. The composition of the mobile phase was changed from 70% ACN to 100% ACN in 5 min and held constant for further 7 min. 5 min post-run time was set to fully reequilibrate the systems. The injection volume was 5 μL and the detection wavelength was set at 220 nm (for naphthalene) and 230 nm (for phthalates). Data collection and management was performed by Agilent OpenLAB CDS software.

**Procedures**

The overall SUPRA phase formation procedure is illustrated in Fig. 1. Specifically, the appropriate volume (5.0–10.0 mL) of an aqueous sample was placed into a glass centrifuge tube, and the specified amounts of NaCl (only for TDTMAB/HFIP solvent), quaternary ammonium salt solution and perfluorinated compound were sequentially added. The mixture was shaken manually for 1–30 s, resulting in the formation of emulsion. The phases were separated by centrifugation at 3000 rpm for 5 min and the volume of SUPRA phase was measured using a microsyringe. For the extraction efficiency measurements, the upper aqueous phase was analysed using the HPLC technique.

For the final DLLME of phthalates, 7.5 mL of the wastewater sample was placed into a 12 mL glass centrifuge tube and spiked with naphthalene at 20 μg/L. Then 0.75 mL of 5.0 mol/L NaCl, 0.20 mL of 0.20 mol/L TDTMAB and 0.20 mL of HFIP were sequentially added and the mixture was shaken manually for 5 s. The phases were separated by centrifugation at 3000 rpm for 5 min, the upper aqueous phase was removed using a syringe, the bottom SUPRA phase was dissolved in 50 μL acetonitrile and analysed using the HPLC technique.

All measurements were performed in triplicate and mean values are reported. Before extraction, the wastewater samples were filtered through a 0.7 μm glass fiber filter.
RESULTS AND DISCUSSION

In situ formation of SUPRA phases

As already mentioned in the introduction, two quaternary ammonium salts (TBAC and TDTMAB) and four perfluorinated compounds (HFIP, TFA, PFPA and HFBA) were selected for preliminary experiments. Eight combinations of quaternary ammonium salt/perfluorinated compound were composed and examined as potential SUPRA solvents. In initial tests, different amounts of perfluorinated compound were added into a 5 mL aqueous solution containing quaternary ammonium salt, then the mixture was shaken for 30 s and centrifuged. It was found that the mixtures of TDTMAB and HFIP did not form SUPRA phases at any concentrations in pure aqueous solutions. Further experiments showed that the TDTMAB/HFIP based SUPRA phase forms only in high ionic strength (≥100 mmol/L NaCl) solutions. Thus, all further experiments with this composition were performed using aqueous solutions containing 0.5 mol/L NaCl. The other seven compositions formed colourless liquid SUPRA phases without the addition of NaCl. Due to the high density of perfluorinated compounds, all the in situ formed SUPRA phases were heavier than water.

In the DLLME techniques, target analytes are usually extracted from 5–10 mL of water samples using small volumes (50–100 µL) of extraction solvents. In the present work, the extraction solvent was formed in situ. Therefore it is important to know what concentrations of SUPRA components generate required solvent volumes. For this reason, the effects of quaternary ammonium salt and perfluorinated compound concentrations on the volume of the formed SUPRA phase were investigated. In this experiment, a small amount of alizarin dye (~0.02 mmol/L) was added to the initial aqueous solution. Relatively hydrophobic alizarin was concentrated in the SUPRA phase and coloured it in an intense red colour. This improved the visibility of SUPRA solvents and facilitated their collection after phase separation. Figure 2 shows the effects of TBAC and TDTMAB concentration on the volume of the formed SUPRA phase. As expected, for all systems, the SUPRA phase volume increases gradually as the concentration of quaternary ammonium salt increases from 5 to 100 mmol/L. A similar behaviour has also been reported by Khaledi et al. [12, 13] in HFIP induced complex SUPRA phases of cationic-anionic surfactant [13] and polyelectrolyte-surfactant mixtures [12]. They concluded that the increase in volume with the surfactant concentration was indicative of a growth of the SUPRA phase that is in a bilayered bicontinuous structure rather than in discrete structures such as micelles. Increasing the quaternary ammonium salt concentration would simply make the structure larger, as opposed to the more densely packed one. In both TBAC and TDTMAB based systems, the HFIP induced much larger SUPRA phase volumes than the perfluorinated acids at comparable concentrations. This may be attributed to the different charge state of perfluorinated compounds: alcohol has a net charge of zero, whereas strong acids are present in an anionic form. Although the structures of these phases are not known at this point, one can assume that the oppositely

![Fig. 2. Effect of TBAC (a) and TDTMAB (b) concentration on the SUPRA phase volume. Aqueous phase volume is 5 mL; amount of perfluorinated compound is 5 mmol](image-url)
charged quaternary ammonium cation-perfluorinated acid anion would form tighter assemblies resulting in lower volumes. It is worth noting that for the TBAC salt (Fig. 2a) perfluorinated acids with a longer fluoroalkyl chain induce larger SUPRA volumes, whereas for the TDTMAB (Fig. 2b) this phenomenon has not been observed. However, the exact reason for this behaviour is not clear.

Figure 3a depicts the behaviour when a fixed concentration of TBAC salt is combined with increased amounts of appropriate perfluorinated compound. The volume of the TBAC/HFIP phase increased gradually with increasing the HFIP amount in a range of 1–5 mmol. In contrast, the SUPRA phase volume remains almost constant for TBAC/HFBA, TBAC/PFPA and TBAC/TFA systems within a range of 2–5, 3–5 and 4–5 mmol of appropriate perfluorinated acid, respectively. At lower amounts of perfluorinated acid, all three mixtures form white precipitates. The initial amount of acid that is needed to form the SUPRA phase decreases in the following order: TFA > PFPA > HFBA. This indicates that the SUPRA phase formation ability of perfluorinated acids with a longer fluoroalkyl chain is more efficient.

Figure 3b illustrates the behaviour when TDTMAB is combined with different amounts of perfluorinated compounds. As the amount of appropriate perfluorinated compound increases from 1 to 5 mmol, the volume of TDTMAB/HFIP and TDTMAB/PFPA phases first decreases and then gradually increases (for TDTMAB/HFIP) or remains almost unchanged (for TDTMAB/PFPA). The volume of TDTMAB/HFBA phase formed was nearly unaffected by the varied amount of HFBA.

Finally, as in the case of TBAC/TFA system, for the TDTMAB solution, the minimum amount of TFA required to form the SUPRA phase is 4 mmol.

The obtained results show that there are some differences among the two quaternary ammonium salts. One possible reason for such differences could be attributed to different initial states of these salts in an aqueous solution. In the concentration range used, TDTMAB forms micelles (critical micelle concentration 3.6–3.7 mmol/L [18]), whereas TBAC exists in the non-micellar state. Additional information about the exact structures of these phases is needed to achieve a better understanding of the involved mechanisms. However, a detailed investigation of these effects is beyond the scope of this study.

**Extraction properties**

The suitability of the SUPRA solvents for liquid-phase microextraction was tested for the extraction of four phthalates from the model aqueous solutions. The comparison of the extraction properties of different solvents should be performed under identical conditions, i.e. using equal or at least similar extraction solvent volumes. For each solvent we have selected such amounts of both SUPRA compounds that gave the final solvent volume of 150 ± 10 µL. The extraction efficiency (EE) of each analyte was calculated according to the following equation

\[
EE(\%) = \left( \frac{c_f - c_i}{c_i} \right) \times 100 \%
\]

**Fig. 3.** Effect of the perfluorinated compound amount on the SUPRA phase volume for TBAC (a) and TDTMAB (b) amphiphiles. Aqueous phase volume is 5 mL; concentration of the quaternary ammonium salt is 25 mmol/L.
where \( c_i \) is the initial concentration of the analyte in the aqueous phase before the extraction and \( c_f \) is the analyte concentration in the aqueous phase after the extraction. The final concentrations of the analytes in the aqueous phase were measured using the HPLC technique (for HPLC conditions see the Experimental section).

The obtained results are presented in Table 1. It was not possible to evaluate higher than 98% EE data for phthalates because their concentrations in the aqueous phase after the extraction were below the limit of quantification. In general, under the employed extraction conditions all developed SUPRA solvents demonstrated a good or even excellent overall extraction efficiency. As expected, for all phthalates their EE values showed a good correlation with their log \( P \) values, listed in Table 1, indicating that hydrophobicity plays a crucial role in the extraction of these compounds from aqueous solutions. Both TFA-based solvents were found to be least effective extractants: the extraction of the most hydrophilic DMP reached efficiencies of 58.9 and 70.2% for TDTMAB/TFA and TBAC/TFA, respectively. Finally, the TDTMAB/HFIP solvent demonstrated the best extractability: using this solvent all phthalates were extracted with higher than 94% extraction efficiencies.

It should be taken into account that by the extraction with perfluorinated acid-based solvents the pH of aqueous phase considerably decreased. Although the pH decrease had no influence on the extraction efficiency of the compounds studied, this may have a significant effect on the extractability of weakly acidic and basics compounds. Thus, these solvents should be useful for the extractions in which acidification of the aqueous phase or the extractant is required.

**Compatibility with RP-HPLC**

HPLC in the reversed-phase mode (RP-HPLC) is the most common analytical technique used in combination with DLLME sample pretreatment procedures \([3-7]\). It is well established that in RP-HPLC the sample solvent with a higher elution strength (i.e. higher hydrophobicity) than the mobile phase leads to peak broadening, extreme distortions or even fragmentation of peaks \([19, 20]\). In addition, the difference in viscosity between the sample solvent and mobile phase also may affect the separation performance. When the sample viscosity greatly exceeded that of the mobile phase, flow instabilities could occur which lead to serious deformations and splitting of sample component peaks \([21]\). Another problem that may occur by the RP-HPLC analysis is the interferences from the solvent itself, its main compounds or impurities which are detected under conditions used.

In liquid-phase microextractions employing conventional hydrophobic extractants, this problem is usually avoided by simple evaporation/reconstitution steps prior to RP-HPLC analysis. In contrast to the common organic solvents, SUPRA solvents are nonvolatile and hence they cannot be removed by evaporation. Thus, before the application of the solvents for the microextraction of phthalates with further RP-HPLC analysis it is worth to check their compatibility with RP-HPLC.

Table 1. Extraction efficiencies of phthalates (1.0 mg/L) from the aqueous solution using different SUPRA solvents (aqueous sample volume 7.5 mL, SUPRA volume 150 ± 10 µL, extraction time 30 s)

<table>
<thead>
<tr>
<th>SUPRA solvent</th>
<th>EE ± SD, %; ( n = 3 )</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>DMF (1.60)</td>
</tr>
<tr>
<td>TBAC/HFIP</td>
<td>87.3 ± 1.6</td>
</tr>
<tr>
<td>TBAC/TFA</td>
<td>70.2 ± 1.3</td>
</tr>
<tr>
<td>TBAC/PFPA</td>
<td>74.8 ± 1.2</td>
</tr>
<tr>
<td>TBAC/HFBA</td>
<td>73.2 ± 1.7</td>
</tr>
<tr>
<td>TDTMAB/HFIP</td>
<td>94.0 ± 1.8</td>
</tr>
<tr>
<td>TDTMAB/TFA</td>
<td>58.9 ± 1.3</td>
</tr>
<tr>
<td>TDTMAB/PFPA</td>
<td>73.4 ± 1.6</td>
</tr>
<tr>
<td>TDTMAB/HFBA</td>
<td>78.7 ± 1.5</td>
</tr>
</tbody>
</table>

*In parentheses are the log \( P \) values obtained from pubchem.ncbi.nlm.nih.gov*
TDTMAB-based SUPRA solvents diluted (1:1, v/v) with ACN. As expected, the sample dissolved in ACN shows four narrow and symmetric peaks. No significant broadening and distortion of the peak profiles was observed for the phthalates dissolved in ACN/SUPRA mixtures indicating that the hydrophobicity of the SUPRA solvents has no remarkable effect on the peak shapes. Most likely, the dilution of the SUPRA solvent with ACN and/or its interaction with the stationary phase during separation breaks the bond network of the solvent and, consequently, reduces the hydrophobicity of the diluent.

However, two unexpected peaks appeared in the chromatograms of phthalates dissolved in perfluorinated acid containing SUPRA solvents. One of them corresponds to an unretained compound and does not interfere in the detection of phthalates. The other broad peak, however, overlaps with the DEP peak or with both DMP and DEP peaks. Moreover, its intensity and retention time depend on the nature of perfluorinated acid and increase in the following order: TFA < PFPA < HFBA. The obtained results indicate that the extra peaks may be attributed to the perfluorinated acid itself, its impurity and/or the formation of a certain compound. This was confirmed by injecting samples of individual perfluorinated acids and their SUPRA solvents (data not shown). In the chromatograms of perfluorinated acid solutions only one peak appeared at about 1.3 min indicating that free acids were unretained under the given conditions. In contrast, by the analysis of SUPRA solvent solutions (without phthalates) two peaks were detected and their chromatographic profiles were quite similar to the extra peak profiles obtained in the corresponding chromatograms of phthalates which are shown in Fig. 4. These results suggest that most likely in

Fig. 4. Chromatograms of a mixture of four phthalates dissolved in pure ACN and in four TDTMAB-based SUPRA solvents diluted (1:1, v/v) with ACN. For chromatographic conditions see the Instrumentation section.
the acetonitrile-rich SUPRA solution perfluorinated acid exists in two forms: unretained hydrophilic free acid and retained less hydrophilic neutral ion pair with an oppositely charged quaternary ammonium cation.

It should be noted that by using UV detection at ≥250 nm, these interferences are completely avoided but with a significant loss of the detection sensitivity of phthalates. Similar chromatographic profiles were also observed for the phthalates dissolved in the four TBAC-based SUPRA solvents (data not shown).

As a conclusion, it seems that at least for some phthalates the perfluorinated acid-based SUPRA solvents are not suitable as extractants and sample diluents for the RP-HPLC analysis. On the other hand, because these solvents exhibited good extraction properties, they may be very promising alternative extractants for other analyte types or in combination with other analytical techniques.

**DLLME of phthalates**

Based on the above results, the TDTMAB/HFIP solvent was selected for the DLLME of phthalates from the real water samples combining DLLME with RP-HPLC analysis. Naphthalene (NAPH) was used as an internal standard. In order to obtain high enrichment factors, the volume ratio of extraction solvent to sample solution should be minimised. For this reason, the effect of TDTMAB/HFIP solvent volume on the extraction efficiency of phthalates and naphthalene was investigated and the obtained results are presented in Table 2.

To obtain the required solvent volumes, different amounts of TDTMAB and HFIP were added to a 7.5 mL of aqueous sample spiked at 1.0 mg/L of each phthalate and the internal standard. As can be seen, by decreasing the SUPRA solvent volume up to 50 μL higher than 95% extraction efficiencies were obtained for all five compounds. Based on these results, 50 μL of TDTMAB/HFIP volume was selected for subsequent experiments.

Next, the effect of extraction time on the extraction efficiency was studied over a range of 1–30 s. No significant difference in the extraction efficiency of all compounds was observed in the time range studied indicating that the SUPRA solvent-based DLLME is time-independent. The final extraction conditions were as follows: the aqueous sample volume 7.5 mL, SUPRA extractant volume 50 μL and extraction time 5 s.

The analytical performance of the method was investigated under the optimised extraction conditions. The results are summarised in Table 3. The calibration curves were linear for a concentration level between 1.0–2.0 and 50.0 μg/L with the correlation coefficients ($R^2$) ranging from 0.9965 to 0.9982. The limits of detection (LODs) and the limits of quantification (LOQs), calculated based on signal to noise ratios of 3 and 10, respectively, were in the ranges 0.3–0.6 and 1.0–2.0 μg/L. The enrichment factors for all studied phthalates were around 75.

Finally, the developed method was applied for the determination of phthalates in two influent and
one effluent (i.e. after treatment) water samples collected from the main wastewater treatment plant of Vilnius. The influent samples were collected at different days. Only DBP and DEHP in the one influent water sample were detected. Unfortunately, the determination of DMP and DEP was impossible due to the interference from co-eluting matrix compounds. Recovery studies were performed by spiking samples with the known concentrations of DBP and DEHP. The results are summarised in Table 4. The average recoveries of spiked samples were in the range from 93.1% to 104.4% with a satisfactory precision (RSD lower than 7.4%). The chromatograms of the unspiked and spiked influent water sample are shown in Fig. 5. The obtained results indicate that the developed method is a promising alternative for the rapid enrichment and determination of common phthalates in aqueous samples.

**CONCLUSIONS**

In this work, eight novel SUPRA solvents based on quaternary ammonium salt-perfluorinated

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte</th>
<th>Found, µg/L</th>
<th>Added, µg/L</th>
<th>Recovery, %</th>
<th>RSD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent water 1</td>
<td>DBF</td>
<td>2.9</td>
<td>10.0</td>
<td>104.4</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>DEHF</td>
<td>2.4</td>
<td>10.0</td>
<td>96.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Influent water 2</td>
<td>DBF</td>
<td>–</td>
<td>5.0</td>
<td>102.9</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>DEHF</td>
<td>–</td>
<td>5.0</td>
<td>93.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Effluent water</td>
<td>DBF</td>
<td>–</td>
<td>10.0</td>
<td>95.5</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>DEHF</td>
<td>–</td>
<td>10.0</td>
<td>97.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

**Table 4. Results and recoveries of phthalates from wastewater samples (n = 3)**

**Fig. 5.** Chromatograms of the (a) unspiked and (b) spiked with 10.0 µg/L of DBP and DEHP influent wastewater sample. For chromatographic conditions see the Instrumentation section.
compound mixtures were prepared and investigated for potential use as extractants in DLLME. The presented solvents were formed \textit{in situ} during the analysis, exhibited higher than water densities and demonstrated good extraction efficiencies for phthalates. The TDTMAB/HFIP solvent was successfully applied for the DLLME of parabens from wastewater samples prior to HPLC analysis. The obtained results demonstrate that the developed solvents may be considered as very promising alternative extractants for DLLME.

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