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Research Article

Surfactant-based ionic liquids for extraction of phenolic compounds combined with rapid quantification using capillary electrophoresis

A rapid liquid phase extraction employing a novel hydrophobic surfactant-based room temperature ionic liquid (RTIL), tetrabutylphosphonium dioctyl sulfosuccinate ([4C$_4$P][AOT]), coupled with capillary electrophoretic-UV (CE-UV) detection is developed for removal and determination of phenolic compounds. The long-carbon-chain RTIL used is sparingly soluble in most solvents and can be used to replace volatile organic solvents. This fact, in combination with functional-surfactant-anions, is proposed to reduce the interfacial energy of the two immiscible liquid phases, resulting in highly efficient extraction of analytes. Several parameters that influence the extraction efficiencies, such as extraction time, RTIL type, pH value, and ionic strength of aqueous solutions, were investigated. It was found that, under acidic conditions, most of the investigated phenols were extracted from aqueous solution into the RTIL phase within 12 min. Good linearity was observed over the concentration range of 0.1–80.0 μg/mL for all phenols investigated. The precision of this method, expressed as RSD, was determined to be within 3.4–5.3% range. The LODs (S/N = 3) of the method were in the range of 0.047–0.257 μg/mL. The proposed methodology was successfully applied to determination of phenols in real water samples.

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1 Introduction

Phenolic compounds are considered priority pollutants as a result of their widespread use, high persistence in the environment, and noted toxicities [1, 2]. Furthermore, when the problem of these pollutants is not addressed, many of these compounds ultimately accumulate in water and/or soil resources [3]. As a consequence, several processes including oxidation, biological degradation, and solvent extraction have been proposed for decontamination of phenol-contaminated environmental compartments [1, 4–9]. However, to date, phenols are still considered intrusive environmental pollutants,

and are frequently chosen as model contaminants. In addition, significant data are available on the removal and elimination of phenols, especially with regards to wastewater treatment [3]. However, the management of highly concentrated phenol wastewater still remains a bottleneck in modern sewage treatment, primarily due to the high cost of sorbents [5–8].

Solvent extraction techniques are often employed as effective separation and pretreatment procedures in analytical science and the chemical industry [10]. In addition, solvent extraction is a widely used extraction procedure with more than satisfactory performance for removal of phenols. However, its wider application is restricted due to the volatility and flammability of organic solvents that are often employed in such procedures [11, 12]. In this regard, room temperature ionic liquids (RTILs) offer a suitable alternative as clean and effective extraction solvents due to their high thermal stability and low volatility [12, 13]. In previous studies, RTILs have been

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Abbreviations: AOT, dioctylsulfosuccinate; **CP**, chlorophenol; **DCP**, dichlorophenol; **NP**, nitrophenol; **RTIL**, room temperature ionic liquid

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successfully explored as substitute solvents for extraction and separation of various compounds, including phenols, from organic or aqueous solutions [14, 15]. In this regard, we have also successfully established a magnetic-based separation approach to extracting various phenolic compounds from aqueous solution by use of a hydrophobic magnetic RTIL (trihexyltetradecylphosphonium tetrachloroferrate) [13].

Various RTILs composed of a diversity of cations and anions have been previously evaluated in a quest to improve extraction efficiencies of these priority pollutants. These studies have focused primarily on traditional RTILs using anions such as $[PF_6]^-$, $[BF_4]^-$, $[Tf_2N]^-$, and cations derived from imidazolium and phosphonium salts [12, 13, 16]. As noted in these references, a major driving force for these extractions is hydrogen bonding and hydrophobic interactions between RTILs and phenols. Moreover, a key to enhancing extraction efficiencies is to accelerate the mass transfer of analytes between the two immiscible phases in order to quickly reach equilibrium, a process that is primarily impacted by interfacial tensions and viscosities of the solvents.

It is well established that surfactants can decrease interfacial tension between a nonaqueous liquid and water and thus increase interactions between the two phases. Therefore, surfactant-based extraction strategies have been used extensively to enhance extraction efficiencies [17, 18]. While Brown et al., have recently reported the first surfactant-based RTILs, which are surface active [19], these surfactant-based RTILs were soluble in water and are therefore not suitable as extraction solvents. For the purposes of extraction, hydrophobic surfactant-based RTILs can be designed and synthesized by using variations in hydrophobicity. Thus, when used as alternative extraction solvents, such molecules should lead to improved separations.

In order to develop a complete protocol for addressing the issue of phenol pollution, it is also desirable and worthwhile to develop a rapid and effective method for monitoring phenols after extraction and cleanup. Among the various methods for determination of phenols, CE is increasingly recognized as a highly attractive and powerful separation tool as a result of its high separation efficiencies, short analysis time, small sample requirements, and low operation costs [20–22].

In this manuscript, we report on a new strategy for solvent extraction of phenols using novel surfactant-based RTILs to replace traditionally used and toxic organic solvents. A CE system is then applied to separation and determination of phenols in the phenols-rich RTIL phase. Distribution ratios of these compounds are determined in order to evaluate extraction efficiency and optimize the extraction process.

2 Materials and methods

2.1 Chemicals and materials

Tetrabutylphosphonium bromide (4C$_4$PBr) (98%), tetrabutylammonium bromide (4C$_4$NBr) (98%), trihexyltetradecyl-

phosphonium chloride (3C$_6$PC$_{14}$Cl) (95%), 1-methy-3-octyl-imidazolium bromide (C$_8$mimBr) (95%), dioctylsulfosuccinate sodium salt (AOT) (96%), SDS, phenol (Ph) (99%), 4-nitrophenol (4-NP) (≥99%), 2-nitrophenol (2-NP) (≥99%), 3-nitrophenol (3-NP) (≥99%), 3-chlorophenol (3-CP) (≥99%), 2,4-dichlorophenol (2,4-DCP) (99%), Na$_2$B$_4$O$_7$·10H$_2$O, NaOH, acetonitrile, and methanol were purchased from Sigma–Aldrich (Milwaukee, WI). All reagents were used as received without further purification.

2.2 Synthesis and characterization

Surfactant-based RTILs, tetrabutylphosphonium dioctylsulfosuccinate ([4C$_4$P][AOT]), tetrabutylammonium dioctylsulfosuccinate ([4C$_4$N][AOT]), trihexyltetradecylphosphonium dioctylsulfosuccinate ([3C$_6$PC$_{14}$][AOT]), 1-methy-3-octylimidazolium dioctylsulfosuccinate ([C$_8$mim][AOT]), and trihexyltetradecylphosphonium dodecylsulfate ([3C$_6$PC$_{14}$][SDS]), were synthesized as follows: 0.44 g of AOT (or 0.35 g of SDS) were added to 10 mL of a mixture of water and methanol (2:1, v/v) under stirring, to form a transparent solution. Then, 1.0 mmol of the counter anion (4C$_4$PBr, 4C$_4$NBr, 3C$_6$PC$_{14}$Cl, or C$_8$mimBr) dissolved in methanol, was added to this solution, and stirred for 24 h. After completion of the reaction, mixed solvents were removed by rotavaporation under vacuum. The resultant viscous liquids were subsequently washed with deionized water. After careful removal of the water phase, the RTILs were further freeze-dried overnight. The final products, ([4C$_4$P][AOT]), ([4C$_4$N][AOT]), ([3C$_6$PC$_{14}$][AOT]), ([C$_8$mim][AOT]), and ([3C$_6$PC$_{14}$][SDS]) were transparent viscous liquids, with respective densities of 0.848, 0.816, 0.824, 0.896, and 0.820 mg/mL. In addition, the solubilities of these compounds were determined using a gravimetric method and all were found to be sparingly soluble in water [23]. These samples were further characterized using nuclear magnetic resonance (^{1}H$^-$NMR) and high-resolution mass spectrometry (HR-MS).

2.3 Preparation of standard stock solution

Stock solutions of 10.0 mg/mL Ph, 4-NP, 2-NP, 3-NP, 3-CP, and 2,4-DCP were prepared in methanol and stored in precleaned amber glass vials at 4°C. Mixed standard stock solutions containing the six phenolic compounds were prepared in methanol and stored at 4°C. Working solutions were prepared daily by diluting the standard stock solutions with deionized water.

2.4 Sampling

Water samples (lake and river water) were collected from LSU University Lake and the Mississippi River (Baton Rouge, LA, USA). Before analysis, samples were centrifuged at 10 000 rpm for 15 min to remove suspended solids. The pH

of the filtered water samples was adjusted to approximately 5.0 with a diluted solution of 0.1 mol/L HNO$_3$.

2.5 Batch extraction experiments

Batch extraction tests were performed in 50.0 mL capped vials. A volume of 0.4 mL of RTIL was added to 48.0 mL of aqueous solution containing a predetermined phenol concentration. Aqueous solutions of HCl and NaOH (0.1 mol/L) were employed for pH adjustment, and NaCl (0.05, 0.10, 0.15, 0.20, 0.25, or 0.30 g/mL) was used to regulate the ionic strength of the sample. Then, the system was vigorously stirred using a vortex during extraction time. After a given period of time, the sample was centrifuged (4500 rpm; 10 min) and 100 μL of the phenols-rich RTIL phase were collected. This phase was then diluted with 100 μL acetonitrile and directly injected into the CE using 0.5 psi for 5 s.

During extraction experiments, the extraction efficiency was reported as distribution ratios (D) and extraction percentages (E) previously described [13]. The following equations were used for computations:

$$D = \frac{C_{RTIL}}{C_W} \tag{1}$$

$$E = \frac{C_{RTIL}}{C_{RTIL} + C_W} \times 100\% = \frac{C_{RTIL} V_{RTIL}}{C_{RTIL} V_{RTIL} + C_W V_W} \times 100\%$$

$$= \frac{D}{D + \left(\frac{V_W}{V_{RTIL}}\right)} \times 100\% \tag{2}$$

where C_W and C_{RTIL} are the respective equilibrium concentration of the phenols in aqueous and RTIL phases and V_W and V_{RTIL} refer to the volumes of aqueous and RTIL phases. The third part of Eq. (2) is only valid once the system has come to equilibrium.

2.6 Capillary electrophoretic analysis

Mixed solutions of the six phenolic compounds were separated and quantified by using a Beckman P/ACE MDQ Capillary Electrophoresis System (Beckman Coulter, Fullerton, CA, USA), equipped with an autosampler and a diode array detector. Untreated fused-silica capillaries (polymicro Technologies Phoenix, AZ, USA) were 50 cm × 50 μm id, with a length of 40 cm between injection and detection. Mobility measurements were run at 25°C with a liquid coolant in the capillary cartridge with an applied voltage of 20 kV. Detection was monitored at 205 nm using an 800 μm × 100 μm aperture to maximize sensitivity. A 20 mM borate buffer solution (pH 10) was prepared using the appropriate combination of Na$_2$B$_4$O$_7$ and NaOH aqueous solution and used as the elution buffer.

3 Results and discussion

3.1 Characterization of [4C$_4$P][AOT], [4C$_4$N][AOT], [C$_8$min][AOT], and [3C$_6$PC$_{14}$][AOT]

The RTILs [4C$_4$P][AOT], [4C$_4$N][AOT], [C$_8$min][AOT], and [3C$_6$PC$_{14}$][AOT] were primarily characterized using HR-MS. Examination of the HR-MS spectra (Supporting Information Fig. 1), showed intense peaks with m/z of 259.3, 242.3, 195.3, and 483.5, corresponding to molecular masses for the respective cations [4C$_4$P]$^+$, [4C$_4$N]$^+$, [C$_8$mim]$^+$, and [3C$_6$PC$_{14}$]$^+$. For the four RTILs, a peak was observed at 421.2 m/z that is characteristic of the [AOT]$^-$ anion. Structures and purities of the four RTILs were also confirmed using ^{1}H NMR spectra (Supporting Information Fig. 2). Examination of the NMR spectra show that the approximate ratios of integral peak areas are in good agreement with the ratios of the number of hydrogen atoms at different shifts in an allowable error range, indicating that [4C$_4$P][AOT], [4C$_4$N][AOT], [C$_8$min][AOT], and [3C$_6$PC$_{14}$][AOT] were successfully synthesized.

3.2 Extraction procedure

3.2.1 Selection of ionic liquids

Selection of specific RTILs is extremely important in this method because it significantly influences the extraction efficiency and ultimate determination of the analytes. In order to obtain a simple and rapid detection method based on CE-UV, it is desirable to directly inject the RTIL phase into the capillary without causing current instabilities [16, 24]. Therefore, five different hydrophobic surfactant-based RTILs were evaluated for phenols extraction. When using [4C$_4$P][AOT] (Fig. 1B) or [4C$_4$N][AOT] (Fig. 1C) as extractants, these compounds exhibited the typical electropherogram of phenols, with parameters such as resolution, number and shape of peaks, baseline, and elution sequence comparable with that obtained from the standard solution without addition of RTILs (Fig. 1A). However, when using [3C$_6$PC$_{14}$][AOT] (Fig. 1D) and [3C$_6$PC$_{14}$][SDS] (Fig. 1E) as extractants, new peaks, and baseline shifts were observed, and the retention times of the analytes were increased, thus increasing their peak broadness. It was observed that the increase in length of the alkyl side chain affected the electrophoretic mobility of the phenols and reduced selectivity. We assumed that this is due to the higher hydrophobicity and viscosity of [3C$_6$PC$_{14}$][AOT] and [3C$_6$PC$_{14}$][SDS], resulting in a lower solute diffusion coefficient. Thus, addition of organic solvents will guarantee complete dissolution or dispersion of these compounds to form a homogeneous system in the CE. For this reason, a higher content of organic solvent (acetonitrile) is needed to release the phenols from [3C$_6$PC$_{14}$][AOT] and [3C$_6$PC$_{14}$][SDS]. However, use of an organic solvent works against the separation process [16, 24, 25]. Additionally, as can be seen in Fig. 1F, the RTIL [C$_8$mim][AOT] produces an intense peak at the beginning of the electropherogram, which overlaps
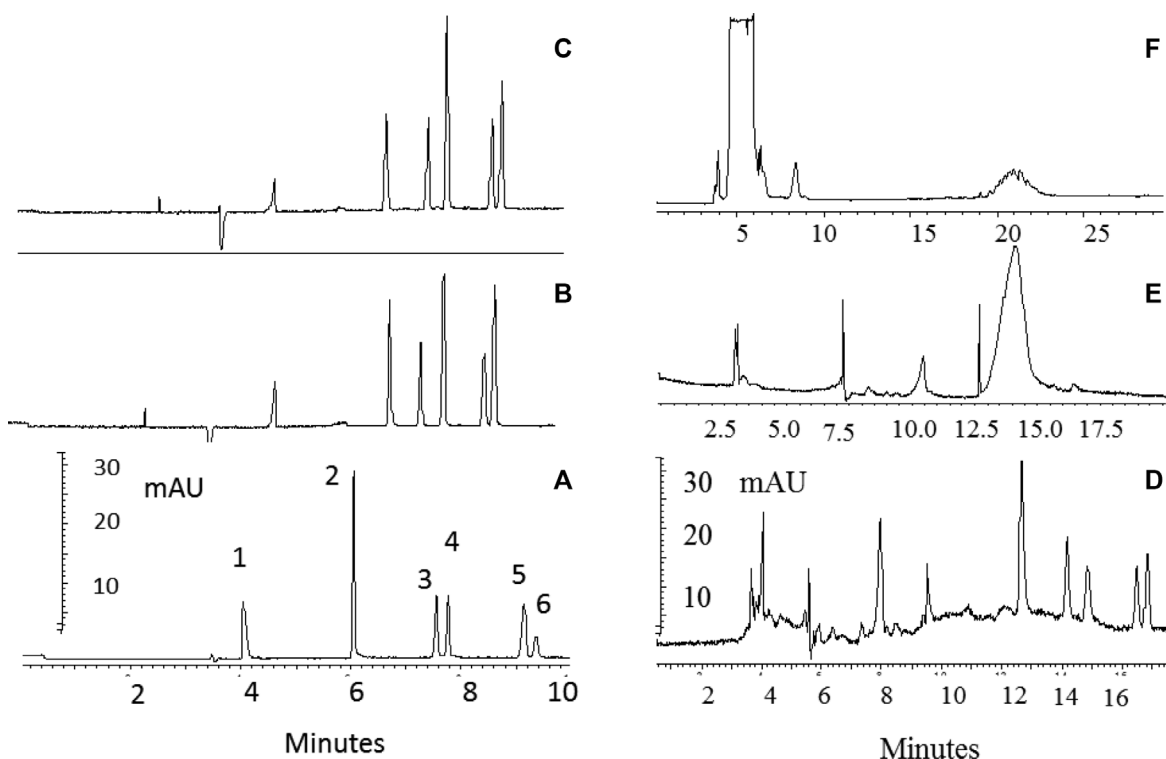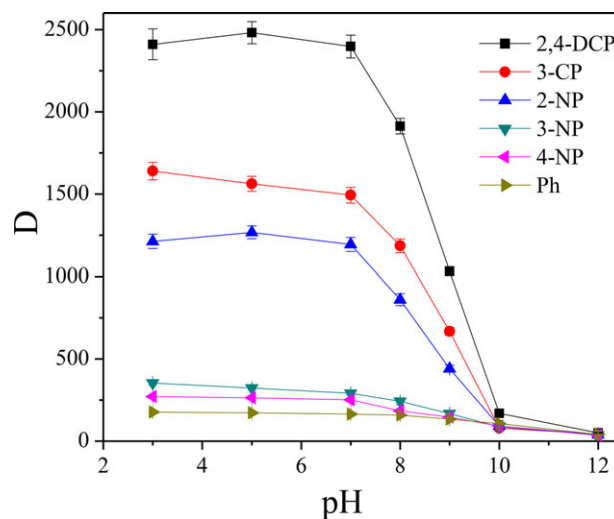
Figure 1. Electropherogram of (A) standard solution of phenols at the concentration of 0.2 mg/L; Electropherograms of the extract of phenols solution after liquid–liquid extraction using (B) [4C$_4$P][AOT], (C) [4C$_4$N][AOT], (D) [3C$_6$PC$_{14}$][AOT], (E) [3C$_6$PC$_{14}$][SDS], (F) [C$_8$mim][AOT] as extractant phase.
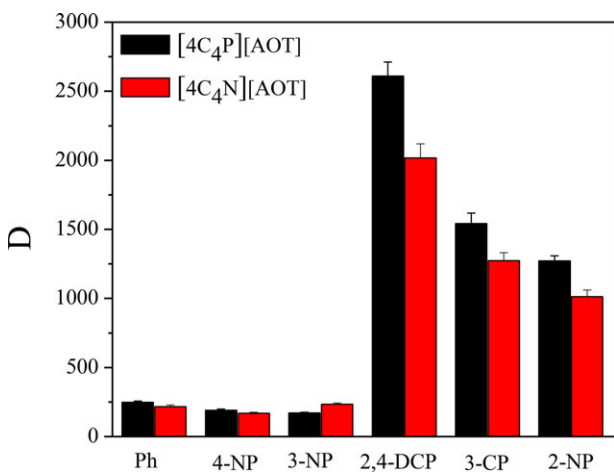
Figure 2. Distribution ratios of phenols after extraction with [4C$_4$P][AOT] and [4C$_4$N][AOT].

Figure 3. Effect of pH on distribution ratios of phenols between [4C$_4$P][AOT] and aqueous phases.

with the peaks of phenols when directly determined by using CE-UV [26]. Based on these results, the RTILs [4C$_4$P][AOT] and [4C$_4$N][AOT] were preferred for evaluation as alternative extraction solvents.

Among the selected two surfactant-based RTILs, the distribution ratios of the phenols, except 3-NP, were higher in [4C$_4$P][AOT] than in [4C$_4$N][AOT] (Fig. 2). Thus [4C$_4$P][AOT] was chosen as the extractant for further experiments.

### 3.2.2 Effect of pH and ionic strength of aqueous solution

In order to investigate the effect of pH on the extraction of targeted phenols, pH of the aqueous phase was varied from pH 3 to 12. Results, illustrated in Fig. 3, revealed that the distribution ratios of all phenols in RTIL phase increased
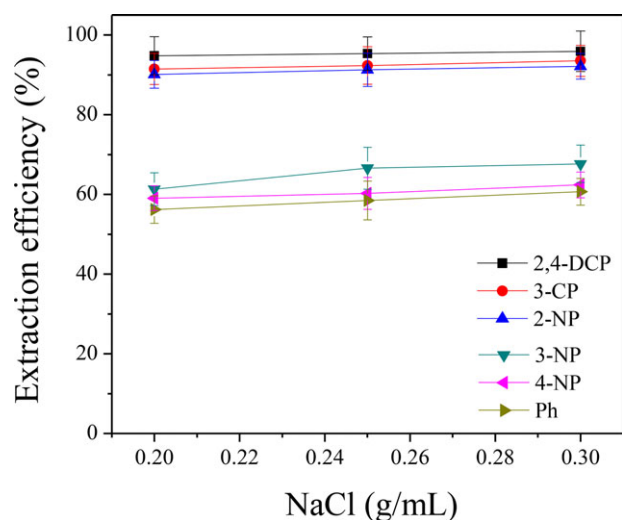
Figure 4. Effect of concentration of salt on the extraction efficiencies of phenols in [4C$_4$P][AOT].

Figure 5. Effect of phase ratio on the extraction efficiencies of phenols in [4C$_4$P][AOT].

from neutral to acidic pH values, reaching a plateau at low pH and sharply decreasing at basic pH values. Since the respective ionization constants (pKa) of 4-NP, 2-NP, 2,4-DCP, 3-NP, 3-CP, and Ph in water are 7.15, 7.23, 7.85, 8.37, 9.05, and 9.89, respectively [21, 22], at acidic pH values the molecular forms of phenols will predominate. The RTILs can participate in multiple types of solvation interactions, such as n–π, dipolar, hydrogen bonding, dispersive, and ionic interactions due to their complex structure and various functional groups [27]. Hydrogen bonding, mainly by the RTIL anion, and hydrophobic interactions between RTILs and phenols facilitate, at acidic pH values, the transfer of analytes from aqueous to RTIL phase [12, 28, 29]. However, at basic pH values, a drop in D of all the phenols is observed, independent of their pKa values. A possible explanation of this behavior is cleavage of the ester group of the RTIL anion through alkaline hydrolysis [30, 31], thus diminishing hydrophobic interactions among the remaining molecular forms of the analytes and the RTIL. Based on the above results, a pH of 5 was selected as an optimum value for subsequent experiments.

The effect of salt addition on the extraction efficiencies of phenols was investigated (Fig. 4) by using NaCl to control the ionic strength of the solution. For extraction of organic solutes from aqueous solutions, the salting-out effect may play a positive role in extraction efficiency, since it reduces the solubility of target analytes in the aqueous phase [26, 32]. In the present technique, it was however observed that extraction efficiencies of phenols remained almost constant with addition of NaCl to the aqueous solution (from 0.20 and up to 0.30 g/mL). The ruggedness evidenced by this method at relatively high salt concentrations (up to 0.30 g/mL) may represent an important advantage for analysis of salty samples. Based on these results, 0.30 g/mL NaCl was selected as the optimum concentration for extraction.
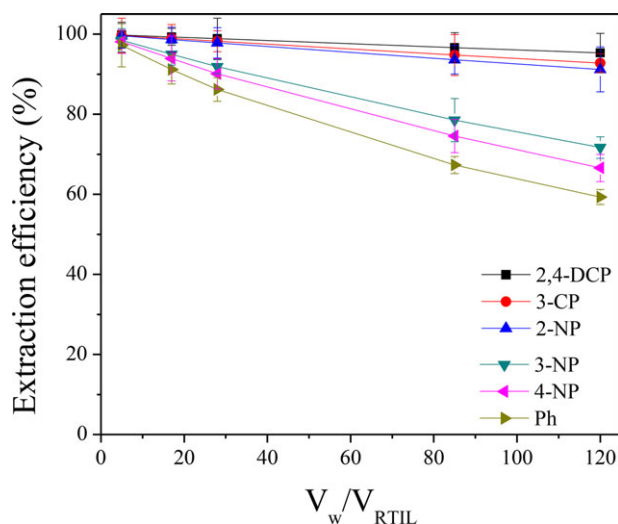
3.2.3 Effect of sample volume and extraction time

The phenol concentration in real samples such as natural waters is usually very low. Thus, the sample volume is one of the most important parameters to optimize during development of a preconcentration method, since this volume determines the sensitivity enhancement of the technique. For this reason, the effect of the phase ratio between the aqueous solution and [4C$_4$P][AOT] on the phenol extraction efficiencies was also examined. As seen in Fig. 5, a clear diminution of extraction efficiencies is observed for 3-NP, 4-NP, and Ph at higher phase ratios, possibly due to their lower distribution ratios. In contrast, extraction efficiencies of 2,4-DCP, 3-CP, and 2-NP remained constant when the phase ratio increased from 5 (2.5 mL/0.5 mL) to 120 (48 mL/0.4 mL). Accordingly, 0.4 mL of [4C$_4$P][AOT] and 48.0 mL of aqueous solution, i.e. V_W:V_{IL} = 120:1, were typically used for further extractions.

Extraction time is an important factor, which influences the extraction efficiency. Maximum efficiency is obtained when the system is at equilibrium, which requires time for mass transfer of analytes between the two immiscible phases [33, 34]. Furthermore, mass transfer and extraction rates are slightly slower as compared to cases where organic solvents are used, due to the higher viscosities of the RTILs [35, 36]. Therefore, the influence of extraction time on extraction of the phenols using [4C$_4$P][AOT] as extraction solvent was investigated. As shown in Fig. 6, the extraction efficiencies of the six phenols rapidly increased when extraction time increased up to 12 min. With additional extraction times, no significant increase was observed. In addition, it was observed that maximum extractions were independent of the molecular structures of the phenols, since a similar trend was observed for each when extracted with [4C$_4$P][AOT]. Furthermore, when compared to traditional RTILs, most of which need at least 20 min [13], the maximum extractions were obtained more rapidly when surfactant-based RTILs were employed. This
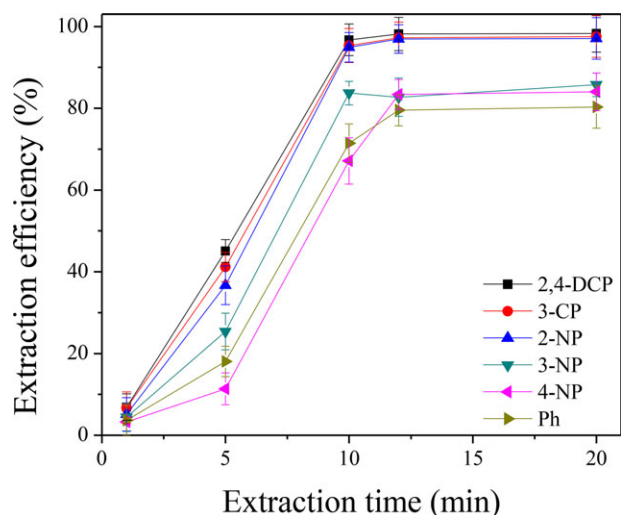
Figure 6. Effect of extraction time on extraction efficiencies of phenols in [4C₄P][AOT].

Table 1. Linear ranges (LR), correlation coefficients (*r*), LODs, LOQs, and RSDs for phenol samples

Analyte	LR (μg/mL)	*r*	RSD (%) (*n* = 5)	LOD (μg/mL)	LOQ (μg/mL)
2,4-DCP	0.1–80	0.9988	3.8	0.047	0.142
3-CP	0.1–80	0.9976	4.6	0.062	0.186
2-NP	0.1–80	0.9964	5.1	0.085	0.255
3-NP	0.1–80	0.9994	3.4	0.257	0.771
4-NP	0.1–80	0.9976	5.3	0.182	0.546
Ph	0.1–80	0.9995	3.7	0.163	0.489

could be due to the ability of the surfactant to reduce the interfacial energy of the two liquid phases, while increasing the solute diffusion coefficient. Therefore, a phase contact time of 12 min was employed as optimum extraction time for the six phenols throughout the extraction.

3.3 Analytical performance

Under optimal conditions, linear range, linearity, LODs, LOQs, and reproducibility of the method were evaluated. As shown in Table 1, good linearity was observed for all target analytes in the concentration range of 0.1–80 μg/mL. All correlation coefficients (*r*) were larger than 0.9964. The LODs, based on a *S/N* of 3, were found to be 0.047–0.257 μg/mL. The LOQs, based on a *S/N* of 10 for the analytes, were between 0.142 and 0.771 μg/mL. The LOD and LOQ values are close to those previously reported [19, 22, 37–39]. The reproducibility of the proposed method, expressed as RSD, was found to be between 3.4 and 5.3%.

3.4 Analysis of water samples

To further evaluate the applicability of the proposed method using real samples, the procedure was applied to determi-

Table 2. Recovery of phenols spiked in water samples

Analyte	Lake water			River water		
	Spiked (μg/mL)	Found[a] (μg/mL)	Recovery (%)	Spiked (μg/mL)	Found[a] (μg/mL)	Recovery (%)
2,4-DCP	0.0	nd[b]		0.00	nd[b]	
	15.0	14.7 ± 0.20	98.0	15.0	14.3 ± 0.10	95.3
	60.0	59.4 ± 0.30	99.0	60.0	58.8 ± 1.50	98.0
3-CP	0.00	nd[b]		0.00	nd[b]	
	15.0	14.6 ± 0.20	97.3	15.0	14.4 ± 0.20	96.0
	60.0	58.1 ± 0.40	96.8	60.0	59.2 ± 2.10	98.7
2-NP	0.00	nd[b]	96.0	0.00	nd[b]	
	15.0	14.4 ± 0.10	96.3	15.0	14.9 ± 0.40	99.3
	60.0	57.8 ± 1.20		60.0	57.8 ± 1.80	96.3
4-NP	0.00	nd[b]		0.00	nd[b]	
	15.0	15.8 ± 0.20	105	15.0	14.6 ± 0.50	97.3
	60.0	59.6 ± 0.60	99.6	60.0	57.3 ± 1.30	95.5
3-NP	0.00	nd[b]		0.00	nd[b]	
	15.0	14.4 ± 0.30	96.0	15.0	16.1 ± 0.20	107
	60.0	57.5 ± 0.80	95.8	60.0	58.4 ± 1.30	97.3
Ph	0.00	nd[b]		0.00	nd[b]	
	15.0	14.2 ± 0.40	94.6	15.0	14.2 ± 0.40	94.6
	60.0	58.4 ± 1.60	97.3	60.0	57.3 ± 2.40	95.5

a) Mean of three determinations ± SD.
b) nd: not detected.

nation of phenols in two water samples, including lake and river water. Both water samples were spiked with phenols at concentrations of 15.0 and 60.0 μg/mL because direct analysis revealed no measurable phenols. Results are presented in Table 2. As seen, recovery values calculated for spiked samples at different concentrations were higher than 90%, suggesting that the proposed surfactant-based RTIL liquid-phase extraction procedure is reliable for the sample examined. In fact, concentrations of the six phenols were dramatically reduced from an initial concentration of at least 15.0 μg/mL to lower than 0.8 μg/mL (calculated as difference between concentrations added to aqueous phase and those found in RTIL phase after the proposed procedure). Furthermore, with the aid of the novel surfactant-based RTIL [4C₄P][AOT], an improvement in sensitivity of 100 with CE was obtained. A similar improvement in sensitivity was also obtained by Wang et al. [16], who proposed a RTIL-based single-drop microextraction with CE for the extraction and determination of phenols from water samples. However, that methodology required a higher concentration of organic solvent to recover and separate the extracted phenols due to the RTIL used as extraction solvent ([BMIM][PF₆]).

4 Concluding remarks

Novel surfactant-based ionic liquids have been synthesized and their properties as alternative extraction solvents for phenols have been evaluated. Evaluation of results shows that this novel surfactant-based RTIL is highly efficient for extraction of phenols. Distribution ratios and thus extraction efficiencies

of analyzed phenols were highly influenced by the extractant RTIL and by the pH and ionic strength of the aqueous solution. At the same time, the extraction phase can be directly injected into the CE-UV in contrast to general RTILs, leading to development of a simple, rapid, and effective analytical method. It is concluded that the present RTIL-based extraction combined with CE-UV has great potential for highly efficient cleanup and rapid analyses of phenols in aqueous samples.

The authors have declared no conflict of interest.

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