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Original Article

Detection of phthalates migration from disposable tablewares to drinking water using hexafluoroisopropanol-induced catanionic surfactant coacervate extraction ☆

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ABSTRACT

Hexafluoroisopropanol (HFIP)-induced sodium dodecyl sulfate/dodecyltrimethylammonium bromide (SDS/DTAB) catanionic surfactant coacervate extraction method coupled with high performance liquid chromatography (HPLC) was used to detect the migration of phthalates from disposable tablewares to drinking water. The concentration factors are larger than 82 and extraction recoveries over 53% for water samples spiked with 100 or 200 ng/mL phthalates. Limit of detection is in the range of 1.0–2.6 ng/mL. Good linearity with correlation coefficients larger than 0.9985 is obtained in the concentration of 20–1500 or 40–3000 ng/mL. Relative recoveries are from 82.4% to 123.6% for water samples spiked with 30/60, 250/500, and 1500/3000 ng/mL phthalates, respectively. Relative standard deviations (RSDs) are 0.4%–7.4% for intraday precision ($n=5$) and 0.6%–7.8% for interday precision ($n=3$). Four of studied phthalates are found in the drinking water samples prepared from four kinds of tablewares.

1. Introduction

Phthalates are the most widely used plasticizers in the plastics industry. They are usually added into polymers to improve their moldability and flexibility. The phthalates with lower molecular weight, such as di-n-butyl phthalate (DBP), are commonly used as solvents to hold color and scent in personal care products and various other consumables [1]. Exposure to phthalates can lead to a variety of harmful effects on human health, including notable developmental and reproductive toxicities, allergic diseases, and carcinogenic threat [2,3]. A toxicogenomics study revealed that phthalates can lead to nephrotoxicity, cardiotoxicity and hepatotoxicity [4]. Therefore, some international and national regulatory organizations have listed several phthalates as priority hazardous substances for supervision. For instance, the European Union listed di-2-ethylhexyl phthalate (DEHP), DBP and butyl benzyl phthalate (BBP) in candidate substances with potential or evident endocrine disrupting action [5,6]. Most recently, several plasticizer incidents on food safety occurred in China. In 2011, a high concentration (600 ppm) of DEHP was detected in probiotics raw materials produced in Taiwan [2]. In 2012, an unacceptable amount (1.08 mg/kg, the permitted maximum amount is 0.3 mg/kg) of DBP was discovered from Jiugui white liquor produced by Jiugui Liquor Co., LTD. in Hunan Province [7]. These incidents and other similar reports have aroused worldwide concerns over phthalate-related food safety issues and environmental pollution. In past several years, the detection of phthalates in beverage [8–11], wine [8,10,12], cleaning and personal care products [6] and various water samples [10,13–16] has been reported. Also, the migration of phthalates from food packaging to food products (especially water and liquid food) has been surveyed [17–20].

Nowadays, polymer-made disposable tablewares, such as disposable cups and bowls, are extensively used in our daily life due to their low cost and easy use. Even worse, they are often abused in some places. In the production of these tablewares, a certain amount of phthalates are added into the polymers to increase their moldability and flexibility. Because phthalates are only physically bound to the polymer chains, they can easily migrate into the food or drinking water during the use of the tablewares [21,22]. Thus, detection of phthalates migration from disposable tablewares to food and drinking water is very important. Many pretreatment techniques for extracting phthalates from complex samples have been reported, including solid-phase extraction (SPE) [11,14,19], liquid-liquid extraction (LLE) [23], solid-phase microextraction (SPME) [8,13,17], dispersive liquid–liquid microextraction (DLLME) [6,10,12], and cloud point extraction (CPE) [15,16].

More recently, a novel sample pretreatment method,

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hexafluoroisopropanol (HFIP)-induced sodium dodecyl sulfate (SDS)/dodecyltrimethylammonium bromide (DTAB) catanionic surfactant coacervate extraction, has been developed by our group [24]. This new method has promising applications for the extraction of analytes in a wide polarity range because of the different polar regions of the coacervate aggregates formed by catanionic surfactant vesicles. In our previous paper, the method was used to extract three strongly polar sulfonamides from environmental water, showing efficient preconcentration and extraction effects [24]. In the present work, we further utilized the novel method, coupled with high performance liquid chromatography (HPLC), to detect phthalates (neutral compounds with weak or non polarity) migration from disposable tablewares to drinking water. It is the first time we applied the new coacervate extraction method for the extraction of weak/non polar compounds and detected the migration of phthalates from disposable tablewares to drinking water.

2. Experimental

2.1. Chemicals and materials

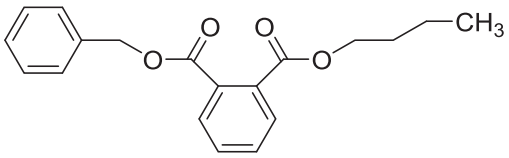
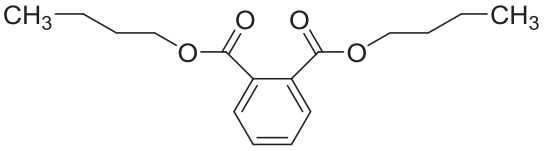
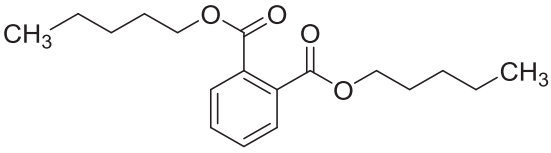
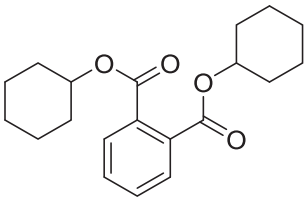
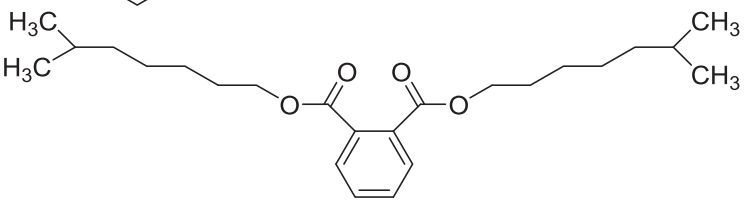
SDS, DTAB and HFIP were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). The standards of BBP, DBP, dipentyl phthalate (DPP), dicyclohexyl phthalate (DCHP), and DEHP were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China), and their structures and physical properties are shown in Table 1. Chromatographic-grade methanol and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals used were of analytical reagent grade unless otherwise indicated. The deionized water used in this work was obtained from a Milli-Q water purification system (Millipore, Molsheim, France). Dixie cups, plastic cups and feeding bottles were purchased from a supermarket in Wuhan (Hubei, China). Paper bowls were obtained from a student canteen of Wuhan University (Hubei, China).

2.2. Preparation of solutions and drinking water samples

The DTAB and SDS stock solutions were prepared as 100 mM in water. The stock solutions of phthalates were prepared as 2 mg/mL in methanol. All the stock solutions were stored at 4 °C in the dark. The mixed standard solutions of phthalates for extraction and HPLC analysis were obtained by appropriately diluting their stock solutions with water.

Drinking water samples were prepared by simulating the normal use of paper cups, plastic cups, paper bowls and feeding bottles as drinking utensils. Briefly, deionized water was heated to 100 °C and then added into a disposable dishware and a feeding bottle, respectively, until the distance between water level and the top boundary of the tablewares reached 1 cm. These water-contained tablewares were allowed to stand for 1 h at room temperature, and then the water was filtered with 0.45 μm cellulose membrane and used as drinking water samples, which were stored at 4 °C in the dark before use.

Table 1
The structures and physical properties of the studied phthalates.

Analyte	Structure	Log *P*	$H_{Acceptor}$
BBP		4.910 ± 0.266	4
DBP		4.752 ± 0.254	4
DPP		5.771 ± 0.254	4
DCHP		5.639 ± 0.257	4
DEHP		8.516 ± 0.261	4

2.3. Extraction procedure

Extraction procedure was similar to that reported previously [24] with slight modification. First, 5 mL of phthalates-spiked water sample or the drinking water sample prepared from the tablewares was pipetted into a 7 mL centrifuge tube with a conical bottom. Then, an appropriate volume of both DTAB and SDS stock solutions and a certain quantity of HFIP (≤ 0.6 mL) were added into the tube in sequence. This solution was vortex mixed for 1 min, waterbath heated for 1 h at 40 °C, and centrifuged at 2400 rpm for 30 min. At this moment, a stable coacervate phase occurred in the bottom of the tube and was transferred to a vial with a microsyringe. The coacervate phase was diluted 1-fold with methanol to reduce viscosity and then injected into the HPLC system.

2.4. HPLC analysis

Chromatographic experiments were performed on a Shimadzu LC-20CE HPLC system (Kyoto, Japan) equipped with a variable wavelength detector and manual/automated injectors with a 10 μL injection loop. An intraMax C_{18} column (250 mm × 4.6 mm, 5 μm) was used, and the column temperature was set at 40 °C. The five phthalates were chromatographically separated by using a gradient mobile phase of acetonitrile-water (v/v) with 80% acetonitrile from 0 to 13 min, 80%–100% acetonitrile from 13 to 14 min, and 100% acetonitrile from 14 to 25 min. The flow rate of mobile phase was set at 1.0 mL/min and detection wavelength was at 275 nm.

2.5. Method validation

The developed coacervate extraction method coupled with HPLC was applied to analyze phthalates-spiked water samples. Water samples spiked with 100 ng/mL BBP, DBP and DEHP as well as 200 ng/mL DPP and DCHP were analyzed to calculate the concentration factor and extraction recovery of five phthalates. Linearity was evaluated by a six-point calibration curve (BBP, DBP and DEHP: 20, 50, 100, 200, 500, 1500 ng/mL; DPP and DCHP: 40, 100, 200, 400, 1000, 3000 ng/mL). Linear equations were produced by plotting the peak area as a function of the concentration of phthalates spiked in water. Limit of detection (LOD) was calculated at signal-to-noise ratio (S/N) of 3. Accuracy and precision were assessed by determining the phthalates-spiked water samples in low (30/60 ng/mL), moderate (250/500 ng/mL) and high (1500/3000 ng/mL) concentrations, respectively. Each concentration-spiked water sample was in quintuplicate.

3. Results and discussion

3.1. Phase composition

Phase compositions of HFIP-induced SDS-DTAB coacervate systems were not investigated in detail in our previous paper [24]. Hence, in this paper, we investigated the effects of total concentration and molar ratio of surfactants, and HFIP content on the phase compositions. The measurement of phase compositions was performed by the method reported previously, and the results are shown in Figs. 1 and 2. As shown in Fig. 1A, the amounts of SDS, DTAB, HFIP and water in the coacervate phase all first increased and then decreased as the SDS-DTAB molar ratio increased from 2:8 to 7:3. In addition, for the DTAB-rich mixed system, the amount of DTAB in the coacervate phase was much larger than that of SDS; however, for both the SDS-rich and the equimolar systems, the amount of DTAB in the coacervate phase was still a bit larger than that of SDS, which was due to the interaction between HFIP and DTAB is much stronger than that between HFIP and SDS (the data will be published later). As shown in Fig. 1B, the amounts of SDS, DTAB, HFIP and water in the coacervate phase all rose almost linearly as the total concentration of surfactants varied from 20 mM to 100 mM. Meantime, the total amount of SDS and DTAB in the aqueous phase also increased with increasing the total concentration of surfactants in the mixed system (Fig. 2A). Fig. 1C and Fig. 2B depict the effect of the HFIP volume content on the amount of four compositions in the coacervate phase and the HFIP amount in the aqueous phase, respectively. As the HFIP content increased, the amount of both SDS and DTAB in the coacervate phase changed very little, but the amount of both HFIP and water in the coacervate phase increased gradually. Similarly, the amount of HFIP in the aqueous phase increased with increasing HFIP content.

3.2. Extraction mechanism

As the HFIP-induced coacervation occurred, the SDS/DTAB aggregates were distributed into the coacervate phase. According to the results of phase compositions (Figs. 1 and 2), large fractions of surfactants and small amounts of HFIP were in the coacervate phase, while small fractions of surfactants and large amounts of HFIP were in the aqueous phase. Because the DTAB amounts are always larger than the SDS amounts for the DTAB-rich, SDS-rich and equimolar mixed systems, the surfactant aggregates in the coacervate phase are positively charged. HFIP has the special properties of high hydrophobicity and strong hydrogen bond donor due to $–CF_3$ and –OH groups [25]. Five studied phthalates are neutral, belong to hydrophobic compounds with log *P* larger than 4.7, and have one or two benzene rings and four hydrogen bond acceptors (Table 1). Thus, it is expected that phthalates can be

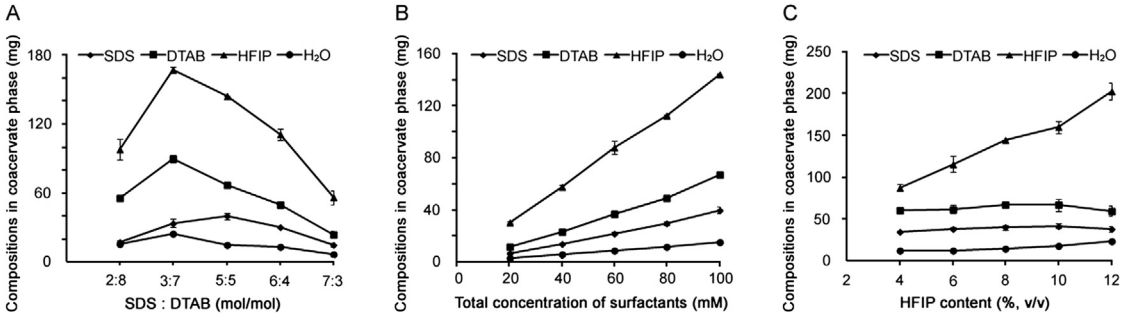


Fig. 1. Effects of (A) SDS/DTAB molar ratio, (B) total surfactant concentration, and (C) HFIP volume content on the compositions of the coacervate phase. Conditions: (A) C_{total} = 100 mM, HFIP = 8% (v/v); (B) SDS: DTAB = 1:1 (mol/mol), HFIP = 8% (v/v); (C) SDS: DTAB = 1:1 (mol/mol), C_{total} = 100 mM. The error bar is the standard deviation for three independent measurements.

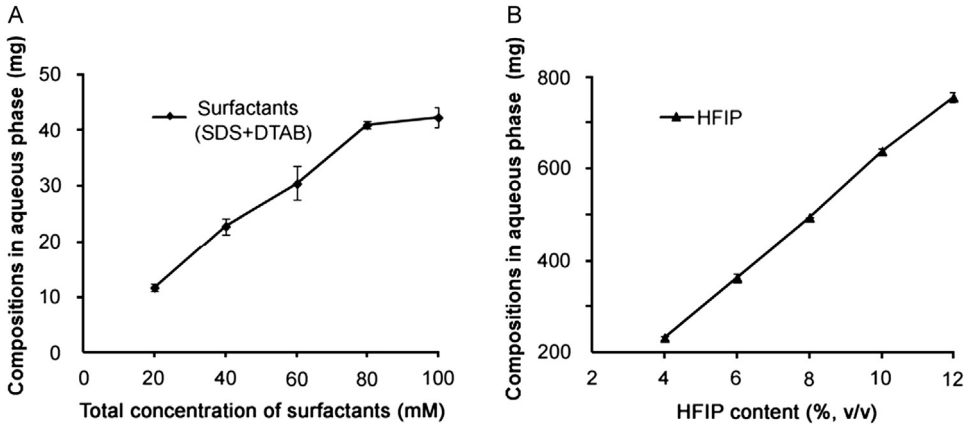


Fig. 2. Effects of (A) total surfactant concentration and (B) HFIP volume content on the compositions of the aqueous phase. Conditions: (A) SDS: DTAB =1:1 (mol/mol), HFIP =8% (v/v); (B) SDS: DTAB=1:1 (mol/mol), C_{total}=100 mM. The error bar is the standard deviation for three independent measurements.

extracted into the coacervate phase through hydrophobic and π-cation interactions with positively surfactant aggregates as well as hydrophobic and hydrogen bond interactions with HFIP.

3.3. Extraction optimization

Extraction conditions for phthalates including the molar ratio and total concentration of surfactants, HFIP addition amount, and equilibrium time were optimized by changing the single factor in turn with other factors unchanged and using phthalates-spiked deionized water samples (100 ng/mL for BBP, DBP and DEHP; 200 ng/mL for DPP and DCHP). Concentration factor (*CF*) and extraction recovery (*ER*) are two important parameters to evaluate the extraction efficiency. Concentration factor can be calculated by the equation of $CF=C_c/C_s$ (C_c is the concentration of analytes in the coacervate phase; C_s is the initial concentration of analytes in water sample), and extraction recovery by the equation of $ER=(C_c \times V_c/C_s \times V_s) \times 100\%$ (V_c is the coacervate phase volume; V_s is the volume of water sample). Phase ratio, which is defined as the ratio of the coacervate phase volume versus the total solution volume, has a close correlation with the concentration factor of analytes. Thus, the variations of phase ratio versus the molar ratio and total concentration of surfactants and the HFIP addition amount were also recorded, respectively, during the optimization of extraction conditions for phthalates.

3.3.1. Effect of surfactant composition

Since the interaction between HFIP and DTAB is much stronger than that between HFIP and SDS, the HFIP-induced coacervation occurs more easily for the DTAB-rich mixed solutions than for the SDS-rich mixed solutions [24]. Therefore, SDS/DTAB molar ratio was specified in the range of 2:8 to 6:4. The effects of the SDS/DTAB molar ratio on the concentration factor and the extraction recovery of phthalates were investigated in 40 mM SDS-DTAB mixed system with 8% (v/v) HFIP addition, and the results are shown in Fig. 3A. As the SDS/DTAB molar ratio varied from 2:8 to 6:4, the extraction recoveries showed the variation trend of first increase and then decrease perhaps due to the fact that the amounts of SDS, DTAB and HFIP in the coacervate phase also first increased and then decreased from 2:8 to 6:4 (mol/mol) (Fig. 1A). However, the concentration factors first decreased and then increased from 2:8 to 6:4, reaching the lowest at 4:6 (mol/mol). This was mainly ascribed to the fact that the coacervate phase volume increases rapidly with the SDS/DTAB molar ratio from 2:8 to 4:6 and then decreases rapidly from 4:6 to 6:4, as shown in Fig. 4A. Though the concentration factor at 2:8 (mol/mol) was larger than that at 3:7 (mol/mol), we still chose 3:7 (mol/mol) as the optimum due to the relative high extraction recoveries and the easy formation of the coacervate phase at this ratio.

3.3.2. Effect of total surfactant concentration

The influences of total surfactant concentration on the concentration factor and the extraction recovery of phthalates were investigated in a 3:7 (mol/mol) SDS/DTAB mixed system with 8% (v/v) HFIP addition, and the results are shown in Fig. 3B. The extraction recoveries increased with the total surfactant concentration varying from 20 mM to 60 mM, while almost remained constant or decreased slightly from 60 mM to 80 mM. This was mainly related to the variation of the phase compositions. As seen in Fig. 1B and Fig. 2A, the amount of surfactants both in the coacervate phase and in the aqueous phase increased with increasing the total surfactant concentration from 20 mM to 80 mM. Furthermore, the amount of surfactants in the coacervate phase increased by 103.3% from 20 to 40 mM, 59.7% from 40 to 60 mM and 32.9% from 60 mM to 80 mM; the amount of surfactants in the aqueous phase increased by 94.8% from 20 to 40 mM, 34.3% from 40 to 60 mM and 34.1% from 60 mM to 80 mM. That is, compared with the amount of surfactants in the aqueous phase, the amount of surfactants in the coacervate phase increased at a faster rate from 20 mM to 60 mM, while at a little slower rate from 60 mM to 80 mM, which may account for the varying tendency of the extraction recoveries versus the total surfactant concentration as indicated above. As to the concentration factors, they declined with increasing the total surfactant concentration from 20 mM to 80 mM. This was primarily because the volume of the coacervate phase increased with the increase of the total surfactant concentration from 20 mM to 80 mM (Fig. 4B). The optimum 20 mM was selected in the following experiments.

3.3.3. Effect of HFIP content

In consideration of both coacervate formation and environmental benefits, HFIP content was set in the range of 4%–12% (v/v). The influences of HFIP content on the extraction recoveries and the concentration factors of phthalates were investigated in a 20 mM SDS-DTAB (3:7, mol/mol) mixed system, and the results are shown in Fig. 3C. Because the amount of surfactants in the coacervate phase changed very little, and the amount of HFIP both in the coacervate phase and in the aqueous phase increased gradually with increasing the HFIP content (Fig. 1C and Fig. 2B), it is expected that the increscent content of HFIP in the mixed system should have very little influence on the extraction recoveries of phthalates. This was proved by the results shown in Fig. 3C-a except for the extraction recoveries at 4% (v/v) HFIP. In fact, the coacervation phenomenon does not very easily occur at 4% (v/v)

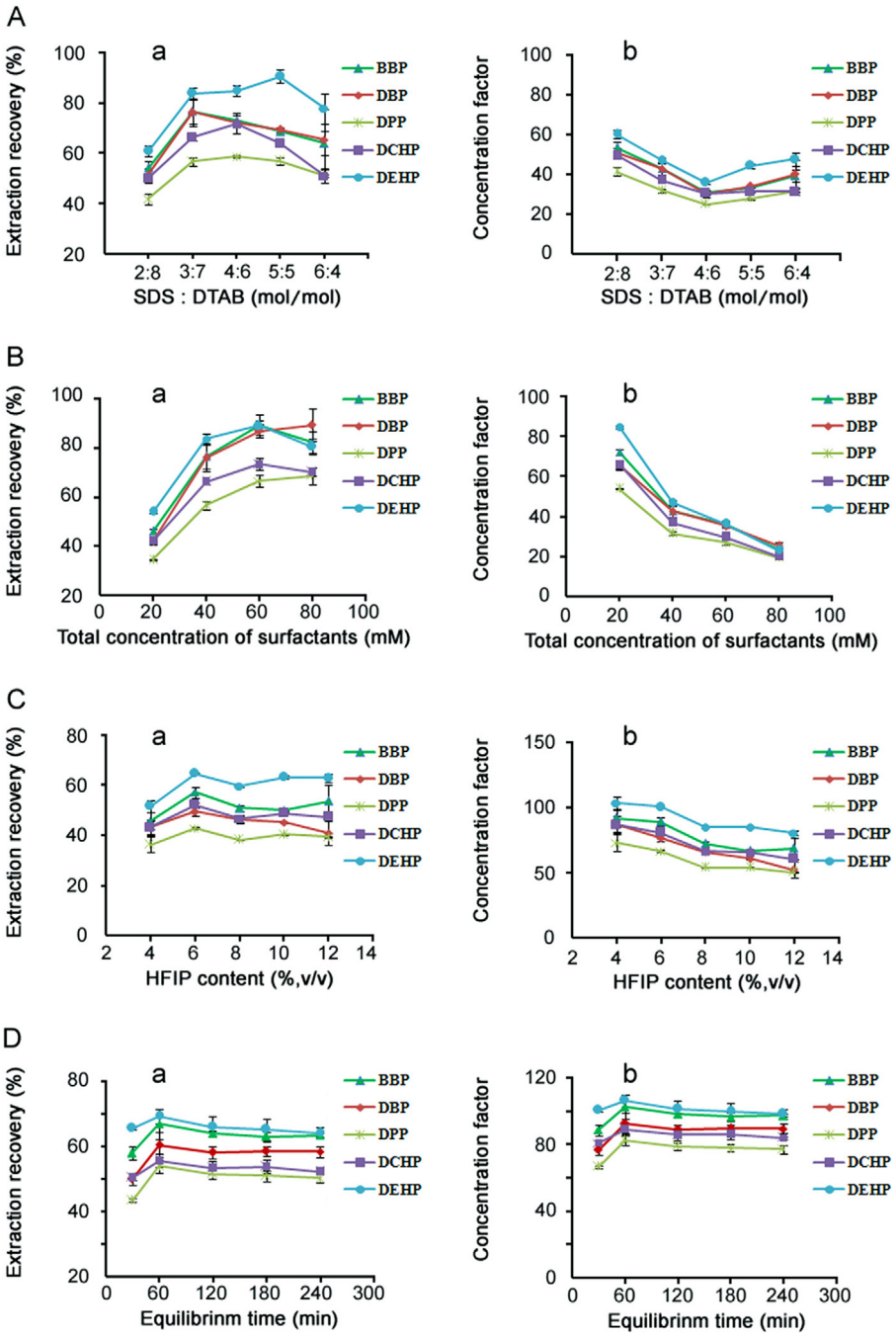


Fig. 3. Effects of (A) SDS/DTAB molar ratio, (B) total concentration of surfactants, (C) HFIP volume content, and (D) equilibrium time on (a) the extraction recovery and (b) the concentration factor of phthalates. The error bar is the standard deviation for three independent measurements.

HFIP, and little precipitates might exist in the coacervate phase sometimes, leading to the loss of phthalates. As a result, the extraction recoveries were a little lower at 4% (v/v) HFIP. As seen in Fig. 3C-b, the concentration factors of phthalates decreased with increasing the HFIP content from 4% to 12% (v/v). This was related to the variation of the coacervate phase volume (Fig. 4C). Given the easy formation of coacervation and the enrichment effect, 6% (v/v) was chosen as the optimal HFIP content.

3.3.4. *Effect of equilibrium time*

The effects of equilibrium time on the extraction recoveries and the concentration factors of phthalates were investigated in a 20 mM SDS-DTAB (3:7, mol/mol) mixed system with 6% (v/v) HFIP addition. As seen in Fig. 3D, as the equilibrium time increased from 30 min to 1 h, both the extraction recoveries and the concentration factors increased obviously, but the further increase in the equilibrium time just led to a slight fluctuation of extraction efficiency. This indicates that the partition equilibrium of phthalates between the aqueous phase and the coacervate phase can be achieved at 1 h. Therefore, we chose 1 h as the optimum equilibrium time.

3.4. *Method validation*

The developed extraction method was used to analyze five phthalates-spiked water samples in the optimum conditions (SDS/DTAB=3:7 (mol/mol), 20 mM total surfactant concentration, 6% (v/v) HFIP, 1 h equilibrium time). As shown in Fig. 5A and B, all the

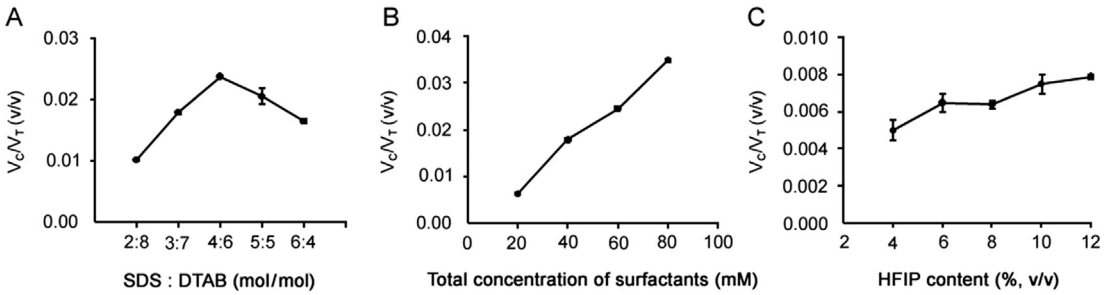


Fig. 4. Plot of the phase ratio versus SDS/DTAB molar ratio, total concentration of surfactants, and HFIP volume content, respectively. V_C: the volume of coacervate phase; V_T: the volume of the total solution. Conditions: (A) C_{total}=40 mM, HFIP =8% (v/v); (B) SDS/DTAB =3:7 (mol/mol), HFIP =8% (v/v); (C) SDS/DTAB=3:7 (mol/mol), C_{total}=20 mM. The error bar is the standard deviation for three independent measurements.

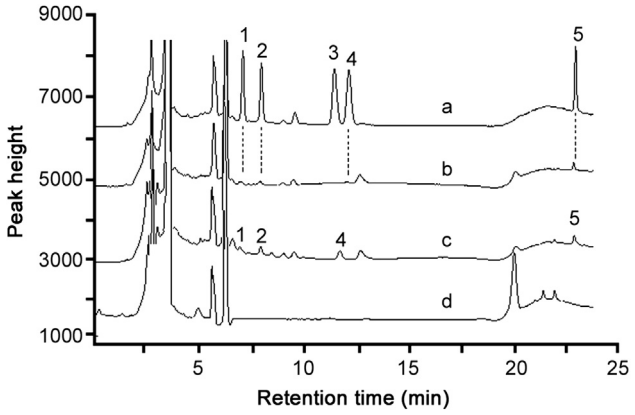


Fig. 5. Chromatograms of water samples analyzed by the proposed coacervate extraction coupled with HPLC-UV. (a) phthalates-spiked deionized water after extraction; (b) phthalates-spiked blank coacervate phase without extraction; (c) the drinking water samples prepared from plastic cups after extraction; and (d) deionized water after extraction (blank coacervate phase). Spiked concentration: 100 ng/mL for BBP, DBP and DEHP; 200 ng/mL for DPP and DCHP. Extraction conditions: 20 mM SDS/DTAB (3:7, mol/mol) with 6% (v/v) HFIP, 1 h equilibrium time. Peaks: 1-BBP, 2-DBP, 3-DPP, 4-DCHP, 5-DEHP.

five phthalates could be greatly preconcentrated in the coacervate phase. Their enrichment factors were in the range of 82.4–106.2 and their extraction recoveries ranged from 53.9% to 69.4% (Table 2). In our previous work, the concentration factors from 17.3 to 49.1 were obtained for three polar sulfonamides using the same coacervate extraction system [24]. Considering the five phthalates (Log P=4.752–8.516) have much stronger hydrophobicity than the three sulfonamides (Log P= −0.074–0.659), we expect that the HFIP-induced catanionic surfactant coacervate extraction has much more excellent extraction and preconcentration efficiency for non-polar compounds than for polar compounds.

As shown in Table 2, good linear correlations (r > 0.9985) were obtained in the range of 20–1500 ng/mL (BBP, DBP, DEHP) and 40–3000 ng/mL (DPP, DCHP). LODs were between 1.0 and 2.6 ng/mL for the five phthalates and the relative recoveries were in the range of 82.4%–123.6%. The intra-day (n=5) precisions were in the range of 0.4%–7.4% and the inter-day (n=3) precisions 0.6%–7.8%. These results indicate that the developed coacervate extraction in combination with HPLC has satisfactory analytical performance for analysis of phthalates in water samples.

3.5. Comparison of this method with other novel methods

Some performances of this method for the extraction and detection of phthalates in water samples were compared with those of other five novel methods reported recently. As seen in Table 3, the proposed coacervate extraction method has several advantages. First, because HFIP, SDS and DTAB are commercially available at a low cost, and very small amount of HFIP (a little expensive) is needed for extraction, the method is very simple, cost-effective and environmentally-friendly compared to the four novel SPE methods with complicated material preparation and/or large amount of organic solvents. Second, the method has much higher or comparable enrichment efficiency and detection sensitivity compared with the three methods using GC. Third, the method has superior or comparable analytical accuracy to the other four methods. In summary, the proposed method is suitable for monitoring phthalates in water samples. However, the problem in need of improvement for the proposed method is the damage of surfactants to the chromatographic column, compared with the SPE methods.

3.6. Tabletion of phthalates migration from disposable tablewares to drinking water

The new extraction method was applied for detection of phthalates migration from feeding bottles, paper bowls, plastic cups, and dixie cups, respectively. The drinking water samples prepared from these tablewares were analyzed using the coacervate extraction coupled with HPLC. As seen in Table 4, one or several phthalates were found in the drinking water samples prepared from all the four kinds of tablewares. Especially for plastic cups, four phthalates displayed high migration levels even up to 26.59 ng/mL for DCHP. Fig. 5C is a representative chromatogram of the drinking water sample prepared from a plastic cup after the coacervate extraction. To reduce the risk of phthalates pollution in drinking water, some organizations have regulated the limit values for phthalates in drinking water. For instance, the maximum contamination levels are 8 and 3 ng/mL for DEHP and DBP, respectively, in China [26], 8 ng/mL for DEHP in the World Health Organization [27], and 6 ng/mL for DEHP in the USA [28]. Apparently, the migration amounts of DEHP (11.44 and 10.13 ng/mL) and DBP (5.83 ng/mL) from paper bowls and plastic cups to drinking water exceeded their maximum contamination levels regulated by the three organizations. Considering the adverse effects of phthalates to human [2–4], the high-frequency and long-term use of disposable tablewares may generate huge potential harm to our health. Hence, it is necessary that we reduce or avoid the use of disposable tablewares (especially plastic tablewares) in our daily life and reduce the addition of phthalates in the polymer materials for the production of disposable tablewares.

4. Conclusions

Phthalates migration from tablewares to drinking water was detected using the HFIP-induced SDS-DTAB coacervate extraction

Table 2
Analytical performance of the developed coacervate extraction method coupled with HPLC-UV for phthalates-spiked water.

Analyte	Concentration (ng/mL)	Recovery (%, $n=5$)	Intra-day precision (RSD%, $n=5$)	Inter-day precision (RSD%, $n=3$)	Linear equation	Linear range (ng/mL)	Correlation coefficient	LOD (ng/mL)	Concentration factor (mean ± SD, $n=3$[a])	Extraction recovery (mean ± SD%, $n=3$[a])
BBP	30	113.3	6.1	5.0	y=116.1x-8.276	20–1500	0.9995	1.0	102.4 ± 7.2	66.9 ± 0.05
	250	94.8	1.2	1.1						
	1500	97.2	6.1	6.6						
DBP	30	107.9	2.1	6.4	y=107.6x+4.825	20–1500	0.9995	1.2	92.6 ± 6.1	60.5 ± 0.04
	250	92	0.4	3.5						
	1500	97.9	5.6	7.0						
DPP	60	89.4	7.4	3.2	y=89.83x-8.979	40–3000	0.9995	2.6	82.4 ± 3.0	53.9 ± 0.02
	500	94.9	1.7	1.9						
	3000	102.7	5.2	5.0						
DCHP	60	82.4	7.4	5.1	y=88.95x-12.82	40–3000	0.9995	2.6	89.0 ± 3.2	55.6 ± 0.02
	500	94.6	1.9	0.6						
	3000	104.1	5.2	4.4						
DEHP	30	123.6	2.3	1.1	y=80.41x-1.115	20–1500	0.9985	1.1	106.2 ± 3.4	69.4 ± 0.02
	250	98.4	1.5	1.0						
	1500	94.9	5.5	7.8						

[a] Water samples spiked with 100 ng/mL BBP, DBP and DEHP as well as 200 ng/mL DPP and DCHP were analyzed.

Table 3
Comparison of the proposed method with other novel methods for determination of phthalates in water samples.

Extraction method	Consumption of organic solvent/ sample	Detection	Phthalates	LOD (ng/mL)	Concentration factor	Recovery (%)	Reference
Fe_3O_4@ZIF-8-SPE	1.1 mL methanol/20 mL	HPLC–DAD	BBP	0.14	–	92.3–96.4	[14]
			DBP	0.12	–	86.6–98.6	
CMET-CPE	0.1 mL isooctane/9 mL	GC–FID	BBP	15.8	82	89.3–96.1	[15]
			DBP	11.5	85	91.1–96.3	
MAG-MIM-dSPE	7.0 mL ethyl acetate – acetic acid (85:15, v/v)+0.5 mL of acetone/10 mL	GC–FID	BBP	0.53	–	89.5–100.2	[11]
			DBP	0.60	–	95.0–101.3	
CAP-D-μ-SPE	0.2 mL methanol/10 mL	HPLC–DAD	BBP	1.0	24.8	92.2–101.3	[16]
			DBP	1.0	24.8	86.2–103.3	
			DEHP	5.0	25.4	93.8–98.7	
C18-functionalized Fe_3O_4@mSiO2 microspheres (micro-SPE)	0.5 mL chloroform/10 mL	GC–MS	BBP	46	–	–	[13]
			DBP	77	–	–	
			DEHP	31	–	–	
HFIP-induced SDS/DTAB coacervate extraction	0.3 mL/5 mL (6% (v/v) HFIP in the total solution)	HPLC–UV	BBP	1.0	102.4	94.8–113.3	This work
			DBP	1.2	92.6	92.0–107.9	
			DPP	2.6	82.4	89.4–102.7	
			DCHP	2.6	89.0	82.4–104.1	
			DEHP	1.1	106.2	94.9–123.6	

ZIF-8-SPE: zeolitic imidazolate framework-8-solid-phase extraction; CMET-CPE: centrifugal microextraction tube-cloud point extraction; MAG-MIM-dSPE: magnetic dummy molecularly imprinted dispersive solid-phase extraction; CAP-D-μ-SPE: anionic surfactant coacervation phase extraction and dispersivemicrosolid-phase extraction; HPLC: high performance liquid chromatography; DAD: diode array detector; GC: gas chromatography; FID: flame ionization detector; MS: mass spectrometer; UV: ultraviolet.

Table 4
Determination of the migration of five phthalates from tablewares to drinking water.

Tableware	Material	Phthalate (ng/mL) (mean ± SD, $n=3$)				
		BBP	DBP	DPP	DCHP	DEHP
Feeding bottle	polypropylene	8.46 ± 0.06	2.46 ± 0.64	ND	ND	ND
Paper bowl	polyethylene	2.33 ± 0.30	ND	ND	ND	11.44 ± 2.06
Plastic cup	polystyrene	9.34 ± 1.81	5.83 ± 1.17	ND	26.59 ± 1.24	10.13 ± 2.34
Dixie cup	polyethylene	ND	ND	ND	ND	2.18 ± 0.62

ND: not detectable.

coupled with HPLC. Four of the five studied phthalates were found in the drinking water samples prepared from the four kinds of disposable tablewares. The concentrations of DBP and DEHP in the drinking water samples prepared from paper bowls and plastic cups exceeded the limit levels for drinking water regulated by some organizations. This suggests that the high-frequency and long-term use of disposable tablewares may be harmful to human health, and both the production and the use of disposable tablewares should be regulated by law. The coacervate extraction is suitable for extracting non/weak polar phthalates, providing high enrichment efficiency. The hydrophobic, π-cation and hydrogen-bond interactions of phthalates with surfactant aggregates and HFIP in the coacervate phase are the main extraction forces.

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