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Application of vesicular coacervate phase for microextraction based on solidification of floating drop

Morteza Moradi, Yadollah Yamini*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

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ABSTRACT

A new, efficient and environmentally friendly method for the analysis of parabens as model compounds was developed using solidified floating vesicular coacervative drop microextraction (SFVCDME). A supramolecular solvent consisting of vesicles of decanoic acid in the nano- and microscale regimes was firstly used as the solvent in solidification of floating drop microextraction. The solvent was produced from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutylammonium (Bu_4N^+). Methylparaben (MP), ethylparaben (EP), and propylparaben (PP) were extracted on the basis of hydrophobic and π–cation interactions and the formation of hydrogen bonds. Microliter volume of vesicular coacervative droplet was delivered to the surface of the aqueous sample, and the sample was stirred for a desired time. The sample vial was cooled by immersing it into an ice bath for 3 min. The solidified solvent was transferred into a suitable vial and melted immediately. Twenty microliter of the vesicular coacervative solvent was directly injected to high-performance liquid chromatography-ultraviolet detection, with no need to dilution or solvent evaporation. Several parameters affecting the microextraction efficiency including sample temperature, stirring rate, pH, salt effect, volume of the solvent and extraction time were investigated and optimized. Under optimum conditions, preconcentration factors and relative recoveries of the studied compounds were obtained in the range of 81–174 and 91–108%, respectively; and the performance of the method was comparable with that of solid-phase extraction as the reference method.

1. Introduction

The esters of *p*-hydroxybenzoic acid are commonly known as parabens, including methyl paraben, ethyl paraben, propyl paraben and butyl paraben. They are widely used as preservatives in a large number of cosmetic, food and pharmaceutical products. Although combinations of two or more parabens are often used to increase the ability of the system to withstand microbial contamination [1–3], there are numerous formulations that contain only one of them. Parabens are extensively used in formulations of personal care products due to having neutral pH, no perceptible odor or taste, and having no discoloration or hardening effect [4,5]. Generally, parabens are stable in the air, and are resistant to hydrolysis in hot and cold water as well as in acidic solutions ($1 \leq pH < 7$). Recently, use of preservatives in consumer products has been the subject of criticism because of their possible side-effects on human health. The Council Directive 76/768/EC of the European Community permits their use with a maximum concentration of 0.4% (w/w) for each one and total maximum concentration of 0.8% (w/w), expressed as *p*-hydroxybenzoic acid [6].

Determination of parabens can be performed by various techniques, such as gas chromatography–mass spectrometry (GC–MS) [7], high-performance liquid chromatography (HPLC) [8–10], microemulsion electrokinetic chromatography (MEEKC) [11,12], and capillary electrochromatography (CEC) [9]. HPLC is the most common method used for detecting these compounds, which is often combined with a pretreatment procedure to remove nonpolar matrices. In order to determine and analyze the parabens in different samples, an extraction or pre-concentration step is often required.

Sample preparation prior to the chromatographic analysis is one of the most crucial steps in the whole analytical procedure to obtain accurate and sensitive results [13–16]. There are several recent reviews on the methodological approach to improve analytical performances [17,18]. Solid-phase microextraction and liquid-phase microextraction (LPME) have emerged as new attractive alternatives for sample preparation, which leads to saving time, labor, and solvent consumption, and therefore can improve the analytical performance of the procedure. Recently, several different types of LPME have been developed, including single drop microextraction (SDME) [19,20], hollow fiber LPME [21–24], and dispersive

* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.
E-mail address: yyamini@modares.ac.ir (Y. Yamini).

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liquid–liquid microextraction (DLLME) [25,26]. Microextraction techniques are fast, simple, inexpensive, environmentally friendly, and compatible with many analytical instruments.

Surfactants are organic compounds that are amphiphilic, and contain both hydrophobic and hydrophilic groups. Therefore, they are soluble in both organic and aqueous solvents. Many surfactant-based extraction methods have been reported up to now [27–33].

The cloud point extraction (CPE) was the first extraction method in which non-ionic surfactants have been used. In this technique, a small volume of the surfactant-rich phase enables that the extraction and preconcentration of the analytes to be performed in a single step. The cloud point refers to the phase separation of neutral surfactants induced by temperature [34]. Non-ionic and zwitterionic surfactants have been used for cloud point extraction. The term "coacervation extraction" or "micelle-mediated extraction" is reserved for the phase separation of ionic amphiphiles induced by other conditions. Cationic surfactants, *e.g.* alkyltrimethylammonium bromides, are known to undergo coacervation in the presence of saturated sodium chloride and 1-octanol. Anionic surfactants such as alkyl sulfates, sulfonates, and sulfosuccinates undergo pH-induced coacervation. Hence, cationic and anionic surfactants can be used for coacervative extraction. Among the four types of surfactants, anionic surfactant-mediated extraction is predominant [35].

The surfactant-rich phase is a nano-structured liquid, recently named as supramolecular solvent (SUPRAS), which is generated from the amphiphiles through a sequential self-assembly process occurring on the molecular and nano-scales [36–42]. Recently, Rubio et al. reviewed both theoretical and practical aspects of using supramolecular solvents in analytical extractions reported over the last decade [43].

The tetrabutylammonium-induced liquid–liquid phase separation in vesicular solutions of alkyl carboxylic acids recently described by Pérez-Bendito et al. [44], presents a high potential for the extraction of bisphenols. The main properties of the SUPRASs are the high concentration of amphiphiles, 1 mg μL^{-1}, and different types of the interactions offered by them for analyte extraction (*i.e.* ionic, hydrogen bonding, π-cation and hydrophobic).

In 2007, a new and simple liquid-phase microextraction method was developed based on solidification of floating droplet (LPME-SFD) by our research group [45] in which the extraction solvent had lower density than water, low toxicity, and proper melting point near room temperature (in the range of 10–30 °C). In this method, a small volume of an extraction solvent was floated on the surface of aqueous solution. The aqueous sample solution was stirred for a defined time. After the extraction, the floated droplet could be collected easily through solidification at low temperature. The solidified organic solvent could be melted quickly at room temperature, and subsequently determined by either chromatographic or spectrometric methods.

In 2008, Pérez-Bendito and coworkers described the potential of coacervates for SDME for the first time [46]. They investigated the parameters affecting the efficiency of single-drop coacervative microextraction (SDCME) using vesicular coacervates as the solvent and chlorophenols as model analytes. They found that, with the experimental setup proposed, maximal stirring rates should be kept at 300 and 600 rpm during the extraction of samples with drop volumes of 40 and 5.0 μL, respectively. The main limitation of SDCME was dislodging of the coacervate drops from the needle tip in higher stirring rates which caused an increase in the extraction time.

Herein, the potential of vesicular coacervates drop (melting point ≈ 10 °C) for LPME-SFD was explored. The effective parameters on the extraction efficiency of parabens including sample temperature, stirring rate, salt effect, pH, volume of the solvent, and the extraction time were investigated and optimized.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical grade. Methyl-, ethyl-, and propyl esters of 4-hydroxy benzoic acid were purchased from Sigma (St. Louis, MO, USA). Decanoic acid was purchased from Fluka (Buchs, Switzerland) and tetrabutyl ammonium hydroxide (Bu_4NOH, 40%, w/v in water) was obtained from Sigma. HPLC-grade methanol and acetonitrile were purchased from Caledon (Ontario, Canada). The ultra-pure water was prepared by a model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea).

Stock solutions of 1000 mg L^{-1} parabens were prepared by dissolving appropriate amount of compounds in methanol and then keeping them stable during three months by being stored in fridge at 4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with ultra-pure water to the required concentrations.

2.2. Apparatus

Chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a 20 μL sample loop and equipped with a Varian 9050 UV–vis detector. Chromatographic data were recorded and analyzed using ChromanaCH software version 3.6.4 (Tehran, Iran). The separations were carried out on an ODS column (250 cm × 4.6 mm, with particle size of 5 μm) from Teknochroma (Barcelona, Spain). A mixture of ultra-pure water and acetonitrile (55:45) for 15 min and then 100% acetonitrile for 10 min (for elution of coacervate phase) at a flow rate of 1.0 mL min^{-1} were used as a mobile phase and the analytes were detected at 254 nm.

2.3. Sample preparation

(a) Cosmetic samples: Five milligram of each sample (sunblock, aftershave gel and skin cream) was accurately weighed and dissolved in a solution mixture containing 2 mL methanol and 8 mL ultra-pure water. Then, 1 mL of a concentrated HCl solution (37 vol.%) was added to the solution and exposed to sonication for 10 min. The solution was diluted to 150 mL with ultra-pure water and finally the pH was adjusted at 6.0. Afterwards, 24 mL of the solution was transferred into an extraction vial.

(b) Water samples: Different water samples, including tap water from our lab (Tehran, Iran), river water (Niasar, Iran), pond water (Tehran downtown, Iran) and urban wastewater from downtown (Tehran, Iran) were collected and the SFVCDME method was applied to extract the parabens. Each water sample was filtered, in order to remove any suspended material. After being filtered, the urban wastewater sample was diluted 1:1 by ultra-pure water. For preconcentration, pH of the samples was adjusted at 6.0 using the described procedure before the analysis. Finally, the interference effect of calcium was removed by adding EDTA (2 mg L^{-1}) as masking agent before extraction, for water samples containing high concentration of calcium.

2.4. Vesicular coacervates preparation

Vesicular coacervates were prepared by mixing 5.15 g of decanoic acid and 3.9 g of tetrabutyl ammonium hydroxide in 200 mL distilled water at pH 7. In order to dissolve the decanoic acid, the mixture was stirred at 1200 rpm for 10 min. Finally, phase separation was achieved by centrifugation of the mixture for 5 min

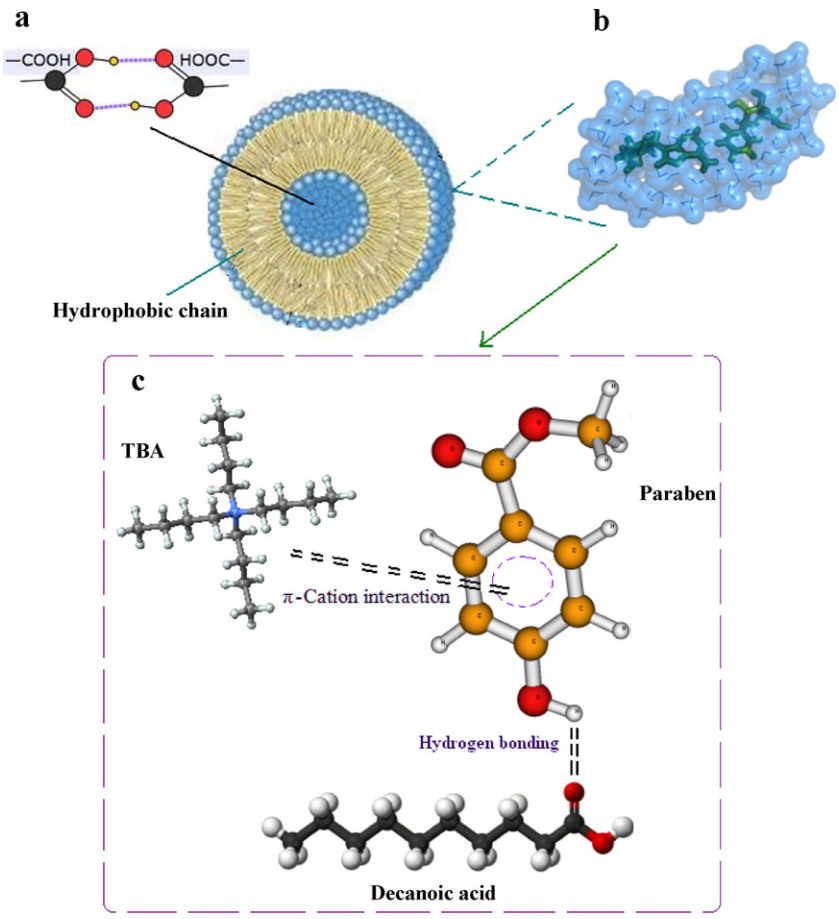

Fig. 1. Schematic representation of solidified floating vesicular coacervative drop microextraction. (a) Chemical interactions can influence vesicle formation and its stability, (b) parabens extraction, and (c) molecular mechanism of microextraction and different interactions between paraben and vesicle.

at 4000 rpm and the obtained vesicular coacervates solvent was used in extraction experiments.

2.5. SFVCDME procedure

A 24 mL aqueous sample solution (pH ≈ 6) containing 100 μg L^{-1} of each paraben was placed in a 25 mL vial and 30 μL of supramolecular solvent was floated on the surface of the sample solution and stirred with a 15 mm × 4 mm magnetic stirring bar for 30 min at 30 °C using an IKA multi-position magnetic stirrer (Staufen, Germany).

A simple water bath placed on the heater-stirrer was employed to control the temperature of the sample solution. After a desired period of extraction, the sample vial was placed into a beaker containing ice pieces and the solution was stirred for 3 min more, at 600 rpm until the supramolecular solvent was solidified. The solidified solvent was subsequently transferred into the conical vial by a simple spatula where it started to melt. Finally, 20 μL of the solvent was injected into HPLC for quantification.

3. Results and discussion

3.1. Vesicular coacervates composition

The vesicular coacervates solvent is produced from aqueous mixtures of protonated (DeA) and deprotonated (De^-) decanoic acid in the presence of tetrabutylammonium cation (Bu_4N^+). In an aqueous solution, DeA and De^- molecules are assembled as small water-soluble vesicles. The addition of Bu_4N^+ to aqueous suspensions of these aggregates results in the formation of larger vesicles consisting of DeA and Bu_4NDe. The driving forces for the formation of these vesicular aggregates are hydrophobic interactions between the hydrocarbon chains of DeA and De^- molecules, hydrogen bonding between their carboxylic and carboxylate groups, and the electrostatic interactions between the carboxylate and quaternary ammonium groups of De^- and Bu_4N^+ molecules, respectively. Bu_4N^+ acts as a coacervating agent. The aggregates in the supramolecular solvent are expected to efficiently extract parabens according to their structure and the parameters related to their extraction, as schematically shown in Fig. 1.

The composition of supramolecular solvent is a key factor which greatly influences its extraction capability. In order to study the effect of varying the composition of vesicular coacervates on the efficiency of the extraction of parabens, the amount of $Bu_4N^+/DeA + De^-$ was varied between 0.1 and 1.0 (molar ratio) and the $DeA + De^-$ was kept constant at 0.15 mol L^{-1}. At 0.5 molar ratios, complete neutralization of De^- occurs whereas at higher ratios, there is the possibility of cation–π interactions between the quaternary ammonium group of Bu_4N^+ non-bonded to De^- and the aromatic rings in the target analytes (Fig. 1) [43,45].

The stirring of samples is an essential step in microextraction methods to reduce the time necessary for reaching the thermodynamic equilibrium. Thus, the stability of vesicular coacervate droplets *versus* time was investigated under stirring conditions. For this purpose, the stirring speed was adjusted at 800 rpm and collected volume of the droplet ($V_{initial}$ = 50 μL) was investigated in the time profile of 15–800 min. After a desired time, the liquid

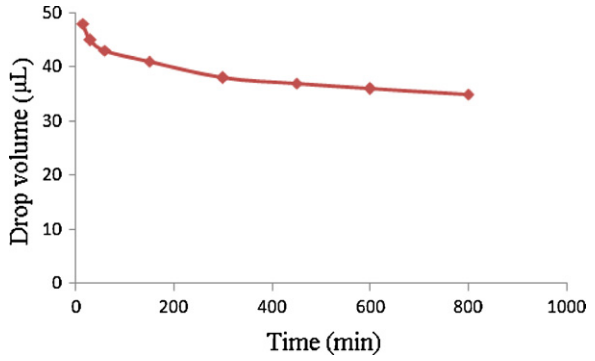

Fig. 2. Stability of 50 μL drop volume in 24 mL of distilled water, stirred at 800 rpm and room temperature, as a function of time.

vesicular droplet was floated to the top of the vial. The vial was thereafter dipped into an ice bath for 3 min. The solidified solvent was transferred into a micro-tube in which it melted rapidly at room temperature. Then remaining volume of solvent was measured using a 50 μL Hamilton syringe. The obtained results are depicted in Fig. 2. As it can be seen, in the primary 60 min, droplet volume decreases from 50 to 42 μL, indicating 16% decrease in collected volume. In the second part (from 60 to 800 min), droplet volume decreases from 42 to 35 μL. As a result, coacervate droplet is stable during the microextraction procedure. This finding is in agreement with previous reported data by Pérez-Bendito [46].

3.2. Optimization of SFVCDME

The extraction efficiency of SFVCDME procedure depends on some important experimental parameters including the composition of vesicular coacervates, pH, temperature, drop volume, stirring rate, ionic strength, and extraction time; which should be investigated in detail. Optimization of the above-mentioned variables was performed by modifying one at a time while keeping the remaining ones constant.

Generally, pH of the sample solution determines the state of analytes in aqueous solution which in turn plays an important role in extraction of pollutants from environmental water samples. The effect of sample pH on the extraction efficiency of the parabens from aqueous samples was investigated in the range of 3–9. The obtained results indicate that the maximal extraction efficiencies were obtained at pH values around 6 (Fig. 3). It seems that at this pH both neutral and ionized analytes were efficiently extracted to the vesicular phase. The extraction of neutral protonated analyte into the vesicular phase is eligible because of conventional interactions; but the extraction of deprotonated charged species seems to be an

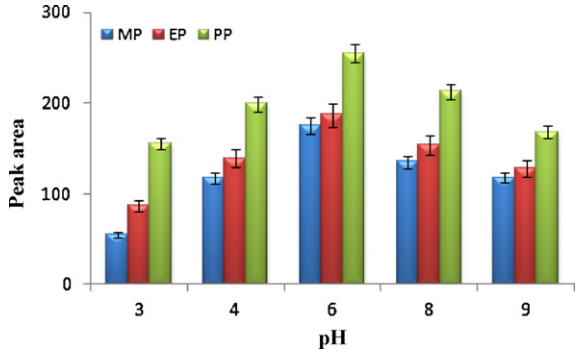

Fig. 3. The effect of pH on the extraction efficiency of parabens. Extraction conditions: sample solution, 24.0 mL of 100 μg L^{-1} of each paraben; drop volume, 20 μL; stirring rate, 700 rpm; extraction time, 30 min.

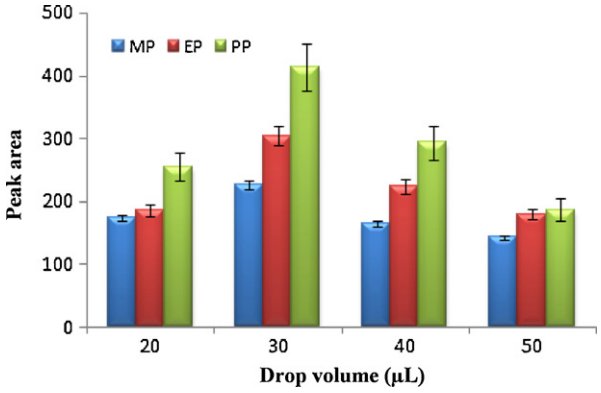

Fig. 4. Effect of supramolecular solvent volume on the SFVCDME efficiency. Extraction conditions: sample solution, 24.0 mL of 100 μg L^{-1} of each paraben; pH 6; stirring rate, 700 rpm; extraction time, 30 min.

interesting phenomenon which has occurred in alkaline medium for parabens and can be the result of ion pair formation between cationic Bu_4N^+ and deprotonated analytes. Therefore, pH 6.0 was selected for further studies.

In a liquid phase extraction, temperature has an influence on both equilibrium and mass transfer. In droplet-based microextraction, temperature has two opposite effects: (I) it facilitates mass transfer of the analytes from the sample to the extraction solvent and thus increases the extraction recovery; (II) high temperature can generate air bubbles around the droplet, thus resulting in droplet instability and sometimes dislodging of the droplet to small bits. The effect of temperature on the extraction efficiency was studied by varying the temperature in the range of 20–60 °C. The results showed that by increasing temperature to 30 °C, extraction efficiency increased as a result of the increase in mass transfer. When the temperature was near 60 °C, the formation of the air bubbles resulted in dislodging of the drops to small bits, therefore the solidified drop volume as well as extraction efficiency was decreased. The temperature of the solution was adjusted at 30 °C for further experiments.

The volume of the solvent influences the extraction recovery and preconcentration factor of the analytes. Increasing the ratio of sample volume to the extraction solvent volume can increase the preconcentration factor to some extent. However, in SFVCDME the total mass of the analyte in the extraction solvent is of higher importance compared to the absolute concentration of the analyte. Accordingly, the droplet volume should be large enough to promote analyte transport to the acceptor phase. In the present work, the phase ratio of donor to acceptor solutions was changed in the range of 1200:1–480:1, by changing the volume of the coacervate phase (20–50 μL) while the volume of the sample solution was kept constant at 24 mL. As it can be seen in Fig. 4, the peak area increases by increasing droplet volume in the range of 20–30 μL, after which there is low decrease in the peak area due to dilution effect resulted from further increase in droplet volume. Accordingly, in further experiments 30 μL of the supramolecular solvent was floated on the surface of the aqueous solution.

In general, the addition of sodium chloride into an aqueous solution increases its ionic strength, which decreases the solubility of the analytes in the sample solution and improves the extraction efficiency. In this study, the effect of adding NaCl in concentration range of 0% to 20.0% (w/v) on the extraction efficiency of the analytes was investigated. The plot of the peak area *versus* NaCl concentration is shown in Fig. 5, which clearly indicates that the peak areas of the analytes experience very small changes in the range of 0–2% and decrease gradually as the concentration of NaCl increases from 2% to 20%. This phenomenon may be explained by

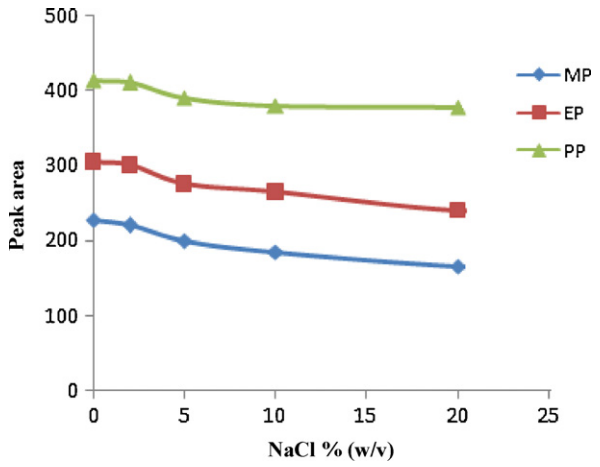

Fig. 5. Effect of salt addition on the SFVCDME efficiency. Extraction conditions: sample solution, 24.0 mL of 100 μg L^{-1} of each paraben; pH 6; drop volume, 30 μL; stirring rate, 700 rpm; extraction time, 30 min.

the fact that electrostatic interactions between polar compounds and salt ions increase in the presence of salt ions, which reduce the capacity of target compounds to move into the extraction phase, and lead to the occurrence of low recoveries [47]. Therefore the proposed method can be used for preconcentration of parabens in samples containing small amounts of salt. It is worthy to note that at higher concentrations of salt (>20%, w/v), the vesicular droplet becomes unstable due to bubble formation. Also NaCl dissolved in water might have changed physical properties of the Nernst diffusion film and reduced the rate of diffusion of the target analytes into the drop [48]. Hence, further extractions were performed without adding NaCl to the solutions.

Stirring of samples reduces the time necessary to reach thermodynamic equilibrium. Based on the film theory of convective-diffusive mass transfer for LPME system, high stirring speed can decrease the thickness of the diffusion film in the aqueous phase, so the aqueous phase mass-transfer coefficient will be increased by increasing the stirring rate (rpm). The effect of stirring rate on the extraction efficiency of parabens in the range of 300–1000 rpm was investigated. The results showed that the extraction efficiency is increased by increasing the stirring rate up to 850 rpm (Fig. 6). This is in agreement with the expected behavior of the solvent microextraction based on the penetration theory of mass transfer of a solute. As stirring rate exceeded 850 rpm, it resulted in dislodging the drops to small bits, as well as a decrease in the collected solvent volume and extraction efficiency.

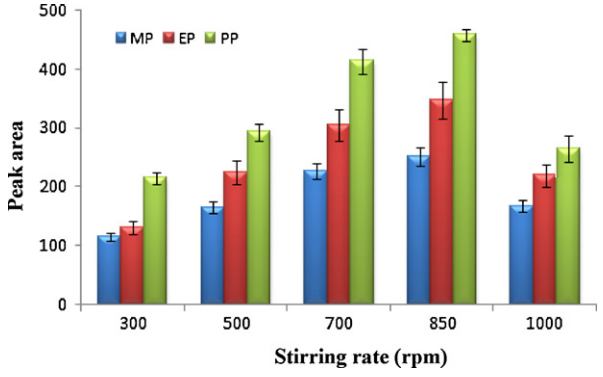

Fig. 6. Effect of stirring rate on the SFVCDME efficiency. Extraction conditions: sample solution, 24.0 mL of 100 μg L^{-1} of each paraben; pH, 6; drop volume, 30 μL; extraction time, 30 min.

In order to gain good precision, sensitivity and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and vesicular phase, together with the maximum extraction of analyte. The effect of extraction time on the extraction efficiency was examined by varying the extraction time from 10 to 40 min at constant experimental conditions. The results revealed that the analytical signals were increased when the extraction time was increased from 10 to 30 min. The extraction time profile indicates that the equilibrium between the two phases was reached after 30 min and thus the extraction time of 30 min was selected in the present study.

3.3. Quantitative analysis

Quantitative parameters of the proposed SFVCDME-HPLC-UV method were calculated under the optimized conditions described in Section 3.2. Linearity of the method was evaluated using water samples spiked with the parabens at fourteen different concentrations ranging from 0.5 to 100 μg L^{-1}. The figures of merit of the proposed method are listed in Table 1. The coefficients of determination (R^2) of the calibration curves were between 0.9933 and 0.9994, and limits of detection (LODs) for the analytes based on a signal to noise ratio (S/N) of 3 varied in the range of 0.2–0.5 μg L^{-1}. Intra-day precision was obtained from five consecutive replicates and expressed as relative standard deviations (RSDs%) whose values were between 3.9 and 6.0%; furthermore, the obtained inter-day RSDs% at five different days were in the range of 8.5–11.9%.

The preconcentration factor (*PF*) was defined as the ratio of the final analyte concentration in the vesicular phase ($C_{f,ves}$) and the initial concentration of analyte ($C_{i,s}$) within the sample solution:

$$PF = \frac{C_{f,ves}}{C_{i,s}} \quad (1)$$

where $C_{f,ves}$ was calculated from a calibration graph obtained from direct injection of parabens standard solutions (0.1–5 mg L^{-1}) in vesicular solution. The obtained *PF*s were in the range of 81–174.

Some characteristics of previously reported methods such as *PF*, LDR and LOD for extraction and determination of the parabens are summarized in Table 2 for comparison. As it can be seen, the proposed SFVCDME method shows a *PF* in most cases compared to the previously reported methods, although the LOD of the proposed method is comparable with those of the methods mentioned in Table 2. Lower consumption of extraction solvent and consequently less organic waste, simplicity, low cost, enhancement of sensitivity, and short analysis time are other advantages of the proposed method. On the other hand, instability of droplets at high stirring rate is a potential disadvantage of this method.

3.4. Analysis of natural water and cosmetic samples

In order to evaluate the applicability of the developed extraction method to analysis of the parabens in the real samples with complex matrices, environmental water and cosmetic samples were extracted and analyzed using the proposed method under the optimum conditions. Sample preparation for the real samples was performed according to Section 2.3.

Three kinds of water samples (tap water, river water and pond water) were analyzed by HPLC-UV after SFVCDME procedures. The results showed that tap and river water samples were all free of parabens contaminations. However, MP and PP were detected to be 7.4 μg L^{-1} and 12.3 μg L^{-1} in pond water, respectively. It is noteworthy that, in some water samples containing high concentration of calcium, vesicular phase could be turbid because of calcium precipitation in the extraction solvent (calcium decanoate was formed). The interference of calcium was removed by addition of EDTA (2 mg L^{-1}) to the samples before delivering the droplet

Table 1
SFVCDME performance and validation data.

Analyte	Linearity		LOD ($\mu g\,L^{-1}$)	Precision[a] (RSD%, $n=5$)		PF[a]
	LDR ($\mu g\,L^{-1}$)	R^2		Intra-day	Inter-day	
MP	1.0–100	0.9994	0.5	3.9	8.5	81
EP	0.5–100	0.9933	0.2	4.3	11.9	143
PP	0.5–100	0.9950	0.2	6.0	10.2	174

[a] Data were calculated based on the extraction of 20 $\mu g\,L^{-1}$ of each paraben.

Table 2
Comparison of the proposed method with other methods developed for extraction and determination of parabens.

Analyte	Sample	Method	LOD ($\mu g\,L^{-1}$)	PF	Linear range ($\mu g\,L^{-1}$)	RSD (%)	Refs.
MP-EP-PP	Creams	SBSE-LC[a]	–	–	30–2500 $ng\,mg^{-1}$	–	[49]
MP-EP-PP	Creams, lotions	SPME-UPLC-DAD[b]	120–150	–	50–160	<5.4	[50]
MP-EP-PP	Creams, shampoo, lotions	SPE-HPLC-C-CAD[c]	500–2100	–	–	<3.8	[51]
MP-EP-PP	Beverage samples	DLLME-GC-FID	0.59–2.92	46–166	1.0–100	<7.0	[52]
MP-EP-PP	Cosmetic products	SFE-GC-MS[d]	0.5–8.3 $ng\,g^{-1}$	–	10–1000 $ng\,g^{-1}$	<10	[53]
MP-EP-PP	Water samples-cosmetic products	SFVCDME-HPLC-UV	0.2–0.5	81–174	0.5–100	<6.0	Proposed method

[a] Stir bar sorptive extraction-liquid chromatography.
[b] Solid phase microextraction-ultra performance liquid chromatography-diode array detector.
[c] Solid phase extraction-high performance liquid chromatography, corona-charged aerosol detection.
[d] Supercritical fluid extraction.

in the sample surface [46]. EDTA can act as a masking agent for minimizing the calcium decanoate formation.

To investigate the relative recoveries, water samples spiked at concentration of 10.0 $\mu g\,L^{-1}$ were extracted under the optimized conditions. Each treatment was in triplicate, and the results are provided in Table 3. The relative recovery (RR%) of the analyte from real sample was obtained from the following equation:

$$\text{Relative recovery}\,(\%) = 100 \times \frac{A_1 - A_2}{A_3} \quad (2)$$

where A_1, A_2 and A_3 are peak areas of the extracted target analyte from spiked natural water, non-spiked natural water and spiked ultra-pure water, respectively. The relative recoveries for the analytes were in the range of 91.2–104.4% and the RSDs ranged from 4.5% to 11.9% in water samples. These results demonstrate that the different matrices of tap, river and pond water used in this experiment had little effect on the SFVCDME efficiency. Chromatograms of pond water for blank and spiking at the concentration level 10.0 $\mu g\,L^{-1}$ of analytes are shown in Fig. 7.

The effectiveness of the SFVCDME-HPLC-UV method for determination of parabens was evaluated by analyzing commercial cosmetic products that were acquired at a local market (Table 4). Fig. 8A shows the chromatogram of a skin cream sample, in which MP and PP were found. The determined concentrations of all parabens were lower than the maximum allowed addition levels. Finally, the recoveries for each paraben from different cosmetic products were determined by adding 0.5 and 1.0 $\mu g\,mg^{-1}$ standards to the prepared sample solution before SFVCDME, and the results are provided in Table 4. The developed method showed high relative recoveries for different cosmetics from 92.2 to 108.8%,

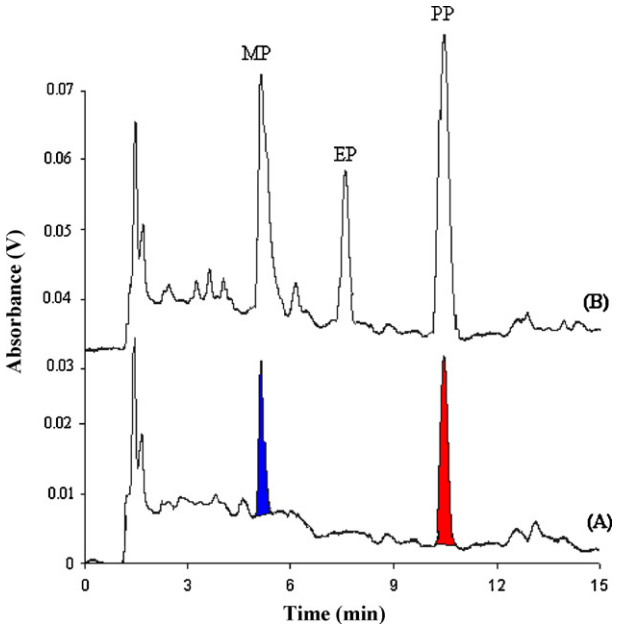

Fig. 7. HPLC-UV chromatograms related to SFVCDME of the parabens of the (A) non-spiked and (B) spiked pond water by 10 $\mu g\,L^{-1}$ of the target analytes.

which ensured the accuracy of the amount of parabens detected in the non-spiked cosmetic samples. Fig. 8 shows SFVCDME-HPLC-UV chromatograms of non-spiked and spiked skin cream at the concentration level of 1.0 $\mu g\,mg^{-1}$ paraben standards.

Table 3
Determination of parabens in water samples.

Analyte	Tap water			Pond water			River water		
	Conc.[a] ($\mu g\,L^{-1}$)	RR[b] (%)	RSD[c] (%)	Conc. ($\mu g\,L^{-1}$)	RR (%)	RSD (%)	Conc. ($\mu g\,L^{-1}$)	RR (%)	RSD (%)
MP	<LOD	100.2	8.0	7.4	98.3	8.1	<LOD	91.2	11.9
EP	<LOD	104.4	4.5	<LOD	95.9	10.2	<LOD	93.2	8.4
PP	<LOD	96.9	11.2	12.3	93.0	6.4	<LOD	97.3	10.1

[a] Initial concentration.
[b] Ten microgram per liter of each analyte was added to calculate relative recovery (RR %).
[c] Data were calculated based on three replicates.

Table 4
Determination of parabens in cosmetic samples.

Sample	Added ($\mu g\,mg^{-1}$)	Found ($\mu g\,mg^{-1}$) (RSD %)[a]			RR (%)		
		MP	EP	PP	MP	EP	PP
Sunblock	0	0.2_1 (7.9)	<LOD	<LOD	–	–	–
	0.5	0.7_4 (9.0)	0.4_6 (10.9)	0.4_8 (5.9)	106.0	92.6	96.8
	1.0	1.2_2 (11.4)	0.9_8 (3.1)	1.0_3 (8.3)	101.3	98.4	103.1
Skin cream	0	0.8_3 (12.9)	<LOD	1.9_3 (11.7)	–	–	–
	0.5	1.3_0 (9.2)	0.5_0 (13.2)	2.4_3 (8.3)	94.2	100.3	92.2
	1.0	1.8_1 (11.6)	0.9_6 (7.7)	2.8_9 (5.3)	98.7	96.0	94.5
Aftershave	0	1.0_2 (7.3)	<LOD	0.4_7 (4.0)	–	–	–
	0.5	1.4_9 (4.5)	0.5_4 (6.3)	1.0_1 (5.4)	94.6	108.7	108.8
	1.0	2.1_0 (6.9)	1.0_3 (8.2)	1.5_2 (10.0)	108.4	103.5	105.2

[a] Data were calculated based on three-replicate experiments.

Table 5
Comparison of the proposed method with the reference method for extraction and determination of the parabens in urban wastewater.

Method		MP	EP	PP
SFVCDME	Initial concentration ($\mu g\,L^{-1}$)	36.9	–	61.3
	RSD (%) ($n=3$)	4.5	–	3.8
SPE	Initial concentration	38.4	–	59.1
	RSD (%) ($n=3$)	3.1	–	7.9

3.5. Solid-phase extraction

Solid-phase extraction (SPE) was applied as an acceptable reference method to confirm the accuracy of the present method for determination of parabens in the effluent of wastewater. The parabens were analyzed in 50 mL diluted urban wastewater using SPE-HPLC procedure according to Ref. [54]. After the C18 SPE column was conditioned according to the manufacturer's recommendations, 50 mL of the sample was passed through the column to extract the parabens. The column was then washed with 2 mL of HCl solution (2%, v/v) to elute probable interferences. Methanol (4 mL) was used to wash the parabens from the column. The volume of eluate was reduced to 100 μL by nitrogen bubbling. Finally, 20 μL of the residue was injected into the HPLC-UV for analysis. The results are provided in Table 5. It was found that the concentration of MP and PP in the wastewater were 38.4 and 59.1 $\mu g\,L^{-1}$ by SPE method and 36.9 and 61.3 $\mu g\,L^{-1}$ by the present method. The results obtained by the proposed method were in accordance with those of the reference method and indicated that the quantitative data can be obtained for determination of parabens in wastewater samples using SFVCDME procedure. This method has several advantages in comparison with SPE extraction due to reduced solvent volume. Furthermore, it is not necessary in the proposed method to evaporate a large volume of toxic organic solvent which is a time-consuming and inappropriate environmental behavior.

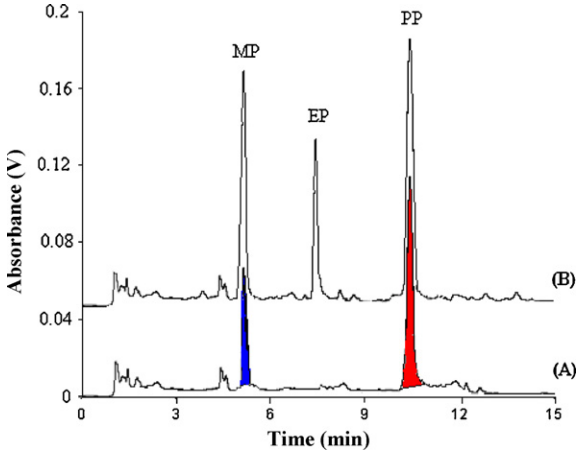

Fig. 8. Chromatograms obtained by the developed SFVCDME method for (A) a non-spiked and (B) spiked skin cream by 1.0 $\mu g\,mg^{-1}$ of the target analytes.

4. Conclusions

Supramolecular solvents have a unique array of physicochemical properties that render them very attractive to replace organic solvents in analytical extractions. In this research, supramolecular solvents made up of tetrabutylammonium-induced vesicles of decanoic acid were proposed as valuable tools for microextraction of parabens from water samples and cosmetic products. Since fresh supramolecular solvent was used for each extraction, there was no memory effect. The proposed SFVCDME technique is attractive enough owing to its simplicity, sensitivity, analytical precision, low consumption of organic solvent, low cost and short sample preparation time.

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