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D-Limonene as a green bio-solvent for dispersive liquid–liquid microextraction of β-cyclodextrin followed by spectrophotometric determination

Nahid Pourreza*, Tina Naghdi

Department of Chemistry, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran

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ABSTRACT

In this paper D-limonene and β-carotene are introduced as two natural products in a dispersive liquid–liquid microextraction (DLLME) method for spectrophotometric determination of β-cyclodextrin (β-CD). Dissolved β-carotene in D-limonene exhibits strong absorption exhibits strong absorption intensity after performing. The absorption intensity of the extracted phase is increased in the presence of β-CD due to its interaction (complex formation) with β-carotene. This increase in the absorbance of the extracted phase is related to the β-CD concentration and was utilized as an analytical signal for determination of β-CD. The effect of chemical variables such as pH of the sample solution, nature and volume of dispersive solvent, volume of extraction solvent and extraction time on the DLLME method was studied and optimum conditions were established. The calibration curve was linear in the range of 1×10^{-4}–6×10^{-3} mol L^{-1} (r = 0.9956) with a limit of detection 4×10^{-5} mol L^{-1}. The relative standard deviation for eight replicate determinations of 1×10^{-3} mol L^{-1} and 5×10^{-3} mol L^{-1} of β-CD was 1.82% and 0.88% respectively. The proposed method was successfully applied to the determination of β-CD in spiked water and pharmaceutical samples and good recoveries in the range of 94.2–108.0% were obtained.

Introduction

Cyclodextrins are water soluble cyclic oligosaccharides with toroidal molecule shapes that are produced from starch by enzymatic conversion [1,2]. β-Cyclodextrin (β-CD) as the most important cyclodextrin containing seven glucose sub-units, presents a relatively hydrophobic cavity and the hydrophilic outer surfaces. β-CD is able to interact with organic and inorganic compounds, which may fit into its cavity and form inclusion complexes. β-CD can act as flavor carrier and overcome some of the formulation and delivery limitations of intractable molecules. Due to its properties, β-CD has found numerous applications in the fields of biotechnology, medicine, cosmetic, food, organic synthesis and analytical chemistry [1,3–5]. On the other hand like other chemicals, β-CD has some drawbacks for example it is toxic for renal and disturbs the biological membranes [6]. Thus, it is of great significance to human health to determine and control β-CD content in food and medicinal products. Various analytical techniques such as fluorimetry [3,7], high performance liquid chromatography [8–10] and spectrophotometric methods [11–13] have been used for the determination of β-CD. However some of these analytical methods may not present sufficient sensitivity or selectivity for the determination of the analyte. Therefore the development of a pretreatment step for sample preconcentration is sometimes required [14].

In recent decades, many methods for this propose have been developed. Dispersive liquid–liquid microextraction (DLLME) is one of the successful miniaturized sample pre-treatment and preconcentration techniques for the determination of various analytes [15–19]. In this technique, an appropriate mixture of microliter volumes of organic extraction solvent (with a density higher/lower than water and immiscible with water) with a high extraction capability for the target analyte, and a small volume of a dispersive solvent (miscible with both aqueous and organic phases), is rapidly injected into a sample solution with a glass syringe. This results in the formation of a cloudy state in the solution. The target analytes in the sample solution are quickly transferred into the extraction solvent because of the large contact surface between the organic and the aqueous phases. Phase separation is carried out by centrifugation and the organic phase

* Corresponding author. Fax: +98 6133337009.
E-mail address: npourreza@scu.ac.ir (N. Pourreza).

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containing the target analyte is accumulated at the bottom/top of a conical vial which is then separated and analyzed by various analytical techniques [20,21].

The promising prospects of DLLME, especially its combined use with chromatographic techniques for organic compounds analysis in environmental water samples have been previously discussed [22]. The DLLME method coupled with capillary electrophoresis has been developed and applied for simultaneous determination of the several sulfonamides [23], mercury [24] and four phenolic environmental estrogens in water samples [25].

However, in order to minimize the health and environmental impact of toxic solvents used in chemical process, substitution of hazardous solvents with bio-based/green solvents obtained from renewable feed stocks has gained worldwide attention. D-Limonene as a natural solvent derived from citrus peels is a biodegradable terpene with low toxicity and cost. It has been used as a valuable replacement for traditional solvents such as methyl ethyl ketone, acetone, toluene, glycol ethers, and numerous fluorinated and chlorinated solvents. It has been considered for many applications like insecticide, cosmetics, and food industry. This rising interest for D-limonene is due to its proved cleansing and degreasing properties [26]. D-Limonene has also been used as an alternative solvent for Soxhlet extraction of fats and oils [27]. In addition to environmental friendly properties of D-limonene; high extraction capability for the target analyte, water immiscibility and having all the requirements for an extraction solvent makes limonene as an alternative solvent to hazardous solvent used in DLLME method. Herein we introduce D-limonene as new green solvents for DLLME method.

One of the applications of β-CD is production of water-soluble complexes with insoluble compounds in water such as β-carotene [28–30]. CDs have also been used as versatile tool in the molecular recognition and sensing. Formation of inclusion complex causes some spectral changes which have been used for the study of host–guest interactions [31,32] and encapsulation of natural colorants [33].

Herein, we have used the interaction between β-CD and β-carotene in D-limonene solvent to develop a novel DLLME procedure as a pre-treatment and preconcentration method for the determination of β-CD. The organic phase containing β-carotene is dispersed into aqueous phase as fine droplets and the inclusion complex of β-carotene and β-CD is transferred to D-limonene. The concentration of β-CD can be monitored by measuring the absorbance of the organic phase. The effect of chemical variables such as pH of the sample solution, nature and volume of the dispersive solvent, volume of the extraction solvent and extraction time on DLLME method was studied and optimum conditions were established.

Experimental section

Apparatus

The absorbance measurements and absorption spectra of the solutions were performed by a GBC UV–vis spectrophotometer model Cintra101 (Sydney, Australia) operating at 466 nm using 350 μL quartz microcells. Measurements of pH were performed by a digital pH-Meter model 632, Metrohm (Herisau, Switzerland) with a combined glass electrode. A centrifuge model BHG HERMLE (Germany) was used for the phase separation. A syringe (1.0 mL, Gastight, Hamilton, Reno, NV, USA) was used.

Reagents

All chemicals were of analytical grade and doubled distilled water was used throughout.

A stock solution of 1×10^{-2} mol L^{-1} of β-CD was prepared by dissolving 1.13498 g of β-CD (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. Working standard solutions were prepared by stepwise dilution of the stock solution. Maleate buffer solution pH 6 was prepared by adding 0.1 mol L^{-1} NaOH (Merck) to 0.1 mol L^{-1} maleic acid (Merck) and adjusting the pH to 6 using a pH meter. 0.05% (w/v) solution of β-carotene (Sigma Aldrich, St. Loius, MO, USA) in D-limonene (Sigma Aldrich) was prepared by dissolving 5 mg of β-carotene in D-limonene and diluting to 10 mL.

General procedure

An aliquot of β-CD solution (so that its final concentration was in the range of 1×10^{-4}– 6×10^{-3}) was placed in a 10 mL volumetric flask containing 0.5 mL of maleate buffer (pH = 6). The resulting solution was diluted to the mark with water and mixed thoroughly. The solution was then transferred to a home-designed glass vial with a glass tube fixed on the side of the vial and a capillary tube attached to the top of the vial. Then a mixture of 1 mL of acetone (as the dispersive solvent) and 200 μL D-limonene (as the extraction solvent) containing 0.05% (w/v) β-carotene was rapidly injected into the sample solution using a 1 mL syringe. This injection led to the formation of cloudy solution which was manually shaken for 40 s. After 3 min standing, the cloudy solution was centrifuged for 5 min at 4000 rpm. Upon centrifugation, the fine droplets of organic solvent float at the top of the glass tube. The organic phase was moved to the capillary tube attached to the top of the vial by adding water to the fixed glass tube on the side of the vial. The upper phase (195 ± 4 μL) was collected and transferred to a 350 μL quartz microcells by a micro-syringe and its absorbance was measured at 466 nm. A blank solution was also run under the same conditions without adding any β-CD. The experimental steps involved in the recommended procedure for β-CD determination are illustrated in Fig. 1.

Sample preparation

The water samples were collected from Karun River (Khuzestan province, Iran) and tap water (Ahvaz, Iran) boiled and filtered before use. An aliquot of the solution was subjected to the general procedure.

For preparation of tablet samples, the acetaminophen, diclofenac, ibuprofen tablets were powdered. 100 mg of each tablet was weighed in a beaker; 50 mL of water was added and spiked with a known concentration of β-CD. The solution was stirred and filtered into a100 mL volumetric flask and diluted to the mark with water. An aliquot of each solution was subjected to DLLME procedure for the determination of β-CD content.

Results and discussions

β-CD forms host–guest inclusion complexes with a number of compounds including β-carotene and some drugs and can enhance the solubility and stability of the guest molecule [4]. Formation of inclusion complex leads to some spectral changes which have been used to study the host–guest interactions [32]. D-Limonene as a solvent lighter than water dissolves and extracts beta-carotene but when beta-cyclodextrin is present due to the formation of inclusion complex more beta-carotene is carried to the solvent and the solution turns orange (Scheme 1). Therefore the absorption intensity at 466 nm is increased in the presence of beta-cyclodextrin. This increase in the absorbance of the extraction solvent phase is proportional to the β-CD concentration and was utilized as an analytical signal for determination of β-CD.

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