Talanta 80 (2009) 789–796

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Development and characterization of a new polyampholyte–surfactant complex applied to the solid phase extraction of bisphenol-A

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ARTICLE INFO

Article history:
Received 29 April 2009
Received in revised form 27 July 2009
Accepted 30 July 2009
Available online 7 August 2009

Keywords:
Polyampholyte
Surfactant
NMR
Solid phase extraction
Sorption
Bisphenol-A

ABSTRACT

This paper presents a material that has both hydrophilic and hydrophobic domains, obtained by combination of a polyampholyte with a surfactant. This material was fully characterized by different spectroscopic techniques and microscopy.

Bisphenol-A (BPA) was chosen as a model molecule to study the interaction with compounds of intermediate polarity. We explored the kinetics and equilibrium of BPA on the surface of the polyampholyte–surfactant complex and found a significantly high loading capacity (2.02 mmol g^{-1}) and complete binding from solutions at concentration levels below 100 μmol L^{-1}.

The complex was encapsulated in agarose gel to be used as solid phase for extraction of BPA from food simulants in contact with polycarbonate bottles under different treatments. Bisphenol was preconcentrated, extracted and analysed by liquid chromatography with an amperometric detector. The instrumental detection limit of the technique was 10 μg L^{-1}, which was lowered to 0.14 μg L^{-1} by the preconcentration step. The BPA released from baby bottles was 2.1 ng cm^{-2} (σ_{n-1}: 0.1) in the first use with distilled water.

1. Introduction

Bisphenol-A (BPA), 2,2-bis(4-hydroxyphenyl) propane, is a chemical substance used mainly in the production of polycarbonate and epoxy resins [1]. A great variety of materials (storage containers, milk bottles, infant feeding bottles, microwave ovenware) derived from polycarbonate cause environmental contamination when they are in contact with water or food due to the leakage of non-polymerized monomers or residues from hydrolysis.

It has been reported that BPA has a weak affinity for estrogen receptors [2], has potential for disrupting thyroid hormone action [3], affects the proliferation of human prostate cancer cells [4] and blocks testosterone synthesis [5] at ng L^{-1} doses.

Due to these toxicological properties, many analytical methodologies, including sample preparation, separation and detection of BPA, have been developed [1].

In 2004, the EU Commission established a specific migration limit (SML) of BPA from food plastic materials of 600 ng g^{-1} [6]. Migration testing is usually carried out with food simulants instead of food, because its analysis usually presents some drawbacks. Simulants have been selected to model different categories of food (aqueous, acidic, alcoholic and fatty) to simplify the testing and evaluate whether a plastic is suitable for a given application [7].

Separation, identification and quantitation of BPA are reliably carried out with mass spectrometric methods, namely liquid chromatography–tandem mass spectrometry [8] and gas chromatography–tandem mass spectrometry [9]. Other methods such as liquid chromatography coupled to fluorescence or electrochemical detection and immunochemical methods have also been reported [1]. When food simulants are used, the sample preparation consists of a preconcentration step by solvent evaporation, liquid–liquid extraction, solid phase extraction (SPE), solid phase microextraction or stir bar sorptive extraction [1].

SPE is by far the most widely used technique for the extraction of BPA-containing liquids [9–12]. The technique uses a copolymer formed with the hydrophilic *N*-vinylpyrrolidone, which acts as a hydrogen acceptor, and the hydrophobic divinylbenzene, which provides reversed-phase retention (Oasis HLB).

A number of different approaches have been used to prepare new sorbents in order to improve particular features such as selectivity or capacity. Synthetic strategies such as the molecularly imprinting technique or the construction of immunoaffinity monoliths have been applied to generate selective binding sites in bulk or surfaces of polymeric matrixes [13–15].

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doi:10.1016/j.talanta.2009.07.065

This paper presents a material that combines a hydrophilic network with hydrophobic regions, and exhibits a notably high loading capacity for BPA. The network is a polyampholyte obtained by reaction of methacrylic acid, ethylene glycol, diglycidyl ether and 2-methylimidazole (poly(EGDE–MAA–2MI)) [16–18], following a new synthetic procedure. The acid form of this polymeric material binds dodecyl sulfate on the surface. The interactions between surfactants and polyelectrolytes have been well reviewed [19–21] and the dominating factor that influences binding is the electrostatic charged neutralization of the polyion by oppositely charged surfactants. The electrostatic binding is an endothermic process driven by entropy. The positive entropy is attributed to the recovery of translational entropy of released counterions by the bound surfactant.

The new material was fully characterized by spectroscopy (^{13}C Nuclear Magnetic Resonance in the solid-state, Fourier Transform-Infrared), thermogravimetry, elemental analysis, nitrogen adsorption and scanning electron microscopy.

The kinetics and sorption equilibrium of BPA on the surface were also studied. The material was also encapsulated in agarose beads and tested as sorbent for the BPA released from baby bottles into food simulants, under different treatments. The analysis was completed by liquid chromatography with electrochemical detection (HPLC-ED), and the performance of the method is discussed.

2. Materials and methods

2.1. Reagents

2-Methylimidazole (2MI; 99 wt%; pK_a: 7.86), bisphenol-A (BPA 99 wt%, MW: 228.29), methacrylic acid (MAA; 99 wt%; pK_a: 4.66), ethylene glycol diglycidyl ether (EGDE; 50 wt% in ethylene glycol dimethyl ether), phenol (99 wt%), methylparaben (99 wt%), propylparaben (99 wt%) and diethyl phthalate (99 wt%) were purchased from Sigma–Aldrich, and benzoyl peroxide from Fluka. Sodium dodecylsulfate (SDS; MW: 288.38; solubility at 20 °C: 10 g in 100 g of water; critical micelle concentration (CMC): 8.2 mmol L^{-1}) and dodecylbenzene sulfonic acid sodium salt (SBDS; MW 348.5; solubility at 20 °C: 32.8 g in 100 g of water; CMC: 1.2 mmol L^{-1}) were purchased from ICN Biomedical.

Baby bottles (250 cm^3) from one brand made of polycarbonate were washed twice with distilled water before use; no further treatment was performed.

Acetonitrile, isopropyl alcohol and methanol from Baxter were HPLC grade. BPA-free distilled water was used for all aqueous solutions. Spectroscopic grade potassium bromide was used for infrared pellets. Hydrochloric acid, sodium chloride, sodium hydroxide, disodium hydrogen phosphate and potassium hydrogen phosphate were of analytical grade.

2.2. Synthesis of the polyampholyte modified with the surfactant

The polyampholyte was synthesized according to previous reports [16–18], from methacrylic acid, ethylene glycol diglycidyl ether and 2-methylimidazole. Then it was washed with water, dried at 60 °C for 24 h and milled in particles with an average diameter of 200 μm. The particles were treated with 0.1 mol L^{-1} HCl to obtain the acid form of the polyampholyte (poly(EGDE–MAA–2MIH$^+$)), and 50 mg were put in contact with three aliquots of 4 mL of 20 mmol L^{-1} sodium dodecyl sulfate (SDS) solution. The adsorption of dodecyl sulfate (DS) on the surface of the poly(EGDE–MAA–2MIH$^+$) was expected to take place under these conditions (Scheme 1). The complex poly(EGDE–MAA–2MIH$^+$)–DS was rinsed with distilled water, filtered, and let to dry at room temperature. Sodium dodecylbenzene sulfonate (SDBS) was also used for the formation of the complex since it absorbs radiation at 273 nm and can be monitored spectrophotometrically.

2.3. Characterization of the poly(EGDE–MAA–2MIH$^+$)–DS complex

The Fourier Transform-Infrared (FTIR) spectra of poly(EGDE–MAA–2MIH$^+$)–DS and polyampholyte were recorded on a Spectrum 1000 PerkinElmer spectrometer using KBr pellets. The material was dried and placed in a desiccator at 20 °C prior to pellet preparation.

High-resolution ^{13}C Nuclear Magnetic Resonance (NMR) solid-state spectra were recorded using the ramp $\{^1\text{H}\} \rightarrow \{^{13}\text{C}\}$ CP-MAS (cross-polarization and magic angle spinning) sequence with proton decoupling during acquisition. All the solid-state NMR experiments were performed at room temperature in a Bruker Avance II-300 spectrometer equipped with a 4-mm MAS probe. The operating frequency for carbons was 75.46 MHz and the spinning rate was 10 kHz. Samples of two batches of each material were studied.

Thermogravimetric measurements were carried out with a TA Instrument SDT Q600, under nitrogen flux over a temperature range from 30 to 400 °C with a heating rate of 10 °C min^{-1}. The average sample size was 10 mg and the measurements were carried out in triplicate.

The surface of two batches of each polymer was characterized using a scanning electron microscope Field Emission SEM (Zeiss Gemini DSM 982) operated at a 0.3 kV acceleration voltage.

Elemental analysis was performed with a CE440 Elemental Analyser device (Exeter Analytical).

The nitrogen adsorption isotherm was collected at 77 K on a Micromeritics Gemini 2360 system. Specific surface area was calculated using the Brunauer–Emmett–Teller equation (BET).

2.4. Surfactant adsorption isotherms

For binding studies, SDS was replaced with SDBS, whose concentration was determined by UV measurements.

Kinetic experiments were performed with a 4 mmol L^{-1} SDBS standard solution under forced convection.

The adsorption isotherm was performed with aliquots of 80 mg of acid polyampholyte dispersed in 10.0 mL of SDBS standard solutions in a concentration range between 0.20 and 8.0 mmol L^{-1}. The suspensions were mixed and thermostated at 20.0 ± 0.5 °C for 16 h to reach equilibrium. The SDBS concentration in the supernatant and standard solutions was analysed spectrophotometrically at 273 nm.

2.5. Bisphenol-A (BPA) uptake

BPA in solution was analysed by liquid chromatography with electrochemical detection (HPLC-ED). The chromatographic system consisted of an HPLC SpectraSYSTEM Isocratic Pump P100, a Rheodyne injection valve (Model 7125) with a 20-μL sample loop, a guard column, and a C-18 bonded column (Hewlett-Packard) 5 μm, 200 mm × 4.6 mm. The mobile phase was methanol:aqueous solution containing 10 mmol L^{-1} KNO$_3$ and 0.25 mmol L^{-1} H$_2$SO$_4$ as supporting electrolyte in a proportion of 55:45, at a flow rate of 0.8 mL min^{-1}.

Amperometric detection was performed with a microprocessor-controlled electrochemical analyser. A thin-layer cell (7 μL volume), equipped with a glassy carbon working electrode (BAS, 7 mm^2 area) and a stainless steel block as auxiliary electrode, operated at +1 V vs. Ag/AgCl.

Stainless steel, PTFE and PEEK were used for the flow system connections.