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High-capacity anion exchangers based on poly (glycidylmethacrylate-divinylbenzene) microspheres for ion chromatography

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ABSTRACT

Poly (glycidylmethacrylate-divinylbenzene) microspheres were prepared by the two-staged swelling and polymerization method and applied to prepare anion exchange stationary phases. Methylamine, dimethylamine, trimethylamine, diethylamine and triethylamine were selected to prepare the quaternary ammonium groups of anion exchangers, respectively. The diameters and surface characteristics of microspheres were measured by scanning electron microscope and nitrogen adsorption-desorption measurements. The anion exchangers were characterized by Fourier transform infrared spectrum, elemental analysis and breakthrough curve methods. The chromatographic performances of anion exchangers were illustrated by separating conventional anions, organic weak acids and carbohydrates. The results indicated that the anion exchange capacities were controllable by changing either the content of glycidylmethacrylate in microspheres or the number of bonded quaternary ammonium layer. Meanwhile, the substituents of quaternary ammonium groups greatly influenced the separation properties of anion exchangers. Finally, the three-layer methylamine-quaternized anion exchanger was successfully applied for the determination of fluoride in tea sample. The content of fluoride was detected to be 0.13 mg g^{-1} without the interference of acetate and formate.

1. Introduction

Ion chromatography (IC) is a powerful analytical technique for determination of ion compounds. Its highly selective separation mainly depends on the stationary phases. Therefore, developing new ion-exchange stationary phases continues to be one of the most challenging research goals in IC [1–4]. For supporting materials of IC stationary phases, organic polymer microspheres have been predominantly employed due to their high chemical stability towards extreme pH conditions. Poly (acrylates), poly (methacrylates) and poly (styrene-divinylbenzene) (PS-DVB) have been commonly applied in IC stationary phases [5–12]. In recent years, glycidylmethacrylate (GMA) has attracted lots of researchers' attention, which can be readily modified to introduce various functional groups. Poly (glycidylmethacrylate-ethylenedimethacrylate) microspheres have been applied to prepare the chromatographic stationary phases [13–18]. GMA can also be copolymerized with divinylbenzene (DVB) to produce poly (GMA-DVB) microspheres for different purposes by diverse methods. Compared with PS-DVB, poly (GMA-DVB) microspheres offer the advantage that the ligand can be covalently immobilized on them by a single chemical reaction step [19–22].

The separation properties of anion exchange stationary phases are mainly dependent on the type and structure of anion exchange sites. The anion exchange functional groups in IC commonly include quaternary ammonium and tertiary amine. Strong anion exchangers are the primary exchangers in IC, with quaternary ammoniums acting as exchange sites. Conventionally, selectivity of the anion exchangers can be changed through optimization of the length, bulkiness and hydrophobicity of the substituents of ammonium functional groups. The retention properties of quaternary ammonium groups are greatly influenced by the substituted alkanol and alkyl groups [23]. The strong anion exchangers are usually synthesized by dendrimer quaternization, in which the supporting microspheres are exposed to amine and diepoxide in a repetitive manner. Dendrimer quaternization has been extensively

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applied to prepare the quaternary ammonium exchanger as the exchange capacity can be controllable, and the synthesized copolymer exhibits a dendrimer (layer) structure [24–30].

As weak electrolytes, organic acids and carbohydrates have interaction with anion exchange resins, which can be separated and determined by IC [31,32]. So, the strong ion-interaction of the chromatographic column is of great importance; high capacity anion exchangers are suitable for the determination of them. In this work, poly (GMA-DVB) microspheres containing three different contents of GMA were prepared by the two-stage swelling and polymerization method and applied for the preparation of high capacity anion exchangers. Methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), diethylamine (DEA) and triethylamine (TEA) were selected to prepare the quaternary ammonium groups by dendrimer quaternization, respectively. The properties of the materials were investigated and characterized in detail. Finally, the three-layer MA-quaternized anion exchanger was applied for the determination of fluoride in tea sample.

2. Experimental

2.1. Apparatus and instruments

All the chromatographic separations of anion-exchange stationary phases were carried out by an ICS-3000 IC system (Thermo fisher, Agawam, USA), equipped with an ICS-3000 dual pump, an ICS-3000 chromatography/detector module, a Dionex AERS-4mm suppressor and an AS auto-sampler. The JY92-Π ultrasonic disrupter (Scientz Biotechnology Co. Ltd., Ningbo, China) was employed to emulsify organic compounds. The scanning electron microscopy (SEM) images were obtained using a Quanta-650 SEM (FEI, Hillsboro, USA). Fourier transform infrared (FT-IR) spectrum was achieved by a Bruker Vector 22 spectrometer (Bruker, Berlin, Germany). Elemental analysis was performed with a Flash EA 1112 elemental analyzer (Thermo fisher, Agawam, USA). The surface characteristics were measured on a surface area and porosity analyzer ASAP 2020 HD88 (Micromeritics, Atlanta, Georgia, USA). The column was packed by a pneumatic-pump K-1900 (Knauer, Berlin, Germany). A water purification system of Millipore Simplicity (Millipore, Agawam, USA) was used to purify the water for all eluents.

2.2. Reagents

Styrene (ST) (99+%, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), DVB (55+%, Zhengguang Chemical Plant, Hangzhou, China) and GMA (97+%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) were used after washing with 10% (w/v) sodium hydroxide aqueous solution. Azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Co., Ltd., China) and benzyl peroxide (BPO) (99+%, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) were recrystallized before use. Polyvinylpyrrolidone (PVP, K-30), dibutyl phthalate (DBP), polyvinyl alcohol (PVA, 1750 ± 50), sodium dodecylsulfonate (SDS), MA, DMA, TMA, DEA, TEA, 1, 4-butanedioldiglycidyl ether (BDDE) (60%) and toluene were purchased from Huipu Chemical Reagent Co., Ltd. (Hangzhou, China). All reagents employed for the synthesis were of analytical grade.

2.3. Chromatographic conditions and sample preparation

12.5 mmol L^{-1} Na_2CO_3+2.0 mmol L^{-1} $NaHCO_3$ (pH=11.1) and 20 mmol L^{-1} Na_2CO_3+3.5 mmol L^{-1} $NaHCO_3$ (pH=11.1) were used to separate the conventional anions; 30 mmol L^{-1} NaOH (pH=12.5) was used to separate the weak organic acids; and 5 mmol L^{-1} NaOH (pH=11.7) was used to separate the carbohydrates. The eluent flow rate was 1.0 mL min^{-1}, the injection volume was 25 μL, the detector was suppressed conductivity detector or pulsed amperometry detector and the system temperature of all chromatographic tests was set at 30 °C. All the concentrations of the anions in the mixed standards of conventional anions, organic acids and carbohydrates were 0.1 mmol L^{-1}. The anions were identified by spiking standards. Preparation of tea sample: 2.0 g of tea sample were soaked in water (50 mL, 100 °C) for 15 min assisted with ultrasonic. Then the solution was transferred to a 500 mL volumetric flask and diluted with water to 500 mL. Before injection, the solution was filtered with a RP-C_{18} SPE column and a 0.22 μm nylon filter to eliminate the organic molecular and solid particles. 30 mmol L^{-1} NaOH was used as eluent for tea sample analysis. Data were collected with Chromeleon 6.80 chromatogram workstation.

2.4. Preparation of anion exchangers

2.4.1. Preparation of poly (GMA-DVB) microspheres

The poly (GMA-DVB) microspheres containing different contents of GMA were prepared by the two-staged swelling and polymerization method. Firstly, mono-dispersed polystyrene seed microspheres were prepared by dispersion polymerization method [33]. The reaction was conducted in a 250 mL four-neck round bottom flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel in a temperature-controlled water bath at 70 °C. 0.3 g PVP and 100 mL mixture of ethanol and water (95:5, v/v) were added to the flask, and then a blend of 0.7 g AIBN and 20 mL styrene was added dropwise within 30 min under the protection of nitrogen. The mixture was stirred at the rotational speed of 250 rpm for 24 h. The beads were collected by suction and washed with excess water, and then the microspheres were stored in 30 mL 1% SDS (m/v) aqueous solution. Secondly, a blend of 2.0 mL polymer seeds solution and 15 mL SDS aqueous solution (0.2%, w/v) was placed into a 500 mL four neck flask. An emulsified solution containing 4.0 g DBP, 30 mL SDS aqueous solution (0.2%, w/v) was added and stirred at the rotational speed of 120 rpm for 24 h. Emulsified mixture comprised 30 g organic compounds and 250 mL PVA aqueous solution (1%, w/v) was prepared by an ultrasonic disrupter and poured into the flask for swelling. The above organic compounds consisted of ST, GMA, DVB, toluene, BPO and SDS. The amount of toluene was equal to the total amount of ST, GMA and DVB, while BPO was only 1.5% of the total amount (w/w). The amount of SDS was 0.25% of the PVA aqueous solution (w/v). After 24 h of swelling, the temperature of water bath was increased to 70 °C under nitrogen atmosphere and lasted for 24 h. Subsequently, the resulting microspheres were washed successively with hot water and alcohol. The crude products obtained were purified by soxhlet extraction with toluene for 48 h and then washed with water and absolute ethyl alcohol followed by drying under vacuum at 60 °C for 24 h. To prepare poly (GMA-DVB) microspheres consisted of different contents of GMA, three emulsified mixtures containing different mass ratios of GMA to DVB (1/5, 3/5, 5/5) were selected to prepare the microspheres, with the mass of DVB being held constant and ST acting as co-monomer. Finally, poly (GMA-DVB) (1/5), poly (GMA-DVB) (3/5) and poly (GMA-DVB) (5/5) microspheres containing three contents of GMA were obtained, respectively.

2.4.2. Preparation of poly (GMA-DVB) anion exchangers

The poly (GMA-DVB) anion exchangers were prepared by the typical dendrimer quaternization. In detail, 20 mL amine (4%, w/v) was added to the poly (GMA-DVB) microspheres (3 g) and allowed to react at 60 °C for 2 h, and later the microspheres were filtered and rinsed with deionized water. Subsequently, 20 mL BDDE (10%, w/v) was added to the amine-modified microspheres and allowed