

Preparation and applications of weak acid cation exchanger based on monodisperse poly(ethylvinylbenzene-co-divinylbenzene) beads

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Abstract

New technology is reported here for the synthesis of an effective weak acid–cation exchanger for ion chromatography. Monodisperse macroporous poly(ethylvinylbenzene-co-divinylbenzene) (PEVB–DVB) beads of 5 μm diameter were prepared by a two-step swelling and polymerization method. Then carboxyl groups were introduced by polymerization of maleic anhydride with unreacted vinyl groups on the resin beads, followed by hydrolysis of the maleic anhydride groups. A column packed with the carboxylate beads was used to separate alkali and alkaline earth metal ions in a single isocratic run. Separations were found to be better than those with similar resin particles that are simply coated with maleic acid. The columns containing the new particles were 100% compatible with solvents commonly used for HPLC. Additionally, the prepared column was stable and could be used for a long time in a wide range of pH. The column gave good resolution, low detection limits and good repeatability for the separation of common cations. Satisfactory results were also obtained for separations of organic amines and of common cations in rainwater.

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1. Introduction

In recent years, considerable advances have been made in developing new stationary phases for IC. Silica is brought as support for preparation of IC matrix. However, silica-based packings are less stable under high or low pH conditions, they cannot, sometimes, satisfy the requirement for the separation of some samples. In most cases, polymer-based packings can be employed even in the pH range from 1 to 14, and this led us to the development of various polymer-based resins in IC [1].

In order to get the satisfactory efficiency, uniformly sized beads (5 μm) should be got firstly. In the search for uniformly sized beads as chromatographic stationary phases, Ugelstad [2] has developed a technique named “activated multi-step swelling and polymerization” method. Uniform beads are prepared by Ugelstad’s method from a great variety of monomers, such as styrene [3], methylmethacrylate, 2-

hydroxyethylmethacrylate, glycidylmethacrylate, vinylphenol, and chloromethylstyrene. This method is excellent, and at least two steps are needed in the swelling process. The first step is the activation of the seed beads by the absorption of a water-insoluble compound. The subsequent step is the absorption of monomer, cross-linker and diluent.

The use of substrates consisting of ethylvinylbenzene (EVB) cross-linked with 55% divinylbenzene (DVB) is a relatively recent advance in the development of IC columns, which permits 100% HPLC solvents compatibility. Consequently, organic solvents can be added to the mobile phase at high concentrations to vary separation selectivity [1,4].

Cation exchange resins are divided into strong acid (e.g. sulfonic acid) and weak acid (e.g. carboxylic or phosphonic acids) types. Cation exchanger with weak acidic group can be used to separate ammonium, alkali and alkaline earth metals in the same eluent condition while strong acid cation exchanger cannot do this [5].

Coating maleic acid as a new way to generate silica based cation exchanger has been investigated previously [6–8].

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However, silica based exchanger can not be used in a wide range of pH or not be compatible to solvents. What is more, its stability is not as good as required for modern ion chromatography.

In this paper, we report a preparation of poly(ethylvinylbenzene-co-divinylbenzene) (PEVB–DVB) beads by two-step swelling and polymerization method in the presence of solvents, linear polystyrene as a porogens, and a new method for chemical modification of PEVB–DVB for the synthesis of a cation exchanger with carboxyl group, a new type of IC stationary phase. The chromatographic properties of the stationary phase for common cations and organic amines are discussed in detail.

2. Experimental

2.1. Reagents

2.1.1. Give purities for monomers

Styrene (Shanghai Chemical Reagent Co. Ltd., Shanghai, China), ethylvinylbenzene (EVB) and divinylbenzene (DVB) (Organic Chemical Factory, Shaoxing, China) were extracted five times with 10% aqueous sodium hydroxide and distilled water, and then dried with anhydrous magnesium sulfate.

Poly(vinylpyrrolidone, k-30) (PVP, k-30) was purchased from Aldrich (USA). Maleic anhydride, azobisisobutyronitrile (AIBN), dibutyl phthalate and cyclohexanol were bought from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Polyvinyl alcohol (PVA) and sodium dodecyl sulfate (SDS) were obtained from Beijing Chemical Reagent Co. Ltd. (Beijing, China). Benzyl peroxide (BPO) was obtained from Linfeng Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were purified by re-crystal and dryness according to GB standard of China.

Aliquots of commercially available stock solutions (1000 mg/L) were used to prepare cation mixtures containing the ions to be investigated. All eluents were prepared with sulfuric acid. Milli-Q water (Millipore, Bedford, MA, USA) was used in all dilutions.

2.2. Instrumentation

The IC system consisted of an HPLC pump (Type YSB-2, Shanghai, China), a manual injection valve (Model 7725, Rheodyne, USA) fitted with 25 μ L sample loop and a conductivity detector (Dinoex 2010i). The eluent flow rate was 1 ml/min throughout all experiments. Neither the column nor the conductivity detector were heated; experiments were conducted at the ambient temperature of ca. 30 °C. There was temperature compensation in the detector with a default value of 1.7% per °C. Data were collected by using an N-2000 double-channel chromatogram workstation. Chinese software, CM 2.1 was used; it had a data acquisition rate of 10 data/s (10 Hz).

2.3. Synthesis of polymer seeds

According to the method reported by Pane et al. [10], monodisperse polystyrene seed beads with low molecular weight were prepared by dispersion polymerization of styrene in alcohol media in the presence of inhibitor under a nitrogen atmosphere. A typical example was as follows. Into a 300 ml flask, 20 g of styrene, 75 g of ethanol (95% in water), 1.0 g of AIBN and 5 g of PVP (k-30) were charged. The mixture was stirred for 8 h with a magnetic stirrer at 70 °C under dry nitrogen. After centrifugal separation, the seed beads obtained were dispersed in an aqueous solution. The particle size of the prepared beads was measured to be 1.7 μ m.

2.4. Preparation of basic substrate

A uniformly mixed solution containing 300 ml of water, 1.5 g of SDS and 1.2 g of St seeds obtained above therein 15 ml of paraffine and 15 ml of toluene were charged into a three-neck flask equipped with a reflux condenser and the resulting mixture was stirred for 10 h at room temperature. Twenty millilitres of EVB, 25 ml of DVB and 0.45 g of BPO were added. The solution was stirred for another 10 h also at room temperature. Subsequently, after 20 g of polyethylene ether alcohol was charged, polymerization was performed under nitrogen stream at 90 °C for 10 h. This polymer was filtrated, washed and dried. What we got were macroporous EVB–DVB polymers with a particle size of 5 μ m. Using this as substrate, a cation exchanger was produced through the following procedure.

2.5. Chemical modification of PEVB–DVB beads

Into a 100 ml flask, 1.2 g of EVB–DVB polymers obtained above was suspended in 40 ml of dry toluene. After addition of 0.1 g of maleic anhydride and 0.01 g of BPO, the suspension was stirred at 78 °C for 2 h to introduce a carboxylic group, thereby preparing a cation exchanger. This polymer was filtered off and washed by methanol and water respectively. The carboxylated polymer is suspended in 2 M NaOH solution and stirred for at least 12 h. The polymer was filtered off and washed several times with water. Finally, the polymer was suspended in a 2 M HCl solution and stirred for 6–24 h depending on the degree of functionalization. The final maleic acid exchanger was filtered off and dried under reduced pressure.

2.6. Column packing procedure

The analytical column (stainless-steel, 250 mm \times 4.6 mm I.D.) was slurry packed with the cation exchanger obtained as above, by pressing with acetonitrile packing solvent under a working pressure of 35 MPa. The solvent was passed through the column at least 250 ml. Finally, the column was conditioned by passing 500 ml of 10 mM H₂SO₄ at a flow rate of 1 ml/min. Aqueous acetonitrile (30% in water) was

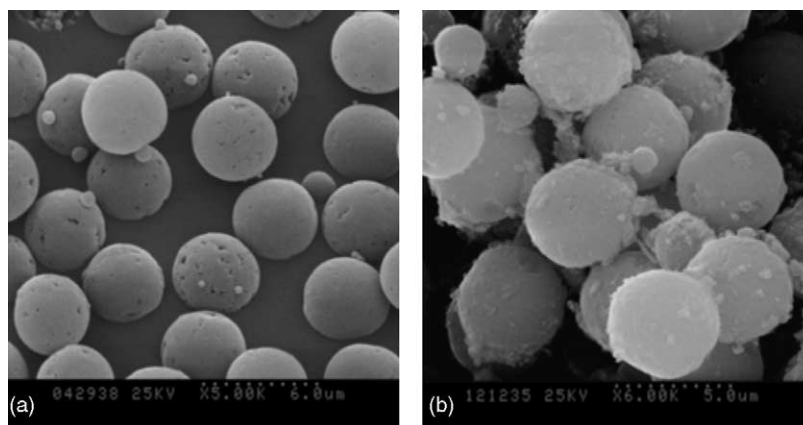


Fig. 1. Scanning electron micrographs of the untreated PEVB–DVB beads (a) and coating maleic acid beads (b).

used as the slurry solvent. The maximum exchange capacity of the column was 745 $\mu\text{eq}/\text{column}$.

3. Results and discussion

3.1. Preparation of monodisperse beads

EVB–DVB polymers were taken into consideration because they are suitable for LC, with great stability against many oxidizing agents and can be used in a wide range of pH. The size of the final beads was well controlled by the seed diameter and the existing amount of organic phase. As organic phase consisting of EVB, DVB and diluents is fully adsorbed by the seeds in an effective swelling range, the final particle diameter could be calculated according to the following simple equation [9]

$$\log D = \log d + \frac{1}{3} \log \frac{M + m}{m} \quad (1)$$

where d and D are the diameters of the seeds and the final beads, respectively, M and m are the amounts of organic phase and the seeds, respectively; the value of $(M + m)/m$ is the swelling multiple. The experimental results showed that when 1.7 μm of seed beads were used and the swelling multiple was controlled to be in the range of 3–25, a series of monosized EVB–DVB resins with particle diameter in the range of 5 μm could be obtained.

Fig. 1(a) shows the scanning electron micrographs of the prepared beads, illustrating that the prepared beads in this study are uniform in size.

3.2. Chemical modification of PEVB–DVB beads

Because there are some extra vinyl groups on the PEVB–DVB beads, maleic anhydride can be polymerized with free vinyl group and with each other. An additional hydrolyzation step produces carboxyl groups, which is the ion exchange site [1].

Fig. 1(b) shows the scanning electron micrographs of the packing, illustrating that the packing in this study is uniform in size and different from the prepared beads. There are some new polymers on the surface of EVB–DVB resins. The grafted polymer on the surface was confirmed.

The IR spectrum of the modified polymer exhibited a large broad adsorption peak at 1735 and 1174 cm^{-1} , corresponding to carboxyl group; adsorption peaks at 1605, 1585, 1500 and 1450 cm^{-1} , corresponding to phenyl group. These results prove that the phenyl groups were really bonded to the EVB–DVB beads.

3.3. Separation of alkali and alkaline earth metals

The column is packed with a weak cation exchanger that was based on spherical polymer beads grafted with poly maleic acid groups. The main application is the determination of alkali and alkaline earth metal within a single isocratic run.

Fig. 2 presents the separation of these cations using 3.5 mmol/L sulfuric acid as eluent. The eluent can be easily prepared without adding other reagents. The cations were separated very well and can be determined and qualified very easily. Table 1 shows RSD and detection limits of them.

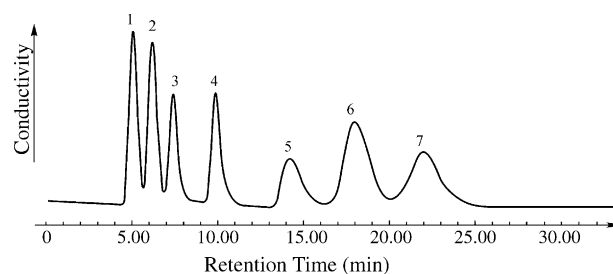


Fig. 2. Separation of a standard solution containing different cations. Conditions: 3.5 mmol/L sulfuric acid; flow rate: 1.0 ml/min; detection: conductivity; sample: 25 μL containing: (1) 1 mg/L lithium, (2) 3 mg/L sodium, (3) 3 mg/L ammonium, (4) 5 mg/L potassium, (5) 3 mg/L magnesium, (6) 6 mg/L calcium and (7) 10 mg/L strontium.

Table 1
RSD and detection limits of standard samples containing seven cations

Cations	RSD (RT) (%)	RSD (peak area) (%)	Detection limits (mmol/L)
Lithium	1.996	3.646	0.690
Ammonium	2.166	4.100	0.626
Sodium	1.689	1.626	1.140
Potassium	2.110	3.661	0.472
Magnesium	2.394	2.811	0.691
Calcium	3.166	2.653	0.601
Strontium	3.648	4.630	0.534

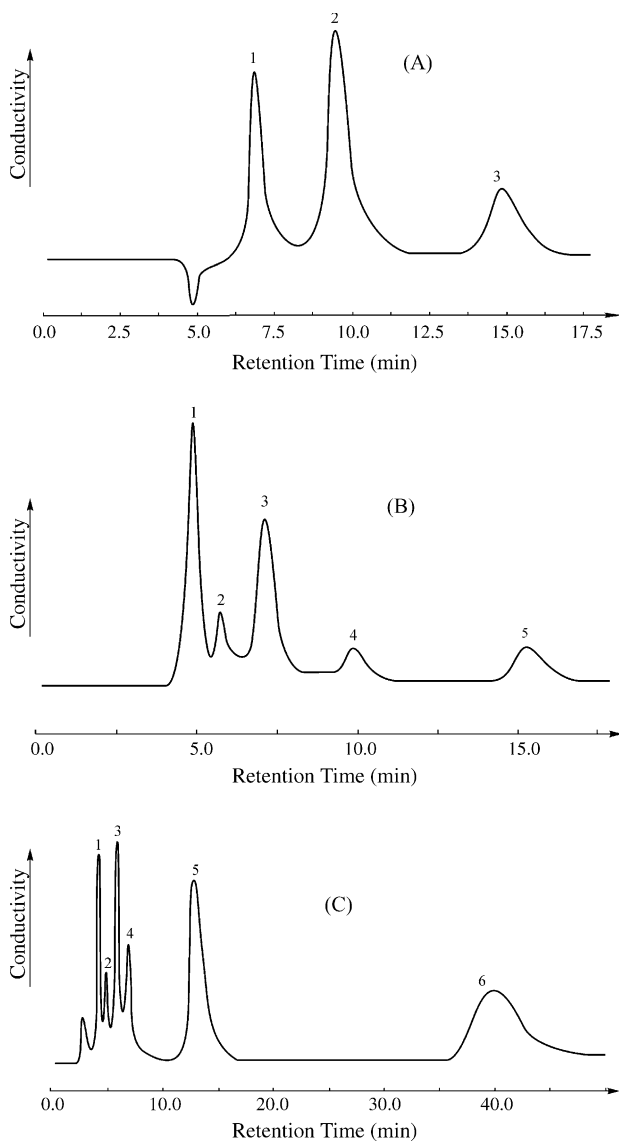


Fig. 3. Separation of organic amines, ammonium, alkali metals. Flow rate: 1.0 mL/min; detection: conductivity. (A) Eluent: 4 mmol/L sulfuric acid. Peaks: 1 = methylamine (13.5 mg/L); 2 = dimethylamine (30 mg/L); 3 = trimethylamine (30 mg/L). (B) Eluent: 4 mmol/L sulfuric acid. Peaks: 1 = sodium (5 mg/L); 2 = ammonium (4 mg/L); 3 = potassium (5 mg/L); 4 = dimethylamine (3 mg/L); 5 = trimethylamine (12 mg/L). (C) Eluent: 5 mmol/L sulfuric acid. Peaks: 1 = sodium (6 mg/L); 2 = ammonium (6 mg/L); 3 = potassium (10 mg/L); 4 = diethylamine (70 mg/L); 5 = triethylamine (140 mg/L).

Table 2
Contents and recoveries of cations in rainwater

Analyte	Content (mmol/L)	Sample added (mmol/L)	Total (mmol/L)	Recovery (%)
Sodium	130	130	255	95.84
Ammonium	843	167	1132	114.48
Potassium	123	127	249	98.21
Magnesium	34	123	153	86.15
Calcium	198	150	383	117.83

3.4. Separation of amines and alkali metals

Amines (methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, and etc.) are used widely in chemical industry. It is important to detect organic amines in industry. The amounts of ammonium and trimethylamine are used to estimate the degree of freshness of food. As food goes bad, both of their concentrations will turn high. So it is important to detect their concentrations in food industry. Fig. 3 shows separation of organic amines, ammonium, alkali metals. Ammonium and trimethylamine can be separated from the common alkali metals with an entirely aqueous–acid eluent system.

3.5. Sample determination

Fig. 4 shows a chromatogram of rainwater collected in Hangzhou, China, on May 15, 2003, without any pretreatment. The determination and recovery data are summarized in Table 2. Results show that the prepared column can be used in the requirement of practical analysis processing.

3.6. Solvent-compatibility and durability

The substrate consisting of ethylenevinylbenzene cross-linked with 55% divinylbenzene permits 100% HPLC solvent compatibility. Consequently, organic solvents, such as acetonitrile or acetone, could be added to the mobile phase at high concentrations to vary separation selectivity. When using aqueous acetonitrile (0–60% in water)–acid as the eluent, the RSD of retention time was no larger than 3%, nearly the same as that without organic solvents. Chromatogram

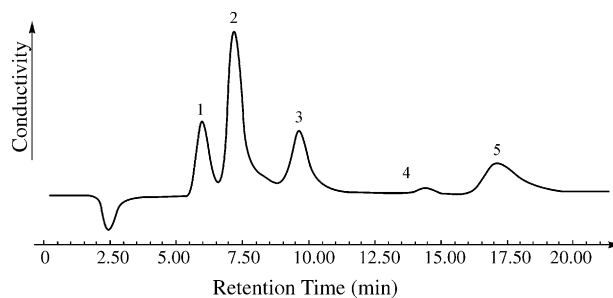


Fig. 4. Chromatogram of cations in rainwater Conditions: 3.5 mmol/L sulfuric acid; flow rate: 1.0 ml/min; detection: conductivity; sample: 25 μ L containing: (1) sodium, (2) ammonium, (3) potassium, (4) calcium, (5) magnesium. Concentrations are listed in Table 2.

of common cations was run again after treating the column with sodium hydroxide solution, hydrochloric acid, acetone and acetonitrile, respectively. The peak widths and retention times nearly had no changes in comparison with no such treating. In addition, the column kept good efficiency and resolution after 500 h use. The durability of the column was better than that of silicon gel. However, alcohol at high concentration could not be added due to esterification reaction.

4. Conclusions

The obtained results show that the beads had the uniformity in particle size and strong particle rigidity. Based on this medium, one new kind of cation exchangers was synthesized by a new chemically modified method. Because the substrate consisting of EVB cross-linked with 55% DVB permits 100% HPLC, the cation exchanger had good solvent compatibility. A better separation, sharpness of the peak shape and fast separation of seven common cations (lithium, sodium, ammonium, potassium, calcium, magnesium and strontium) indicate that the prepared beads in this study could be used to stationary phase for IC. Good resolution, low detection limits and good repeatability were obtained within a single isocratic run. Consequently, a satisfactory result can be obtained when using the column to determine low molecular weight amines. All of these facts represent that highly cross-linked PEVB–DVB (55%) grafted with poly(butadiene-maleic acid

groups is an effective tool for the generation of a new class of high performance cation exchangers.

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