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Sulfoacylated macroporous polystyrene–divinylbenzene: a new type of cation exchanger for the analysis of multivalent metal cations

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Abstract

The basic idea, conception, synthesis and performance of a new type of high-performance liquid chromatography (HPLC) cation exchangers are presented. Friedel–Crafts acylation as a starting operation for functionalization of size exclusion polymers turned out to be versatile and easily controllable. The resulting sulfoacylated HPLC cation exchangers show HETP values of 0.02–0.05 mm for a 5–6 μm resin. In contrast to directly sulfonated resins the HETP values decrease with increasing exchange capacity. The exchangers can be varied in exchange capacity, structure of the exchange site and spacer arm length. The influence of the pore size of the substrate on selectivity is much stronger than that of the spacer arm. The upper limit of exchange capacity is about 1.5 mmol/ml. Characterization of the resins by IR spectroscopy is possible. The separation of Fe, Pb, Cu, Zn, Ni, Co, Cd, Mn, Ca and Mg using a tartaric acid elution system is presented. Detection is performed by post-column reaction with Zn-EDTA/PAR. © 1997 Elsevier Science B.V.

Keywords: Sulfoacylated cation exchanger; Stationary phases, LC; Metal cations; Polystyrene–divinylbenzene polymers

1. Introduction

The world of strong cation exchangers can be classified by two extremes. First there are high capacity PS–DVB exchangers such as Dowex 50W with a high chemical stability and a poor chromatographic performance [1,2]. Second, there are very good performing HPLC cation exchangers based on silica-gel such as Nucleosil SA with a medium capacity and an insufficient chemical stability [3,4]. Directly sulfonated PS–DVB with low exchange capacity are of minor importance for alkaline ion separations with suppressed conductivity detection [5].

The exchange capacity of a cation exchanger is a product attribute that has to be chosen taking into account several factors. The higher the exchange capacity the larger is the sample amount that can be injected without major disturbance of the chromatographic separation. The amount of analyte available for the detection process is linearly correlated to the exchange capacity when all other parameters are kept constant. Dilution as the most preferred sample pretreatment in suppressed ion chromatography lowers the amount of analyte present for detection.

The most important limitation for increasing exchange capacity is the detection technique. Suppressed conductivity detection [5] allows only dilute eluents with weak eluting ions. In cation chromatog-

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raphy suppression is restricted to alkaline and alkaline earth cations due to precipitation of hydroxides in the suppressor. Non-suppressed conductivity detection allows an increase in exchange capacity, but ternary or quaternary eluents show large system peaks. Both sample amount and ionic strength of the sample will increase the system peaks and decrease sensitivity. Direct photometry [6–10] as an alternative detection technique is usually not disturbed by high eluent concentrations. Unfortunately most of the analytes of interest in ion chromatography show no UV absorbance. A way out is indirect photometric detection [5,11], whose application is limited to low exchange capacities. The sensitivity of indirect photometry is dominated by the absorbance of the eluent. High absorbance coefficients combined with high concentrations of the absorbing species lead to an absorbance that is outside the working range of common photometers.

Post-column reaction (PCR) detection systems are available for alkaline earth, transition and heavy metals. They are based on a transformation of the non-absorbing metal ion with a photometric reagent into a complex with high absorption coefficient [8,12–14]. This detection system is ideally suited for high capacity exchangers. The combination of sensitive detection and large sample amounts leads to an analytical technique for ultra trace determination [15].

An upcoming analytical technique is on-line coupling of ion chromatography and atomic spectrometry. An atomic spectrometry device, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS), acts in a coupling application as a chromatographic detector with some unique features [16–18]. The detector is highly element selective and allows sensitive detection of almost every metal and a number of non-metal elements. In comparison to the common detection techniques the use of an atomic spectrometry device shows less restrictions concerning the eluent composition.

The conclusion is a need for new packing materials especially designed for modern detection techniques. For cation chromatography of polyvalent cations, the following list of desirable properties can be compiled:

- high exchange capacity
- pH-stability from pH 0–14
- stable against oxidation and reduction
- high chromatographic efficiency and low back pressure
- selectivity comparable to common packing materials

The presently available materials do not meet most of the listed requirements. More sophisticated applications of ion chromatography such as speciation or ultra trace analysis [19] need a highly flexible synthesis of cation exchangers, whereas capacity and selectivity are the main parameters that have to be controlled. Therefore a method for the preparation of cation exchanger should fulfil some more requirements:

- easily adjustable and reproducible exchange capacity
- control of selectivity by variation of the structure of the exchange site (e.g. for cation exchanger different types of sulfonic acids)
- variation of substrate structure (pore size, size exclusion characteristics)
- variation of substrate polarity (hydrophilic/hydrophobic)

Our attempt to meet most of the points mentioned above starts with rigid PS–DVB copolymers of high crosslinkage and small particle size. Instead of commonly used direct sulfonation or chloromethylation a synthesis based on Friedel–Crafts acylation should allow a versatile and controllable preparation of cation exchangers.

2. Experimental

2.1. Basic substrate

Only PS–DVB polymers were taken into consideration because of their suitability for HPLC and stability against most oxidizing agents, acids and bases. The aimed level of chromatographic efficiency requires a particle size of 5 μm. A further restriction was the availability of bulk materials for a reduction of starting costs. We selected three macroporous PS–DVB polymers of very high crosslinkage as starting materials. The physical properties of the materials supplied by BioRad, Munich, Germany (trade name BioGel) and by Polymer Standard

Table 1
Physical properties of the size exclusion resins used as basic material for the development of sulfoacylated cation exchangers

Physical property	BioGel SEC 3	BioGel SEC 7	PSS GPC SDV 100 Å
Type	PS–DVB	PS–DVB	PS–DVB
Particle size (μm)	5	5	6
Mean pore size d_{P50} (nm)	3	7	10
Pore volume (ml g^{-1})	0.67	1.3	0.5–0.8
Surface area (m^2 g^{-1})	500	450	400
Maximum pressure (MPa)	20	20	16
Crosslinkage (% DVB)	High	High	55

Service, Germany (trade name Z-gel) are given in Table 1. All materials were originally designed for organic phase size exclusion chromatography.

2.2. *Sulfoacylation of highly crosslinked PS–DVB*

The Friedel–Crafts acylation of highly crosslinked PS–DVB polymers using ω-halogenoacyl chlorides was carried out as outlined in [20–22]. The PS–DVB cores were suspended in dry 1,2-dichloroethane and reacted using varying amounts of ω-halogenoacyl chlorides and aluminum chloride as Lewis catalyst. The reaction was quenched by addition of tetrahydrofuran (THF). Subsequent extraction with THF–water, aqueous hydrogen chloride and finally methanol was used for almost complete removal of aluminum chloride. An expected simplification of the procedure by using BF_3–etherate as Lewis catalyst was not successful. It can be assumed that the Lewis acidity of BF_3 is insufficient to give an acceptable reaction rate even when the temperature was increased up to 40°C.

The sulfonic acid exchangers were prepared by a two-step S_N reaction using dimethyl sulfide as first step reagent. Dimethyl sulfide substitutes the chloride atom to create a more hydrophilic salt, which allows the conversion of raw product into a sulfonic acid exchanger using aqueous sodium sulfite solution.

One problem of the procedure described in the literature is the degree of breakage of the rigid PS–DVB cores during the reactions. The problem of breakage increased with increasing pore size of the polymer. The material with 3-nm pore size showed nearly no degradation, the 10-nm pore size material purchased by PSS had the biggest problems with breakage. A simple way to avoid a high degree of breakage was to shorten the time of all steps of the synthesis procedure, whereas the first one seemed to be the most critical. A well performing procedure enabling the synthesis of a wide range of reproducible capacities is described below.

2.2.1. *Synthesis procedure*

A 2-g amount of the macroporous PS–DVB polymer was suspended in 25 ml of dry 1,2-dichloroethane in a pre-dried 250-ml flask. After addition of a variable amount of ω-halogenoacyl chlorides the suspension was stirred for 15 min for complete homogenization. Afterwards the stoichiometric amount of anhydrous $AlCl_3$ was added. The color of the reaction mixture immediately turns dark red. Ten minutes after addition of $AlCl_3$ the reaction was stopped by addition of 100 ml THF. The polymer was filtered off and extracted for 1 h each with THF–water (1:1, v/v), 2 *M* HCl in water, water and methanol, respectively.

The acylated polymer was suspended in 15 ml dimethyl sulfide and 20 ml methanol and stirred for 12 h. The polymer was filtered off and washed several times with methanol. Finally the polymer in the sulfonium form was suspended in a 1 *M* Na_2SO_3 solution and stirred for 6–24 h depending on the degree of functionalization. A low grade of functionalization lead to a hydrophobic sulfonium salt that reacted more slowly with aqueous sodium sulfite. The reaction temperature for the final step was slowly increased from 20–80°C over 6 h. The final sulfonic acid exchanger was filtered off and dried.

2.3. Instrumentation

The HPLC system consisted of a HPLC pump (Type 64, Knauer, Berlin, Germany), a pneumatic injection valve (Knauer) with a 20-μl sample loop, a variable wavelength detector (Type 87.00, Knauer). 100 mm×4 mm I.D. stainless steel columns (Vertex, Knauer) were used as analytical columns. Post-column detection of the ions was realized by reaction with 4-(2-pyridylazo)-resorcinol (PAR), Zn-EDTA, $0.25\cdot10^{-4}$ M Zn-EDTA, $1\cdot10^{-4}$ M PAR, 2 M NH_3. The post-column reagent was added to the eluate in the post-column reactor by a single piston HPLC-pump (LDC Analytical) and absorption was monitored at 495 nm. The whole system control and the readout of the detector were processed by a computing system.

2.4. Reagents

All reagents were of analytical or high purity grade. Aliquots of commercially available stock solutions (1000 mg/l) were used to prepare cation mixtures containing the ions to be investigated in a range of 2–60 mg/l. All eluents were prepared with tartaric acid (Fluka, Switzerland, microselect grade) and Millipore water with a minimum resistance of 18 MΩ. The pH was adjusted with 4 M NaOH solution (from NaOH p.a. containing less than 0.0002% K^+, Merck, Darmstadt, Germany). The concentration and the pH of the eluents varied from 0.1–0.25 M tartaric acid and 2.7–3.96 pH value.

2.5. Infrared spectroscopy

All infrared spectra were recorded with a Perkin–Elmer Model 1710 infrared Fourier transform spectrometer. All spectra were recorded from 450–4000 cm^{-1} with a resolution of 4 cm^{-1} corresponding to 10 scans per spectra. The polymeric samples were dispersed in KBr and pressed into pellets.

2.6. Column packing procedure

A slurry packing technique was used for the polymeric materials. The slurry composition depended on the exchange capacity of the polymer. For resins up to 0.2 mmol/ml exchange capacity an amount of 800 mg resin was dispersed into 10 ml toluene and ultrasonic shaken for 15 min. After addition of 10 ml cyclohexanole and further ultrasonic shaking for 10 min the mixture was homogeneous. For high degrees of functionalization a mixture of 10 ml water and 10 ml ethanol was used as slurry. The packing-system consisted of an HPLC-pump (Type 364, Knauer), a slurry reservoir (20 ml volume), joining units and stainless-steel analytical columns. The packing material was immediately pressed into the column with methanol (low functionalization) or water (high functionalization) at a working pressure of 25 MPa. The minimum volume of solvent pumped through the column was 150 ml. After sealing the columns were conditioned with 200 ml water at a flow-rate of 1 ml/min.

3. Results and discussion

3.1. Selection of synthesis procedure

Sulfonation with sulfuric acid as the classical way to generate polymer based cation exchanger had been investigated previously [4]. Chromatographic performance, control of the degree of functionalization and long-term chemical stability are not as good as required for modern ion chromatography. The main reason for the low chromatographic performance is the direct attachment of the exchange site to the aromatic substrate. A simple coating of PS–DVB with aliphatic sulfonic acids increased chromatographic performance by nearly one order of magnitude [23]. Ideally a procedure of synthesis should lead to aliphatic sulfonic acid exchange sites with variable spacer length between the polymeric substrate and the exchange site. As it is impossible to force hydrophilic agents to react directly with the hydrophobic PS–DVB resin a multi-step synthesis has to be chosen. An easy way to generate the desired sulfonic acid exchange sites with variable spacer length is Friedel–Crafts acylation with various ω-halogenoacyl chlorides and subsequent reaction with dimethyl sulfide/sodium sulfite [20–22].

3.2. Control of the degree of functionalization

The degree of functionalization can be controlled by variation of the amount of ω-chloroacyl chloride. Fig. 1 shows the dependence of cation exchange capacity on the amount of ω-chloropropionyl chloride used for the Friedel–Crafts acylation. All other experimental parameters such as amount of polymer, catalyst, temperature and reaction time are kept constant. A nearly linear dependence between capacity and amount of reagent is observed below an exchange capacity of 0.35 mmol/ml. Above 0.5 mmol/ml the slope of the curve decreases rapidly. For higher degrees of functionalization a control by means of reaction time is the more efficient way. Total functionalization of the polymer using a huge excess of ω-chloropropionyl chloride and 48 h reaction time at room temperature leads to an exchange capacity of 1.49 mmol/ml or 1.8 mmol/g.

3.3. Reactivity of ω-chloroacyl chlorides

Reactivity of different ω-chloroacyl chlorides was investigated using fixed experimental conditions. A total reaction time of 10 min at room temperature and stoichiometric amounts of ω-chloroacyl chlorides and catalyst were used. Under these conditions the reactivity of ω-chloroacetyl chloride, ω-chloropropionyl chloride and ω-chlorobutyryl chloride was 0.45:1:0.19. This order of reactivity is generally valid for highly crosslinked, macroporous PS–DVB resins. The exact data are true for low to medium degrees of functionalization.

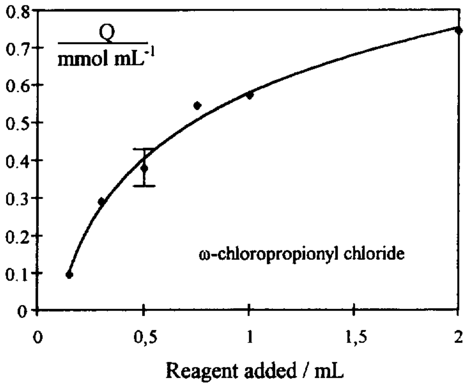

Fig. 1. Dependence of exchange capacity Q on the amount of ω-halogenoacyl chloride. Experimental conditions: 2 g BioGel SEC 7, stoichiometric amount of $AlCl_3$ (1:1), 25 ml 1,2-dichloroethane, ω-chloropropionyl chloride.

3.4. Infrared spectroscopic investigations

Use of FTIR spectroscopy led to the spectra shown in Fig. 2. The spectrum of the native BioGel SEC7 is shown in Fig. 2a, the acylated polymer in Fig. 2b and the spectrum obtained for the sulfopropionylated resin in Fig. 2c. Characteristic C–C-aromatic stretching are present at 1600–1585 cm^{-1}, 1580–1430 cm^{-1} and in the finger print region at 1300–1000 cm^{-1}. After Friedel–Crafts acylation a single absorption band at 1680–1700 cm^{-1} is to be expected. If ω-chloropropionyl chloride is used a second absorption band at 1720–1710 cm^{-1} is observed (Fig. 2b). An explanation could be a side reaction or an isomeric effect [24].

The band at 840 cm^{-1} is typical for 1,4-disubstituted benzene ring, the band at 700 cm^{-1} occurs when single substitution is present. With increasing reaction time and/or increasing amount of acylating reagent the band at 840 cm^{-1} increases instead of the

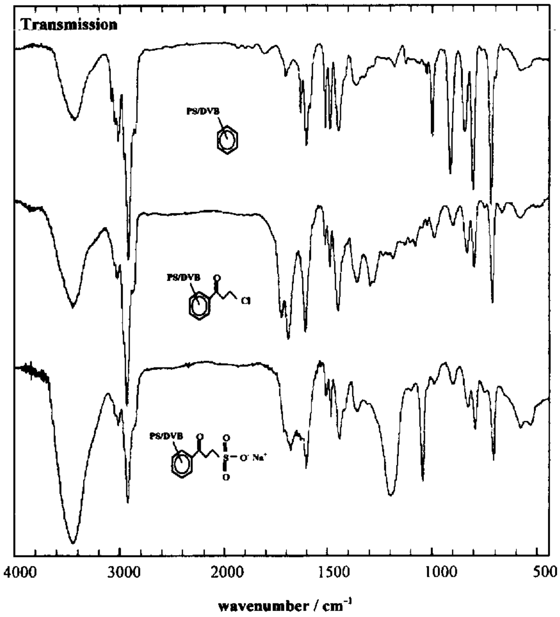

Fig. 2. FT-IR spectra of BioGel SEC 7 (a, top), chloropropionylated BioGel SEC 7 (b, middle) and the finally sulfopropionylated cation exchanger (c, bottom).

band at 700 cm^{-1}. This is caused by increasing disubstitution of the benzene ring. Probably the band at 840 cm^{-1} can be used as quantitative indicator for the degree of functionalization.

The most important absorption band of sulfoacylated PS–DVB in comparison to the acylated product is the strong and broad band of the asymmetric S–O valence oscillation at 1180 cm^{-1}. This band and the symmetric derivatives at 1040 and 1010 cm^{-1} depend on the degree of functionalization. Other bands of interest are the strong water absorption at 3500 and 1680–1620 cm^{-1} because of the hygroscopic sulfonic acid group.

3.5. Side-reactions of the functionalization procedure

Possible products of side reactions during the Friedel–Crafts acylation are shown in Fig. 3. The product (a) occurs as a combination of Friedel–Crafts acylation and alkylation. This type of side reaction increases the degree of crosslinkage and leads to a less hydrophobic surface because of the added carbonyl group. Similar conclusions belong to product (c), an intramolecular type of the reaction scheme discussed for product (a). An indication for product (c) is the second carbonyl band obtained at 1710–1720 cm^{-1}. The five ring should lead to the largest increase in wave numbers. Product (a) is present, but the difference in wave numbers between this carbonyl group and the carbonyl group present after the standard Friedel–Crafts acylation is too small to show a different absorption band even when a polymeric substrate is present. Investigations with different ω-chloroacyl chlorides showed an increase in the width of the 1680–1700 cm^{-1} absorption band. Product (b) is a hydrolyzed product of a Friedel–Crafts alkylation. The amount of this side reaction product was determined by titrimetry to less than 5%.

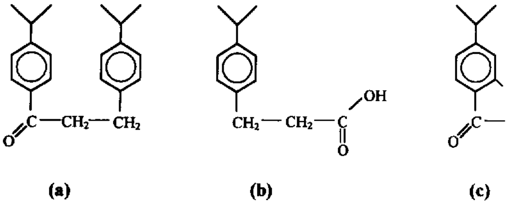

Fig. 3. Products of possible side reactions of a Friedel–Crafts acylation of PS–DVB using ω-chloropropionyl chloride.

3.6. Influence of pore size of the basic substrate

Figs. 4 and 5 compare the chromatographic behavior of high capacity cation exchangers with different basic substrates. In Fig. 4, the BioGel SEC3 with an average pore diameter of 3 nm was used as sulfopropionylated resin with 0.40 mmol/ml exchange capacity. Selectivity for Pb^{2+} and Zn^{2+} was close to zero but all other investigated elements are well resolved from each other. It should be stressed that the resolution of Ca^{2+}, Mn^{2+} and Mg^{2+} is excellent. That behavior is similar to that of the silica based cation exchanger Nucleosil SA with an exchange capacity of only 0.15 mmol/ml. In comparison, Fig. 5 shows the chromatogram obtained for the same analytes on a 7-nm pore size basic substrate with the same exchange site and a volume capacity of 0.43 mmol/ml. Using exactly the same elution system as for the 3-nm pore size column the resolution of Mn^{2+}, Ca^{2+} and Mg^{2+} decreased to zero. In contrast, the coelution of Zn^{2+} and Pb^{2+} is eliminated by moving the Pb^{2+} peak behind Ni^{2+}. Generally, the basic substrate seems to have the most

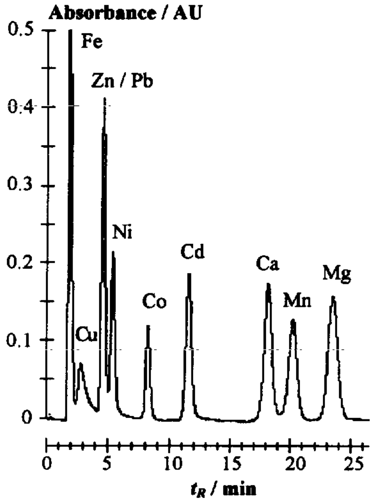

Fig. 4. Separation of di- and trivalent metal cations on a sulfopropionylated BioGel SEC 3 cation exchanger (Q=0.40 mmol/ml bed volume). Chromatographic conditions: 0.175 M tartaric acid (pH 3.42) adjusted with NaOH, 1 ml/min flow-rate, post-column detection with Zn-EDTA-PAR.

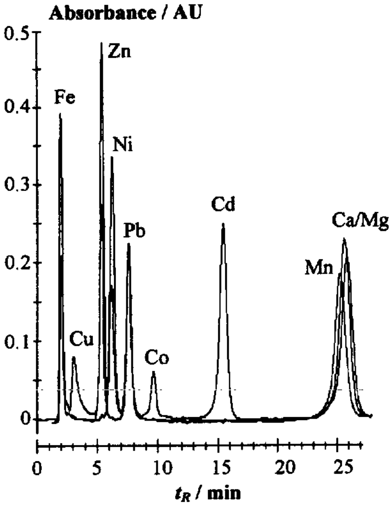

Fig. 5. Separation of di- and trivalent metal cations on a sulfopropionylated BioGel SEC 7 cation exchanger (Q=0.43 mmol/ml bed volume). Overlay of several chromatograms. Chromatographic conditions as in Fig. 4.

important influence on retention characteristics of sulfoacylated cation exchangers.

3.7. Influence of the spacer arm

Figs. 6 and 7 show the overlay of chromatograms of several divalent cation obtained on a sulfoacetylated and on a sulfobutyrylated resin of low exchange capacity. Basic substrate and elution system is equal for both resins. The exchange capacity differed from 0.13 for the sulfoacetylated to 0.10 mmol/ml for the sulfobutyrylated resin. In contrast to the major influence of the basic substrate, the length of the spacer arm seems to have only minor influence on resin selectivity. The evenly spaced peaks in Fig. 7 suggest a somewhat better selectivity for the sulfobutyrylated resin. A minor drawback for sulfobutyrylated resin is the lower reactivity of ω-chlorobutyryl chloride.

3.8. Comparison of figures of merit for sulfopropionylated and sulfonated resins

However, as shown in Figs. 8 and 9 the chromatographic performance is influenced by the exchange capacity. The data are observed for the same substrate with nearly identical exchange capacities and the same elution system. The only difference between the data shown in Figs. 8 and 9 is the kind of functionalization. As shown in Fig. 8 the HETP

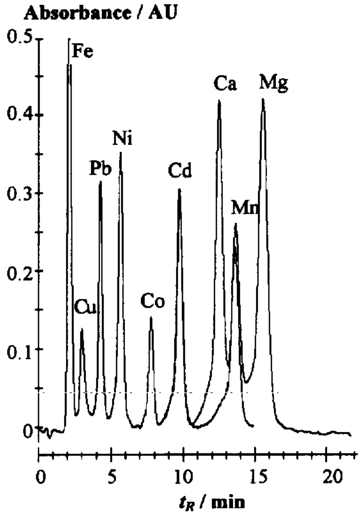

Fig. 6. Separation of di- and trivalent metal cations on a sulfoacetylated BioGel SEC 7 cation exchanger (Q=0.13 mmol/ml bed volume) as overlay of several chromatograms. Chromatographic conditions: 0.1 M tartaric acid (pH 3.10) adjusted with NaOH, for other conditions see Fig. 4.

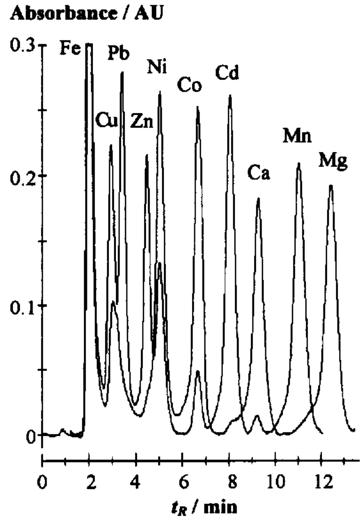

Fig. 7. Separation of di- and trivalent metal cations on a sulfobutyrylated BioGel SEC 7 cation exchanger (Q=0.10 mmol/ml bed volume) as overlay of several chromatograms. Chromatographic conditions as in Fig. 6.

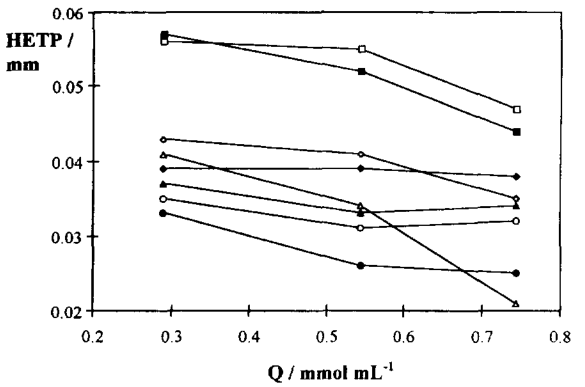

Fig. 8. Influence of exchange capacity on plate height (HETP) for sulfopropionylated cation exchangers based on BioGel SEC 3. Eluent 0.25 *M* tartaric acid (pH 3.3) adjusted with NaOH, flow-rate 1 ml/min. Figure captions: (◇) Zn^{2+}, (■) Ni^{2+}, (♦) Co^{2+}, (△) Cd^{2+}, (●) Mn^{2+}, (△) Ca^{2+}, (○) Mg^{2+}, (□) Pb^{2+}.

value for sulfopropionylated resins decreased with increasing exchange capacity. This behavior is in strong contrast to the one shown in Fig. 9 for sulfonated PS–DVB. The different behavior of sulfonated and sulfopropionylated resins can be explained by the different process of functionalization. In case of sulfonation using the small reactive agent SO_3^+ the increased functionalization leads to a deeper penetration of the core with exchange sites. Therefore, the maximum length of the diffusion pathway increases resulting in an increase of HETP values.

On the other hand, the Friedel–Crafts acylation requires a reagent–catalyst complex close to the surface of the resin. Smaller pores are not functionalized because of the bigger size of the reagent. In addition, the steric approach of the exchange site could prevent some parts of the exchanger from the access by analytes. In sum, the diffusion pathways are decreased and efficiency is increased.

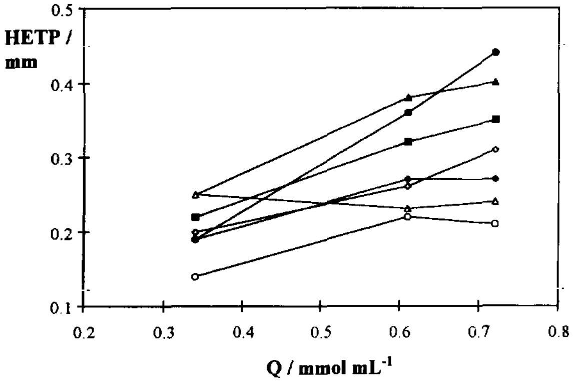

Fig. 9. Influence of exchange capacity on plate height (HETP) for directly sulfonated cation exchangers based on BioGel SEC 3. Eluent 0.25 *M* tartaric acid (pH 3.3) adjusted with NaOH, flow-rate 1 ml/min. For symbols see Fig. 8.

For sulfopropionylated resins the influence of exchange capacity differs from element to element. Most dramatic increase in efficiency with increasing exchange capacity was observed for the late eluting Ca^{2+} and Mn^{2+} as well as fore the early eluting Pb^{2+}. In case of Pb^{2+} the increase is mainly caused by an increased retention compared to Co^{2+} as internal standard. Therefore, the influence of the post column reaction detection system on the HETP-values for Pb^{2+} decreased. In case of Ca^{2+} and Mn^{2+} the increase in efficiency is undoubtedly caused by the increased functionalization. In detail, the higher degree of functionalization leads to a more hydrophilic surface and to a blocking of parts of the exchanger. Other elements such as Ni^{2+} and Co^{2+} show only a minor dependence on the degree of functionalization. Ni^{2+} shows always higher HETP values than the near by eluting ions Zn^{2+} and Co^{2+}. Probably the elution system itself is the limiting factor for Ni^{2+}. The behavior of the elements on sulfonated resins has been discussed previously [4].

4. Conclusions

Sulfoacylation of highly crosslinked PS–DVB is an effective tool for the generation of a new class of high performance cation exchangers. In contrast to sulfonation of PS–DVB the performance of the cation exchangers is dramatically increased and can be compared to silica based HPLC cation exchanger.

First applications dealt with transition metals because of the huge amount of data available for those ions on silica based and on directly sulfonated cation exchangers. Interesting features of the synthetic procedure are the flexibility to render the exchange site, to use several structural different substrates and to manipulate exchange capacity over two orders of magnitude. The upper level of exchange capacity is just a factor of three below the exchange capacity of fully sulfonated PS–DVB. The sulfoacylated exchangers are stable against pH from 0–14, inert against oxidizing reagents such as HNO_3 up to a concentration of 4 *M* and stable against fluoride.

Acknowledgments

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